

References and Notes

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- We draw carbonium ion XI with the Cr(CO)₃ groups in the transoid configuration, since, as molecular models show, this would minimize nonbonded repulsive interactions between CO ligands of the two Cr(CO)₃ groups. An x-ray diffraction study of the phenylbis(tricarbonylironcyclobutadiene)methyl cation (BF₄⁻ salt) established a transoid arrangement of the Fe(CO)₃ groups in that species,¹⁶ and a transoid arrangement of Cr(CO)₃ groups was found in (π , π '-biphenyl)tricarbonylchromium, in which a planar organic ligand is present.¹⁸
- A general rule of thumb is that going from a neutral metal carbonyl to a cationic metal carbonyl, e.g., Cr(CO)₆ → Cr(CO)₆⁺, with a +1 charge raises ν (CO) by ~100 cm⁻¹.²⁵
- The assignment of the structure shown in XX is based solely on the known preferred site of reactivity of pyrrole in Friedel-Crafts acylations and alkylations.²⁹
- The N–H resonances in this and the other two primary amine derived products were not observed. This is a general phenomenon in the ¹H NMR spectroscopy of primary and secondary amines since the N–H resonances are considerably broadened owing to the electric quadrupole moment of the ¹⁴N nucleus: ref 30.

Control of Regioselectivity and Excited Singlet Reaction Rates by Substitution in the Di- π -methane Rearrangement. Mechanistic and Exploratory Photochemistry^{1,2}

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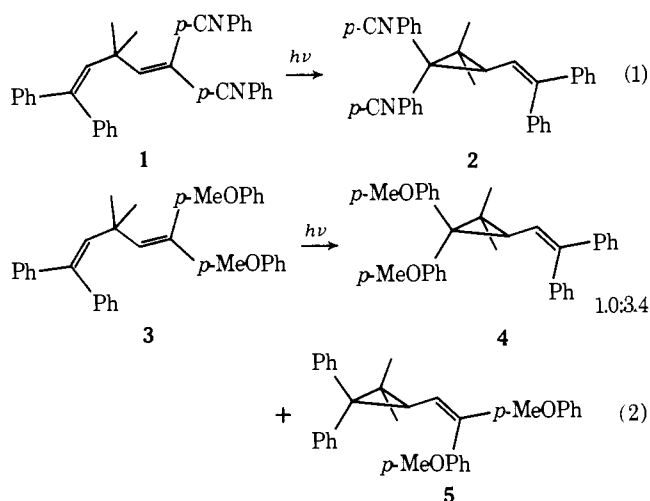
Abstract: A series of 1,1,5,5-tetraaryl-3,3-dimethyl-1,4-pentadienes—with methoxy, cyano, and chloro substitution—was synthesized. The photochemistry of these compounds was investigated. Regioselectivity as a function of substitution was determined for the di- π -methane rearrangement. Reaction efficiencies were obtained. Also, single photon counting with deconvolution was employed to obtain the excited singlet rearrangement rates. The many facets of the rearrangement were investigated theoretically. SCF-CI calculations with multiple singly and doubly excited configurations were employed where necessary. A number of new concepts resulted. Our ΔP matrix treatment was used to determine the locus of excitation initially and during the reaction. Also, the experimental rate constants were found to parallel the calculated energies of bridging of the excited singlets to give the corresponding cyclopropyldicarbonyl diradicals. A hitherto unrecognized phenomenon of reaction inhibition by excessive vertical excited state stabilization was encountered. The electronic structure of the states of the cyclopropyldicarbonyl diradical was determined. Finally, control of the regioselectivity was considered from a theoretical standpoint.

Introduction

In our previous papers dealing with the divinyl version of the di- π -methane rearrangement^{2,3} we observed an enhancement of the reaction efficiency and excited singlet rate constant on introduction of *p*-cyano groups. Conversely, we noted an

efficiency and a rate inhibition arising from *p*-dimethylamino and *p*-methoxy substitution. Also unusual regioselectivity was encountered in which *p*-cyanophenyl groups appeared on the three-ring of product while *p*-methoxyphenyl and *p*-dimethylaminophenyl groups appeared preferentially on the

vinyl group. Note eq 1 and 2.

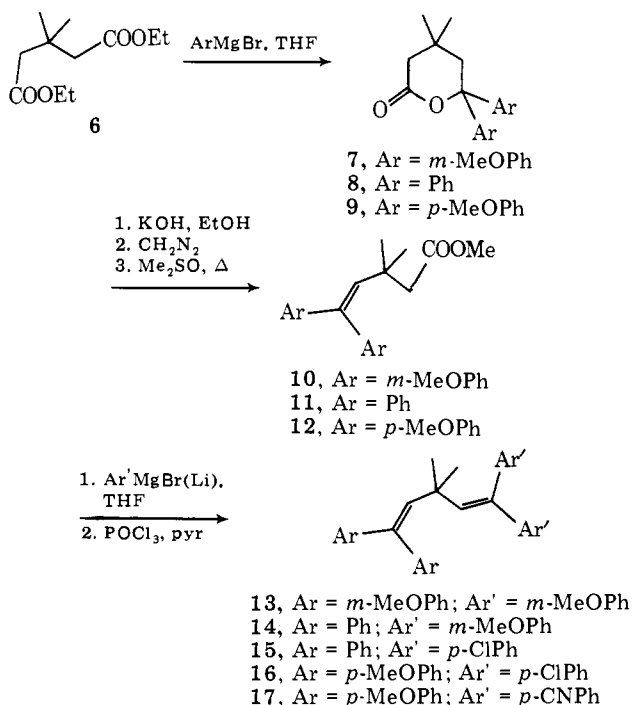


The dramatic regioselectivity effects demanded further investigation in order to determine their generality and to ascertain their bearing on the reaction mechanism. Similarly, the substituent effect on the excited state rates promised to provide information on the mechanism. Finally, we were interested in studying dienes having both electron-donating and electron-withdrawing groups to search for any special effects deriving from intervention of dipolar, or zwitterionic, species.

The substituents chosen for the present study were *p*-cyano, *p*-chloro, *m*-methoxy, and *p*-methoxy, since these promised to provide a relatively complete pattern of di- π -methane systems when coupled with our previous examples.

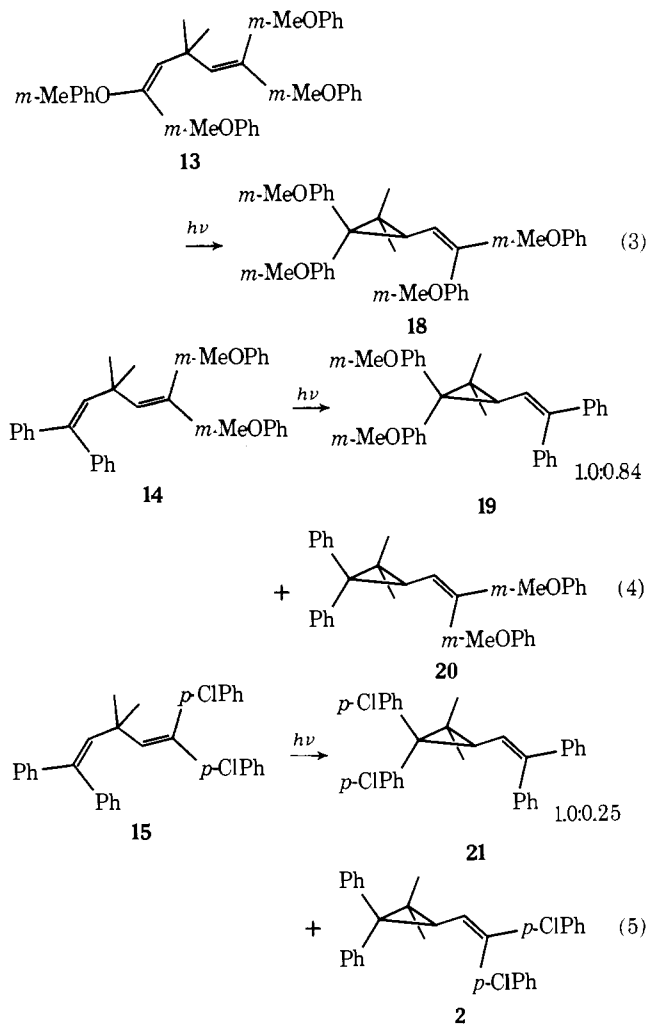
Synthesis of Diene Reactants. The dienes of interest were synthesized as outlined in Chart I; details are given in the

Chart I. Synthesis of Di- π -methane Reactants



Experimental Section. This synthetic approach has proven both practical and general.

Exploratory Photochemistry and Product Structure Elucidation. The five dienes (i.e., **13-17**) were first irradiated preparatively with the results given in eq 3-7.



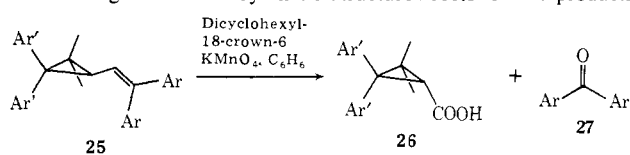
The product structures were in accord with the NMR, UV, IR, and mass spectral data. However, for reasons given earlier,⁴ the assigned structures were confirmed by degradation and synthesis. This is outlined in Chart II and detailed in the Experimental Section. In general, degradation proved more convenient. However, in the case of the minor photoproduct derived from irradiation of the dichlorodiene **15** insufficient

Table I. Quantum Yield Results

Reactant	Additive	λ_{irrad} , nm	Φ_r^a
Tetra- <i>m</i> -methoxy diene 13		310	0.30
	<i>m</i> -Methoxyacetophenone	317	<0.0018
Di- <i>m</i> -methoxy diene 14		300	0.086 (19), 0.072 (20)
	<i>m</i> -Methoxyacetophenone	317	<0.0018
Di- <i>p</i> -chlorodiene 15		295	0.11 (21), 0.029 (22)
	<i>m</i> -Methoxyacetophenone	317	<0.0018
Di- <i>p</i> -chloro-di- <i>p</i> -methoxy diene 16		310	0.13
	<i>m</i> -Methoxyacetophenone	317	<0.0017
Di- <i>p</i> -cyano-di- <i>p</i> -methoxy diene 17		310	0.053
	<i>m</i> -Methoxyacetophenone	317	<0.0018
Tetra- <i>p</i> -cyano diene 29^b		310	0.38
Benzophenone plus benzhydrol		356	0.24
Benzophenone plus benzhydrol	Tetra- <i>m</i> -methoxydiene 13	356	0.041
Benzophenone plus benzhydrol	Di- <i>p</i> -chloro diene 15	356	0.041

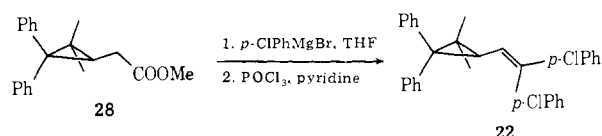
^a Extrapolated quantum yields (zero percent conversion) are given; for individual runs see Experimental Section. ^b 1,1,5,5-Tetrakis(*p*-cyanophenyl)-3,3-dimethyl-1,4-pentadiene, ref 3.

Chart II. Degradative and Synthetic Structure Proofs of Photoproducts



Vinylcyclopropane	Ar	Ar'	% 26^a	% 27^a
18	<i>m</i> -MeOPh	<i>m</i> -MeOPh	68	76
19	Ph	<i>m</i> -MeOPh	76	57
20	<i>m</i> -MeOPh	Ph	60	67
21	Ph	<i>p</i> -ClPh	60	75
22	<i>p</i> -ClPh	Ph	<i>b</i>	28
23	<i>p</i> -MeOPh	<i>p</i> -ClPh	38	83
24	<i>p</i> -MeOPh	<i>p</i> -CNPh	21	88

^a Yield of purified degradation product. ^b Too little material used to isolate degradation product.



material was available for isolation of all degradative fragments, and the photoproduct **22** was independently synthesized. Finally, we note that in each case the photoproducts were vinylcyclopropanes as expected from the di- π -methane rearrangement.⁶

Quantum Yield Determinations. The Black Box apparatus as well as the semimicro optical bench described previously⁷ and additionally the electronic actinometer⁸ proved particularly useful. Assays were performed with high-pressure liquid chromatography except in one case where 270-MHz NMR was employed. The usual precautions⁵ required in quantum yield determinations were followed. Owing to product light absorption it was necessary to extrapolate a series of runs to zero conversion for each diene. The results of direct irradiations are summarized in Table I and detailed in the Experimental Section.

The sensitized runs were carried out with *m*-methoxyacetophenone. As seen in Table I no di- π -methane rearrangement could be detected. Additionally, runs were carried out using a benzophenone plus benzhydrol combination under concentration conditions comparable to the *m*-methoxyacetophenone runs. No di- π -methane rearrangement was effected and yet quenching of the usual pinacolization resulted. Thus energy transfer without triplet rearrangement was found.

Single Photon Counting Measurement of Rate Constants.

We have noted⁹ in the past that excited state rate constants are correlated more safely with theory than are quantum yields. Thus we proceeded to determine these using our method¹⁰ based on single photon counting and relative fluorescence quantum yields. The basic technique and precautions followed in the previous paper^{2b} were utilized. Details are outlined in the Experimental Section. A summary is found in Table II.

It is to be noted that two types of experimental information are incorporated in the measurements. One is the relative fluorescence intensities at low (i.e., 77 K) temperature and room temperature, this ratio being our magic multiplier M .¹⁰ Most commonly fluorescence is more intense at low temperature and, as seen in Table II, M is greater than unity. Interestingly, the present set of compounds exhibits a larger range of M values than usual.

The second type of information obtained is the low-temperature rate of singlet decay as determined by single photon counting. These data are also included in Table II.

The magic multiplier is used by eq 8 to afford the room temperature rate of singlet decay which is too rapid to measure directly.

$${}^1k_{\text{dt}}^{\text{rt}} = M({}^1k_{\text{dt}}^{77}) \quad (8)$$

With the room temperature decay rates known, one can utilize the definition of the quantum yield to solve for the rate of excited singlet reacting to give product; note the equation¹¹

$${}^1k_r = \phi_r({}^1k_{\text{dt}}^{\text{rt}}) \quad (9)$$

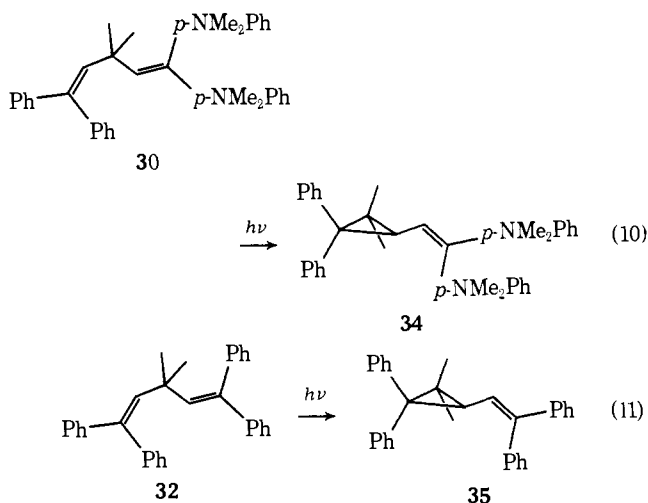
Interpretative Discussion. Systematic Effects and Unusual Behavior in the Systems Studied. The results described above include several intriguing aspects. Two, in particular, constitute new phenomena and become understandable when subjected to theoretical considerations. The first is the remarkable excited singlet rate inhibition by *p*-methoxy, *m*-methoxy, and *p*-chloro substituents. Even more remarkable rate inhibition is observed in our accompanying paper^{2b} where *p*-dimethylamino, as well as methoxy, was studied. Thus, 1,1-bis(*p*-*N,N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**30**)^{2b} (note eq 10) rearranges at a rate of $5.4 \times 10^7 \text{ s}^{-1}$ contrasted with a rate of $1.5 \times 10^{11} \text{ s}^{-1}$ ¹⁰ for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**32**), the parent unsubstituted tetraphenyldiene. Note eq 11. The corresponding cyano-substituted dienes are even more rapid,³ and the compounds of the present study provide a spectrum of rates.

The second intriguing aspect is the remarkable control of regioselectivity in which *p*-dimethylaminophenyl^{2b} and *p*-methoxyphenyl groups appear on the residual double bond of vinylcyclopropane product and in which *p*-cyanophenyl groups appear³ on the product three-ring. *m*-Methoxyphenyl and

Table II. Emission and Single Photon Counting Results

Reactant	$\lambda_{em},^a$ nm	M^b	Temp. K	τ	$^1k_{dt},$ s^{-1}	1k_r, s^{-1}
Di- <i>p</i> -dimethylamino ^c diene 30	360	70	300 77	50 ps 3.5 ns	2.0×10^{10} 2.9×10^8	5.4×10^7
Tetra- <i>p</i> -methoxy diene 31 ^c	335	95	300 77	26 ps 1.9 ns	3.9×10^{10} 5.2×10^8	1.7×10^9
Di- <i>p</i> -chloro diene 15	304	19	300 77	43 ps 0.83 ns	2.3×10^{10} 1.2×10^9	3.3×10^9
Di- <i>p</i> -chloro-di- <i>p</i> -methoxy diene 16	333	68	300 77	40 ps 2.6 ns	2.5×10^{10} 3.8×10^8	3.3×10^9
Di- <i>p</i> -methoxy diene 3 ^c	330	75	300 77	29 ps 2.7 ns	3.5×10^{10} 3.7×10^8	3.4×10^9
Di- <i>m</i> -methoxy diene 14	326	260	300 77	18 ps 4.8 ns	5.5×10^{10} 2.1×10^8	8.6×10^9
Tetra- <i>m</i> -methoxy diene 13	327	170	300 77	22 ps 3.7 ns	4.6×10^{10} 2.7×10^8	1.4×10^{10}
Tetraphenyl ^d diene 32	310	225	300 77	0.55 ps 0.12 ns	1.8×10^{12} 8.0×10^9	1.5×10^{11}
Di- <i>p</i> -cyano diene 1 ^e			300	0.50 ps	2.3×10^{12}	2.2×10^{11}
Tetra- <i>p</i> -cyano diene 29 ^e			300	0.43 ps	2.0×10^{12}	7.6×10^{11}
Di- <i>p</i> -chloro ethylene 33 ^f	308	9.6	300 77	104 ps 1.0 ns	9.6×10^9 1.0×10^9	

^aWavelength of emission maximum. ^b Magic multiplier. ^c Reference 2b. ^d Reference 10. ^eReference 3. ^f1,1-Bis(*p*-chlorophenyl)ethylene.

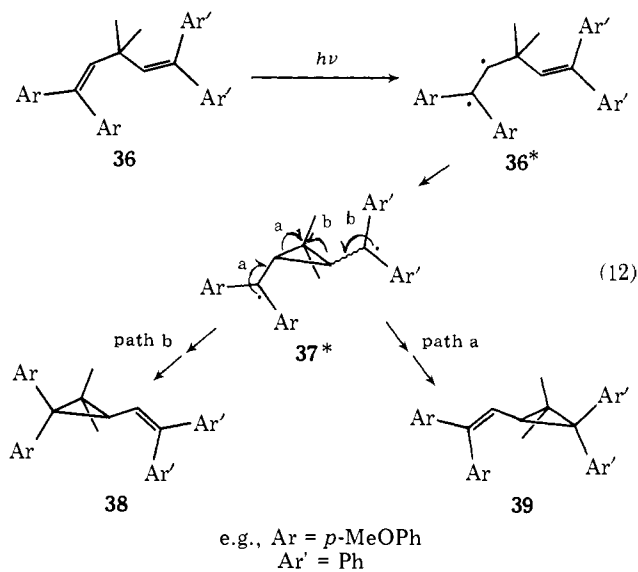


p-chlorophenyl groups also tend to be found on the product three-ring.

Finally, in our consideration of aryl substituent effects we must deal with the question of whether we are dealing with ground or excited state aromatic groups, since we know¹² that this will control the nature of substituent effects.

The qualitative valence bond representation of the di- π -methane rearrangement is given in eq 12. This representation alone does not lead to an understanding of the above effects. For example, one might have predicted both *p*-cyano and *p*-methoxy to have stabilized the intermediate bridged diradical **37** and increased the reaction rate.

Interpretative Discussion. The ΔP Matrix Concept. In order to interpret a number of the electronic effects in our present study we need to consider the ΔP matrix treatment which we have introduced briefly in our previous publication.^{1b} Thus a simple method of determining the distribution of electronic excitation makes use of excited and ground state bond orders. For each pair of atomic or basis orbitals, r and t , the change in bond order on excitation is given by $\Delta P_{rt} = P_{rt}^* - P_{rt}^0$. Lacking excitation at this site in the molecule, the excited state bond order (i.e., P_{rt}^*) will be unchanged from the ground-state bond order (i.e., P_{rt}^0) and ΔP_{rt} will be zero. Thus excitation will



be found in those portions of the excited molecule where the ΔP_{rt} 's are nonzero. Negative ΔP_{rt} 's indicate that the excited state is more antibonding than the ground state at this location while positive ΔP_{rt} 's indicate greater bonding character.

The advantage of the method is that it can utilize the bond orders derived from either very sophisticated calculations as SCF-CI or, alternatively, from simple one-electron (e.g., Hückel) calculations. Even qualitative MOs can be used to afford qualitative predictions.

Interpretative Discussion. SCF-CI Calculations. Also required in order to interpret the experimental results were SCF-CI calculations to correlate with observation. In view of the size of the tetraaryl pentadienes and diradicals, we utilized the 1,5-diaryl-1,4-pentadiene moiety and derived diarylcyclopropyldicarbonyl diradical as models. The basis set orbitals utilized are given in Figure 1. Beyond the diene and the bridged diradical, some additional species along the reaction coordinate were inspected. The method involved standard¹⁴ SCF calculations followed by configuration interaction of the SCF wave functions resulting. Here we included both singly and doubly

Table III. Calculated Bridging Energies for S_1 with Experimental $\log(^1k_r)$'s

Reactant	$\log(^1k_r)$	ΔE , eV	Reactant	$\log(^1k_r)$	ΔE , eV
Di- <i>p</i> -dimethylamino diene 30	7.74	-1.28	Di- <i>m</i> -methoxy diene 14	9.93	-1.28
Tetra- <i>p</i> -methoxy diene 31	9.23	-1.53	Tetra- <i>m</i> -methoxy diene 13	10.14	-1.27
Di- <i>p</i> -chloro diene 15	9.52	-1.51	Tetraphenyl diene 32	11.18	-1.64
Di- <i>p</i> -chloro-di- <i>p</i> -methoxy diene 16	9.52	-1.47	Di- <i>p</i> -cyano diene 1	11.34	-1.68
Di- <i>p</i> -methoxy diene 3	9.53	-1.52	Tetra- <i>p</i> -cyano diene 29	11.89	<i>a</i>

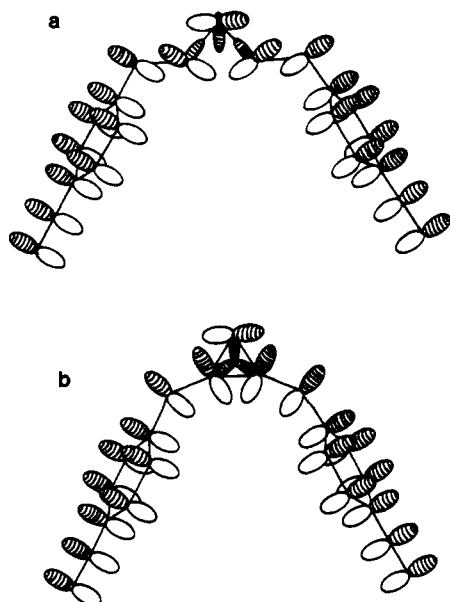
^aNot calculated.

Figure 1. (a) Basis set for diaryl diene; (b) basis orbital set for diaryl cyclopropyldicarbonyl diradical.

excited configurations. All possible singly and doubly excited configurations were subjected to a perturbation treatment; those leading to appreciable energy lowering were included, along with ground state, in configuration interaction. This meant that, typically, 100 singly and 5050 doubly excited configurations were tested with 40–50 singly excited and 200 doubly excited configurations being retained in the final configuration interaction. For more details see the section on Calculations.

One final comment is required, this pertaining to the cyclopropyldicarbonyl diradical model utilized to represent the reacting molecule. This corresponds to the qualitative valence bond structure (i.e., **37**) which we have found most useful in previous discussions of the mechanism.^{6a,b} On the other hand, we have made frequent use of a Möbius cyclic orbital array^{2b,6b,13} since this seems best in accord with the observed¹³ reaction stereochemistry. The two arrays are related. The Möbius array includes orbitals and overlap needed for the latter stages of the reaction (vinyl disengagement from the methane carbon and product three-ring formation). The present array emphasizes the bridging stage of the reaction and includes all orbitals required for the cyclopropyldicarbonyl three-ring. Hence no discord exists.

Interpretative Discussion. Variation of Rates with Substituents. As noted above, the striking rate inhibition by electron-donating substituents required explanation. This inhibition seemed anomalous since in the case of para-substituted aryl-vinylmethanes^{1b,14b} and divinylmethane systems bearing

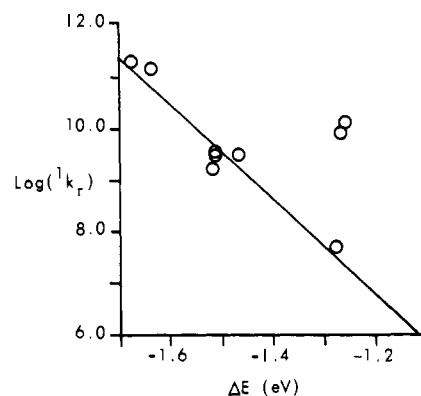
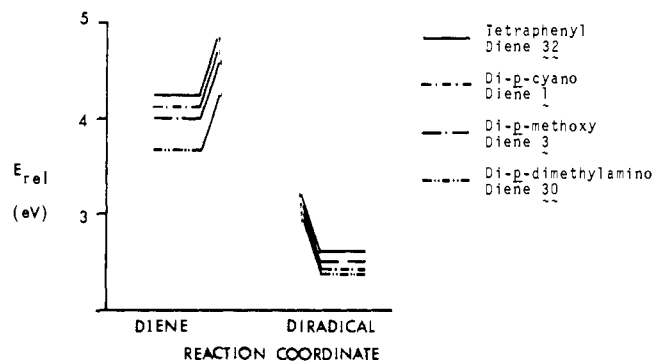
Figure 2. Correlation between $\log(^1k_r)$ and bridging energies; correlation coefficient (excluding meta-substituted compounds) = 0.96.

Figure 3. Energetics of bridging.

substituents directly on the vinyl group,^{1b,15} both methoxy and cyano groups accelerate the rates.

In order to understand the effect of substituents we used the SCF-CI calculations described above to determine energies of bridging of the two vinyl groups in the first excited state, that is, the energy of proceeding from vertical S_1 to excited cyclopropyldicarbonyl diradical. The calculated bridging energies are collected in Table III and also plotted in Figure 2 vs. $\log(^1k_r)$. Except for two meta-substituted cases the fit to linearity is remarkably good.

Since the quantum mechanical calculations nicely fit experiment, to understand the source of the anomalous rate inhibition by methoxy and dimethylamino it seemed necessary only to dissect the energetics of the calculations. This is seen most readily by reference to Figure 3. Here the SCF ground-state energies for the reactant pentadienes are taken as a common zero.¹⁶

It is seen that there is selective stabilization of the vertical excited states of dienes having dimethylamino and methoxy groups, stabilization considerably in excess of that of the

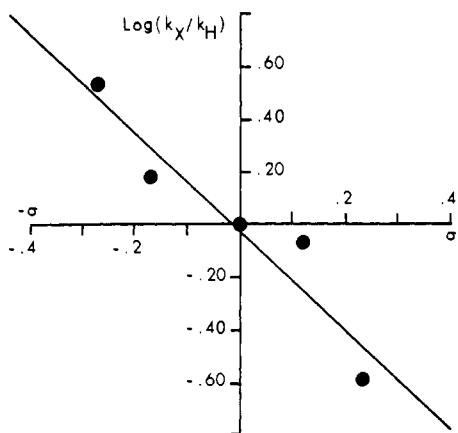
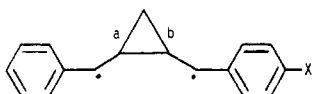


Figure 4. Plot of $\log(k_X/k_H)$ vs. Hammett σ , corr coeff = 0.96.



X = CN; bond a fission is favored by 0.24 eV.

X = OMe; bond b fission is favored by 0.11 eV.

Figure 5. SCF-CI prediction of relative ease of bond *a* vs. *b* fission.

Table IV. Regioselectivity and the Hammett σ

Reactant	k_X/k_H^a	$\text{Log}(k_X/k_H)$	σ_X^b
Di- <i>p</i> -methoxy ^c diene 3	3.41	0.532	-0.27
Di- <i>p</i> -methyl ^d diene 40	1.52	0.182	-0.18
Tetraphenyl ^e diene 32	1.00	0.000	0.00
Di- <i>m</i> -methoxy diene 14	0.84	-0.076	0.12
Di- <i>p</i> -chloro diene 15	0.25	-0.595	0.23

^a Ratio obtained from ratio of photoproduct quantum yields. ^b Ref 17. ^c Reference 2b. ^d 1,1-Bis(*p*-methylphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, ref 18. ^e Reference 19.

bridged diradicals. Thus the inhibition derives of excessive vertical starting state stabilization in the bridging process. This assumes that the rates of bridging and reaction will become more rapid as bridging exothermicity increases. This may be due to an activation barrier which parallels the overall energetics of bridging but we have no evidence on this point.

Interestingly, in the case of the *p*-methoxy-substituted compounds it was observed both experimentally and in the calculations that introduction of methoxy groups at one end of the pentadiene system resulted in a massive rate inhibition while further addition to give substitution at both ends did not greatly change the observed or calculated rates. This is understandable if excitation is localized in the lower energy styryl-like chromophore of unsymmetrical systems. Then the energy of the excited di-*p*-methoxy diene (i.e., **3***) will be the same as that of the excited tetra-*p*-methoxy diene (i.e., **31***) both having the same excited bis(*p*-methoxyphenyl)vinylic chromophore in common. That the two vinyl chromophores are either uncoupled or at most weakly interacting is supported by the observation of no special, long-wavelength fluorescence. The observed fluorescence in all cases was that of the isolated diarylvinylic moieties; note Table II. In addition, our subsequent discussion (vide infra) of excitation distribution supports this view.

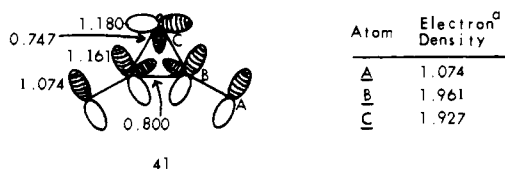


Figure 6. Electron densities for orbitals and atoms of the unsubstituted cyclopropylidene diradical in S_1 . a: Note a density of 2.0 at a two-orbital site (B and C) or a density of 1.0 at a one-orbital site (A) corresponds to neutrality.

Turning again to Figure 3, we note that all of the cyclopropylidene diradicals are stabilized relative to the unsubstituted diradical. Such stabilization by cyano, methoxy, and dimethylamino is in agreement with organic mechanistic reasoning. While in the cases of dimethylamino and methoxy these effects are outweighed by the greater starting S_1 stabilization noted above, for *p*-cyano there is slightly greater diradical than S_1 reactant stabilization in accord with the observed ca. twofold rate enhancement for *p*-cyano substitution (note Table II).

In suggesting stabilization by para substituents, we are assuming as noted above that such stabilization is that characteristic of ground-state aromatic groups. This point is discussed subsequently.

Interpretative Discussion. Regioselectivity. As noted above a distinctive pattern is observed wherein *p*-cyanophenyl, *m*-methoxyphenyl, and *p*-chlorophenyl groups tend to appear on the three-ring of di- π -methane product while *p*-methoxyphenyl and *p*-dimethylaminophenyl tend to appear on the double bond of product.

The first aspect derives from the plot in Figure 4 of $\log(R_X)$ vs. Hammett σ for substituent X. Here R_X is the regioselectivity defined as the ratio of product with the substituted phenyl group on vinyl to product with this group on the three-ring. This ratio is equivalent to k_X/k_H where k_X is the rate of cyclopropylidene diradical opening to afford the $\text{Ar}_2\text{C}=\text{CH}$ -moiety while k_H is the rate of opening to form the $\text{Ph}_2\text{C}=\text{CH}$ - moiety (corresponding to arrows *a* and *b* in eq 12). The corresponding data are listed in Table IV.

Interestingly, the plot has a negative slope (i.e., $\rho < 0$). A negative ρ signifies that the carbinyl carbon becomes more positive or less negative (vide infra) as a π bond is engendered at this site.

Another consequence derives from the plot in Figure 4. If one uses the σ values of *p*-cyano and *p*-dimethylamino (+0.66 and -0.83, respectively), the extrapolated plot leads to a prediction of a regioselectivity of 17:1 in favor of the observed *p*-cyano photoproduct **2** while the prediction for the dimethylamino photoproduct **34** is 40:1. Considering that most photochemical runs are not to complete conversion, the apparent absence of the minor photoproducts is in agreement with theory.

A second approach to regioselectivity was calculation of the relative energy increase on a 20% diminution of the bonding of each three-ring bond of the cyclopropylidene diradical. Thus, an SCF-CI calculation was run with all integrals corresponding to either bond *a* or bond *b* diminished by this percentage. This is summarized in Figure 5. It is seen that bond *a* fission is predicted where X is a cyano and bond *b* fission is predicted where X is methoxy. This is in agreement with observation as discussed above and in Table IV.

The calculations on the basic, unsubstituted cyclopropylidene diradical species **41** show the carbinyl centers to be electron rich in both S_1 and S_0 (note Figure 6). Since the three-ring opening processes leading onward to product dissipate this density at one carbinyl center or the other, it will be the cyano-substituted center which loses electron density more

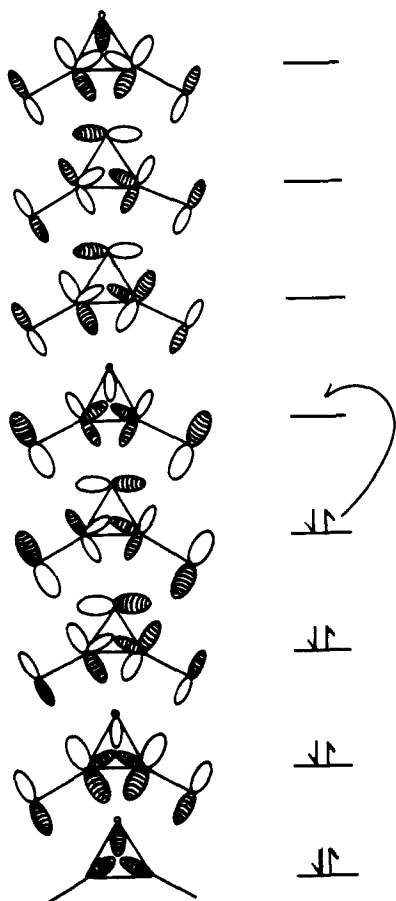


Figure 7. SCF molecular orbitals of the unsubstituted cyclopropyldicarbonyl diradical.

reluctantly. Conversely, the *p*-methoxy substituted side opens more readily.

Interpretative Discussion. Nature of the Excited State and the ΔP Matrix. We need to consider both the excited states of the diene reactants and also those of the bridged cyclopropyldicarbonyl diradicals.

The latter can be discussed from a qualitative viewpoint and will be considered first. Our understanding of the diradical excited state is aided by reference to Figure 7 which gives the SCF MOs. The dominant configuration in our SCF-CI treatment derives from the HOMO-LUMO excitation depicted. This is true for both the truncated species **41** and the diphenyl substituted model **42** in Figure 8. In the latter only the HOMO and LUMO are shown.

Inspection of Figure 7 suggests strengthening of the central σ bond, formed on bridging, in the excited state relative to ground state. This accords with the tendency of such ground-state diradicals to undergo fission of this bond compared with excited-state formation of the bond and preference for fission of the other three-ring bonds.

Another feature of the system is that HOMO and LUMO include the carbonyl *p* orbitals in negative and positive linear combinations, respectively. Beyond this, reference to Figure 8 reveals that the same negative and positive linear combinations persist in the substituted examples, except that these centers are now characteristic of the benzyl radical moiety. In fact, we see in Figure 8 that the benzylic-like moieties are essentially unchanged on excitation from HOMO to LUMO and that these portions of the molecule must be ground state in nature.

A more quantitative picture is useful in treatment of the reactant dienes. Thus Figure 9 shows two typical situations, one having *p*-cyano substitution and the other having *p*-me-

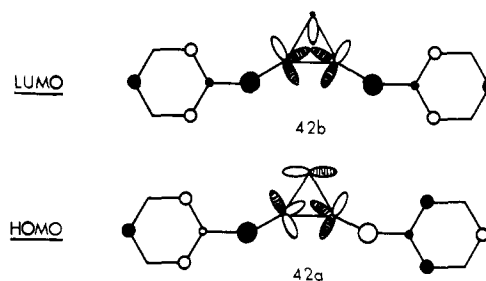


Figure 8. HOMO and LUMO of the diphenylcyclopropyldicarbonyl diradical.

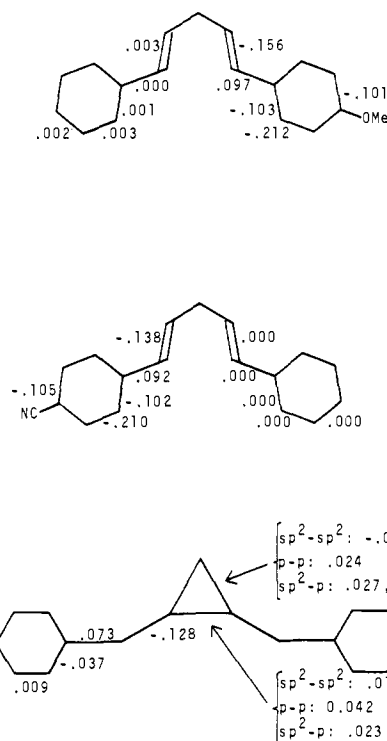


Figure 9. ΔP_{rt} 's for two diaryl dienes and diphenylcyclopropyldicarbonyl diradical.

thoxy. The ΔP_{rt} values are included. It is seen that appreciable ΔP values are found in the diarylvinyli moieties but not in the diphenylvinyli groups, thus signifying that electronic excitation is localized in the substituted styryl-like chromophore. This justifies the discussion above made in connection with interpretation of substituent effects on the rates.

Using ΔP_{rt} 's (note Figure 9 again) we confirm our qualitative conclusion that the aryl groups are essentially unexcited in the bridged diradicals; thus these elements are quite small in the aryl moieties and excitation is localized in the three-ring. This explains why ground-state substituent effects are seen in both stabilizing the diradicals (note Figure 3) and in the correlation of regioselectivity with ground-state σ constants (vide supra)

Interpretative Discussion. Zwitterionic Species. An intriguing suggestion has been made by Salem²⁰ that the di- π -methane rearrangement may go via a zwitterionic state having the gross structure of our cyclopropyldicarbonyl diradical. With this in mind we inspect the results obtained from the di-*p*-chloro-di-*p*-methoxy (i.e., **16**) and di-*p*-cyano-di-*p*-methoxy (i.e., **17**) dienes. Each of these had electron-withdrawing groups at one end and donating groups at the other end of the molecule. Rates could not be obtained because of anomalous emission due to internal exciplexing in the case of the cyano derivative. However, a quantum yield of 0.053 for

diene **17** is unexceptional and reveals no enhanced "push-pull" reactivity. The rate for the chloro diene **16** (note Table II) fits the rate plot of Figure 2 with a point lying near its structurally similar analogues having only independent chromophores.

Conclusion

The work considered above illustrates the utility of dissection of excitation energy and the importance of considering vertical excited state stabilization by substituents along with the effect of these substituents along the reaction coordinate. An especially important result deriving from this study is that substituents can behave as ordinary ground-state moieties or, instead, as excited-state groups. Furthermore, all gradations of excitation are theoretically possible. The ΔP matrix treatment allows one to decide whether ground- or excited-state reasoning is appropriate when substituents are introduced. Finally, the di- π -methane rearrangement is seen to be understood in ever-increasing depth.

Experimental Section²¹

5,5-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic Acid Lactone. To a solution of *m*-methoxyphenylmagnesium bromide, made from 11.2 g (60.0 mmol) of *m*-bromoanisole and 1.78 g (75.0 mg-atoms) of magnesium in 75 mL of tetrahydrofuran, was added 5.40 g (25.0 mmol) of diethyl 3,3-dimethylglutarate²² in 8.0 mL of tetrahydrofuran. The solution was refluxed for 2.0 h, treated with 6.0 mL of saturated aqueous ammonium chloride, diluted with ether, dried, and filtered through Celite. Concentration in vacuo afforded 10.88 g of a yellow oil. The oil was chromatographed on a 3.0 × 41 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column and 500-mL fractions were collected: fraction 1, hexane; 2, 5% ether in hexane; 3, 10% ether, 4, 15% ether. Fractions 3–4 gave 4.49 g (52.1%) of a yellow oil. Bulb-to-bulb distillation (165–185 °C at 0.07 Torr) afforded 4.15 g (48.2%) of 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone, a colorless oil which crystallized upon standing, mp 63–65 °C. Recrystallization did not change the melting point. The spectral data follow: NMR (CDCl₃) τ 2.5–3.4 (m, 8 H, aromatic), 7.43 (s, 2 H, CH₂), 7.84 (s, 2 H, CO₂CH₂), 8.93 (s, 6 H, CH₃); IR (film) 5.73 μ ; high-resolution MS (calcd for C₂₁H₂₄O₄, *m/e* 340.167 45). *m/e* 340.167 63

Anal. Calcd for C₂₁H₂₄O₄: C, 74.08; H, 7.11. Found: C, 74.10; H, 7.12.

Methyl 5,5-Bis(*m*-methoxyphenyl)-3,3-dimethyl-4-pentenoate. A solution of 928 mg (2.89 mmol) of 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone, 1.00 g (18.0 mmol) of potassium hydroxide, and 30 mL of 95% ethanol was refluxed for 2.0 h, concentrated in vacuo, taken up in ether and water, and cautiously acidified to a methyl orange end point with concentrated hydrochloric acid avoiding relactonization. The ether layer, after washing with water and brine, was dried and concentrated in vacuo to afford 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid as a colorless oil. The oil in 100 mL of ether was treated with diazomethane generated from 2.12 g of Du Pont EXR-101 as described by Moore and Reed.²³ After 2 h at room temperature, excess diazomethane was blown off with nitrogen and the solution concentrated to 845 mg of essentially pure methyl 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoate as a pale yellow oil. The NMR showed (CDCl₃) τ 2.3–3.5 (m, 8 H, aromatic), 6.31 (s, 6 H, OCH₃), 6.43 (s, 3 H, CO₂CH₃), 7.52 (s, 3 H, CH₂ and OH), 9.18 (s, 6 H, CH₃).

The oil in 20.0 mL of dimethyl sulfoxide was heated at 175–180 °C for 2.5 h, diluted with water, ether extracted, washed with water and brine, dried, and concentrated to 752 mg of a yellow oil. The oil was chromatographed on a 3.0 × 48 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether; 5, 4% ether; 6, 5% ether; 7, 6% ether. Fractions 6–7 afforded the methyl 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-4-pentenoate as 494 mg (55.9%) of colorless oil. The spectral data follow: NMR (CDCl₃) τ 2.5–3.5 (m, 8 H, aromatic), 3.90 (s, 1 H, vinyl), 6.26 (s, 3 H, OCH₃), 6.30 (s, 3 H, OCH₃), 6.40 (s, 3 H, OCH₃), 7.70 (s, 2 H, CH₃O₂CCH₂), 8.93 (s, 6 H, CH₃); IR (CHCl₃) 5.76 μ ; high-resolution MS *m/e* 354.181 97 (calcd for C₂₂H₂₆O₄; *m/e* 354.183 10).

Anal. Calcd for C₂₂H₂₆O₄: C, 74.54; H, 7.40. Found: C, 74.68; H, 7.42.

1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene.

To a solution of *m*-methoxyphenylmagnesium bromide, prepared from 1.01 g (5.40 mmol) of *m*-bromoanisole and 0.134 g (5.50 mg-atoms) of magnesium, in 15.0 mL of tetrahydrofuran was added 480 mg (1.35 mmol) of methyl 5,5-bis(*m*-methoxyphenyl)-3,3-dimethyl-4-pentenoate in 10.0 mL of tetrahydrofuran. The solution was refluxed for 2.5 h, quenched with 0.54 mL of saturated aqueous ammonium chloride, diluted with ether, dried, and filtered through Celite. Concentration in vacuo yielded 919 mg of essentially pure 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-4-penten-1-ol as a yellow oil. The NMR showed (CDCl₃) τ 2.4–3.5 (m, 16 H, aromatic), 3.90 (s, 1 H, vinyl), 6.33 (s, 12 H, OCH₃), 7.25 (s, 1 H, OH), 7.43 (s, 2 H, CH₂), 9.15 (s, 6 H, CH₃).

Without further purification this oil was refluxed for 16 h with 1.30 mL (14.3 mmol) of phosphorus oxychloride in 25.0 mL of pyridine, diluted with water, ether extracted, washed with 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to 753 mg of yellow oil. The oil was chromatographed on a 1.2 × 46.5 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 75-mL fractions were collected: fraction 1, hexane; 2–4 2% ether in hexane; 5–7, 3% ether; 8–10, 4% ether. Fractions 4–7 yielded 557 mg (79.3%) of 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene as a colorless oil which crystallized upon standing, mp 72.5–74 °C. Recrystallization from hexane did not change the melting point. The spectral data follow: NMR (CDCl₃) τ 2.5–3.4 (m, 16 H, aromatic), 4.03 (s, 2 H, vinyl), 6.23 (s, 6 H, OCH₃), 6.40 (s, 6 H, OCH₃), 8.97 (s, 6 H, CH₃); UV (EtOH) λ_{\max} 262 nm (ϵ 17 700); high-resolution MS *m/e* 520.262 01 (calcd for C₃₅H₃₆O₄, *m/e* 520.261 35).

Anal. Calcd for C₃₅H₃₆O₄: C, 80.73; H, 6.97. Found: C, 80.52; H, 7.13.

1,1-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene.

To a solution of *m*-methoxyphenylmagnesium bromide, prepared from 4.00 g (21.3 mmol) of *m*-bromoanisole and 0.610 g (25.0 mg-atoms) of magnesium in 30 mL of tetrahydrofuran, was added 1.57 g (5.30 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-butenate² in 15 mL of tetrahydrofuran. The solution was refluxed for 1.0 h, then stirred at room temperature for 2.0 h. The solution was treated with 2.13 mL of saturated aqueous ammonium chloride, diluted with ether, then filtered through Celite. The filtrate was concentrated in vacuo to yield 2.39 g (94.3%) of essentially pure 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol as a colorless oil. The NMR showed (CDCl₃) τ 2.5–3.5 (m, 18 H, aromatic), 3.83 (s, 1 H, vinyl), 6.33 (s, 6 H, OCH₃), 7.07 (s, 1 H, OH), 7.60 (s, 2 H, CH₂), 9.17 (s, 6 H, CH₃).

Without further purification a portion of the oil (2.33 g, 4.87 mmol) was refluxed in 45.0 mL of pyridine with 2.23 mL (24.4 mmol) of phosphorus oxychloride for 3.0 h. The solution was poured onto ice and ether extracted. The ether extract was washed with water, 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 2.07 g of a pale yellow oil. The crude product was chromatographed on a 2.8 × 43 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column; 500-mL fractions were collected. Fractions 1–2, hexane; 3–5, 1% ether in hexane. Fractions 4–5 yielded 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as a colorless oil, 1.82 g (81.2%). The spectral data follow: NMR (CDCl₃) τ 2.5–3.5 (m, 18 H, aromatic), 3.96 (s, 2 H, vinyl), 6.22 (s, 3 H, OCH₃), 6.33 (s, 3 H, OCH₃), 8.93 (s, 6 H, CH₃); MS (70 eV) *m/e* (rel abundance) 461 (3.9), 460 (13), 417 (13), 294 (22), 293 (100), 280 (22), 264 (12), 233 (19), 227 (18), 220 (18), 167 (24), 165 (17), 105 (10), 91 (19), 77 (6); UV (EtOH) λ_{\max} 250 nm (ϵ 19 600); high-resolution MS *m/e* 460.240 61 (calcd for C₃₃H₃₂O₂; *m/e* 460.240 22).

Anal. Calcd for C₃₃H₃₂O₂: C, 86.04; H, 7.01. Found: C, 86.30; H, 7.08.

1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol.

To a solution of *p*-chlorophenylmagnesium bromide, prepared from 2.60 g (13.6 mmol) of *p*-chlorobromobenzene and 0.363 g (14.9 mg-atoms) of magnesium, in 30.0 mL of tetrahydrofuran was added 0.94 g (3.20 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate² in 20.0 mL of tetrahydrofuran. The solution was refluxed for 1.0 h, quenched by the addition of 1.40 mL of saturated aqueous ammonium chloride, diluted with ether, dried, and filtered through

Celite. The filtrate was concentrated in vacuo to 1.69 g of yellow oil. The oil was chromatographed on a 3.5 \times 36 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fractions 1–2, hexane; 3–4, 5% ether in hexane. Fractions 3–4 afforded 1.20 g (79.7%) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol as a colorless solid, mp 111–112 °C. Recrystallization from hexane yielded 1.12 g (74.7%) of colorless crystals: mp 114–115.5 °C; NMR (CDCl₃) τ 2.5–3.2 (m, 18 H, aromatic), 3.93 (s, 1 H, vinyl), 7.07 (s, 1 H, OH), 7.48 (s, 2 H, CH₂), 9.17 (s, 6 H, CH₃); IR (CHCl₃) 2.77, 2.84 μ ; high-resolution MS *m/e* 486.151 87 (calcd for C₃₁H₂₈Cl₂O, *m/e* 486.151 72).

Anal. Calcd for C₃₁H₂₈Cl₂O: C, 76.37; H, 5.78. Found: C, 76.51; H, 5.96.

1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. An improved preparation utilized the POCl₃–pyridine elimination of 500 mg (1.03 mmol) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol at pyridine reflux for 20 h to give (84.5%) 408 mg of diene, mp 90–91 °C (lit.³ 89–90.5 °C). The spectral data were identical with those reported previously,³ additionally: UV (EtOH) λ_{\max} 252 nm (ϵ 26 200).

1,1-Bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. To a solution of *p*-chlorophenylmagnesium bromide, prepared from 2.60 g (13.6 mmol) of *p*-chlorobromobenzene and 0.363 g (14.9 mg-atoms) of magnesium, in 40.0 mL of tetrahydrofuran was added 1.00 g (3.40 mmol) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoate in 20.0 mL of tetrahydrofuran. The solution was refluxed for 1.0 h, quenched by addition of 1.3 mL of saturated aqueous ammonium chloride, diluted with ether, dried, and filtered through Celite. The filtrate was concentrated in vacuo to 2.10 g of yellow oil. The oil was chromatographed on a 3.0 \times 35 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 250-mL fractions were collected: fractions 1–2, hexane; 3–4, 4% ether in hexane; 5–6, 8% ether; 7–8, 24% ether. Fractions 6–7 yielded 1.25 g (69.3%) of 1,1-bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-penten-1-ol as an essentially pure colorless oil. The NMR showed τ 2.5–3.5 (m, 16 H, aromatic), 4.06 (s, 1 H, vinyl), 6.33 (s, 3 H, OCH₃), 6.36 (s, 3 H, OCH₃), 6.87 (s, 1 H, OH), 7.53 (s, 2 H, CH₂), 9.18 (s, 6 H, CH₃).

Without further purification the oil was refluxed in 20.0 mL of pyridine with 2.08 mL (22.9 mmol) of phosphorus oxychloride for 10.5 h. The solution was poured onto ice, ether extracted, washed with 10% hydrochloric acid, water, and brine, dried, and concentrated in vacuo to 1.19 g of pale yellow oil. The oil was chromatographed on a 3.0 \times 35 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether. Fraction 3 afforded 960 mg (79.4%) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene as a colorless oil which crystallized from isopentane as colorless crystals, 416 mg (34.4%), mp 79–81 °C. The spectral data follow: NMR (CDCl₃) τ 2.5–3.2 (m, 16 H, aromatic), 4.07 (s, 1 H, vinyl), 4.14 (s, 1 H, vinyl), 6.27 (s, 3 H, OCH₃), 6.34 (s, 3 H, OCH₃), 8.97 (s, 6 H, CH₃); MS (70 eV) *m/e* (rel abundance) 532 (2), 531 (8), 530 (18), 529 (10), 528 (28), 293 (38), 281 (22), 280 (100), 235 (14), 202 (12), 195 (22), 175 (14), 165 (23), 161 (19), 139 (13), 135 (35), 121 (43), 115 (15), 105 (14), 97 (13), 91 (25), 81 (32), 77 (22); UV (EtOH) λ_{\max} 263 nm (ϵ 30 100), 247 (33 300); high-resolution MS *m/e* 528.162 61 (calcd for C₃₃H₃₀Cl₂O₂, *m/e* 528.162 28).

Anal. Calcd for C₃₃H₃₀Cl₂O₂: C, 74.83; H, 5.71. Found: C, 74.64; H, 5.90.

1,1-Bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-penten-1-ol. The aryllithium used in this procedure was prepared by the method of Parham.²⁴ At –100 °C a solution of 1.54 g (8.46 mmol) of *p*-bromobenzonitrile in 38.0 mL of tetrahydrofuran with 11.0 mL of hexane was treated with 5.76 mL (1.47 M, in hexane, 8.46 mmol) of *n*-butyllithium solution. The temperature did not rise above –92 °C during the addition. After 10.0 min at –100 °C, a solution of 1.50 g (4.23 mmol) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoate² in 9.0 mL of tetrahydrofuran was added at such a rate that the temperature did not rise above –92 °C. The solution was warmed to room temperature over 3 h, poured into water, ether extracted, washed with water and brine, dried, and concentrated in vacuo to 2.32 g of yellow oil. The oil was chromatographed on a 2.5 \times 50 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fraction 1, 1% ether in hexane; 2, 2% ether; 3, 4% ether; 4, 6% ether;

5–7, 8% ether; 8–14, 10% ether. Fractions 10–14 yielded 1.18 g of yellow oil. The oil was chromatographed on a 2.7 \times 71 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fraction 1, hexane; 2, 5% ether in hexane; 3–10, 10% ether in hexane. Fractions 7–10 yielded 0.789 g (50.1%) of 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-penten-1-ol as a pale yellow solid, mp 145–149 °C. Recrystallization from chloroform–hexane gave 594 mg (37.7%) of colorless crystals: mp 151–152 °C; NMR (CDCl₃) τ 2.50 (s, 8 H, aromatic), 2.98, 3.22 (AB q, 8 H, *J* = 9 Hz, aromatic), 4.03 (s, 1 H, vinyl), 6.24 (s, 6 H, OCH₃), 6.47 (s, 1 H, OH), 7.43 (bs, 2 H, CH₂), 9.15 (s, 6 H, CH₃); IR (CHCl₃) 2.77, 2.86 μ ; high-resolution *m/e* 528.240 87 (calcd for C₃₅H₃₂N₂O₃, *m/e* 528.241 38).

Anal. Calcd for C₃₅H₃₂N₂O₃: C, 79.51; H, 6.10. Found: C, 79.33; H, 6.23.

1,1-Bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 530 mg (1.00 mmol) of 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-penten-1-ol, 1.84 mL (20.0 mmol) of phosphorus oxychloride, and 25.0 mL of pyridine was refluxed for 16 h, poured onto ice, and ether extracted. Washing with water, 10% hydrochloric acid, saturated sodium bicarbonate, and brine, followed by drying and concentration in vacuo, afforded 459 mg of a yellow oil. The oil was chromatographed on a 1.7 \times 104 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500 mL fractions were collected: fraction 1, 1% ether in hexane; 2, 2% ether; 3, 3% ether; 4–9, 4% ether. Fractions 7–9 yielded 293 mg of yellow oil. This oil was chromatographed on a preparative, thick layer, silica gel plate (40.0 g, E. Merck GF-254) eluted with ether–hexane; the second of three bands yielded 141 mg (27.7%) of pale yellow solid, which crystallized upon standing. Recrystallization from chloroform–hexane gave 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene as colorless crystals, mp 163–165 °C. The spectral data follow: NMR (CDCl₃) τ 2.2–3.4 (m, 16 H, aromatic), 3.95 (s, 1 H, vinyl), 4.27 (s, 1 H, vinyl), 6.27 (s, 3 H, OCH₃), 6.33 (s, 3 H, OCH₃), 8.95 (s, 6 H, CH₃); IR (CHCl₃) 4.28 μ ; MS (70 eV) *m/e* (rel abundance) 510 (100), 495 (40), 479 (3), 467 (9), 293 (12), 280 (15), 255 (17), 240 (12), 227 (26), 149 (19), 135 (11), 121 (27), 83 (11); UV (EtOH) λ_{\max} 265 nm (ϵ 30 500), 248 (31 700), 236.5 (33 500); high-resolution MS *m/e* 510.231 09 (calcd for C₃₆H₃₀N₂O₂, *m/e* 510.230 72).

Anal. Calcd for C₃₆H₃₀N₂O₂: C, 82.31; H, 5.92. Found: C, 82.15; H, 5.72.

Exploratory Photolysis of 1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 551 mg (1.06 mmol) of 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene in 500 mL of anhydrous *tert*-butyl alcohol was purged with purified nitrogen²⁵ for 1.0 h before and during the photolysis. The solution was irradiated for 45 min through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure lamp. Concentration in vacuo afforded 578 mg. A portion of this oil (537 mg) was chromatographed on a 3.0 \times 174 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 40-mL fractions were collected: fractions 1–65, 0.25% ether in hexane; 66–95, 0.50% ether; 96–235, 0.75% ether; 236–345, 1% ether; 346–365, 1.25% ether; 366–425, 1.50% ether; 426–540, 1.75% ether; 541–825, 2.00% ether. Fractions 600–710 yielded 238 mg of pale yellow oil. Fractions 715–825 yielded 244 mg of a yellow oil (mass balance 94.1%).

Fractions 600–710 were chromatographed on a 1.2 \times 45 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether; 5, 4% ether. Fraction 5 gave 205 mg of a colorless oil, spectroscopically identical with 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene.

Fractions 715–825 were chromatographed on a 1.2 \times 44 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether; 5–6, 4% ether. Fraction 6 yielded 208 mg of 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane as a colorless oil. The spectral data follow: NMR (CDCl₃) τ 2.5–3.5 (m, 16 H, aromatic), 4.23 (d, 1 H, *J* = 11 Hz, vinyl), 6.20 (s, 3 H, OCH₃), 6.23 (s, 3 H, OCH₃), 6.26 (s, 3 H, OCH₃), 6.30 (s, 3 H, OCH₃), 7.84 (d, 1 H, *J* = 11 Hz, cyclopropyl), 8.73 (s, 3 H, CH₃), 9.00 (s, 3 H, CH₃); MS (70 eV) *m/e* (rel abundance) 520 (100), 505 (5), 478 (15), 477 (43), 399 (15), 371 (19), 370 (19), 294 (15), 293 (22), 281 (23), 280

(87), 279 (15), 278 (21), 265 (37), 251 (22), 228 (23), 227 (82), 149 (21), 135 (17), 121 (39); UV (EtOH) λ_{\max} 277 nm (ϵ 19 500), 283 (sh) (17 800); high-resolution MS m/e 520.259 30 (calcd for $C_{35}H_{36}O_4$, m/e 520.261 35).

Anal. Calcd for $C_{35}H_{36}O_4$: C, 80.73; H, 6.97. Found: C, 80.71; H, 7.01.

Exploratory Photolysis of 1,1-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 452 mg (0.98 mmol) of 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 500 mL of anhydrous *tert*-butyl alcohol was purged using purified nitrogen.²⁵ The solution was irradiated for 60 min through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure lamp. The solution was concentrated in vacuo to 518 mg of yellow oil. The oil was chromatographed on a 3.0×175 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 40-mL fractions were collected: fractions 1–35, hexane; 36–725, 0.25% ether in hexane; 726–825, 0.50% ether; 826–900, 1.0% ether. Fractions 410–560 yielded 195 mg of yellow oil. Fractions 590–760 yielded 89 mg of yellow oil. Fractions 775–900 afforded 145 mg of a yellow oil (mass balance 94.9%).

Fractions 410–560 were chromatographed on a 1.2×45 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether. Fractions 3–4 yielded 142 mg of colorless oil which was spectroscopically identical with 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene.

Fractions 590–760 were chromatographed on a 1.2×32 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether. Fractions 3–4 afforded 79 mg of 2,2-dimethyl-1,1-diphenyl-3-(1,1-bis(*m*-methoxyphenyl)vinyl)cyclopropane as a colorless oil. The spectral data follow: NMR ($CDCl_3$) τ 2.4–3.5 (m, 18 H, aromatic), 4.30 (d, 1 H, $J = 11$ Hz, vinyl), 6.16 (s, 3 H, OCH_3), 6.28 (s, 3 H, OCH_3), 7.86 (d, 1 H, $J = 11$ Hz, cyclopropyl), 8.70 (s, 3 H, CH_3), 9.03 (s, 3 H, CH_3); IR ($CHCl_3$) 3.24, 3.27, 3.28, 3.30, 3.32, 3.40, 3.41, 3.42, 3.48, 3.52, 6.27, 6.34, 6.75, 6.89, 7.00, 7.22, 7.27, 7.64, 7.81, 8.10, 8.34, 8.55, 8.68, 8.99, 9.29, 9.60, 10.09, 11.05, 11.42, 14.37 μ ; MS (70 eV) m/e (rel abundance) 460 (81), 417 (23), 294 (19), 293 (84), 280 (31), 265 (18), 233 (55), 228 (16), 227 (65), 221 (21), 220 (73), 205 (27), 167 (33), 165 (34), 121 (26), 105 (23), 91 (34), 85 (65), 83 (100); UV (EtOH) λ_{\max} 274 nm (ϵ 15 800); high-resolution MS m/e 460.240 61 (calcd for $C_{33}H_{32}O_2$, m/e 460.240 23).

Anal. Calcd for $C_{33}H_{32}O_2$: C, 86.04; H, 7.01. Found: C, 85.99; H, 7.08.

Fractions 775–900 were chromatographed on a 1.2×31 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 3% ether. Fractions 3–4 afforded 127 mg of 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane as a colorless oil. The spectral data follow: NMR ($CDCl_3$) τ 2.3–3.4 (m, 18 H, aromatic), 4.26 (d, 1 H, $J = 11$ Hz, vinyl), 6.23 (s, 3 H, OCH_3), 6.33 (s, 3 H, OCH_3), 7.83 (d, 1 H, $J = 11$ Hz, cyclopropyl), 8.70 (s, 3 H, CH_3), 9.02 (s, 3 H, CH_3); IR ($CHCl_3$) 3.23, 3.25, 3.27, 3.29, 3.32, 3.40, 3.42, 3.48, 3.52, 6.27, 6.32, 6.71, 6.80, 6.89, 6.95, 7.17, 7.24, 7.59, 7.76, 7.97, 8.20, 8.61, 8.86, 8.95, 9.30, 9.59, 10.03, 10.65, 11.03, 11.44, 11.63, 14.43, 15.08 μ ; MS (70 eV) m/e (rel abundance) 460 (84), 417 (27), 294 (32), 293 (100), 280 (49), 265 (20), 233 (18), 227 (20), 191 (19), 167 (51), 165 (14), 121 (19), 91 (24); UV (EtOH) λ_{\max} 276 nm (ϵ 19 000), 283 (17 300); high-resolution MS m/e 460.240 61 (calcd for $C_{33}H_{32}O_2$, m/e 460.240 23).

Anal. Calcd for $C_{33}H_{32}O_2$: C, 86.04; H, 7.01. Found: C, 86.20; H, 7.09.

Exploratory Photolysis of 1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 445 mg (0.949 mmol) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 255 mL of anhydrous *tert*-butyl alcohol was purged with purified nitrogen.²⁵ The solution was irradiated for 1.0 h through a 2-mm Corex filter using a Hanovia 450-W medium-pressure lamp. The solution was concentrated to 451 mg of yellow oil. The oil was chromatographed on a 2.8×187 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 40-mL fractions were collected: fractions 1–450, hexane. Fractions 1–159 gave 20 mg of yellow oil. Fractions 160–223 gave 185 mg of yellow

oil. Fractions 224–254 afforded 33 mg of yellow oil. Fractions 255–350 gave 138 mg of yellow solid, mp 140–165 °C. Fractions 351–450 afforded 27 mg of a colorless oil (mass balance 90.6%).

Fractions 1–159 were a trace of unidentifiable oil.

Fractions 160–223, recrystallized from ethanol, gave 79 mg of colorless, crystalline solid, mp 90–91 °C (lit.³ 89–90.5 °C), which was identified as 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene.

Fractions 224–254 were apparently a mixture of secondary photolysis products, not readily identifiable.

Fractions 255–350, recrystallized from pentane, yielded 88 mg of 1,1-bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane as a colorless, crystalline solid, mp 169–170 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.4–3.0 (m, 18 H, aromatic), 4.43 (d, 1 H, $J = 10$ Hz, vinyl), 7.94 (d, 1 H, $J = 10$ Hz, cyclopropyl), 8.73 (s, 3 H, CH_3), 9.07 (s, 3 H, CH_3); IR ($CHCl_3$) 3.25, 3.27, 3.32, 3.40, 3.42, 3.48, 6.28, 6.73, 6.94, 7.15, 8.28, 9.00, 9.16, 9.72, 9.86, 10.78, 12.30 μ ; UV (EtOH) λ_{\max} 268 nm (ϵ 19 000), 234 (29 000); high-resolution MS m/e 468.138 81 (calcd for $C_{31}H_{26}Cl_2$, m/e 468.141 15).

Anal. Calcd for $C_{31}H_{26}Cl_2$: C, 79.30; H, 5.59. Found: C, 79.08; H, 5.74.

Fractions 351–450 crystallized from isopentane to yield 2,2-dimethyl-1,1-diphenyl-3-(2,2-bis(*p*-chlorophenyl)vinyl)cyclopropane as a colorless solid, mp 171–173.5 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.5–3.2 (m, 18 H, aromatic), 4.42 (d, 1 H, $J = 10$ Hz, vinyl), 7.95 (d, 1 H, $J = 10$ Hz, cyclopropane), 8.74 (s, 3 H, CH_3), 9.02 (s, 3 H, CH_3); IR ($CHCl_3$) 3.25, 3.27, 3.32, 3.42, 3.48, 6.27, 6.72, 6.93, 7.22, 8.26, 9.00, 9.18, 9.89, 10.75, 11.05, 11.61, 12.05 μ ; UV (EtOH) λ_{\max} 273 nm (ϵ 18 000); high-resolution MS m/e 468.140 63 (calcd for $C_{31}H_{26}Cl_2$, m/e 468.141 15).

This material was spectroscopically identical with that obtained synthetically (vide infra).

Exploratory Photolysis of 1,1-Bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 416 mg (0.787 mmol) of 1,1-bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene in 200 mL of anhydrous *tert*-butyl alcohol was purged with purified nitrogen. The solution was irradiated for 3.0 h through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure lamp. The solution was concentrated in vacuo to 449 mg of yellow oil. The oil was chromatographed on a 2.8×187 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 40-mL fractions were collected: fractions 1–50, hexane; 51–380, 0.5% ether in hexane. Fractions 230–295 afforded 236 mg of colorless oil. Fractions 296–380 gave 144 mg of a yellow solid, mp 206–217 °C (mass balance 91.3%).

Fractions 230–295 were spectroscopically identical with 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene.

Fractions 296–380 were recrystallized from ethyl acetate to 80 mg of 1,1-bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane as a colorless solid, mp 225–226 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.4–3.3 (m, 16 H, aromatic), 4.59 (d, 1 H, $J = 10$ Hz, vinyl), 6.15 (s, 3 H, OCH_3), 6.22 (s, 3 H, OCH_3), 8.07 (d, 1 H, $J = 10$ Hz, cyclopropyl), 8.88 (s, 3 H, CH_3), 9.05 (s, 3 H, CH_3); IR ($CHCl_3$) 3.30, 3.32, 3.41, 3.48, 5.53, 6.23, 6.37, 6.63, 6.73, 6.83, 6.94, 7.16, 7.27, 7.79, 8.06, 8.20, 8.48, 8.55, 8.98, 9.17, 9.70, 9.87, 10.80, 12.02 μ ; MS (70 eV) m/e (rel abundance) 528 (4), 515 (2), 513 (3), 293 (5), 280 (7); UV (benzene) λ_{\max} 283 nm; high-resolution MS m/e 528.162 42 (calcd for $C_{33}H_{30}Cl_2O_2$, m/e 528.162 28).

Anal. Calcd for $C_{33}H_{30}Cl_2O_2$: C, 74.83; H, 5.71. Found: C, 74.67; H, 5.82.

Exploratory Photolysis of 1,1-Bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 338 mg (0.663 mmol) of 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene in 200 mL of anhydrous *tert*-butyl alcohol was purged with purified nitrogen²⁵ for 1 h before and during the photolysis. The solution was irradiated for 45.0 min through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure lamp. The solution was concentrated in vacuo affording 393 mg of yellow oil. The oil was chromatographed on a 1.8×96 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 500-mL fractions were collected: fraction 1, hexane; 2, 2% ether in hexane; 3, 4% ether; 4, 6% ether; 5, 8% ether; 6, 10% ether; 7, 12% ether; 8–10, 14% ether; 11, 20% ether; 12, 40% ether; 13, ether.

Fraction 8 afforded 179 mg of yellow solid, mp 163–165 °C. Fractions 9–10 gave 106 mg of yellow solid, mp 101–102 °C. Fractions 11–13 afforded 28 mg of yellow oil (mass balance 92.6%).

Fraction 8, recrystallized from chloroform–hexane, gave 161 mg of a colorless solid, mp 164–165 °C, which was spectroscopically identical with 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene.

Fractions 9–10 were chromatographed on a 1.2 × 34 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 5% ether in hexane; 3, 7.5% ether; 4, 10% ether; 5, 12.5% ether; 6, 15% ether; 7, 17.5% ether. Fractions 6–7 afforded 101 mg of 1,1-bis(*p*-cyanophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane as a colorless solid, mp 101–102 °C. Recrystallization did not raise the melting point. The spectral data follow: NMR (CDCl₃) τ 2.2–3.4 (m, 16 H, aromatic), 4.62 (d, 1 H, J = 10 Hz, vinyl), 6.12 (s, 3 H, OCH₃), 6.22 (s, 3 H, OCH₃), 7.79 (d, 1 H, J = 10 Hz, cyclopropyl), 8.72 (s, 3 H, CH₃), 9.02 (s, 3 H, CH₃); IR (CHCl₃) 3.26, 3.30, 3.32, 3.36, 3.50, 3.52, 4.30, 6.24, 6.63, 6.83, 6.94, 7.12, 7.25, 7.78, 8.05, 8.20, 8.28, 8.49, 8.55, 9.03, 9.73, 9.82, 10.87, 11.39 μ ; MS (70 eV) m/e (rel abundance) 510 (100), 495 (40), 479 (8), 467 (24), 293 (36), 281 (22), 280 (47), 278 (17), 265 (16), 255 (24), 240 (12), 241 (12), 228 (10), 227 (42), 226 (11), 221 (12), 175 (12), 161 (19), 149 (53), 135 (44), 121 (39), 116 (14); UV (EtOH) λ_{\max} 272 nm (ϵ 22 300), 250 (43 000); high-resolution m/e 510.230 58 (calcd for C₃₅H₃₀N₂O₂, m/e 510.230 72).

Anal. Calcd for C₃₅H₃₀N₂O₂: C, 82.31; H, 5.92. Found: C, 82.24; H, 6.07.

Fractions 11–13 could not be further characterized.

3,3'-Dimethoxybenzophenone Hydrazone. A solution of 1.00 g (4.13 mmol) of 3,3'-dimethoxybenzophenone,²⁶ 1.03 g (20.7 mmol) of hydrazine hydrate, and 13.0 mL of *n*-butyl alcohol was refluxed for 22 h, poured into water, and ether extracted. The ether was washed with water and brine, dried, and concentrated in vacuo to 1.02 g (96.8%) of pale yellow oil, which crystallized when cooled. The pasty solid was sublimed, under aspirator pressure, to 716 mg (67.9%) of 3,3'-dimethoxybenzophenone hydrazone as a colorless, crystalline solid, mp 52–54 °C. The spectral data follow: NMR (CDCl₃) τ 2.4–3.3 (m, 8 H, aromatic), 4.3–4.7 (bs, 2 H, NH₂), 6.18 (s, 3 H, OCH₃), 6.21 (s, 3 H, OCH₃); IR (film) 2.93, 3.04, 3.11, 3.26, 3.32, 3.37, 3.40, 3.44, 3.47, 3.52, 6.29, 6.34, 6.73, 6.83, 6.87, 6.99, 7.51, 7.58, 7.76, 7.88, 8.00, 8.20, 8.48, 8.55, 8.63, 8.73, 9.25, 9.35, 9.54, 10.08, 10.15, 11.43, 12.33, 12.80, 13.69, 13.94, 14.26, 14.47 μ ; MS (70 eV) m/e (rel abundance) 257 (18), 256 (100), 255 (32), 242 (8), 241 (14), 240 (18), 225 (16), 135 (18), 123 (18), 108 (24), 92 (20), 77 (28); high-resolution MS m/e 256.121 28 (calcd for C₁₅H₁₆N₂O₂, m/e 256.121 17).

Anal. Calcd for C₁₅H₁₆N₂O₂: C, 70.28; H, 6.30. Found: C, 70.49; H, 6.14.

3,3-Bis(*m*-methoxyphenyl)-4,4-dimethylcyclopropanecarboxylic Acid. A mixture of 3.00 g (11.7 mmol) of 3,3'-dimethoxybenzophenone hydrazone, 5.06 g (23.4 mmol) of yellow mercuric oxide, 1.04 mL of saturated potassium hydroxide in ethanol, 1.67 g (11.8 mmol) of anhydrous sodium sulfate, and 25.0 mL of ether was stirred at room temperature for 6.0 h. The mixture was filtered through glass wool, concentrated in vacuo, dissolved in pentane, filtered through glass wool, and concentrated in vacuo in an acid-washed flask. To bis(*m*-methoxyphenyl)diazomethane as a purple oil was added 25.0 mL of ethyl 3,3-dimethylacrylate. The solution was heated at 55–60 °C for 261 h, then vacuum distilled under aspirator pressure to 70 °C. The 3.91 g of residual oil was washed with pentane; the pentane was concentrated in vacuo to 3.40 g of yellow oil. The oil was refluxed in 150 mL of 95% ethanol with 1.12 g (20.0 mmol) of potassium hydroxide for 1.5 h, concentrated in vacuo, and partitioned between water and ether. The ether was dried and concentrated to 3.07 g of yellow oil. The oil was refluxed in 150 mL of 95% ethanol with 2.24 g (40.0 mmol) of potassium hydroxide for 13.0 h, concentrated in vacuo, dissolved in water, acidified with concentrated hydrochloric acid to methyl orange end point, and ether extracted. The ether was washed with water and brine, dried, and concentrated in vacuo to 871 mg of yellow oil. Trituration with and recrystallization from hexane afforded 676 mg (17.9%) of 3,3-bis(*m*-methoxyphenyl)-4,4-dimethylcyclopropanecarboxylic acid as a colorless, crystalline solid, mp 168–169.5 °C. Recrystallization from ether–pentane gave 191 mg (5.05%) of colorless crystals, mp 172–172.5 °C. The spectral data follow: NMR (CDCl₃) τ 2.7–3.5 (m, 8 H, aromatic), 6.23 (s, 6 H, OCH₃), 7.72 (s, 1 H, cyclopropyl), 8.50 (s, 3 H, CH₃), 8.90 (s, 3 H, CH₃); IR (CHCl₃)

2.7–4.3 (broad band), 3.32, 3.39, 3.48, 3.53, 5.88, 6.27, 6.33, 6.71, 6.85, 7.00, 7.19, 7.27, 7.63, 7.78, 8.20, 8.63, 9.00, 9.17, 9.58, 9.74, 10.64, 11.43, 14.49, 15.04 μ ; MS (70 eV) m/e (rel abundance) 327 (14), 326 (64), 312 (15), 311 (75), 294 (11), 293 (54), 281 (23), 280 (37), 266 (12), 265 (37), 227 (10), 203 (11), 173 (39), 159 (20), 121 (21); high-resolution MS m/e 326.151 88 (calcd for C₂₀H₂₂O₄, m/e 326.151 80).

Anal. Calcd for C₂₀H₂₂O₄: C, 73.58; H, 6.80. Found: C, 73.47; H, 6.94.

3,3-Bis(*p*-chlorophenyl)-4,4-dimethylcyclopropanecarboxylic Acid. A solution of 3.07 g (11.7 mmol) of bis(*p*-chlorophenyl)diazomethane²⁷ in 25.0 mL of ethyl 3,3-dimethylacrylate was heated at 55 °C for 156 h, then vacuum distilled under aspirator pressure to 85 °C. The residual oil was washed with hexane; the hexane was concentrated in vacuo to 3.10 g of crude ethyl 3,3-bis(*p*-chlorophenyl)-4,4-dimethylcyclopropanecarboxylate as a yellow oil. The oil was refluxed for 16 h in 75 mL of methanol with 6.56 g (117 mmol) of potassium hydroxide, concentrated in vacuo, dissolved in water, acidified with concentrated hydrochloric acid to methyl orange end point, and ether extracted. The ether was washed with water and brine, dried, and concentrated to 1.40 g of yellow oil. The oil was chromatographed on a 3.8 × 34 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 250-mL fractions were collected: fractions 1–2, 10% ether in hexane; 3–4, 20% ether; 5, 30% ether. Fractions 4–5 yielded 496 mg (12.7%) of 3,3-bis(*p*-chlorophenyl)-4,4-dimethylcyclopropanecarboxylic acid as a colorless solid, mp 183–184 °C. Recrystallization from hexane gave 433 mg (11.1%) of colorless crystals, mp 184–185 °C. The spectral data follow: NMR (CDCl₃) τ 0.8 (bs, 1 H, CO₂H), 2.80 (s, 4 H, aromatic), 2.85 (s, 4 H, aromatic), 7.77 (s, 1 H, cyclopropyl), 8.55 (s, 3 H, CH₃), 8.92 (s, 3 H, CH₃); IR (CHCl₃) 2.9–3.7 (broad band), 3.27, 3.34, 3.37, 3.42, 5.87, 6.30, 6.95, 7.10, 7.22, 7.55, 7.67, 7.86, 8.12, 8.30, 8.86, 9.02, 9.67, 10.105, 10.56, 10.83, 11.26, 11.75, 11.93 μ ; MS (70 eV) m/e (rel abundance) 336 (3), 334 (5), 321 (2), 319 (4), 301 (7), 299 (15), 289 (8), 288 (12), 275 (4), 273 (4), 255 (4), 253 (10), 41 (100); high-resolution MS m/e 334.054 02 (calcd for C₁₈H₁₆Cl₂O₂, m/e 334.052 73).

Anal. Calcd for C₁₈H₁₆Cl₂O₂: C, 64.47; H, 4.81. Found: C, 64.62; H, 5.04.

2,2-Dimethyl-1,1-diphenyl-3-(2,2-bis(*p*-chlorophenyl)vinyl)cyclopropane. Using a modification of the general method of Zimmerman and Cotter,³ 4,4-diphenyl-5,5-dimethylcyclopropanecarboxylic acid³ was transformed into 2,2-dimethyl-1,1-diphenyl-3-(2,2-bis(*p*-chlorophenyl)vinyl)cyclopropane. A colorless, crystalline solid, mp 175–177 °C, was isolated in 34.5% overall yield. The spectral data were identical with those of the material obtained as the minor photoproduct from direct irradiation of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (vide supra).

Anal. Calcd for C₃₁H₂₆Cl₂: C, 79.30; H, 5.59. Found: C, 79.61; H, 5.65.

Characterization of 1,1-Bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane. A solution²⁸ of 100 mg (0.268 mmol) of dicyclohexyl-18-crown-6, 40.2 mg (0.254 mmol) of potassium permanganate, and 21.0 mg (0.040 mmol) of 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane in 15.0 mL of benzene was stirred at room temperature 60 h, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with 10% aqueous sodium hydroxide and brine, dried, and concentrated in vacuo to 91 mg of colorless oil. The oil was chromatographed on a 1.2 × 45 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 50-mL fractions were collected: fractions 1–2, hexane; 3–4, 1% ether in hexane; 5–6, 2% ether; 7–8, 3% ether; 9–10, 4% ether, 11–12, 5% ether. Fractions 9–10 yielded 4.9 mg (76%) of colorless oil, spectroscopically identical with 3,3'-dimethoxybenzophenone. Fractions 11–12 yielded 7.2 mg of colorless oil which was spectroscopically identical with 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane. The 10% aqueous sodium hydroxide was acidified to methyl orange end point with concentrated hydrochloric acid, ether extracted, washed with water and brine, dried, and concentrated to 11.7 mg of colorless oil. The oil was chromatographed on a 1.2 × 45 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 50-mL fractions were collected: fraction 1, hexane; 2, 2% ether in hexane; 3, 4% ether, 4, 6% ether; 5, 8% ether; 6, 10% ether; 7, 12% ether; 8, 14% ether; 9, 16%

ether; 10, 18% ether; 11, 20% ether; 12, 24% ether; 13, 28% ether; 14, 32% ether; 15, 40% ether; 16, 50% ether; 17, 75% ether. Fractions 15–17 afforded 10.7 mg of colorless oil which crystallized from hexane as 5.9 mg (68%) of colorless solid, mp 168–169 °C. The solid was spectroscopically identical with 3,3-bis(*m*-methoxyphenyl)-4,4-dimethylcyclopropanecarboxylic acid (vide supra).

Characterization of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane. A solution²⁸ of 100 mg (0.268 mmol) of dicyclohexyl-18-crown-6, 40.2 mg (0.254 mmol) of potassium permanganate, and 21.6 mg (0.047 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane in 15 mL of benzene was stirred at room temperature for 95 h, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with water, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to 100.2 mg of yellow oil. The oil was chromatographed on a 1.2 × 32 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1–3, hexane; 4–5, 1% ether in hexane; 6–7, 2% ether; 8–9, 3% ether; 10–11, 10% ether; 12–13, 20% ether; 14–15, 40% ether. Fractions 6–7 afforded 6.3 mg of colorless oil spectroscopically identical with 2,2-dimethyl-1,1-diphenyl-3-(2,2-bis(*m*-methoxyphenyl)vinyl)cyclopropane. Fraction 8–9 afforded 5.4 mg (67%) of a colorless oil which was spectroscopically identical with 3,3'-dimethoxybenzophenone. Fractions 14–15 gave 25.9 mg of colorless oil which crystallized from hexane yielding 6.5 mg (74%) of colorless solid, mp 225–231 °C. Recrystallization from benzene-hexane afforded 5.3 mg (60%) of colorless crystals, mp 232–235 °C (lit.¹⁹ 232–234 °C), which were spectroscopically identical with 3,3-diphenyl-4,4-dimethylcyclopropanecarboxylic acid.

Characterization of 1,1-Bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. A solution²⁸ of 100 mg (0.268 mmol) of dicyclohexyl-18-crown-6, 40.2 mg (0.254 mmol) of potassium permanganate, and 17.7 mg (0.038 mmol) of 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane in 15 mL of benzene was stirred for 92.5 h at room temperature, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with saturated aqueous sodium bicarbonate, water, and brine, dried, and concentrated in vacuo to a yellow oil. The oil was chromatographed on a 1.2 × 33 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fractions 1–3, hexane; 4–5, 0.25% ether in hexane; 6–7, 0.5% ether; 8–9, 1% ether; 10–11, 3% ether; 12–13, 6% ether; 14–15, 12% ether; 16–17, 20% ether; 18–19, 40% ether. Fractions 6–7 afforded 4.1 mg (90%) of a colorless solid, mp 42–44 °C. Sublimation at 65 °C under aspirator pressure yielded 2.6 mg (57%) of colorless crystals, mp 45.5–47.5 °C (lit.²² 49 °C), which were spectroscopically identical with benzophenone. Fractions 8–10 gave 6.3 mg of colorless oil, spectroscopically identical with 1,1-bis(*m*-methoxyphenyl)-2,2-dimethyl-3,3-(1,1-diphenylvinyl)cyclopropane. Fractions 18–19 yielded 20.1 mg of colorless oil which crystallized from hexane as 6.2 mg (76%) of colorless solid, mp 168.5–170 °C, whose spectral data were identical with those of 3,3-bis(*m*-methoxyphenyl)-4,4-dimethylcyclopropanecarboxylic acid (vide supra).

Characterization of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-bis(*p*-chlorophenyl)vinyl)cyclopropane. A solution²⁸ of 19.7 mg (0.053 mmol) of dicyclohexyl-18-crown-6, 8.4 mg (0.053 mmol) of potassium permanganate, and 5.0 mg (0.011 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-bis(*p*-chlorophenyl)vinyl)cyclopropane in 2.0 mL of benzene was stirred at room temperature for 38 h, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with water and brine, dried, and concentrated in vacuo to 12.4 mg of yellow oil. The oil was chromatographed on a 4.7 × 20 cm, 10.0-g silica gel thick layer plate (E. Merck, GF-254), eluted twice with 5% ether in hexane. Collection of the most mobile band yielded 2.0 mg (80%) of a colorless solid, mp 120–141 °C. Sublimation at 95–110 °C at aspirator pressure gave 0.7 mg (28%) of a colorless solid, mp 145–148 °C (lit.²² 147–148 °C). This material was spectroscopically identical with 4,4'-dichlorobenzophenone.

Characterization of 1,1-Bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. A solution²⁸ of 197 mg (0.530 mmol) of dicyclohexyl-18-crown-6, 83.7 mg (0.530 mmol) of potassium permanganate, and 50.0 mg (0.106 mmol) of 1,1-bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane in 20.0 mL of ben-

zene was stirred at room temperature for 38 h, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with water and brine, dried, and concentrated in vacuo to 137.1 mg of yellow oil. The oil was chromatographed on a 1.2 × 48 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fractions 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 5% ether; 5, 10% ether; 6, 20% ether; 7, 40% ether; 8, 60% ether. Fraction 3 afforded 18.0 mg (93%) of a colorless oil, which was molecularly distilled at 65 °C under aspirator pressure, to yield 14.5 mg (75%) of benzophenone as colorless crystals, mp 47–48 °C (lit.²² 49 °C).

Fractions 7–8 gave 20.4 mg (60%) of a colorless oil which was spectroscopically identical with 3,3-bis(*p*-chlorophenyl)-4,4-dimethylcyclopropanecarboxylic acid (vide supra).

Characterization of 1,1-Bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane. A solution²⁸ of 288 mg (0.77 mmol) of dicyclohexyl-18-crown-6, 122 mg (0.77 mmol) of potassium permanganate, and 51.2 mg (0.096 mmol) of 1,1-bis(*p*-chlorophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane in 20.0 mL of benzene was stirred at room temperature for 43 h, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with 15% aqueous potassium chloride and brine, dried, and concentrated in vacuo to 84.0 mg of oily solid. The paste was chromatographed on a 1.2 × 33 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 2% ether; 4, 4% ether; 5, 6% ether; 6, 8% ether; 7, 10% ether; 8, 15% ether; 9, 20% ether; 10, 25% ether; 11, 30% ether. Fractions 5–6 afforded 19.4 mg (83%) of a colorless, crystalline solid, mp 143–144 °C (lit.²² 146 °C), which was spectroscopically identical with 4,4'-dimethoxybenzophenone.

Fractions 9–11 gave 11.8 mg (38%) of a colorless solid, mp 184–185 °C, which was spectroscopically identical with 3,3-bis(*p*-chlorophenyl)-4,4-dimethylcyclopropanecarboxylic acid (vide supra).

Characterization of 1,1-Bis(*p*-cyanophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane. A solution of 152.4 mg (0.410 mmol) of dicyclohexyl-18-crown-6, 64.7 mg (0.410 mmol) of potassium permanganate, and 41.8 mg (0.082 mmol) of 1,1-bis(*p*-cyanophenyl)-2,2-dimethyl-3-(2,2-bis(*p*-methoxyphenyl)vinyl)cyclopropane in 22.0 mL of benzene was stirred for 48 h at room temperature, then filtered through Celite. The precipitate was washed with 10% hydrochloric acid and ether. The filtrate was ether extracted, washed with 10% aqueous sodium hydroxide and brine, dried, and concentrated in vacuo to 163.2 mg of a yellow oil. The oil was chromatographed on a 1.2 × 32 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column, and 125-mL fractions were collected: fraction 1, hexane; 2, 1% ether in hexane; 3, 3% ether; 4, 4% ether; 5, 5% ether; 6, 6% ether; 7, 7% ether. Fractions 5–7 afforded 17.4 mg (88%) of colorless solid, mp 144–145 °C (lit.²² 146 °C), which was spectroscopically identical with 4,4'-dimethoxybenzophenone.

The 10% aqueous sodium hydroxide wash was acidified to methyl orange end point with concentrated hydrochloric acid, ether extracted, washed with water and brine, dried, and concentrated in vacuo to 41.6 mg of yellow oil. The oil was chromatographed on a 1.2 × 48 cm, slurry packed, silicic acid (Mallinckrodt, Silicar CC-7, 100–200 mesh) column, and 125-mL fractions were collected: fraction 1, 10% ether in hexane; 2, 30% ether; 3, 60% ether; and 4, ether. Fractions 3–4 yielded 12.8 mg (49%) of colorless solid, mp 105–110 °C. Recrystallization from chloroform-hexane afforded 5.5 mg (21%) of a colorless solid, mp 236–238 °C (lit.³ 236–238 °C), whose spectral data were identical with those of 3,3-bis(*p*-cyanophenyl)-4,4-dimethylcyclopropanecarboxylic acid.

Photolysis Equipment for Quantum Yield Determination. Quantum yields were performed on the "black box"⁷ or on the microoptical bench.⁷ Light output was measured by a digital actinometer⁸ calibrated by ferrioxalate actinometry.²⁹

For microbench runs, the monochromator inlet slit was set at 5.4 mm and the exit slit at 3.0 mm, to give a band pass of 22 nm at half-peak height.

For "black box" runs the two filter solutions used were filter A (a) 1.0 M cobalt sulfate in 5% sulfuric acid, (b) 2.0 M nickel sulfate in 5% sulfuric acid, (c) 0.1 M cupric sulfate in 5% sulfuric acid (this combination gave a transmission maximum at 317 nm (28% trans-

mission) and was opaque above 356 nm and below 282 nm); filter B (a) 0.19 M nickel sulfate in 10% sulfuric acid, (b) 1.0 M cobalt sulfate in 5% sulfuric acid, (c) 0.66 M stannous chloride in 15% hydrochloric acid (this combination gave a transmission maximum at 356 nm (19% transmission) and was opaque above 390 nm and below 330 nm). All runs were purged with purified nitrogen²⁵ for 1.0 h before and during each run.

Direct Quantum Yields. 1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. All runs were performed on the microoptical bench apparatus, in 42.0 mL of anhydrous *tert*-butyl alcohol, irradiated at 310 nm. All runs were analyzed by high-pressure liquid chromatography using two 1 ft \times 1/8 in. columns, packed with 10- μ porous silica 3-cyanopropyl-coated silica gel beads,³⁰ and eluting with 15% ether in anhydrous hexane with 0.05% methanol. Benzophenone was used as an internal standard.

Run 1. Starting diene used, 0.0360 mmol; 0.0288 mEinstein absorbed; vinylcyclopropane formed, 0.003 16 mmol; Φ = 0.110; 8.8% conversion.

Run 2. Starting diene used, 0.0330 mmol; 0.0158 mEinstein absorbed; vinylcyclopropane formed, 0.002 46 mmol; Φ = 0.156; 7.3% conversion.

Run 3. Starting diene used, 0.0431 mmol; 0.0314 mEinstein absorbed; vinylcyclopropane formed, 0.003 93 mmol; Φ = 0.125; 9.1% conversion.

Run 4. Starting diene used, 0.0500 mmol; 0.0114 mEinstein absorbed; vinylcyclopropane formed, 0.002 34 mmol; Φ = 0.204; 4.7% conversion.

Run 5. Starting diene used, 0.0358 mmol; 0.00514 mEinstein absorbed; vinylcyclopropane formed, 0.001 20 mmol; Φ = 0.234; 3.4% conversion.

Direct Quantum Yields. 1,1-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. All runs were performed on the microoptical bench apparatus, in 42.0 mL of anhydrous *tert*-butyl alcohol, irradiated at 300 nm. All runs were analyzed by high-pressure liquid chromatography using three 1 ft \times 1/8 in. columns, packed with 10- μ silica gel beads³⁰ and eluting with 2.5% ether in hexane. Benzophenone was used as an internal standard.

Run 1. Starting diene used, 0.0276 mmol; 0.0251 mEinstein absorbed; major vinylcyclopropane formed, 0.001 82 mmol; Φ_{major} = 0.073; minor vinylcyclopropane formed, 0.001 41 mmol; Φ_{minor} = 0.056; 11.8% conversion.

Run 2. Starting diene used, 0.0407 mmol; 0.0317 mEinstein absorbed; major vinylcyclopropane formed, 0.002 33 mmol; Φ_{major} = 0.073; minor vinylcyclopropane formed, 0.001 96 mmol; Φ_{minor} = 0.062; 10.5% conversion.

Run 3. Starting diene used, 0.0270 mmol; 0.0311 mEinstein absorbed; major vinylcyclopropane formed, 0.002 20 mmol; Φ_{major} = 0.071; minor vinylcyclopropane formed, 0.001 87 mmol; Φ_{minor} = 0.060; 15.0% conversion.

Run 4. Starting diene used, 0.0358 mmol; 0.0124 mEinstein absorbed; major vinylcyclopropane formed, 0.001 01 mmol; Φ_{major} = 0.081; minor vinylcyclopropane formed, 0.000 84 mmol; Φ_{minor} = 0.068; 5.2% conversion.

Direct Quantum Yields. 1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. All runs were performed on the microoptical bench in 42.0 mL of anhydrous *tert*-butyl alcohol. Run 1 was irradiated at 295 nm while the remaining runs were irradiated at 300 nm. All runs were analyzed by manual integration of the expanded vinyl region of NMR spectra obtained from the 270-MHz Fourier transform instrument; 600 full-width spectra were collected. An internal standard of 1,1-bis(*p*-methoxyphenyl)ethylene was used.

Run 1. Starting diene used, 0.0421 mmol; 0.0146 mEinstein absorbed; major vinylcyclopropane formed, 0.001 75 mmol; Φ_{major} = 0.120; minor vinylcyclopropane formed, 0.000 45 mmol; Φ_{minor} = 0.031; 5.2% conversion.

Run 2. Starting diene used, 0.104 mmol; 0.0280 mEinstein absorbed; major vinylcyclopropane formed, 0.003 01 mmol; Φ_{major} = 0.107; minor vinylcyclopropane formed, 0.000 77 mmol; Φ_{minor} = 0.027; 3.6% conversion.

Run 3. Starting diene used, 0.116 mmol; 0.0521 mEinstein absorbed; major vinylcyclopropane formed, 0.005 63 mmol; Φ_{major} = 0.108; minor vinylcyclopropane formed, 0.001 71 mmol; Φ_{minor} = 0.033; 6.3% conversion.

Run 4. Starting diene used, 0.113 mmol; 0.0400 mEinstein absorbed; major vinylcyclopropane formed, 0.004 93 mmol; Φ_{major} =

0.123; minor vinylcyclopropane formed, 0.001 00 mmol; Φ_{minor} = 0.025; 4.4% conversion.

Direct Quantum Yields. 1,1-Bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. All runs were performed on the microoptical bench, in 42.0 mL of anhydrous *tert*-butyl alcohol, irradiated at 310 nm. All runs were analyzed by high-pressure liquid chromatography using three 1 ft \times 1/8 in. columns packed with 10- μ porous silica gel beads,³⁰ eluting with 1.0% ether in hexane. The internal standard was 4-chlorobenzophenone.

Run 1. Starting diene used, 0.0462 mmol; 0.0393 mEinstein absorbed; vinylcyclopropane formed, 0.003 63 mmol; Φ = 0.092; 7.9% conversion.

Run 2. Starting diene used, 0.0287 mmol; 0.0148 mEinstein absorbed; vinylcyclopropane formed, 0.001 47 mmol; Φ = 0.100; 5.1% conversion.

Run 3. Starting diene used, 0.0319 mmol; 0.007 14 mEinstein absorbed; vinylcyclopropane formed, 0.000 83 mmol; Φ = 0.116; 2.6% conversion.

Direct Quantum Yields. 1,1-Bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. All runs were performed on the microoptical bench, in 42.0 mL of anhydrous *tert*-butyl alcohol, irradiated at 310 nm. All runs were analyzed by high-pressure liquid chromatography using a 1 ft \times 1/8 in. column, packed with 10- μ porous silica gel beads eluting with 6.5% ether in hexane.³⁰ 4,4'-Dimethoxybenzophenone was used as an internal standard.

Run 1. Starting diene used, 0.0173 mmol; 0.008 56 mEinstein absorbed; vinylcyclopropane formed, 0.000 41 mmol; Φ = 0.048; 2.4% conversion.

Run 2. Starting diene used, 0.0238 mmol; 0.009 71 mEinstein absorbed; vinylcyclopropane formed, 0.000 47 mmol; Φ = 0.048; 2.0% conversion.

Run 3. Starting diene used, 0.0287 mmol; 0.0323 mEinstein absorbed; vinylcyclopropane formed, 0.001 35 mmol; Φ = 0.042; 4.7% conversion.

Direct Quantum Yields. 1,1,5,5-Tetrakis(*p*-cyanophenyl)-3,3-dimethyl-1,4-pentadiene. All runs were performed on the microoptical bench, in 42.0 mL of anhydrous *tert*-butyl alcohol, irradiated at 310 nm. All runs were analyzed by high-pressure liquid chromatography using three 1 ft \times 1/8 in. columns, packed with 10- μ porous silica gel beads,³⁰ eluting with 37.5% ether in hexane. The internal standard was 4-hydroxybenzophenone.

Run 1. Starting diene used, 0.0314 mmol; 0.005 59 mEinstein absorbed; vinylcyclopropane formed, 0.001 56 mmol; Φ = 0.28; 5.0% conversion.

Run 2. Starting diene used, 0.0311 mmol; 0.002 52 mEinstein absorbed; vinylcyclopropane formed, 0.000 82 mmol; Φ = 0.33; 2.6% conversion.

Sensitized Quantum Yield. 1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 50.2 mg (0.0965 mmol, 1.29×10^{-3} M) of 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene and 1.20 mL of *m*-methoxyacetophenone² in 75.0 mL of *tert*-butyl alcohol was irradiated in the "black box" apparatus through filter A with 3.25 mEinstein of light. Removal of solvent and sensitizer in vacuo afforded a colorless oil which contained no vinylcyclopropane as shown by NMR analysis. Assuming that 3.0 mg could be detected $\Phi_{\text{sens}} < 1.8 \times 10^{-3}$.

Sensitized Quantum Yield. 1,1-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 49.9 mg (0.108 mmol, 1.44×10^{-3} M) of 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 1.20 mL of *m*-methoxyacetophenone in 75.0 mL of *tert*-butyl alcohol was irradiated in the "black box" apparatus through filter A with 3.35 mEinstein of light. Removal of solvent and sensitizer in vacuo afforded a colorless oil which contained no vinylcyclopropane as shown by NMR analysis. Assuming 3.0 mg could be detected $\Phi_{\text{sens}} < 1.8 \times 10^{-3}$.

Sensitized Quantum Yield. 1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 51.0 mg (0.109 mmol, 1.45×10^{-3} M) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 1.20 mL of *m*-methoxyacetophenone in 75.0 mL of *tert*-butyl alcohol was irradiated in the "black box" apparatus through filter A with 3.55 mEinstein of light. Removal of solvent and sensitizer in vacuo afforded a colorless oil which contained no vinylcyclopropane as shown by NMR analysis. Assuming that 3.0 mg could be detected $\Phi_{\text{sens}} < 1.8 \times 10^{-3}$.

Sensitized Quantum Yield. 1,1-Bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 61.0 mg

Table V. Calculation Results

Compd	E_{SCF}^{Di} , eV	$E_1^{Di} - E_{SCF}^{Di}$, eV	$E_0^{Di} - E_1^{Di}$, eV	$E_1^{Bi} - E_{SCF}^{Di}$, eV	$E_1^{Bi} - E_1^{Di}$, eV	Obsd ^b spectral transition, eV
Di- <i>p</i> -dimethylamino diene 30	-346.737	3.688	4.218	2.400	1.288	3.87 ^c
Tetra- <i>p</i> -methoxy diene 31	-400.899	4.042	4.411	2.516	1.526	4.23 ^c
Di- <i>p</i> -chloro diene 15	-345.784	4.146	4.414	2.631	1.515	4.32 ^c
Di- <i>p</i> -chlorodi- <i>p</i> -methoxy diene 16	-391.839	4.042	4.411	2.573	1.469	4.23, 4.32 ^c
Di- <i>p</i> -methoxy diene 3	-354.844	4.042	4.411	2.527	1.515	4.23 ^c
Di- <i>m</i> -methoxy diene 14	-354.841	3.935	4.344	2.669	1.266	^d
Tetra- <i>m</i> -methoxy diene 13	-400.890	3.935	4.344	2.661	1.274	^d
Tetraphenyl diene 32	-308.787	4.261	4.478	2.622	1.639	4.42 ^c
Di- <i>p</i> -cyano diene 1	-340.996	4.130	4.263	2.447	1.683	4.3 ^e

^a Di = diene; Bi = biradical; subscript 0 = ground state; subscript 1 = excited singlet; subscript SCF = SCF ground state. ^b Spectral transition of the corresponding substituted styrene. ^c Reference 43. ^d Not available. ^e Estimated from UV and emission spectra of a synthetic sample.

(0.115 mmol, 1.53×10^{-3} M) of 1,1-bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene and 1.20 mL of *m*-methoxyacetophenone in 75.0 mL of *tert*-butyl alcohol was irradiated in the "black box" apparatus through filter A with 3.26 mEinsteins of light. Removal of solvent and sensitizer in vacuo afforded a colorless oil which contained no vinylcyclopropane as shown by NMR analysis. Assuming that 3.0 mg could be detected $\Phi_{sens} < 1.7 \times 10^{-3}$.

Sensitized Quantum Yield. 1,1-Bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene. A solution of 55.7 mg (0.109 mmol, 1.45×10^{-3} M) of 1,1-bis(*p*-cyanophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene and 3.20 mL of *m*-methoxyacetophenone in 75.0 mL of *tert*-butyl alcohol was irradiated in the "black box" apparatus through filter A with 3.35 mEinsteins of light. Removal of solvent and sensitizer in vacuo afforded a colorless oil which contained no vinylcyclopropane as shown by NMR analysis. Assuming that 3.0 mg could be detected $\Phi_{sens} < 1.8 \times 10^{-3}$.

Energy Transfer Test and Triplet Quantum Yields. Quenching of Benzophenone Triplets by 1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene and by 1,1-Bis(4-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. The irradiations were carried out on the "black box" apparatus using filter B (330–390 nm). A solution of 0.400 g (2.20 mmol, 2.93×10^{-2} M) of benzophenone and 0.200 g (1.09 mmol, 1.45×10^{-2} M) of benzhydrol in 75.0 mL of *tert*-butyl alcohol was irradiated. Similarly, a solution of 0.400 g of benzophenone, 0.200 g of benzhydrol, and 0.050 g (0.096 mmol, 1.28×10^{-3} M) of 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene in 75.0 mL of *tert*-butyl alcohol and a solution of 0.400 g of benzophenone, 0.200 g of benzhydrol, and 0.050 g (0.107 mmol, 1.43×10^{-3} M) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 75.0 mL of *tert*-butyl alcohol were irradiated. Chromatography of each photomixture on a 2.5×45 cm, silicic acid (Mallinckrodt, Silicar CC-7) column eluting with ether-hexane completely separated the benzopinacol from the other components.

Run 1. No quencher; benzophenone recovered, 0.243 g; benzopinacol, 0.221 mg; $\Phi = 0.241$; 0% quenching.

Run 2. Quencher, 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene; benzophenone, 0.374 g; benzopinacol, 0.037 mg; $\Phi = 0.041$; 83% quenching.

Run 3. Quencher, 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene; benzophenone, 0.371 g; benzopinacol, 0.034 g; $\Phi = 0.041$; 83% quenching.

The diene recovered out of runs 2 and 3 contained less than 5.0 mg of vinylcyclopropane as estimated by NMR. The quantum yield for benzophenone-sensitized photoreaction must be < 0.005 in each case.

Emission Studies. Purification of Solvent. Isopentane and methylcyclohexane were purified by repeated washings with 10% fuming

sulfuric acid until the washings were colorless, refluxed over a saturated potassium permanganate in 10% sulfuric acid solution, washed with water, distilled from phosphorus pentoxide in nitric acid washed glass, passed through a 2.0×80 cm column of alumina containing 10% silver nitrate discarding early and late fractions, and finally distilled in nitric acid washed glass. Solvents prepared in this manner were transparent in the ultraviolet and emission free.

Absolute ethanol, USP grade, was distilled from calcium oxide, through a 1.0-m metal helix packed column. The solvent prepared in this manner was transparent in the ultraviolet and emission free.

Single Photon Counting. The apparatus and procedure have been described in detail previously.¹⁰ The method uses a high-pressure (ca. 80 psi) nitrogen flash lamp with a half-width of ca. 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.¹⁰ Independent studies established³¹ a 32-ps error limit. Experiments were run to a minimum of 1000 counts in the highest channel when collecting at less than 5% of the 25–40 kHz lamp frequency. The 5% factor assures that few double photons are collected. Excitation was in the range 260–300 nm. Optical densities were adjusted to 0.8–2.5 at the excitation wavelengths. 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.

1,1,5,5-Tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene, 3.7 ns, 2.7×10^8 s⁻¹, 14, 6%.

1,1-Bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 4.7 ns, 2.1×10^8 s⁻¹, 10, 13%.

1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 0.85 ns, 1.2×10^9 s⁻¹, 6, 18%.

1,1-Bis(*p*-chlorophenyl)-5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene, 2.6 ns, 3.8×10^8 s⁻¹, 7, 17%.

1,1-Bis(*p*-chlorophenyl)ethylene, 1.0 ns, 1.0×10^9 s⁻¹, 5, 20%.

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. Excitation wavelengths in the range 260–270 nm were used. The magic multipliers were obtained from individual samples by integration of the emission intensity bands

at the two temperatures. Values obtained were as follows: 1,1,5,5-tetrakis(*m*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene, $M = 170$ (3 runs); 1,1-bis(*m*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, $M = 260$ (3 runs); 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, $M = 19$ (2 runs); 1,1-bis(*p*-chlorophenyl)-5,5-(*p*-methoxyphenyl)-3,3-dimethyl-1,4-pentadiene, $M = 68$ (3 runs); 1,1-bis(*p*-chlorophenyl)ethylene, $M = 9.6$ (2 runs).

Calculations. The Pople semiempirical SCF method^{32,33} (complete neglect of differential overlap) was used for closed-shell SCF ground-state calculations. Excited-state energies and wave functions were obtained from configuration interaction that included both singly and doubly excited configurations. For systems of n basis orbitals, all excitations from MO 2 to MO $n - 1$ inclusive were used. Important configurations were selected from this set, as determined by the extent of the perturbations³⁴ on the first two excited states by a representative set of dominant singly excited configurations. Thus, the final secular problem was reduced to under 250 configurations.

Configurations were represented by linear combinations of Slater determinants such that each configuration was an eigenfunction of spin operator S^2 . These are reported by Murrell and McEwen.³⁵ Standard techniques^{36a} for the reduction of many electron integrals then gave general formulas used to calculate matrix elements between configurations.³⁶

Valence state ionization potentials were taken from Hinze and Jaffe,³⁷ except for heteroatoms, where values compiled by Nishimoto³⁸ were used. The Pariser-Parr method³² was used to calculate atomic orbital repulsion integrals.

Resonance integrals were evaluated by the following expression:³⁹

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

where S_{ij} is the overlap integral,⁴⁰ and I_i and I_j are the respective valence state ionization potentials for the orbitals i and j . Only "nearest-neighbor" resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene using a CI calculation that included single and double excitations. Resonance integrals for heteroatoms bonded to carbon were obtained empirically by spectral fitting to suitable compounds.

Standard geometries for starting distyrylmethanes were assumed, based on model compounds reported.⁴¹ Geometries for 1,4-biradical species were extrapolated from a reported INDO calculation with geometry optimization for the ground-state 2-vinylcyclopropylcarbinyl radical.⁴² Our results are listed in Table V. The weakest point of our calculations is an exaggerated weighting of the ground-state configuration.¹⁶ Transition energies using the SCF ground-state configuration as S_0 are included since this minimizes the problem.

Calculations were performed with programs that utilized a PDP-11/T55 computer having 32K 16-bit words core. Direct access to and from two disks (1.2 million words/disk) allowed usage of large matrices encountered in the CI calculations.^{36c}

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References and Notes

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