The Aryl Vinyl Methane Version of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: A series of aryl vinyl methane systems was studied with a view toward comparing the rearrangement with that of divinyl methane counterparts. One remarkable difference is found in the effect of substituents on the excited singlet rearrangement rate. While in tetraaryl-1,3-pentadienes *p*-methoxy substitution inhibits the S_1 rate, in aryl vinyl methanes such para substitution enhances the rate. Another difference is that substitution on the methane carbon is needed for the divinyl methane version but is not for the aryl vinyl type rearrangement; the rate inhibition due to lack of central substitution was measured. A still further difference is a ca. two orders of magnitude S_1 rate inhibition in the rearrangement of phenyl vinyl methanes compared with divinyl methane systems. Our study included a variety of points of mechanistic interest to the di-π-methane rearrangement. The effect of replacing the diphenylvinyl with a styryl group was studied. The S_1 rearrangement rate was found to be fivefold faster with the additional phenyl group present, this comparison utilizing the *trans*-styryl stereoisomer. Similarly, a much more rapid rate of radiationless conversion to ground state is encountered with the extra phenyl group. The *cis*-styryl system was found to give only isomerization to trans isomer and with remarkable efficiency; a rationale is given. SCF-CI calculations on the excited state transformation are described. Our ΔP matrix treatment when applied to the vertical excited state predicts aryl vinyl bridging. Also, the ΔP treatment allows one to ascertain that the aryl moiety remains essentially unexcited during the rearrangement. Diminished rates of aryl-vinyl vs. vinyl-vinyl bridging are derived from the SCF-CI calculations.

Introduction

In our previous study[2] we investigated substituent effects on the divinyl version of the di-π-methane rearrangement.[3] It was of considerable interest to study the aryl vinyl counterpart[3,4] from a quantitative and mechanistic standpoint in order to determine and understand differences between these two versions of the di-π-methane rearrangement. One very elegant study by Hixson[5] has appeared. Our approach was to use our single photon counting capabilities to obtain S_1 rearrangement and decay rates and to use SCF-CI calculations to correlate with the experiment.

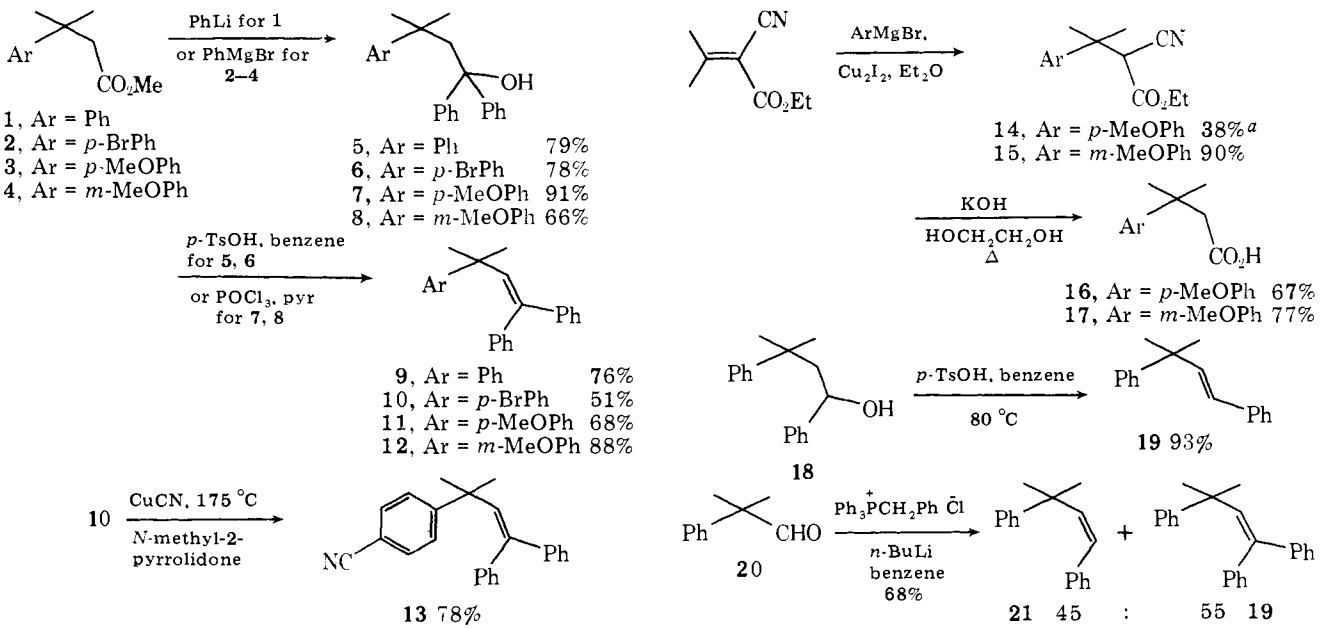
Results

Synthesis of Photochemical Reactants, Exploratory Photolyses, and Product Structure Proofs. Of the eight aryl vinyl methanes studied, the syntheses of seven (**9–13, 19, 21**) are outlined in Chart I; the eighth (i.e., **22**), studied previously by Griffin,[4a] was prepared similarly. These syntheses are described in detail in the Experimental Section.

Exploratory photolyses were run. Arylcyclopropanes were formed by a di-π-methane rearrangement except for cis aryl styryl methane **21,** which underwent only cis-trans isomerization. The mechanism in the case of **22** may be special and is discussed below. The reactions are depicted in eq 1–3.

The structures of the photoproducts derived from synthesis and degradation as well as spectral data. The (note Chart II) 1,1,2-triphenyl-3,3-dimethylcyclopropane (**23**) and the *cis*- and *trans*-1,2-diphenyl-3,3-dimethylcyclopropanes (**38** and

Chart I. Synthesis of Photochemical Reactants



[a] Cu_2I_2 omitted.

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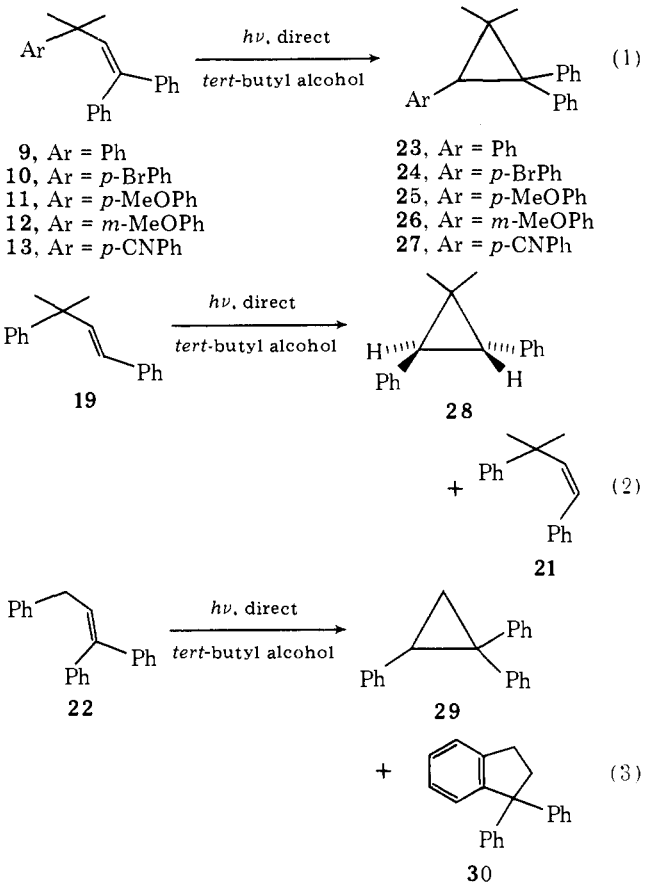


28, respectively) were synthesized. The remaining cyclopropanes (**24–27**) were interconverted with compounds of known structure as detailed in Chart II.

Results. Quantum Yield Determinations. The quantum yields were determined using both the Black Box[6] and semimicro optical bench[6] apparatus we have described previously. We used both standard ferrioxalate actinometry[7] and an electronic actinometer.[8] The precaution was taken in all direct irradiations to have at least two low-conversion (<10%) runs differing in extent of reaction by more than a factor of 2. These runs are listed in Table I. Also, sensitized runs were carried out. *m*-Methoxyacetophenone was used throughout. However, in the case of phenyl vinyl methane **9** we also used benzophenone + benzhydrol. The benzophenone-benzhydrol test[10] led to 93% quenching of benzopinacol formation but no di-π-methane product, thus demonstrating energy transfer without reaction. Similarly, the other sensitized runs led to no di-π-methane rearrangment. These runs also are included in Table I.

Further details of the quantum yield runs are given in the Experimental Section.

Single Photon Counting and Emission Studies. Excited singlet rearrangement rates were needed for correlation with mechanism.[11] These were obtained using our combination of single photon counting with simulated deconvolution[12] coupled with the use of the temperature dependence of fluorescence emission.[12] The details of the technique are given in our original publication and also in a number of subsequent papers utilizing the method.[12,13] Details specific to the present work are given in Table II and the Experimental Section.

Attention should be called to the fact that M is our "magic multiplier" [12] which is given by the ratio of the fluorescence intensity at 77 K to that room temperature, $^1k_{dt}$ is the excited singlet decay rate, and ^1k_r is the rate of excited singlet reaction (i.e., defined as $^1k_r = \phi_r(^1k_{dt})$).

Results. SCF-CI Calculations. In order to understand the many phenomena we encountered in the present and related di-π-methane investigations, we felt that a convenient theoretical treatment of excited states was required. For this we developed an SCF-CI treatment. The Pople-Pariser-Parr method[14] with hybrid orbitals included in the orbital basis set was used for SCF calculations. The SCF wave functions were then used to generate as many as 100 singly and 5050 doubly excited configurations. From these, the important configurations were selected by use of a perturbation approach.[15] In the approach a perturbing configuration was appended to the CI secular matrix comprised of the ground-state configuration and up to 25 of the most important singly excited configurations, and then direct solution of the secular problem gave the state energy lowering due to the perturbing configuration. Each configuration was tested and those giving appreciable energy lowering were retained for the final configuration interaction. Typically ca. 50 singly excited and 200 doubly excited configurations were obtained. The calculations were run on a PDP-11T/55 computer by using the 2.4 million word disk storage as virtual memory. For this a swapping algorithm was developed. Details are given in the Experimental Section.

Owing to the complexity of the aryl vinyl methanes and diradicals, we used the 1,3-diaryl-1-propene moiety and the derived aryl substituted spirocyclopropyldicarbinyl diradical as models. The basis set orbitals are given in Figure 1.

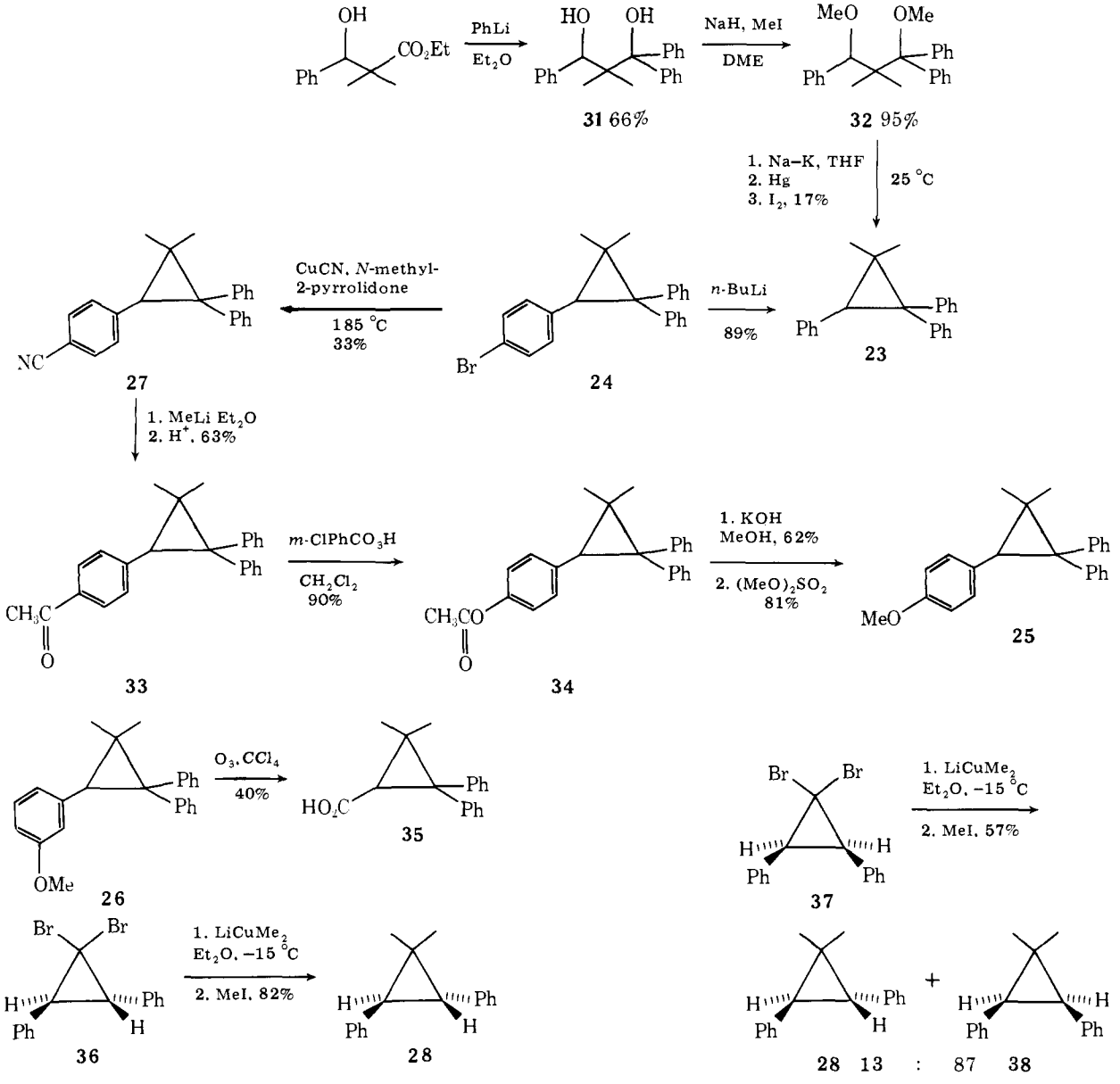
Interpretative Discussion. Questions Posed and to Be Discussed. There are several aspects of interest deriving from the experimental results obtained for the aryl vinyl methane version of the di-π-methane rearrangement. The first is the totally

Table I. Quantum Yields

Reactant	Additive	λ_{irrad}, nm	Φ_r[a]
Phenyl vinyl methane		283	0.036
9	Benzophenone + benzhydrol	333	<0.0024
	m-Methoxyacetophenone	325	<0.0024
p-MeO-phenyl vinyl methane		283	0.058
11	*m*-Methoxyacetophenone	325	<0.0020
m-MeO-phenyl vinyl methane		283	0.024
12	*m*-Methoxyacetophenone	325	<0.000 93
p-CN-phenyl vinyl methane		283	0.044
13	*m*-Methoxyacetophenone	325	<0.0013
Nordimethyl phenyl vinyl		283	0.0074 (**29**), 0.0014 (**30**)
methane **22**	*m*-Methoxyacetophenone	325	<0.00042
Phenyl *trans*-styryl		280	0.40 (0.42[b]) (**28**), 0.065 (**21**)
methane **19**	*m*-Methoxyacetophenone	325	<0.0032 (**28**), 0.50[c] (**21**)
Phenyl *cis*-styryl methane		280	0.40 **19**
21	*m*-Methoxyacetophenone	325	0.45[c] **19**

[a] Each value is the average of several runs. [b] See ref 9. [c] Extrapolated to zero percent conversion.

Chart II. Product Structure Proofs



different pattern of substituent effects compared with that encountered in the divinyl methane version. Thus both *p*-methoxy and *p*-cyano groups accelerate the S_1 rate of reaction in the aryl vinyl methane rearrangement. This contrasts with the divinyl methane cases where *p*-methoxy inhibits the reaction while *p*-cyano accelerates it.[2,16] A second observation is the relatively slow S_1 rates encountered in the present aryl vinyl methane rearrangements compared with the divinyl methane version. A third point is that the diphenylvinyl systems (**9, 11–13**) react considerably more rapidly than the styryl counterparts (for example, **19**). Also the nordimethyl phenyl vinyl methane **22** has an unusually unreactive excited singlet. Finally, it will be necessary to consider if the differences between the *m*- and *p*-methoxyphenyl compounds are characteristic of ground or excited[17] state moieties. Thus there is the intriguing question whether in general the migrating aryl groups are electronically excited or ground state in character during the rearrangement. This will determine whether meta or ortho-para interaction of substituents will be encountered.

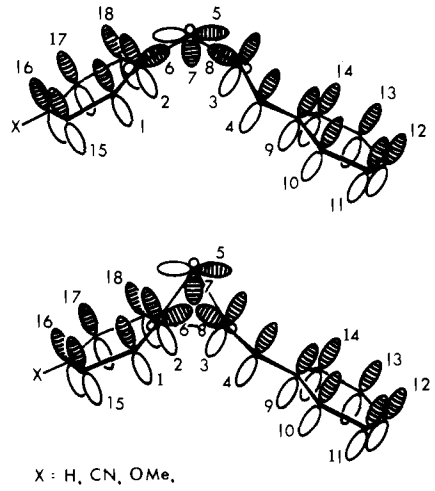


Figure 1. Orbital basis sets used in SCF-CI calculations for aryl vinyl methanes.

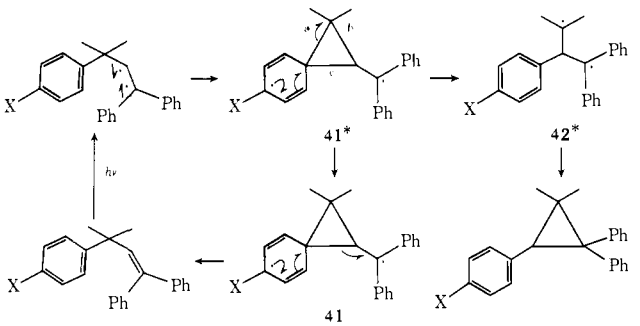
Interpretative Discussion. Rate Inhibition by Loss of Aromaticity in the Excited State. The first striking observation in our results is the finding of lower S_1 rates of reaction compared with our parallel studies[2,13b,16] in the divinyl methane version of the di-π-methane rearrangement. For example, the S_1 rate for phenyl vinyl methane **9** is almost two orders of magnitude slower than for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-penta-

Table II. Emission and Single Photon Counting Results

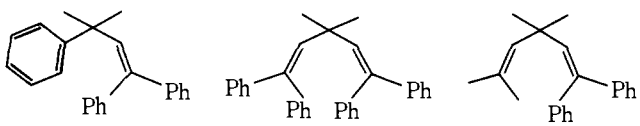
Reactant	λ_{max},[a] nm	M^b	Temp, °K	τ	$^1k_{dt}$, s^{-1}	^1k_r, s^{-1}
Phenyl vinyl methane **9**	310	202	77	3.9 ns	2.6×10^8	
			295	19 ps	5.2×10^{10}	1.9×10^9
p-MeO-phenyl vinyl methane **11**	310	289	77	1.8 ns	5.7×10^8	
			295	6.2 ps	1.6×10^{11}	9.3×10^9
m-MeO-phenyl vinyl methane **12**	310	132	77	2.6 ns	3.8×10^8	
			295	20 ps	5.0×10^{10}	1.2×10^9
p-CN-phenyl vinyl methane **13**	310	281	77	5.9 ns	1.7×10^8	
			295	21 ps	4.8×10^{10}	2.1×10^9
Nordimethyl phenyl vinyl methane **22**	310	202	77	3.9 ns	2.6×10^8	
			295	19 ps	5.2×10^{10}	3.8×10^8
Phenyl *trans*-styryl methane **19**	310	*c*	295	978 ps	1.0×10^9	4.1×10^8

[a] Wavelength of emission maximum [b] Magic multiplier. [c] Not measured.

Chart III. Mechanism for Aryl Migration Involving Loss of Aromaticity



diene (**39**), the divinyl methane counterpart. Another comparison is between phenyl vinyl methane **9** and 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**40**). Part of the rapidity of tetraphenyl diene **39** derives from its considerable stabilization, after excited state bridging, by extra phenyl groups compared with phenyl vinyl methane **9**. The example of hexadiene **40** shows that the aryl vinyl methanes are at the slow end of the rate spectrum. In the case of **9** aromaticity is lost while in **40** a π bond is lost.[18]



9 $k_r = 1.9 \times 10^9\ s^{-1}$ **39** $1.4 \times 10^{11}\ s^{-1}$ **40** $6.9 \times 10^9\ s^{-1}$

Consideration of the qualitative valence bond mechanism in Chart III suggests that a major factor in rate inhibition is loss of aromaticity in the migration of the compounds presently studied. Thus it is the migrating aryl group in **41*** which has lost its aromaticity.

While the inhibition of the S_1 rearrangement rate is attributed to aromaticity loss in the excited state, it still has not been stated whether the aromatic ring destroyed is itself electronically excited. This point will be discussed subsequently.

Finally, it should be noted that the situation is ambivalent. Thus, while photochemistry involves many examples of aryl migrations, a fair number deriving from our own research,[19] evidence is developing that such loss of aromaticity is not without its energetic penalty.[19f]

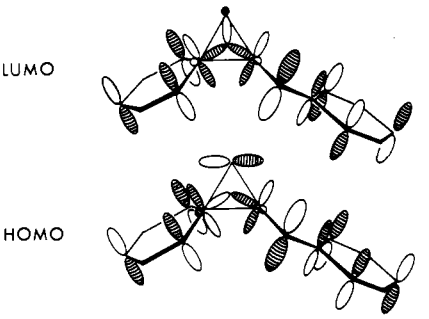


Figure 2. HOMO and LUMO of cyclopropyldicarbinyl diradical species.

Interpretative Discussion. Nature of the Electronic Excitation. As a prelude to utilizing the SCF-CI calculations described above, it is worthwhile to consider the nature of the excitation process in the cyclopropyldicarbinyl species **41***. The predominant configuration, being weighted 90%, is HOMO to LUMO. These two MOs are pictured in Figure 2. Interestingly, we see that the benzylic and spirocyclohexadienyl moieties of these two MOs differ little. However, the LUMO uses a positive combination of the two moieties while the HOMO takes a negative combination. The positive and negative relationships are, of course, determined by the basis set as defined by Figure 1.

Since the two moieties corresponding to ordinary benzylic and pentadienyl radicals are little changed by HOMO to LUMO excitation, we make the preliminary judgment that excitation does not appreciably involve the migrating phenyl group or the benzylic (taken as a model for benzhydryl) group in the cyclopropyldicarbinyl diradical species **41***. This contrasts considerably with the starting vertical excited state where one would expect excitation to be in the diphenylvinyl moiety. This preliminary discussion is reinforced by more quantitative theory below.

Interpretative Discussion. Application of SCF-CI Calculations and the ΔP Concept. We have described in preliminary form[1b] a technique for treating excited state calculations to ascertain which portions of the molecule are electronically excited and how the energy of excitation is partitioned around the molecule. While it is possible to merely compare wave functions for the ground and excited states, a simpler approach defines a ΔP matrix in which each element ΔP_{rt} is given by $P^*_{rt} - P^0_{rt}$. Here the terms P^*_{rt} and P^0_{rt} are the bond orders between atoms r and t for the excited and ground states; the corresponding diagonal terms P_{rr} represent electron densities.

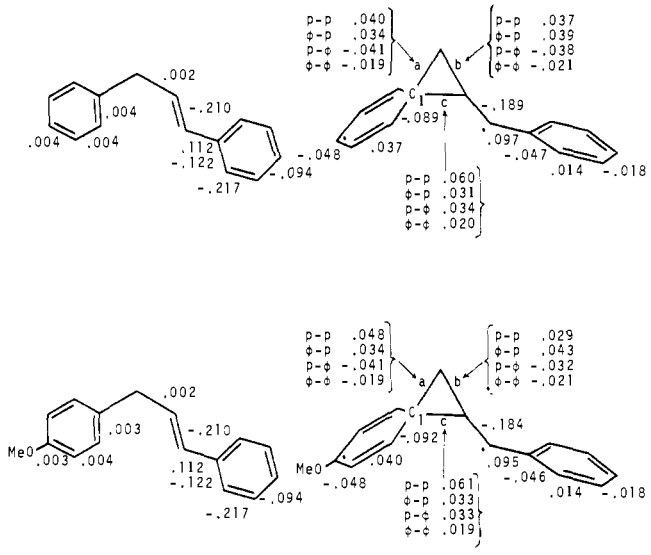


Figure 3. ΔP_{rt} treatment for aryl vinyl methanes and the derived cyclopropyldicarbinyl diradicals.

Where the elements of the ΔP matrix are zero or very small that part of the molecule has an excited state wave function very close or equal to that of the ground state, and that part is unexcited. In portions with very negative or positive elements, the molecule is appreciably perturbed on excitation. A negative ΔP_{rt} element signifies that the excited state has become more antibonding between orbitals r and t and that excitation energy is concentrated at this point. Where the ΔP_{rt} element is positive the excited state has become more bonding than the ground state at this site and energy is withdrawn from this portion.

The first application of this treatment is to the vertical excited state of our aryl vinyl methane reactants. For simplicity, as noted above, throughout a diphenylvinyl group is simulated by a styryl moiety. Figure 3 reveals that the ΔP elements in the aryl groups of the aryl styryl methane model compound are appreciable only in the styryl moiety. This means that the aryl group which migrates in the di-π-methane rearrangement is essentially unexcited in S_1. Also included in Figure 3 are ΔP elements for the corresponding cyclopropyldicarbinyl diradicals. Here the excitation is seen to diffuse throughout the system. The largest ΔP elements are (3,4), (4,9), (1,2), (2,3), and (2,18); here the orbital numbering is defined in Figure 1. Thus the excitation is predominantly concentrated in the cyclopropyldicarbinyl moiety. Relatively little excitation is left in the styryl phenyl group after bridging. Also, except for the ortho-C_1 (i.e., 1,2 and 2,18 overlap), the migrating aromatic ring is only slightly excited.

Another point of interest is that at the onset of bridging, where 2,3 overlap between π moieties becomes appreciable, a positive (more bonding than ground state) ΔP_{23} is found. Excited state bridging is thus enhanced.

Interpretative Discussion. Alternative Approach to Energy Partition. The ΔP treatment is approximate since all bonds do not contribute equally energetically. This is due to differences in hybridization and overlap between different sets of orbitals. Another approach is to use instead the partitioned electronic energy. This is most readily done for a single S_1 configuration derived from SCF calculations. By dissection of the energy of a singlet wave function we obtain the equation

$$\Delta E_{rt}(k\rightarrow m) = [P_{rt,m} - P_{rt,k}]F_{rt}^{AO} + [2P_{rt,m}P_{rt,k} - P_{rr,m}P_{tt,k}]\gamma_{rt} \quad (4)$$

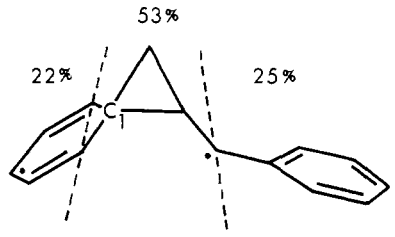


Figure 4. ΔE_{rt} treatment for the cyclopropyldicarbinyl diradical, excitation energy partitioning.

Here the $P_{rt,m}$ and $P_{rt,k}$ are one-electron bond orders in MOs m and k, respectively. $P_{rr,m}$ and $P_{tt,k}$ are one-electron densities for MOs m and k. F_{rt}^{AO} is the SCF matrix element between AOs r and t, and γ_{rt} is the usual repulsion integral. It is important to note that for any pair of different AOs we need to double the energy given, since r may take either orbital assignment and t the other. For diagonal terms this is not done. Summation of $\Delta E_{rt}(k\rightarrow m)$ over all values of r and t leads to the usual[20] total excitation energy for the entire molecule. A parallel dissection of the ground-state energy into localized components is given[20,21] by the equation

$$^0E_{rt} = P_{rt}^{tot}[F_{rt} + H_{rt}] + (1/2)Z_rZ_t\gamma_{rt} \quad (5)$$

Here the total bond order is used, the Z's are core charges, and the last term is excluded for $r = t$. Also we must again double the energy for $r \neq t$. Summation over all values of r and t in eq 5 gives the familiar ground-state energy in the SCF approximation.

We can use dissection of the electronic excitation energies, as given in eq 4; and also we can add the ground-state contributions, as given in eq 5, to give us the total (rather than relative) energy contribution to a molecular portion of an excited state. This gives us an E_{rt} matrix.

The use of the ΔE_{rt}'s from eq 4 is more exact than use of ΔP's but more cumbersome. Since S_1 weights the HOMO to LUMO configuration 90%, we dissect the local energetic contributions to this excitation process in Figure 4. Interestingly, for the cyclopropyldicarbinyl diradical 32% of the excitation energy is localized in the system of six p orbitals of the migrating phenyl group and 22% if we exclude C-1, which is part of the cyclopropyl moiety.

Looking at the local energetic changes in the excited state during the bridging process (i.e., using eq 4 plus 5) we determine that there is an energy rise of 3.63 eV if we use the six phenyl p orbitals plus the sp^2 hybrid at C-1 and observe its change.[22] Were we to inspect only the effect on the ortho-meta-para-meta-ortho system in the same process, we find a 2.35-eV energy rise.[22] This accords with our finding above of diminished S_1 bridging rates where aryl groups are destroyed. Also, we have noted that the S_1 vertical excited state had the excitation localized very heavily in the substituted vinyl moiety and not in the phenyl about to migrate. Thus a ground-state phenyl group is lost in migration.

Interpretative Discussion. Substitution Control of S_1 Rates and Regioselectivity. The first item to be considered is the regioselectivity. Although opening of diradical **41*** may be thought to be necessarily controlled by the demand for rearomatization, nevertheless regioselectivity provides a useful test of our energy dissection treatment using the E_{rt} matrix. In inspecting the cyclopropyldicarbinyl diradical **41*** (note Chart III) from this viewpoint a comparison of bonds a and b reveals that bond a is weaker by 0.52 eV. This includes four different types of overlaps for each bond, namely, p-p, ϕ-ϕ, p-ϕ, and ϕ-p (refer to Figure 3).

Another method of dissection using simple bond orders for the S_1 excited state of the diradical also leads to the same prediction that spiro bond a is weaker than b in all examples

Table III. S_1 Excited State Bond Orders for the Three-Ring of the Cyclopropyldicarbinyl Diradical Derived from 9[a]

Bond a		Bond b		Bond c	
r,t	P_{rt}	r,t	P_{RT}	r,t	P_{rt}
2,5	0.457	3,5	0.490	2,3	0.435
2,7	0.325	3,7	0.352	2,8	0.319
5,6	0.417	5,8	0.415	3,6	0.347
6,7	0.576	7,8	0.578	6,8	0.567
Total	1.775		1.835		1.668

[a] Refer to the basis set orbitals and numbering convention in Figure 1.

Table IV. Calculated Energies of Bridging in the S_1 Excited State for Aryl Vinyl Methanes

Reactant	ΔE, eV	Reactant	ΔE, eV
Phenyl vinyl methane **9**	−1.23	*p*-MeO-phenyl vinyl methane **11**	−1.34
p-CN-phenyl vinyl methane **13**	−1.40	*m*-MeO-phenyl vinyl methane **12**	−1.18
p-Methoxystyryl phenyl methane **47**	−1.04		

studied (phenyl vinyl methane **9**, *p*-methoxyphenyl vinyl methane **11**, *m*-methoxyphenyl vinyl methane **12**, and *p*-cyanophenyl vinyl methane **13**). These are given in Table III for the cyclopropyldicarbinyl diradical derived from phenyl vinyl methane **9**.

Thus, dissection of the electronic energy of the S_1 excited state, either in bond order or energetic terms, can be a useful tool in predicting reactivity. We note, however, that one can conceive of situations where the weakest bond is not the one leading to photochemical product; a case would be in a single step of a complex reaction with this step reversible and the other steps product controlling.

The next aspect needing discussion is the S_1 rate pattern observed (note Table II). It is to be noted that the rate pattern involving *p*-hydrogen, *p*-methoxy, and *p*-cyano is parallel to that observed by Hixson[5] where relative rates were obtained. Furthermore, our absolute rates agree well with the relative rates obtained.

The rates of the aryl vinyl methane rearrangement follow that which one would predict from odd-electron stabilization at the para position of spirocyclopropyldicarbinyl diradical **41*** in Chart III. Thus, *p*-methoxyphenyl vinyl methane **11** and *p*-cyanophenyl vinyl methane **13** both have more rapid S_1 rates than phenyl vinyl methane **9**. SCF-CI calculations of the energy of bridging in the S_1 excited state predict that both the *p*-cyano and *p*-methoxy substituted phenyl vinyl methanes react more exothermically than the unsubstituted case. However, these two substituted compounds are predicted to have similar S_1 rates with the *p*-cyano case being slightly faster than *p*-methoxyphenyl vinyl methane; note Table IV. Actually, *p*-methoxyphenyl vinyl methane **11** has a faster rate than the *p*-cyano compound experimentally. Thus, the calculations are qualitatively correct for predicting the rate enhancement with para substitution.

The *m*-methoxyphenyl vinyl methane **12** is an interesting example since a priori it might have shown either ground-state migratory aptitude behavior or excited-state characteristics. As a result of excited state meta transmission[17] it should show enhanced reactivity if this moiety were appreciably excited during migration. On the other hand, if relatively unexcited, simple resonance reasoning showing little interaction of odd-electron density with the meta position predicts an S_1 rate not too different from the phenyl vinyl analogue. Our discussion above notes that the migrating aryl group is unexcited in the vertical excited state of the aryl vinyl methane and, furthermore, remains relatively unexcited during migration. Thus, our SCF-CI calculations predict an S_1 rate of reaction slightly slower than that of the unsubstituted analogue in accord with observation.

One interesting point bears on the bisnordimethyl vinyl methane **22**. Ordinarily a di-π-methane rearrangement does not proceed without central substitution. However, in the case of the aryl vinyl methane version of the di-π-methane rearrangement, Hixson[23] has shown that the rearrangement does occur. However, this lack of central methyl substitution is not without its energetic penalty as is seen from the rates in Table II, for the S_1 rate is diminished by a factor of 5 compared with the dimethyl relative (i.e., **9**). The same effect has previously been noted by Hixson.[23] The effect of central substitution may derive from an entropy contribution in which approach of the vinyl and aryl groups is enhanced by methyl crowding. Alternatively it may arise as a result of a diminished probability of opening of bond *a* relative to bond *c* (note Chart III).

Another effect deriving from our work is the diminished rate for styryl aryl methanes compared with diphenyl vinyl reactants (note Table II for rates); the quantum yields are high, however. This diminished rate may derive from decreased diradical stabilization in the bridging process, since a benzylic center is engendered in the bridging process rather than a benzhydryl one, thus affording less bridging energy to be gained.

The high styryl quantum yield relative to the diphenyl vinyl examples may come merely from the slower rate of radiationless decay and longer lifetimes of styryl chromophores compared with diphenylvinyl groups. This is seen in our k_{dt}'s in Table II. A long lifetime for β-*tert*-butylstyrene (9 ns) has been reported by Hixson.[9]

The failure of the *cis*-styryl vinyl methane **21** to rearrange, giving only cis-trans isomerization, may come from the fact that the two phenyl groups would have to approach one another and become cis on a developing three-ring or, alternatively, from a very rapid rate of cis-trans isomerization leading to decay. Thus, in our previous stereochemical studies[24] we noted that cis groups on the vinyl group incorporated into the product three-ring become cis to the π moiety left in the product.

Interpretative Discussion. Vertical Excited State Stabilization as a Factor in Substituent Effects. Finally we are left with an enigma. In the present study we observed a different order of substituent effects on the rate than encountered in previous studies involving divinyl methane systems. In the case of 1,1,5,5-tetraaryl 1,4-pentadienes[2,13b] we found that *p*-cyano substitution enhanced the S_1 rates while *p*-methoxy and especially *p*-dimethylamino diminished the rates. In our present study both electron-donating and -withdrawing substituents enhance the rate. Our present situation is similar to that of divinyl methane systems having cyano or methoxy directly on the vinyl surviving in photoproduct.[25]

The dichotomy is understood by reference to Figure 5. Thus in a photochemical reaction the vertical excited state is the effective reactant whose rate is measured. In the case of di-π-methanes having a common excited diphenylvinyl moiety the rate of bridging is controlled only by the energy demands along this pathway; a reasonable supposition is that the energy of activation will parallel the energy required for complete bridging. The systems presently under study fall into this category since the substituted aryl group is effectively unexcited in the S_1 reactants. The same is true of the methoxyvinyl and cyanovinyl diphenylvinyl methanes[25] (**43** and **44**) since, again, the substituent is not part of the excited chromophore.

In contrast, the tetraaryl 1,4-pentadienes have the substituent as part of the excited chromophore. Thus the starting

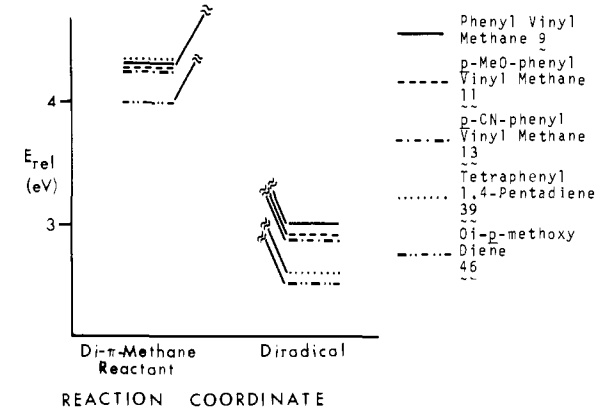
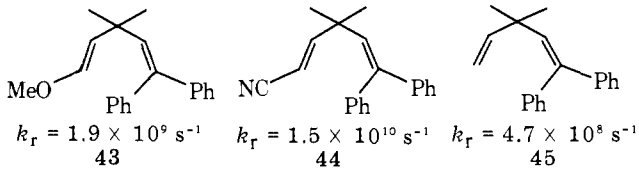


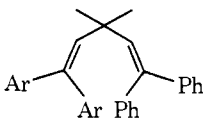
Figure 5. Energetics of bridging.



$k_r = 1.9 \times 10^9\ s^{-1}$ **43** $k_r = 1.5 \times 10^{10}\ s^{-1}$ **44** $k_r = 4.7 \times 10^8\ s^{-1}$ **45**

vertical S_1 energy is not the same for all reactants. With excessive stabilization of the S_1 reactant, one might anticipate a rate lowering. This will be most pronounced where the vertical S_1 stabilization is greater than stabilization at the diradical stage of the reaction. This effect has been encountered in a related study.[2]

We note also that such vertical excited state stabilization accounts nicely for the rate inhibition to phenyl migration observed by Hixson[5] for 1-(*p*-methoxyphenyl)-3-phenyl-1-propene (**47**). Thus our SCF-CI calculations predict a less exothermic energy for bridging in the S_1 excited state for *p*-methoxy substitution on the styryl aromatic ring (note Table IV).



46, Ar = *p*-MeOPh
$k_r = 3.4 \times 10^9\ s^{-1}$

Conclusion

The present study reveals a pattern of substituent effects which can be understood on a theoretical basis. There is promise of enlarging the scope of the di-π-methane rearrangement by improved theoretical understanding. More importantly, some new methods of treating excited state reactivity have proven useful. Significantly, these derive from the philosophy that one can understand mechanistic organic photochemistry on the basis of the excited state surface energetics. Thus, given a choice, an excited state selects the pathway with minimum barriers and maximum exothermicity.[26]

Experimental Section[27]

1,1,3-Triphenyl-3-methyl-1-butanol. Phenyllithium was prepared from 25.5 mL (38.0 g, 0.242 mol) of bromobenzene and 3.54 g (0.510 mol) of lithium in 150 mL of ether and 15.5 g (80.7 mmol) of methyl 3-methyl-3-phenylbutanoate[28] in 100 mL of anhydrous ether was added with stirring at 0 °C. The mixture was then refluxed for 2 h. This was hydrolyzed with saturated ammonium chloride, ether extracted, washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 25.5 g of an orange oil which crystallized upon cooling. Crystallization from 95% ethanol gave 20.1 g (79%) of 1,1,3-triphenyl-3-methyl-1-butanol, mp 59–62 °C. Recrystallization from 95% ethanol gave mp 61–62 °C. The spectral data follow: IR (CCl_4) 2.78, 3.23, 3.26, 3.29, 3.36, 3.41, 3.47, 6.27, 6.71, 6.79, 6.92, 7.23, 7.32, 7.42, 7.80, 8.48, 8.64, 8.93, 9.28, 9.40, 9.70, 9.84, 10.12, 11.04, 11.52, 14.40, 15.43 μ; NMR (CCl_4) τ 2.50–3.10 (m, 15 H, aromatic), 7.20 (s, 2 H, CH_2), 8.45 (s, 1 H, OH), 8.85 (s, 6 H, CH_3).

Anal. Calcd for $C_{23}H_{24}O$: C, 87.29; H, 7.65. Found: C, 87.07; H, 7.59.

1,1,3-Triphenyl-3-methyl-1-butene. A solution of 20.1 g (63.5 mmol) of 1,1,3-triphenyl-3-methyl-1-butanol and 0.40 g of *p*-toluenesulfonic acid in 300 mL of benzene was refluxed with azeotropic removal of water for 5 h. The solution was then washed with saturated sodium carbonate and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford a yellow oil. This was triturated in pentane to give 8.24 g of the desired dehydration product, mp 45–47 °C. The remaining residue was chromatographed on a 94 × 4 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 500-mL fractions to obtain the following chromatogram: fractions 1–3, nil; 4–9, 8.30 g of 1,1,3-triphenyl-3-methyl-1-butene as a crystalline solid. The crystalline material was combined and recrystallized from 95% ethanol to afford 14.4 g (76%) of 1,1,3-triphenyl-3-methyl-1-butene, mp 52–53 °C. The spectral data follow: IR (CCl_4) 3.26, 3.27, 3.31, 3.38, 3.48, 6.27, 6.35, 6.72, 6.86, 6.94, 7.23, 7.35, 8.15, 9.12, 9.32, 9.72, 10.33, 10.78, 11.00, 11.48, 11.83, 13.98, 14.40, 15.57 μ; NMR (CCl_4) τ 2.93 (s, 15 H, aromatic), 3.68 (s, 1 H, vinyl), 8.72 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 250 nm (ε 14 400).

Anal. Calcd for $C_{23}H_{22}$: *m/e* 298.172 15; C, 92.56; H, 7.44. Found: *m/e* 298.171 67; C, 92.70; H, 7.52.

Preparative Direct Irradiation of 1,1,3-Triphenyl-3-methyl-1-butene. A solution of 2.04 g (6.85 mmol) of 1,1,3-triphenyl-3-methyl-1-butene and 700 mL of dry *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.00 h and then irradiated for 6.42 h under vanadous purified nitrogen through a 1-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The photolysate was concentrated and NMR showed ca. 70% conversion to 1,1,2-triphenyl-3,3-dimethylcyclopropane and no absorptions due to other products. The residue was chromatographed on a 125 × 4 cm silica gel column (MCB, grade 62, 60–200 mesh) taking 500-mL fractions. Fractions 1–8, hexane, nil; 9–12, hexane, 552 mg of 1,1,3-triphenyl-3-methyl-1-butene; 13, hexane, 106 mg of a mixture of starting material and cyclopropane photoproduct; 14–16, hexane, 448 mg of 1,1,2-triphenyl-3,3-dimethylcyclopropane; 17–22, 4% ether in hexane, 753 mg of cyclopropane photoproduct. The cyclopropane product from fractions 14–22 was recrystallized from 95% ethanol to give 693 mg, mp 79–80 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.40, 3.48, 6.26, 6.71, 6.92, 7.22, 7.28, 7.62, 8.30, 8.98, 9.28, 9.75, 10.38, 11.05, 14.33, 15.46 μ; NMR ($CDCl_3$) τ 2.50–3.10 (m, 15 H, aromatic), 7.38 (s, 1 H, benzylic cyclopropyl), 8.65 (s, 3 H, CH_3), 8.86 (s, 3 H, CH_3); UV λ_{max} (95% EtOH) 262 nm (ε 1152), 274 (521).

Anal. Calcd for $C_{23}H_{22}$: C, 92.56; H, 7.44. Found: C, 92.63, H, 7.35.

1,1,3-Triphenyl-2,2-dimethyl-1,3-propanediol. Phenyllithium was prepared from 4.84 g (0.696 mol) of lithium and 36.6 mL (54.6 g, 0.348 mol) of bromobenzene in 170 mL of anhydrous ether under nitrogen. A solution of 8.00 g (38.8 mmol) of ethyl 2,2-dimethyl-3-phenyl-3-hydroxypropanoate[29] in 125 mL of anhydrous ether was added dropwise at 0 °C over 20 min under nitrogen with stirring. The mixture was refluxed for 5 h, and then hydrolyzed with saturated ammonium chloride. The mixture was ether extracted, washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give an orange oil. Trituration from chloroform at 0 °C and then crystallization from chloroform gave 8.48 g (65.8%) of diol, mp 206–209 °C. Recrystallization from chloroform brought the mp to 208–210 °C. The spectral data follow: IR ($CHCl_3$) 2.78, 2.90, 3.27, 3.30, 3.34, 6.29, 6.72, 6.82, 6.93, 7.23, 8.67, 9.75, 11.20, 14.35–15.20 μ; NMR ($CDCl_3$) τ 2.84 (s, 15 H, aromatic), 4.73 (s, 1 H, OH), 4.95 (d, J = 3 Hz, 1 H, PhC*H*), 7.57 (d, J = 3 Hz, 1 H, OH), 8.90 (s, 3 H, CH_3), 9.07 (s, 3 H, CH_3).

Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.09; H, 7.28. Found: C, 83.19; H, 7.30.

1,1,3-Triphenyl-2,2-dimethyl-1,3-dimethoxypropane. To a solution of 2.01 g (6.03 mmol) of 1,1,3-triphenyl-2,2-dimethyl-1,3-propanediol and 8.24 mL (18.8 g, 0.132 mol) of methyl iodide in 30 mL of dimethoxyethane (distilled from lithium aluminum hydride) under nitrogen

was added 2.20 g (91.7 mmol) of sodium hydride (56% dispersion in mineral oil ether washed and dried). The mixture was stirred for 1 h and filtered. The filtrate was washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford 2.07 g (95%) of NMR pure diether, mp 107–110 °C and mp 109–110 °C after recrystallization from hexane. The spectral data follow: IR ($CHCl_3$) 3.26, 3.34, 3.40, 3.53, 6.27, 6.71, 6.94, 7.22, 7.33, 7.59, 8.50, 8.68, 8.81, 9.16, 9.33, 9.43, 10.58, 11.13, 11.65, 14.30–15.20 μ; NMR ($CDCl_3$) τ 2.10–2.40 (m, 4 H, aromatic), 2.50–3.00 (m, 11 H, aromatic), 6.00 (s, 1 H, benzylic), 7.00 (s, 3 H, OCH_3), 7.33 (s, 3 H, OCH_3), 8.67 (s, 3 H, CH_3), 9.37 (s, 3 H, CH_3).

Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.18; H, 7.78.

1,1,2-Triphenyl-3,3-dimethylcyclopropane. To a solution of 514 mg (1.43 mmol) of 1,1,3-triphenyl-2,2-dimethyl-1,3-dimethoxypropane in 15 mL of dry tetrahydrofuran (distilled from lithium aluminum hydride and redistilled from the lithium radical anion of naphthalene) was added 0.6 mL of 1:1 (mole ratio) sodium–potassium alloy. The resultant red solution was stirred under nitrogen for 2 h at room temperature, then 1 mL of mercury was added slowly followed by 10 mL of iodine in tetrahydrofuran (100 mg/mL) at which point the mixture became yellow. The mixture was stirred for an additional 0.25 h and then filtered. Ether was added and this was washed with sodium thiosulfate. The wash was ether extracted and the combined ether phases were washed with water, saturated sodium carbonate, and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford 395 mg of an oil. The reaction was repeated using the identical procedure to give a combined total of 800 mg which was chromatographed on a 3 × 43 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 300-mL fractions. The following chromatogram was obtained: fractions 1–6, 244 mg, unidentified; 7–10, 146 mg (17%) of 1,1,2-triphenyl-3,3-dimethylcyclopropane. Fractions 7–10 were recrystallized from 95% ethanol to give colorless, crystalline 1,1,2-triphenyl-3,3-dimethylcyclopropane identical in all respects (IR, NMR, mp 79–80 °C) with that obtained from the direct irradiation of 1,1,3-triphenyl-3-methyl-1-butene. A mixture melting point was undepressed.

3-(*p*-Bromophenyl)-3-methylbutanoic Acid. To a solution of 60 g (1.5 mol) of sodium hydroxide in 300 mL of ice and water was added 37 mL (112 g, 0.70 mol) of bromine with stirring under nitrogen. A solution of 75 mL of 20% sodium hydroxide was added followed by dropwise addition of 40 g (0.157 mol) of 4-(*p*-bromophenyl)-4-methyl-2-pentanone.[30] The mixture was stirred for 21 h at room temperature and then chloroform extracted. Sodium bisulfite was added to decolorize the solution which was then acidified with concentrated hydrochloric acid with cooling. The resulting oil layer was separated and the aqueous phase extracted with dichloromethane. The combined oil and extracts were washed with water and saturated sodium chloride. The extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo to afford 36.6 g of NMR pure crystalline acid. Recrystallization from hexane gave 24.2 g (57.8%), mp 60–61 °C (lit.[30] 60–61 °C). The spectral data follow: IR (CCl_4) 2.92–3.30, 3.37, 3.41, 3.46, 3.60–4.10, 5.87, 6.71, 6.80, 7.10, 7.18, 7.32, 7.62, 7.85, 8.13, 8.41, 8.94, 9.12, 9.36, 9.93, 10.75, 12.30, 12.40, 13.75, 14.00 μ; NMR (CCl_4) τ −1.3 (s, 1 H, $-CO_2H$), 2.64 (d, J = 9.0 Hz, 2 H, aromatic), 2.87 (d, J = 9.0 Hz, 2 H, aromatic), 7.42 (s, 2 H, CH_2), 8.57 (s, 6 H, CH_3).

Methyl 3-(*p*-Bromophenyl)-3-methylbutanoate. To a stirred solution of 19.0 g (73.9 mmol) of 3-(*p*-bromophenyl)-3-methylbutanoic acid in 200 mL of benzene and 0.80 mL of dimethylformamide was added 11.0 mL (18.4 g, 0.154 mol) of thionyl chloride. The solution was stirred at room temperature for 5 h followed by addition of 100 mL of methanol and reflux for 3 h. The reaction mixture was concentrated in vacuo and ether was added. This was washed with water and the wash was ether extracted. The combined extracts were washed with water, saturated sodium carbonate, again with water, and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give an oil. Short-path distillation gave 16.9 g (84%) of analytically pure ester, bp 108 °C (0.75 mm). The spectral data follow: IR (CCl_4) 3.23, 3.28, 3.36, 3.45, 5.75, 6.28, 6.69, 6.78, 6.95, 7.14, 7.30, 7.40, 7.51, 8.30, 8.55, 8.83, 9.10, 9.31, 9.76, 9.92, 12.18, 12.30, 13.80 μ; NMR (CCl_4) τ 2.63 (d, J = 9.0 Hz, 2 H, aromatic), 2.88 (d, J = 9.0 Hz, 2 H, aromatic), 6.54 (s, 3 H, $-CO_2CH_3$), 7.48 (s, 2 H, CH_2), 8.60 (s, 6 H, CH_3).

Anal. Calcd for $C_{12}H_{15}O_2Br$: *m/e* 270.025 59; C, 53.13; H, 5.58. Found: *m/e* 270.025 495; C, 52.85; H, 5.65.

1,1-Diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butanol. Phenylmagnesium bromide was prepared from 2.00 g (0.0823 mol) of magnesium turnings and 8.53 mL (12.7 g, 80.4 mmol) of bromobenzene in 100 mL of anhydrous ether. This was added dropwise with stirring under nitrogen to a solution of 8.75 g (32.4 mmol) of methyl 3-(*p*-bromophenyl)-3-methylbutanoate in 50 mL of ether over 0.75 h followed by stirring at reflux for 4 h. The solution was hydrolyzed with enough saturated ammonium chloride to precipitate the salts and give a clear supernatant which was decanted and concentrated in vacuo to afford 11.2 g of a pale yellow oil. Chromatography on a 38 × 4.5 cm silica gel column (MCB, grade 62, 60–200 mesh) taking 500-mL fractions gave the following: fraction 1, hexane, nil; 2–4, hexane, 278 mg of biphenyl; 5, 1% ether in hexane, 689 mg of impure alcohol; 6–9, 1% ether in hexane, 9.87 g (78%) of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butanol as a colorless oil. This material molecularly distilled at 172 °C (0.025 mm) without residue. The spectral data follow: IR (CCl_4) 2.76, 3.22, 3.25, 3.28, 3.35, 3.40, 3.45, 6.25, 6.68, 6.85, 7.10, 7.26, 7.34, 8.55, 9.02, 9.32, 9.59, 9.80, 12.00, 14.08 μ; NMR (CCl_4) τ 2.65–3.05 (m, 14 H, aromatic), 7.18 (s, 2 H, CH_2), 8.28 (s, 1 H, OH), 8.85 (s, 6 H, CH_3).

Anal. Calcd for $C_{23}H_{23}OBr$: *m/e* 394.093 28; C, 69.86; H, 5.87. Found: *m/e* 394.092 36; C, 69.95; H, 5.83.

1,1-Diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene. A mixture of 10.5 g (26.6 mmol) of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butanol and 0.60 g of *p*-toluenesulfonic acid in 150 mL of benzene was refluxed for 2 h with azeotropic removal of water. The mixture was washed with saturated sodium carbonate, water, and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give an oil. This was triturated from cold pentane to afford 5.14 g (51%), mp 70–72 °C, of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene. Recrystallization from 95% ethanol brought the mp to 71.0–72.5 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.37, 3.42, 3.48, 6.28, 6.73, 6.80, 6.85, 6.93, 7.18, 7.30, 7.34, 8.20, 8.45, 8.78, 9.13, 9.32, 9.70, 9.93, 10.97, 11.78, 12.20, 12.40, 13.78, 13.98, 14.27, 14.40 μ; NMR (CCl_4) τ 2.30–2.60 (m, 14 H, aromatic), 3.73 (s, 1 H, vinyl), 8.72 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 250 nm (ε 21 900).

Anal. Calcd for $C_{23}H_{21}Br$: *m/e* 378.080 51; C, 73.39; H, 5.63. Found: *m/e* 378.080 92; C, 73.19; H, 5.61.

1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene. A mixture of 5.00 g (13.3 mmol) of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene, 1.47 g (16.4 mmol) of cuprous cyanide, and 25 mL of *N*-methyl-2-pyrrolidone was heated at 175 °C for 5.5 h. After cooling, the mixture was shaken with a solution of 2.00 g of sodium cyanide in 50 mL of water. This was benzene extracted, washed with 10% sodium cyanide and then water, decolorized with Norite, dried over anhydrous sodium sulfate, and concentrated in vacuo to give an oil. Trituration from pentane and crystallization from hexane gave 3.34 g (77.6%) of 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene, mp 66–68 °C. Recrystallization from 95% ethanol brought the mp to 68.5–69.5 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.36, 3.41, 3.48, 4.48, 6.23, 6.67, 6.70, 6.84, 6.93, 7.17, 7.28, 7.34, 8.20, 8.45, 8.78, 9.17, 9.32, 9.70, 9.81, 10.96, 12.00, 12.30, 13.85, 14.24, 14.38 μ; NMR (CCl_4) τ 2.60 (d, J = 9.0 Hz, 2 H, aromatic), 2.79 (d, J = 9.0 Hz, 2 H, aromatic), 2.88 (m, 8 H, aromatic), 3.41 (m, 2 H, aromatic), 3.67 (s, 1 H, vinyl), 8.62 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 235 nm (ε 29 700), 250 (25 900).

Anal. Calcd for $C_{24}H_{21}N$: *m/e* 323.167 40; C, 89.12; H, 6.55. Found: *m/e* 323.166 87; C, 89.33; H, 6.62.

Preparative Direct Irradiation of 1,1-Diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene. A solution of 1.12 g (2.97 mmol) of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene and 700 mL of dry *tert*-butyl alcohol was purged with vanadous purified nitrogen for 1.0 h and then irradiated for 1.0 h under deoxygenated nitrogen through a 1-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to obtain a brown oil for which NMR analysis showed ca. 40% conversion. This was chromatographed on a 125 × 2.5 cm column of a 3:1 mixture of silicic acid (Mallinckrodt silica, CC-7, 200–325 mesh) and diatomaceous earth (Eagle-Picher Celatom) slurry packed in hexane. The following chromatogram was obtained taking 250-mL fractions: fractions 1–21, hexane, nil; 22–33, hexane, 456 mg of 1,1-diphenyl-3-(*p*-bromophenyl)-3-methyl-1-butene; 34–35, hexane, 57 mg of a mixture of starting material and 1,1-diphenyl-2-(*p*-bro-

mophenyl)-3,3-dimethylcyclopropane; 36-42, hexane, 126 mg of 75% cyclopropane photoproduct and 25% starting material; 43-48, 0.5% ether in hexane, 78 mg of cyclopropane photoproduct with 15% starting material; 49-57, 1% ether in hexane, 185 mg of cyclopropane photoproduct and 10% starting material. Fractions 36-42 were combined and chromatographed on a 20 cm × 10 cm × 2 mm silica gel plate (EM grade 60, GF-254). After developing twice with hexane, two bands were observed. The leading edge of the broad, fast-moving band gave 31.8 mg of starting material. The remaining portion of the band afforded 75 mg of photoproduct containing 4% starting material (by NMR). The nonmoving band gave 2 mg, unidentified. Fractions 43-54 were combined and chromatographed on a 25 cm × 25 cm × 2 mm silica gel plate. After developing three times with hexane, two bands were observed; the leading edge of the fast-moving band gave 91 mg of 60% photoproduct and 40% starting material and the remaining portion afforded 146 mg of the cyclopropane photoproduct. The nonmoving band gave 5 mg, unidentified. The cyclopropane product was combined and recrystallized from 95% ethanol to give 199 mg, mp 102-103 °C. The spectral data follow: IR (CCl_4) 3.24, 3.27, 3.30, 3.32, 3.36, 3.38, 3.42, 3.48, 6.27, 6.72, 6.86, 6.93, 7.21, 7.27, 8.02, 8.28, 8.97, 9.27, 9.64, 9.76, 9.93, 11.63, 12.18, 12.40, 13.80, 14.17, 14.38, 14.80 μ; NMR (CCl_4) τ 2.60-3.00 (m, 12 H, aromatic), 3.38 (d, J = 9.0 Hz, 2 H, aromatic), 7.48 (s, 1 H, benzylic cyclopropyl), 8.70 (s, 3 H, CH_3), 8.88 (s, 3 H, CH_3); UV λ_{max} (95% ethanol) 269 nm (ϵ 1425), 273 (1075), 284 (467).

Anal. Calcd for $C_{23}H_{21}Br$: C, 73.39; H, 5.63. Found: C, 73.30; H, 5.76.

Preparative Direct Irradiation of 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene. A solution of 1.05 g (3.25 mmol) of 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene in 700 mL of dry *tert*-butyl alcohol (distilled from calcium hydride) was purged with vanadous purified nitrogen for 1 h and then irradiated for 1.33 h under deoxygenated nitrogen through a 1-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The photolysate was then concentrated in vacuo to give a yellow oil which was chromatographed on a 90 × 2.7 cm silica gel column (MCB, grade 62, 60-200 mesh) slurry packed in hexane. The following chromatogram was obtained by taking 250-mL fractions and eluting with hexane initially, but increasing to 12% dichloromethane in hexane at a rate of 2% per liter: fractions 1-36, nil; 37-47, 544 mg of 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene; 48-50, 118 mg of a mixture containing 52.7% (by NMR) 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane and starting material; 51-60, 3% ether in hexane, 255 mg of cyclopropane photoproduct. Fractions 51-60 were recrystallized from 95% ethanol to give 208 mg, mp 178-180 °C. Recrystallization from 95% ethanol brought the mp to 180-181 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.36, 3.41, 3.48, 4.48, 6.23, 6.67, 6.70, 6.84, 6.93, 7.18, 7.28, 7.34, 8.20, 8.45, 8.78, 9.17, 9.32, 9.70, 9.81, 10.96, 12.00, 12.30, 13.85, 14.24, 14.38, 14.80 μ; NMR (CCl_4) τ 2.64 (d, J = 9.0 Hz, 2 H, aromatic, partially obscured by other aromatic), 2.60-3.10 (m, 10 H, aromatic), 3.17 (d, J = 9.0 Hz, 2 H, aromatic), 7.43 (s, 1 H, benzylic cyclopropyl), 8.65 (s, 3 H, CH_3), 8.85 (s, 3 H, CH_3); UV μ_{max} (95% EtOH) 255 nm (ϵ 24 070), 276 (10 500), 285 (3510).

Anal. Calcd for $C_{24}H_{21}N$: *m/e* 323.167 40; C, 89.12; H, 6.55. Found: *m/e* 323.167 19, C, 89.05; H, 6.52.

1,1,2-Triphenyl-3,3-dimethylcyclopropane from 1,1-Diphenyl-2-(*p*-bromophenyl)-3,3-dimethylcyclopropane. To a solution of 100 mg (0.263 mmol) of 1,1-diphenyl-2-(*p*-bromophenyl)-3,3-dimethylcyclopropane in 10 mL of anhydrous ether at 0 °C under nitrogen was added 1.00 mL (1.47 mmol) of 1.47 M *n*-butyllithium in pentane. This was stirred for 3 h and saturated ammonium chloride then added followed by ether extraction. The extracts were washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford a colorless oil. This was chromatographed on a 25 cm × 25 cm × 2 mm silica gel (EM, GF-254) plate eluting twice with hexane. Three bands were observed; the top band gave 70 mg (89%) of 1,1,2-triphenyl-3,3-dimethylcyclopropane pure by NMR assay. Recrystallization from 95% ethanol gave 35 mg, mp 78-80 °C, of cyclopropane that was identical in all respects (NMR, IR, melting point) with an independently synthesized sample. A mixture melting point was undepressed.

1,1-Diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane from 1,1-Diphenyl-2-(*p*-bromophenyl)-3,3-dimethylcyclopropane. A mixture of 87.7 mg (0.233 mmol) of 1,1-diphenyl-2-(*p*-bromophenyl)-3,3-dimethylcyclopropane and 40 mg (0.447 mmol) of cuprous cyanide in 1 mL of *N*-methyl-2-pyrrolidone was heated at 175 °C under nitrogen for 3 h. The mixture was cooled, shaken with 5 mL of 5% sodium cyanide and then water, dried, and concentrated in vacuo to afford 32.4 mg of an oil which crystallized upon standing. Recrystallization from absolute ethanol gave 25 mg (33%) of 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane, mp 178-180 °C; a mixture melting point with cyclopropane obtained from the direct irradiation of 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene was undepressed and NMR and IR spectra were superimposable.

Ethyl 2-Cyano-3-(*p*-methoxyphenyl)-3-methylbutanoate. Anisylmagnesium bromide was prepared from 9.84 g (0.404 mol) of magnesium turnings and 29.4 mL (44.2 g, 0.236 mol) of *p*-bromoanisole in 200 mL of tetrahydrofuran (distilled from lithium aluminum hydride) under nitrogen. A solution of 30.6 g (0.200 mol) of ethyl 2-cyanocrotonate in 100 mL of tetrahydrofuran was added dropwise at 0 °C with stirring. The mixture was stirred for 8 h at room temperature and poured into ice and saturated ammonium chloride. This was ether extracted and the combined extracts were washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give 28.2 g of an orange oil. Short-path distillation of the crude product gave 20.1 g (38%) of pure ethyl 2-cyano-3-(*p*-methoxyphenyl)-3-methylbutanoate, bp 148-158 °C (0.06 mm). The spectral data follow: IR (CCl_4) 3.29, 3.34, 3.37, 3.41, 3.45, 3.53, 4.44, 5.73, 6.22, 6.63, 6.86, 6.94, 7.18, 7.30, 7.57, 7.69, 7.87, 7.99, 8.42, 8.47, 8.57, 8.83, 9.01, 9.15, 9.66, 12.09 μ; NMR (CCl_4) τ 2.77 (d, J = 9.0 Hz, 2 H, aromatic), 3.23 (d, J = 9.0 Hz, 2 H, aromatic), 6.02 (q, J = 7.0 Hz, 2 H, $-CO_2CH_2CH_3$), 6.24 (s, 3 H, OCH_3), 6.47 (s, 1 H, CH), 8.41 (s, 6 H, CH_3), 8.94 (t, J = 7.0 Hz, 3 H, $-CO_2CH_2CH_3$).

Anal. Calcd for $C_{15}H_{19}O_3N$: C, 68.92; H, 7.33. Found: C, 68.91; H, 7.40.

3-(*p*-Methoxyphenyl)-3-methylbutanoic Acid. A mixture of 19.5 g (74.8 mmol) of ethyl 2-cyano-3-(*p*-methoxyphenyl)-3-methylbutanoate, 42.9 g (0.768 mol) of potassium hydroxide, and 150 mL of ethylene glycol was refluxed for 10 h. This was then ether extracted; the glycol phase was diluted with water, acidified with hydrochloric acid, and ether extracted. The combined extracts were washed with water and brine. Treatment with Norite, drying over anhydrous magnesium sulfate, and concentration in vacuo afforded a slightly orange crystalline solid. This was triturated from hexane to give 10.4 g (67%) of acid, mp 82-86 °C. This was recrystallized from hexane to give pure crystalline acid, mp 85-86 °C (lit.[31] mp 70-71 °C). The spectral data follow: IR (CCl_4) 2.96-3.31, 3.37, 3.52, 5.85, 6.20, 6.32, 6.61, 6.83, 6.94, 7.09, 7.22, 7.30, 7.69, 7.97, 8.06, 8.42, 9.09, 9.62, 9.90, 10.27, 12.05 μ; NMR (CCl_4) τ −0.4 (br s, 1 H, $-CO_2H$), 2.83 (d, J = 9.0 Hz, 2 H, aromatic), 3.25 (d, J = 9.0 Hz, 2 H, aromatic), 6.24 (s, 3 H, OCH_3), 7.44 (s, 2 H, CH_2), 8.56 (s, 6 H, CH_3).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.42; H, 7.80.

Methyl 3-(*p*-Methoxyphenyl)-3-methylbutanoate. A solution of 10.3 g (49.4 mmol) of 3-(*p*-methoxyphenyl)-3-methylbutanoic acid and 7.04 mL (98.8 mmol) of thionyl chloride in 125 mL of benzene was stirred at room temperature for 2.5 h; 75 mL of methanol was added and the solution was then refluxed for 2.5 h. The solvent was removed in vacuo and ether added. The solution was washed with water, saturated sodium carbonate, water, and brine, then dried over anhydrous sodium sulfate and concentrated in vacuo to afford 10.7 g (97%) of NMR pure ester. Molecular distillation of 610 mg at 110 °C (1.5 mm) gave 530 mg of analytically pure ester. The spectral data follow: IR (CCl_4) 3.22, 3.25, 3.29, 3.33, 3.36, 3.39, 3.48, 5.75, 6.21, 6.32, 6.59, 6.78, 6.91, 7.14, 7.25, 7.35, 7.52, 7.60, 7.90, 8.16, 8.31, 8.70, 8.93, 9.42, 9.54, 11.68 μ; NMR (CCl_4) τ 2.84 (d, J = 9.0 Hz, 2 H, aromatic), 3.31 (d, J = 9.0 Hz, 2 H, aromatic), 6.29 (s, 3 H, OCH_3), 6.54 (s, 3 H, $-CO_2CH_3$), 7.52 (s, 2 H, CH_2), 8.58 (s, 6 H, CH_3).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.06; H, 8.14.

1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butanol. To 2.84 g (0.117 mol) of magnesium turnings was added 10 mL (16.4 g, 0.104 mol) of bromobenzene in 90 mL of anhydrous ether with stirring under nitrogen over 0.5 h. The mixture was refluxed for an additional 0.75 h and then cooled to 0 °C. A solution of 9.89 g (44.6 mmol) of methyl 3-(*p*-methoxyphenyl)-3-methylbutanoate in 75 mL of anhydrous ether was added dropwise with stirring over 40 min. The mixture was refluxed for 4 h and poured into saturated ammonium chloride and ice. This was ether extracted and the combined extracts were washed with water and saturated sodium chloride, dried over anhydrous magne-

sium sulfate, and concentrated in vacuo to give 15.5 g of a red oil. The residue was chromatographed on a 4 × 45 cm silica gel (MCB, grade 62, 60–200 mesh) column taking 500-mL fractions to give the following chromatogram: fractions 1–5, hexane, 408 mg of biphenyl; 6, hexane, nil; 7–8, 1.5% ether in hexane, nil; 9–14, 3% ether in hexane, 14.2 g (91%) of NMR pure alcohol as a colorless oil. Analytically pure alcohol was obtained by chromatography of 450 mg on a 25 cm × 25 cm × 2 mm silica gel (EM, GF-254) plate. Elution twice with 3% ether in hexane and three times with 5% ether in hexane gave three bands. The middle band afforded 405 mg of the alcohol. The spectral data follow: IR (CCl_4) 2.81, 3.24, 3.29, 3.38, 3.42, 3.48, 4.52, 6.21, 6.25, 6.33, 6.60, 6.70, 6.84, 6.90, 7.20, 7.31, 7.41, 7.69, 7.99, 8.42, 8.98, 9.39, 9.66, 12.02, 12.55, 12.87, 13.35, 13.89, 14.25 μ; NMR (CCl_4) τ 2.60–3.04 (m, 12 H, aromatic), 3.31 (d, J = 9.0 Hz, 2 H, aromatic), 6.32 (s, 3 H, OCH_3), 7.21 (s, 2 H, CH_2), 8.30 (s, 1 H, OH), 8.88 (s, 6 H, CH_3).

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.17; H, 7.63.

1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. To a solution of 2.00 g (5.78 mmol) of 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butanol in 15 mL of pyridine (distilled from calcium hydride) was added 1.07 mL (1.80 g, 11.7 mmol) of phosphorus oxychloride. The solution was refluxed under nitrogen for 5 h and then poured into 75 mL of water. This was ether extracted and washed with water, 5% hydrochloric acid, again with water, then with saturated sodium carbonate and saturated sodium chloride. The extracts were dried over anhydrous sodium sulfate and concentrated in vacuo to give 1.89 g of crystalline 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. This was recrystallized from hexane–ether to give 1.30 g (68.4%), mp 73.5–74.0 °C. The spectral data follow: IR (CCl_4) 3.27, 3.31, 3.38, 3.45, 3.48, 3.53, 4.68, 5.28, 5.33, 5.56, 5.71, 6.23, 6.27, 6.35, 6.66, 6.72, 6.85, 6.94, 7.12, 7.25, 7.36, 7.73, 8.00, 8.51, 8.85, 9.06, 9.16, 9.36, 9.71, 9.95, 10.31, 10.78, 11.05, 11.49, 12.15, 12.82, 14.49 μ; NMR (CCl_4) τ 2.80–3.20 (m, 12 H, aromatic), 3.38 (d, J = 9.0 Hz, 2 H, aromatic), 3.71 (s, 1 H, vinyl), 7.29 (s, 3 H, OCH_3), 8.73 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 250 nm (ε 16 400), 277 (7220), 285 (4430).

Anal. Calcd for $C_{24}H_{24}O$: *m/e* 328.182 71; C, 87.76; H, 7.37. Found: *m/e* 328.182 39; C, 87.86; H, 7.32.

Preparative Direct Irradiation of 1,1-Diphenyl-2-(*p*-methoxyphenyl)-3-methyl-1-butene. A solution of 1.52 g (4.63 mmol) of 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene in 700 mL of *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.00 h and irradiated through a 1-mm Corex filter for 2.00 h with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The progress in reaction was followed by NMR. Clean conversion to 1,1-diphenyl-3-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane up to 60% conversion (by NMR) was observed. The photolysate was concentrated in vacuo and chromatographed on an 81 × 2.8 cm silicic acid (30% by weight Celite) column containing 2% phosphor. The following chromatogram was obtained by taking 250-mL fractions: fractions 1–12, hexane, nil; 13–15, hexane, 495 mg of starting material; 16–17, hexane, 235 mg of a 60:40 mixture of starting material and the cyclopropane photoproduct; 18–22, 297 mg of cyclopropane; 23–28, 5% ether in hexane, 257 mg of cyclopropane product as an oil. The combined cyclopropane product was triturated from cold pentane and the crystalline material was recrystallized from pentane to give 160 mg of 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane, mp 74–75 °C. The spectral data follow: IR (CCl_4) 3.25, 3.27, 3.31, 3.33, 3.39, 3.48, 3.52, 6.25, 6.67, 6.71, 6.90, 6.94, 7.30, 7.75, 8.00, 8.47, 9.01, 9.66, 12.05, 13.70, 14.28 μ; NMR (CCl_4) τ 2.60–3.10 (m, 10 H, aromatic), 3.34 (d, J = 9.0 Hz, 2 H, aromatic), 4.46 (d, J = 9.0 Hz, 2 H, aromatic), 6.31 (s, 3 H, OCH_3), 7.50 (s, 1 H, benzylic cyclopropyl), 8.70 (s, 3 H, CH_3), 8.89 (s, 3 H, CH_3); UV λ_{max} (95% EtOH) 273 nm (ε 2081), 282 (2081), 291 (1587).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.70; H, 7.42.

1,1-Diphenyl-2-(*p*-acetylphenyl)-3,3-dimethylcyclopropane. To a solution of 350 mg (1.08 mmol) of 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane in anhydrous ether was added 4.00 mL (6.80 mmol) of 1.70 M methyllithium with stirring under nitrogen. This was refluxed for 17 h and then poured into 5% hydrochloric acid. After heating for 3 h on a steam bath, the mixture was extracted with dichloromethane, washed with water, saturated sodium carbonate, and saturated sodium chloride, dried, and concentrated in vacuo to afford 256 mg of a semicrystalline solid. This was chromatographed on a 25 cm × 25 cm × 2 mm silica gel plate (EM, PF-254) eluting four times with 10% ether in hexane to give four bands. The second band from the top afforded 230 mg (62.7%) of NMR pure 1,1-diphenyl-2-(*p*-acetylphenyl)-3,3-dimethylcyclopropane as a colorless, crystalline solid, mp 40–45 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.29, 3.38, 3.40, 3.47, 5.93, 6.23, 6.69, 6.84, 6.89, 6.99, 7.25, 7.35, 7.62, 7.88, 8.23, 8.40, 8.94, 9.24, 9.72, 10.43, 10.75, 11.11, 11.83, 12.00, 14.10, 14.33 μ; NMR (CCl_4) τ 2.41 (d, J = 8.0 Hz, 2 H, aromatic), 2.67–3.00 (m, 10 H, aromatic), 3.22 (d, J = 8.0 Hz, 2 H, aromatic), 7.40 (s, 1 H, benzylic cyclopropyl), 7.57 (s, 3 H, $-COCH_3$), 8.67 (s, 3 H, CH_3), 8.85 (s, 3 H, CH_3).

Anal. Calcd for $C_{25}H_{24}O$: *m/e* 340.182 71. Found: *m/e* 340.181 10.

1,1-Diphenyl-2-(*p*-acetoxyphenyl)-3,3-dimethylcyclopropane. A mixture of 190 mg (0.558 mmol) of 1,1-diphenyl-2-(*p*-acetylphenyl)-3,3-dimethylcyclopropane and 344 mg (2.00 mmol) of *m*-chloroperbenzoic acid in 10 mL of dichloromethane was stirred at room temperature under nitrogen for 29 h. This was shaken with 10% sodium sulfite, extracted with dichloromethane, washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give 200 mg of a yellow, crystalline solid. Recrystallization from 95% ethanol gave 180 mg (90%), mp 144.5–146 °C. The spectral data follow: IR ($CHCl_3$) 3.23, 3.27, 3.33, 3.40, 3.42, 3.48, 5.73, 6.25, 6.63, 6.70, 6.82, 6.91, 7.29, 8.16, 8.35, 8.54, 8.94, 9.24, 9.73, 9.82, 10.87, 11.00, 11.83, 14.14, 14.35 μ; NMR (CCl_4) τ 2.60–3.10 (m, 10 H, aromatic), 3.21 (s, 4 H, aromatic), 7.48 (s, 1 H, benzylic cyclopropyl), 7.83 (s, 3 H, CH_3CO_2-), 8.68 (s, 3 H, CH_3), 8.88 (s, 3 H, CH_3).

Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.03; H, 6.81.

1,1-Diphenyl-2-(*p*-hydroxyphenyl)-3,3-dimethylcyclopropane. A solution of 150 mg (0.423 mmol) of 1,1-diphenyl-2-(*p*-acetoxyphenyl)-3,3-dimethylcyclopropane and 10 mL of 20% methanolic potassium hydroxide was refluxed for 2 h and then poured into 10% hydrochloric acid. This was ether extracted, washed with water and saturated sodium chloride, dried, and concentrated in vacuo to afford 125 mg of a yellow oil. Chromatography on a 25 cm × 25 cm × 2 mm silica gel (EM, PF-254) plate eluting twice with 10% ether in hexane gave 83 mg (62.2%) of NMR pure phenol as a colorless oil from the middle band of the three bands resolved. The spectral data follow: IR (CCl_4) 2.77, 2.94, 3.24, 3.26, 3.27, 3.29, 3.36, 3.40, 3.42, 3.49, 6.20, 6.26, 6.61, 6.70, 6.75, 6.91, 7.21, 7.26, 7.50, 7.93, 8.50, 8.94, 9.24, 9.63, 9.74, 10.55, 10.78, 10.95, 11.14, 12.00, 14.14, 14.35, 14.81 μ; NMR (CCl_4) τ 2.57–3.17 (m, 10 H, aromatic), 3.37 (d, J = 9.0 Hz, 2 H, aromatic), 3.57 (d, J = 9.0 Hz, 2 H, aromatic), 5.63 (br s, 1 H, OH), 7.50 (s, 1 H, benzylic cyclopropyl), 8.70 (s, 3 H, CH_3), 8.89 (s, 3 H, CH_3).

Anal. Calcd for $C_{23}H_{22}O$: *m/e* 314.167 06. Found: *m/e* 314.166 96.

1,1-Diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane. To a mixture of 80 mg (0.256 mmol) of 1,1-diphenyl-2-(*p*-hydroxyphenyl)-3,3-dimethylcyclopropane, 0.5 g of potassium carbonate, and 0.5 mL of 10% methanolic potassium hydroxide in 20 mL of acetone was added 0.20 mL (0.266 g, 2.11 mmol) of dimethyl sulfate followed by 5 h of reflux. This was poured into saturated potassium carbonate, ether extracted, washed with water and saturated sodium chloride, dried, and concentrated in vacuo to afford a yellow oil. The residue was chromatographed on a 25 cm × 25 cm × 2 mm silica gel plate (EM, PF-254). Elution with 5% ether in hexane resolved five bands. The top band afforded 68 mg (81%) of NMR pure 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane. Trituration and recrystallization from cold pentane gave 35 mg of cyclopropane, mp 75.5–77.0 °C, with identical IR and NMR spectra with the cyclopropane obtained from the direct irradiation of 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. A mixture melting point with photochemically obtained cyclopropane was not depressed.

1,1,3-Triphenyl-1-propene.[32] This was obtained by a variation of the literature method. A solution of 4.00 g (13.9 mmol) of 1,1,3-triphenyl-1-propanol[32] in 200 mL of benzene with 800 mg (4.21 mmol) of *p*-toluenesulfonic acid was refluxed for 7.5 h with azeotropic removal of water. The solution was washed with water, saturated sodium carbonate, and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give 3.68 g of 1,1,3-triphenyl-1-propene as an oil. This was chromatographed on a 71 × 2.5 cm silica gel column eluting with hexane and taking 500-mL fractions to give the following chromatogram: fractions 1–2, nil; 3–7, 3.57 g (95%) of 1,1,3-tri-

phenyl-1-propene as a colorless oil. Molecular distillation of 444 mg at 155 °C (0.25 mm) afforded 413 mg of analytically pure material. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.38, 6.25, 6.68, 6.89, 6.93, 7.35, 9.34, 9.73, 14.37 μ; NMR (CCl_4) τ 2.60–3.00 (m, 15 H, aromatic), 3.78 (t, J = 8.0 Hz, 1 H, vinyl), 6.55 (d, J = 8.0 Hz, 2 H, CH_2); UV λ_{max} (95% EtOH) 250 nm (ϵ 17 900), 263 (13 200), 269 (8770), 285 (927).

Anal. Calcd for $C_{21}H_{18}$: *m/e* 270.140 85; C, 93.28, H, 6.72. Found: *m/e* 270.140 87; C, 93.30; H, 6.67.

Preparative Direct Irradiation of 1,1,3-Triphenyl-1-propene. A solution of 1.03 g (3.81 mmol) of 1,1,3-triphenyl-1-propene and 1.0 L of dry *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.0 h and then irradiated with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well for 4.5 h under nitrogen. NMR analysis showed the presence of 1,1,3-triphenyl-1-propene (52%), 1,1,2-triphenylcyclopropane (38.5%), and 1,1-diphenylindan (9.5%). The photolysate was concentrated in vacuo and chromatographed on a 130 × 4 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane taking 250-mL fractions: fractions 1–18, nil; 19–32, 428 mg of 1,1,3-triphenyl-1-propene; 33–37, 207 mg of 1,1,2-triphenylcyclopropane; 38–39, 107 mg of a mixture of 33% 1,1-diphenylindan and 67% cyclopropane; 40–47, 96 mg of a mixture containing 58% indan and 42% cyclopropane. Fractions 33–37 were recrystallized from hexane to give 78 mg of 1,1,2-triphenylcyclopropane, mp 48.5–49.0 °C (lit.[33] 48.5–49.0 °C) identical in all respects with an authentic sample prepared by the literature method.[33,34] Fractions 40–47 crystallized upon standing in methanol and were recrystallized from methanol to give 41 mg of indan photoproduct, mp 65.5–67.0 °C (lit.[35] 68–69 °C). NMR and mass spectra agreed with those reported.[35]

Direct Irradiation of 1,1,2-Triphenylcyclopropane. A solution of 499 mg (1.85 mmol) of 1,1,2-triphenylcyclopropane and 500 mL of *tert*-butyl alcohol (distilled from calcium hydride) was purged with deoxygenated nitrogen for 1.0 h and then irradiated through a 1-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Aliquots were taken at time intervals and analyzed by NMR. No 1,1-diphenylindan could be detected after 3 h irradiation. At this time an unidentified product began to appear.

Ethyl 2-Cyano-3-(*m*-methoxyphenyl)-3-methylbutanoate. *m*-Anisylmagnesium bromide was prepared from 1.44 g (60.1 mmol) of magnesium and 10.23 g (54.7 mmol) of *m*-bromoanisole in 35 mL of tetrahydrofuran (distilled from sodium) under nitrogen. Copper(I) iodide (10 mg, 0.052 mmol) was added after 0.5 h and the mixture stirred for an additional 10 min. A solution of 9.00 g (58.8 mmol) of ethyl 2-cyanocrotonate in 25 mL of tetrahydrofuran was added all at once at 0 °C with stirring. The mixture was stirred for 2 h at 0 °C then quenched with 30 mL of cold saturated ammonium chloride. The green mixture was ether extracted and the combined extracts were washed with 10% sodium hydroxide solution and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield 13.9 g of a yellow oil. Short-path distillation of the crude product gave 12.89 g (89.6%) of pure ethyl 2-cyano-3-(*m*-methoxyphenyl)-3-methylbutanoate, bp 120–140 °C (0.05 mm), that analyzed satisfactorily. The spectral data follow: IR (CCl_4) 3.36, 3.40, 3.44, 3.53, 4.45, 5.72, 6.24, 6.40, 6.71, 6.83, 6.98, 7.17, 7.30, 7.56, 7.72, 8.03, 8.23, 8.44, 8.83, 9.01, 9.13, 9.48, 9.62, 10.72, 11.33, 11.45, 11.72, 14.29 μ; NMR ($CDCl_3$) τ 2.40–3.30 (m, 4 H, aromatic), 5.96 (q, J = 7.0 Hz, 2 H, $-CO_2CH_2CH_3$), 6.20 (s, 3 H, $-OCH_3$), 6.26 (s, 1 H, CH), 8.40, (s, 6 H, CH_3), 8.92 (t, J = 7.0 Hz, 3 H, $-CO_2CH_2CH_3$).

Anal. Calcd for $C_{15}H_{19}O_3N$: *m/e* 261.136 48. Found: *m/e* 261.137 41.

3-Methyl-3-(*m*-methoxyphenyl)butanoic Acid. A mixture of 2.00 g (7.66 mmol) of ethyl 2-cyano-3-(*m*-methoxyphenyl)-3-methylbutanoate, 4.80 g of potassium hydroxide (72.7 mmol), and 65 mL of ethylene glycol was heated to 180 °C for 6 h. After cooling to room temperature, water was added and the mixture was ether extracted. The aqueous phase was acidified with 4 N hydrochloric acid and ether extracted and the combined extracts were washed with saturated sodium chloride. Drying over anhydrous magnesium sulfate and concentrating in vacuo afforded a light brown oil. After treatment with Norite, the oil crystallized slowly upon standing. Crystallization from hexane yielded 1.22 g (76.6%) of NMR pure acid. Recrystallization from hexane gave mp 78–79 °C. The spectra data Follow: IR (CCl_4) 2.86–4.05, 5.87, 6.25, 6.32, 6.72, 6.83, 6.91, 6.99, 7.09, 7.32, 7.62, 7.74, 7.94, 8.08, 8.26, 8.51, 9.03, 9.23, 9.50, 10.64, 11.24, 11.45, 11.74, 13.51, 14.28 μ; NMR ($CDCl_3$) τ 2.64–3.36 (m, 4 H, aromatic), 6.20 (s, 3 H, $-OCH_3$), 7.36 (s, 2 H, CH_2), 8.55 (s, 6 H, CH_3).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.47; H, 7.75.

Methyl 3-(*m*-Methoxyphenyl)-3-methylbutanoate. A solution of 1.64 g (7.9 mmol) of 3-methyl-3-(*m*-methoxyphenyl)butanoic acid and 1.10 mL (15.8 mmol) of thionyl chloride in 20 mL of benzene was stirred at room temperature for 5 h. The mixture was concentrated in vacuo and 20 mL of anhydrous methanol was added all at once. The solution was heated to reflux for 18 h. Excess methanol was removed in vacuo and the yellow residue was taken up in ether and washed with water, saturated sodium carbonate, and saturated sodium chloride. Drying over anhydrous magnesium sulfate and concentrating in vacuo afforded 1.50 g (85.5%) of NMR pure methyl ester as a liquid. Molecular distillation at 75 °C (0.2 mm) afforded analytically pure ester. The spectral data follow: IR (CCl_4) 3.25, 3.34, 3.39, 3.44, 3.53, 5.76, 6.25, 6.33, 6.72, 6.84, 6.91, 7.00, 7.19, 7.32, 7.42, 7.58, 7.75, 8.03, 8.22, 8.47, 8.53, 8.87, 9.05, 9.26, 9.51, 9.80, 10.95, 11.23, 11.50, 11.79, 14.32 μ; NMR ($CDCl_3$) τ 2.60–3.40 (m, 4 H, aromatic), 6.18 (s, 3 H, $-OCH_3$), 6.44 (s, 3 H, $-CO_2CH_3$), 7.36 (s, 2 H, CH_2), 8.54 (s, 6 H, CH_3).

Anal. Calcd for $C_{13}H_{18}O_3$: *m/e* 222.125 58. Found: *m/e* 222.125 44.

1,1-Diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butanol. To 0.37 g (16.7 mmol) of magnesium turnings in 5 mL of anhydrous ether was added 1.3 mL (2.40 g, 15.3 mmol) of bromobenzene in 10 mL of anhydrous ether under nitrogen with stirring. The mixture was stirred for an additional 0.5 h, then cooled to 0 °C. A solution of 0.95 g (4.30 mmol) of methyl 3-(*m*-methoxyphenyl)-3-methylbutanoate in 15 mL of anhydrous ether was added dropwise with stirring. The mixture was stirred for 19 h and poured into 50 mL of saturated ammonium chloride, and 20 mL of water was added. The mixture was ether extracted and the combined extracts were washed with saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield 1.45 g of a yellow oil. The residue was chromatographed on a 2.8 × 96 cm silica gel (grade 62, 60–200 mesh) column containing 2% of no. 2282 green Sylvania phosphor, slurry packed in hexane. Elution, collecting 500-mL fractions, gave the following: fractions 1–2, hexane, nil; 3–4, hexane, 156 mg of biphenyl; 5–7, hexane, nil; 8–15, 3% ether in hexane, 986 mg (66%) of NMR pure alcohol as a colorless oil. Further purification was obtained by chromatography of 190 mg on a 25 × 25 × 0.2 cm silica gel (EM, GF-254) plate. Elution twice with 5% ether in hexane gave two bands. The lower band afforded 163 mg of alcohol. The spectral data follow: IR (CCl_4) 2.80, 3.25, 3.28, 3.31, 3.34, 3.38, 3.41, 3.45, 3.50, 3.53, 6.27, 6.33, 6.73, 6.85, 6.92, 7.01, 7.22, 7.35, 7.42, 7.59, 7.75, 8.02, 8.55, 8.93, 9.09, 9.52, 9.71, 9.85, 10.12, 11.05, 11.34, 11.42, 11.76, 14.29 μ; NMR ($CDCl_3$) τ 2.40–3.40 (m, 14 H, aromatic), 6.24 (s, 3 H, $-OCH_3$), 7.12 (s, 2 H, CH_2), 8.12 (s, 1 H, -OH), 8.84 (s, 6 H, CH_3).

Anal. Calcd for $C_{24}H_{26}O_2$: *m/e* 346.193 28. Found: *m/e* 346.194 91.

1,1-Diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene. To a solution of 3.63 g (10.5 mmol) of 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butanol in 65 mL of pyridine (distilled from calcium hydride) was added 1.92 mL (3.21 g, 21.0 mmol) of phosphorus oxychloride. The solution was heated to reflux under nitrogen for 14 h, cooled to room temperature, and poured into 100 mL of water. The mixture was ether extracted and the combined organic extracts were washed with 10% aqueous hydrochloric acid and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield 3.26 g of a yellow oil. The residue was placed on a 4.0 × 70 cm silica gel (grade 62, 60–200 mesh) column, slurry packed in hexane. The following 500-mL fractions gave fractions 1–10, hexane, nil; 11–13, 1% ether in hexane, 3.03 g (88%) of the desired olefin as a colorless oil. This crystallized from pentane upon standing. Recrystallization from hexane yielded colorless crystals, mp 30–31 °C. The spectral data follow: IR (CCl_4) 3.25, 3.27, 3.31, 3.34, 3.38, 3.44, 3.49, 3.53, 6.25, 6.33, 6.70, 6.74, 6.84, 6.92, 6.98, 7.20, 7.35, 7.59, 7.75, 7.97, 8.20, 8.31, 8.47, 8.55, 8.81, 9.06, 9.34, 9.52, 9.71, 11.26, 11.49, 11.76, 12.15, 13.87, 14.29, 15.46 μ; NMR ($CDCl_3$) τ 2.60–3.40 (m, 14 H including 10 H at 2.72, aromatic), 3.55 (s, 1 H, vinyl), 6.18 (s, 3 H, $-OCH_3$), 8.65 (s, 6 H, CH_3); UV λ_{max} (95% ethanol) 251 nm (ϵ 15 300), 280 (4590), 294 (360).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 87.62; H, 7.29.

Preparative Direct Irradiation of 1,1-Diphenyl-3-(*m*-methoxy-

phenyl)-3-methyl-1-butene. A solution of 1.03 g (3.13 mmol) of 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene in 700 mL of *tert*-butyl alcohol was purged with vanadous purified nitrogen for 1 h prior to and during irradiation. The solution was irradiated through a 2-mm Corex filter with a 450-W Hanovia medium-pressure mercury arc lamp in a quartz immersion well. The progress of the reaction was monitored by NMR. Clean conversion to 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane up to 43% was observed. After 5.5 h irradiation was discontinued and the photolysate was concentrated in vacuo. The oily residue was chromatographed on a 2.8 × 86 cm silica gel (Grace 62, 60–200 mesh) column containing 2% of no. 2282 green Sylvania phosphor, slurry packed in hexane. The following 500-mL fractions were obtained: fractions 1–2, hexane, nil; 3, hexane, 2 mg of an oil identified by NMR as 1,1-diphenyl-2-methylpropene; 4–17, hexane, nil; 18–23, 4% CH_2Cl_2 in hexane, 428 mg of starting olefin; 24–26, 1% ether in hexane, 130 mg of starting olefin and cyclopropane product; 27–28, 1% ether in hexane, 430 mg of cyclopropane product with a trace of starting olefin. Fractions 27–38 were combined and placed on a 2.5 × 77 cm silica gel (Grace 62, 60–200 mesh) column slurry packed in hexane to give the following 500-mL fractions: fractions 1–10, hexane, nil; 11–12, hexane, 27 mg of starting olefin and cyclopropane product; 13–19, hexane, 274 mg of pure cyclopropane photoproduct that crystallized slowly at −15 °C. Recrystallization from anhydrous methanol yielded colorless crystals of 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane, mp 58.5–59.5 °C. The spectral data follow: IR (CCl_4) 3.25, 3.28, 3.31, 3.34, 3.40, 3.42, 3.50, 3.53, 6.26, 6.34, 6.72, 6.86, 6.93, 7.29, 7.62, 7.78, 7.89, 8.00, 8.13, 8.40, 8.55, 8.62, 8.98, 9.13, 9.29, 9.52, 9.62, 9.77, 10.47, 11.05, 11.24, 11.53, 11.90, 14.22, 14.39, 15.27 μ; NMR ($CDCl_3$) τ 2.40–3.80 (m, 14 H, aromatic), 6.42 (s, 3 H, $-OCH_3$), 7.40 (s, 1 H, cyclopropyl), 8.66 (s, 3 H, CH_3), 8.88 (s, 3 H, CH_3); UV λ_{max} (95% ethanol) 256 nm (ε 1300), 263 (1590), 270 (2140), 277 (2810), 285 (2740).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.59; H, 7.47.

Characterization of 1,1-Diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane. Degradation to 1,1-Diphenyl-2,2-dimethyl-3-cyclopropylcarboxylic Acid. Ozone (from a Welsbach ozonator) was bubbled through a well-stirred solution of 41 mg (0.125 mmol) of 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane in 25 mL of carbon tetrachloride at room temperature for 20 min. The cloudy mixture was poured into a solution of 15 mL of 20% sodium hydroxide, 25 mL of 30% hydrogen peroxide, and 75 mL of water and heated to reflux for 0.25 h on a steam bath. The phases were separated and the aqueous layer was ether extracted and then acidified to pH 3 with 4 N hydrochloric acid. The aqueous solution was ether extracted and the combined extracts were washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Concentrating in vacuo gave 21 mg of an off-white solid. Recrystallization from hexane–ether afforded 16 mg (40%) of acid identical in all respects with an authentic sample[36] and with mp 232–234 °C. A mixture melting point was undepressed.

***trans*-1,3-Diphenyl-3-methyl-1-butene.** A solution of 3.71 g (15.5 mmol) of 1,3-diphenyl-3-methyl-1-butanol[37] and 700 mg (3.68 mmol) of *p*-toluenesulfonic acid in 175 mL of benzene was refluxed for 6.5 h with azeotropic removal of water. The solution was cooled and ether was added followed by washing with water, saturated sodium carbonate, water again, and saturated sodium chloride. Drying and concentration in vacuo afforded 3.22 g (93%) of NMR pure *trans*-1,3-diphenyl-3-methyl-1-butene. Chromatography of 870 mg on a 100 × 3 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane taking 250-mL fractions gave 662 mg of material containing ca. 0.5% *cis*-1,3-diphenyl-3-methyl-1-butene (by VPC on column E, vide infra) and also an unidentified impurity in fractions 7–9; fractions 10–12 afforded 186 mg of analytically pure (analyzed by VPC as greater than 99.99% pure) material. The spectral data follow: IR (film) 3.24, 3.27, 3.30, 3.37, 3.41, 3.48, 6.25, 6.70, 6.92, 7.25, 7.35, 9.13, 9.34, 9.73, 10.36, 13.14, 13.37, 14.28 μ; NMR (CCl_4) τ 2.50–3.00 (m, 10 H, aromatic), 3.70 (s, 2 H, vinyl), 8.52 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 250 nm (ε 21 500), 260 (14 900), 283 (1700), 293 (1200).

Anal. Calcd for $C_{17}H_{18}$: *m/e* 222.140 85; C, 91.84, H, 8.16. Found: *m/e* 222.140 77; C, 91.75; H, 8.19.

***cis*-1,3-Diphenyl-3-methyl-1-butene.** To a suspension of 5.04 g (13.0 mmol) of benzyltriphenylphosphonium chloride in 50 mL of benzene (distilled from calcium hydride) was added 8.78 mL (12.9 mmol) of 1.47 M *n*-butyllithium while stirring under nitrogen at room temperature. After stirring for 2.5 h a solution of 1.75 g (11.8 mmol) of 2-phenyl-2-methylpropanal[38] in 25 mL of benzene was added and the solution was refluxed for 10 h. The mixture was hydrolyzed by addition of ca. 1 mL of water, cooled, filtered, and concentrated in vacuo. Hexane was added followed by filtration and concentration in vacuo, and this process was repeated to afford a yellow oil. NMR showed this to be a 55:45 mixture of trans:cis styryl compounds. The crude residue was chromatographed on a 90 × 2.7 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 250-mL fractions to give the following chromatogram: fractions 1–2, nil; 3–4, 493 mg of *cis*-1,3-diphenyl-3-methyl-1-butene having satisfactory elemental analysis and containing less than 1% of *trans*-1,3-diphenyl-3-methyl-1-butene by VPC analysis on column E (vide infra); 5–13, 1.30 g of a mixture of cis and trans styryl compounds. The spectral data follow: IR (CCl_4) 3.24, 3.27, 3.29, 3.33, 3.37, 3.41, 3.48, 6.25, 6.69, 6.85, 6.92, 7.26, 7.34, 8.14, 8.56, 8.85, 9.12, 9.33, 9.74, 14.04, 14.35 μ; NMR (CCl_4) τ 2.60–3.30 (m, 10 H, aromatic), 3.61 (d, J = 13.0 Hz, 1 H, vinyl), 4.21 (d, J = 13.0 Hz, 1 H, vinyl), 8.67 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 265 nm (ε 3132), 253 (6456), 243 (8064), 240 (8092).

Anal. Calcd for $C_{17}H_{18}$: *m/e* 222.140 85; C, 91.84; H, 8.16. Found: *m/e* 222.140 55; C, 91.90; H, 8.07.

***trans*-1,2-Diphenyl-3,3-dimethylcyclopropane.** To a stirred suspension of 2.89 g (15.2 mmol) of cuprous iodide in 10 mL of anhydrous ether at −22 °C under nitrogen was added 16 mL (27.2 mmol) of 1.7 M ethereal methyllithium. After 0.5 h, a solution of 530 mg (1.55 mmol) of *trans*-1,2-diphenyl-3,3-dibromocyclopropane[39] in 20 mL of ether was added. After 36 h at −15 °C, an additional 15.2 mmol of ethereal lithium dimethylcuprate was added; 2 mL of methyl iodide was added after an additional 24 h at −15 °C, and the mixture was stirred for 3 h and poured into 5 N ammonium hydroxide. This was ether extracted, washed with water and saturated sodium chloride, dried, and concentrated in vacuo to afford an oil. Since VPC analysis (column E) showed the presence of 1.5% *trans*-stilbene, the crude residue was dissolved in 10 mL of dichloromethane, and solid sodium acetate and 2.0 mL of 40% peracetic acid were added. This was stirred for 16 h, then poured into water, extracted with dichloromethane, washed with water, saturated sodium carbonate, and saturated sodium chloride, dried, and concentrated in vacuo to afford a yellow oil. The residue was chromatographed on a 1.7 × 70 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 250-mL fractions. In fractions 5–7, 284 mg (82.5%) of *trans*-1,2-diphenyl-3,3-dimethylcyclopropane was obtained. Molecular distillation at 90–92 °C (0.70 mm) afforded 270 mg of analytically pure material. Low-temperature recrystallization from methanol gave a colorless, crystalline solid, mp 25–26 °C. The spectral data follow: IR (CCl_4) 3.23, 3.26, 3.30, 3.36, 3.38, 3.42, 3.48, 6.24, 6.67, 6.91, 7.25, 7.85, 8.12, 8.27, 9.29, 9.50, 9.69, 10.48, 10.98, 11.45, 13.59, 14.28 μ; NMR (CCl_4) τ 2.79 (s, 10 H, aromatic), 7.68 (s, 2 H, benzylic cyclopropyl), 9.02 (s, 6 H, CH_3); UV λ_{max} (95% EtOH) 254 nm (ε 589), 257 (622), 260 (679), 263 (681), 265 (670), 270 (506), 274 (363).

Anal. Calcd for $C_{17}H_{18}$: *m/e* 222.140 85, C, 91.84; H, 8.16. Found: *m/e* 222.140 77; C, 91.68; H, 8.20.

***cis*-1,2-Diphenyl-3,3-dibromocyclopropane.** A mixture of 1.25 g (6.94 mmol) of *cis*-stilbene and 8.50 g (16.0 mmol) of phenyl(tribromomethyl)mercury[40] in 10 mL of benzene was heated at reflux under nitrogen for 1.5 h. The reaction was repeated exactly as above and the combined runs were filtered and concentrated in vacuo to give an orange oil. NMR showed *cis*- and *trans*-1,2-diphenyl-3,3-dibromocyclopropanes in a ratio of 82:18, respectively. Longer reaction times led to a greater amount of the trans isomer and an unidentified by-product. The crude residue was chromatographed on a 90 × 1.7 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 250-mL fractions: fractions 1–3, 1.01 g of isomeric stilbenes; 4–5 200 mg of a mixture of stilbenes and cyclopropane product; 6–7, 969 mg of NMR pure *cis*-1,2-diphenyl-3,3-dibromocyclopropane; 8–13, 644 mg of a mixture of isomeric cyclopropanes. *cis*-1,2-Diphenyl-3,3-dibromocyclopropane giving satisfactory combustion analysis was obtained by chromatography of 314 mg from fractions 6–7 on a 25 cm × 25 cm × 2 mm silica gel (EM, GF-254) plate eluting three times with 2% ether in hexane. Two bands were observed; the top band gave 217 mg of the pure cyclopropane as a slightly yellow oil. The spectral data follow: IR (CCl_4) 3.26, 3.30, 6.23, 6.68, 6.87, 6.91, 9.28, 9.33, 9.62, 9.71, 13.79, 13.97, 14.33 μ; NMR (CCl_4) τ 2.67–3.17 (m, 10 H, aromatic), 6.68 (s, 2 H, benzylic cy-

clopropyl); MS (70 eV) *m/e* (%) no parent, 273 (8.3), 271 (9.0), 192 (77), 191 (100), 165 (46).

Anal. Calcd for $C_{15}H_{12}Br_2$: C, 51.17; H, 3.44. Found: C, 50.88; H, 3.60.

***cis*-1,2-Diphenyl-3,3-dimethylcyclopropane.** To a solution of 15.2 mmol of ethereal lithium dimethylcuprate (prepared as above for *trans*-1,2-diphenyl-3,3-dimethylcyclopropane) at −20 °C under nitrogen was added 969 mg (2.75 mmol) of *cis*-1,2-diphenyl-3,3-dibromocyclopropane in 20 mL of ether. The mixture was kept at −15 °C for 36 h, and a fresh 15.2 mmol of ethereal lithium dimethylcuprate was then added. After 24 h at −15 °C, 2 mL of methyl iodide was then added. The mixture was stirred for 3 h, poured into 5 N ammonium hydroxide, ether extracted, washed with water and saturated sodium chloride, dried, and concentrated in vacuo to afford 549 mg of a yellow oil. Treatment with 2 mL of 40% peracetic acid in 10 mL of dichloromethane for 16 h followed by quenching in water, ether extraction, water and brine wash, drying, and concentration in vacuo afforded 533 mg of a yellow oil. This was chromatographed on a 90 × 1.7 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane taking 250-mL fractions: fractions 1–5, nil; 6, 99 mg of 25% *trans*- and 75% *cis*-cyclopropane; 7–9, 252 mg of *cis*-cyclopropane containing ca. 8% of the *trans*-cyclopropane isomer. Fractions 7–9 were triturated at −72 °C from pentane to give 247 mg (40%), mp 48.0–52.5 °C, of *cis*-1,2-diphenyl-3,3-dimethylcyclopropane. Recrystallization from pentane at −72 °C gave 73 mg, mp 56–57 °C. The spectral data follow: IR (CCl_4) 3.24, 3.26, 3.30, 3.33, 3.39, 3.42, 3.46, 3.49, 6.24, 6.68, 6.87, 6.91, 7.19, 7.26, 8.31, 8.91, 9.22, 9.28, 9.37, 9.69, 10.31, 10.64, 10.89, 10.99, 11.20, 13.99, 14.28 μ; NMR (CCl_4) τ 2.70–3.20 (m, 10 H, aromatic), 7.78 (s, 2 H, benzylic cyclopropyl), 8.56 (s, 3 H, CH_3), 8.89 (s, 3 H, CH_3); UV λ_{max} (95% EtOH) 260 nm (ε 892), 267 (780), 275 (492).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.92; H, 8.06.

Preparative Direct Irradiation of *trans*-1,3-Diphenyl-3-methyl-1-butene. A solution of 471 mg (2.12 mmol) of *trans*-1,3-diphenyl-3-methyl-1-butene in 700 mL of dry *tert*-butyl alcohol (distilled from calcium hydride) was degassed with deoxygenated nitrogen for 1 h and irradiated for 0.25 h through a 1-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo to give a yellow oil. Analysis by VPC on column E showed the presence of 53% *trans*-1,3-diphenyl-3-methyl-1-butene, 40% *trans*-1,2-diphenyl-3,3-dimethylcyclopropane, and 7% *cis*-1,3-diphenyl-3-methyl-1-butene. No *cis*-1,2-diphenyl-3,3-dimethylcyclopropane could be detected by VPC or by NMR. This was chromatographed on a 100 × 3 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 50-mL fractions: fractions 1–25, nil; 26–33, 126 mg of a mixture containing 24% *cis*-1,3-diphenyl-3-methyl-1-butene and 76% *trans*-1,2-diphenyl-3,3-dimethylcyclopropane (by NMR); 34–40, 191 mg of a mixture containing 45% *trans*-1,2-diphenyl-3,3-dimethylcyclopropane and *trans*-1,3-diphenyl-3-methyl-1-butene (by NMR); 41–50, 151 mg of *trans*-1,3-diphenyl-3-methyl-1-butene. Fractions 26–33 were rechromatographed on a 100 × 3 cm silica gel column eluting with hexane taking 50-mL fractions: fractions 1–31, nil; 32–35, 15.2 mg of *cis*-1,3-diphenyl-3-methyl-1-butene identical with respect to NMR and VPC retention time (column E, vide infra) with an authentic sample; 36–40, 55.7 mg of a mixture containing 24% *cis*-1,3-diphenyl-3-methyl-1-butene and *trans*-cyclopropane photoproduct (by NMR); 41–60, 57 mg of pure (by VPC, column E) *trans*-1,2-diphenyl-3,3-dimethylcyclopropane. Fractions 41–60 were crystallized from methanol at low temperature to give material identical in all respects (IR, NMR, VPC, and mp 23–26 °C) with an authentic sample of *trans*-cyclopropane.

Preparative Sensitized Irradiation of *trans*-1,3-Diphenyl-3-methyl-1-butene. A solution of 350 mg (1.58 mmol) of *trans*-1,3-diphenyl-3-methyl-1-butene and 523 mg (3.49 mmol) of *m*-methoxyacetophenone in 250 mL of *tert*-butyl alcohol was degassed for 2.5 h with deoxygenated nitrogen. The Black Box[6] irradiation apparatus and filter solution B (vide infra) were used; after 4 h of irradiation aliquots showed no further change in composition. Analysis by NMR and VPC (column E, vide infra) gave 58% *cis*-1,3-diphenyl-3-methyl-1-butene and 42% *trans*-styryl starting material. The photolysate was concentrated in vacuo and chromatographed on a 90 × 2 cm silica gel column eluting with hexane taking 250-mL fractions. The following chromatogram was obtained: fractions 3–4, 141 mg of *cis*-styryl and 44% *trans*-styryl compounds; 6–9, 103 mg of *trans*-styryl starting material. The total mass balance was 100%. All fractions were analyzed by VPC (column E below) and no cyclopropane products could be detected.

Preparative Sensitized Irradiation of *cis*-1,3-Diphenyl-3-methyl-1-butene. A solution of 725 mg (3.26 mmol) of *cis*-1,3-diphenyl-3-methyl-1-butene and 1.70 g (11.3 mmol) of *m*-methoxyacetophenone in 700 mL of dry *tert*-butyl alcohol was degassed for 1 h with deoxygenated nitrogen, and then irradiated for 1 h through a Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo. Analysis by NMR gave 55% *trans*-1,3-diphenyl-3-methyl-1-butene and 45% *cis*-styryl starting material. The mixture was chromatographed on a 92 × 2.7 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane and taking 100-mL fractions. Fractions 1–5, nil; 6–16, 205 mg of *cis*-styryl starting material; 17–21, 291 mg of a mixture containing 41% *cis*-styryl starting material and 59% *trans*-styryl compound; 22–29, 208 mg of *trans*-styryl compound. The total mass balance was 97%. Fractions were analyzed by VPC on column E (vide infra). No cyclopropane products were detected.

Summary of Analytical Procedures. The procedure for analyses involved addition of a weighed amount of internal standard to a sample and analysis either by high-pressure liquid chromatography (HPLC) or gas chromatography (VPC). For HPLC, the following columns were used: Column A, 10 ft × ⅛ in. Corasil/C-18 eluting with 50% acetonitrile in water (v/v) at 1.5 mL/min flow rate; column B, 2 ft × ⅛ in. silica microbeads[41] (particle size 10–30 μ) eluting with 1.5% ether in hexane at 1.5 mL/min flow rate; column C, 2 ft × ⅛ in. C-18 coated silica microbeads[41] (particle size 10–30 μ) eluting with 50% acetonitrile in water (v/v) at 0.12 mL/min flow rate. For VPC analyses, the following columns were used: column D, 6 ft × 0.25 in. 3% Carbowax 20M on 80/100 mesh Chromosorb W at 200 °C with nitrogen as carrier gas at 36 mL/min flow rate; column E, 6 ft × 0.25 in. 10% QF-1 on Chromosorb W at 130 °C with nitrogen carrier gas at 28.5 mL/min flow rate. Peak areas were measured by planimetry and the detector, UV at a wavelength of 254 nm for HPLC, flame ionization for assay by VPC, was calibrated for the relative responses of the components using a known mixture.

Photolysis Equipment and Procedure for Quantum Yield Determinations. Quantum yield irradiations employed either the Black Box apparatus previously described[6] or the microbench apparatus.[6] For Black Box irradiations the light from a high-pressure mercury lamp centered at the focus of a parabolic aluminum reflector was passed through a cell containing three compartments for filter solutions. The photolysis cell consisted of two identical compartments, each 12 cm in diameter with a 5-cm optical path, having a volume of 750 mL. A cell perpendicular to the main beam received light from a beam splitter. Light output was monitored by ferrioxalate actionometry[7] and the light absorbed in the reaction cell was determined by the splitting ratio technique. Alternatively, light was monitored with an electronic actinometer[8] that utilized two 1P28 photomultipliers, one which received light diverted 90° by the beam splitter, the other which monitored light not absorbed by the photolysate, and also a multiplexed voltage to frequency converter and two digital counters. This was calibrated against ferrioxalate actinometry for each run. When digital actinometry was used, a single compartment cell of 750 mL volume for the photolysate was employed.

All irradiations employed dry *tert*-butyl alcohol (distilled from calcium hydride) as solvent. Vanadous purified nitrogen[42] was passed through the photolysis solution for 1.0 h before and also during irradiations. For sensitized irradiations, degassing was conducted for 2 h prior to photolysis.

For direct irradiations that employed the Black Box filter solution combination A was used: 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid in the first compartment, 0.8 M cobalt sulfate heptahydrate in the second compartment, and 2×10^{-4} M bismuth trichloride in 20% hydrochloric acid in the third compartment. The UV transmission was 254 to 307 nm with a maximum of 38% at 283 nm. For sensitized irradiations on the Black Box, the following filter solutions were used: filter solution combination B, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid in the first compartment, 0.8 M cobalt sulfate heptahydrate in the second compartment, and 0.02 M stannous chloride dihydrate in 15% hydrochloric acid in the third compartment. The UV transmission was from 308 to 356 nm with a maximum at 325 nm of 20%; filter solution combination C, 1.0 M nickel sulfate hexahydrate in 5% sulfuric acid, 1.07 M cobalt sulfate heptahydrate in 5% sulfuric acid, and 0.04 M stannous chloride dihydrate in 15% hydro-

chloric acid. The UV transmission was 314 to 363 nm with a maximum of 22% at 333 nm.

For irradiations employing the microbench apparatus, light from an HBO 200-W high-pressure mercury lamp was passed through a Bausch and Lomb monochromator set at 280 nm for direct irradiations and 325 nm for sensitized irradiations. The monochromator entrance slit was set at 5.3 mm and the exit slit at 3.0 mm to give a band-pass of ca. 20 nm at half-peak height. For direct irradiations only, a solution filter of 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid with 2.2-cm path length was additionally used to exclude 360-nm light.

tert-Butyl alcohol solvent was degassed 0.75 h prior to photolysis with oxygen-free nitrogen. Cells of 40-mL volume were used.

Unless otherwise noted, workup consisted of concentration in vacuo and analysis by HPLC or VPC as described above.

Summary of Quantum Yield Results for the Direct Irradiation of 1,1,3-Triphenyl-3-methyl-1-butene. The Black Box apparatus and filter solution A were used. After workup, 1,1,1-triphenylethane was added as an internal standard and assay was performed by HPLC on column A. The retention times were as follows: triphenylethane, 20 min; 1,1,2-triphenyl-3,3-dimethylcyclopropane, 27 min; 1,1,3-triphenyl-3-methyl-1-butene, 35 min. The data are listed as follows: starting 1,1,3-triphenyl-3-methyl-1-butene (mmol), light absorbed, 1,1,2-triphenyl-3,3-dimethylcyclopropane formed (mmol), quantum yield of formation, percent conversion.

Run 1. 1,1,3-Triphenyl-3-methyl-1-butene (1.64 mmol), 3.39 mEinsteins, 1,1,2-triphenyl-3,3-dimethylcyclopropane (0.124 mmol), $\Phi = 0.0367$, 7.6% conversion.

Run 2. 1,1,3-Triphenyl-3-methyl-1-butene (1.72 mmol), 5.60 mEinsteins, 1,1,2-triphenyl-3,3-dimethylcyclopropane (0.193 mmol), $\Phi = 0.0344$, 11.1% conversion.

Run 3. 1,1,3-Triphenyl-3-methyl-1-butene (1.67 mmol), 1.61 mEinsteins, 1,1,2-triphenyl-3,3-dimethylcyclopropane (0.0574 mmol), $\Phi = 0.0356$, 3.4% conversion.

Quantum Yield for the Sensitized Irradiation of 1,1,3-Triphenyl-3-methyl-1-butene. The Black Box apparatus and filter solution B were used. A solution of 297 mg (0.997 mmol) of 1,1,3-triphenyl-3-methyl-1-butene and 1.09 g (7.27 mmol) of *m*-methoxyacetophenone in 750 mL of *tert*-butyl alcohol absorbed 13.59 mEinsteins. The photolysate was concentrated in vacuo and chromatographed on a 90 × 2.7 cm silica gel column (MCB, grade 62, 60–200 mesh) eluting with hexane taking 500-mL fractions. Each fraction was analyzed for 1,1,2-triphenyl-3,3-dimethylcyclopropane by NMR: fractions 1–2, nil; 3–7, 297 mg (0.997 mmol) of starting material and no trace of cyclopropane product (0.033 mmol would have been detected in any one fraction); the mass balance was 100%. The quantum yield for cyclopropane formation is less than 0.0024.

Summary of Quantum Yield Results for the Direct Irradiation of 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene. The Black Box apparatus and filter solution A as described above were used. After workup, *p*-bromobenzophenone was added an internal standard and assay was performed by HPLC on column B. The retention times were as follows: *p*-bromobenzophenone, 8 min; 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene, 13 min; 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane, 18 min. The data are listed as follows: starting material (mmol), light absorbed, 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane (mmol), quantum yield, % conversion.

Run 1. 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene (0.939 mmol), 1.47 mEinsteins, 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane (0.0644 mmol), $\Phi = 0.0438$, 6.85% conversion.

Run 2. 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene (0.953 mmol), 1.66 mEinsteins, 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane (0.0731 mmol), $\Phi = 0.0441$, 7.7% conversion.

Quantum Yield for the Sensitized Irradiation of 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene. The Black Box apparatus and filter solution B were used as described above. A solution of 303 mg (0.939 mmol) of 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene and 1.22 g (8.13 mmol) of *m*-methoxyacetophenone in 750 mL of *tert*-butyl alcohol absorbed 5.76 mEinsteins. The photolysate was concentrated in vacuo and *p*-bromobenzophenone was added as an internal standard. Analysis by HPLC (column B) gave 0.907 mmol of starting material and no 1,1-diphenyl-2-(*p*-cyanophenyl)-3,3-dimethylcyclopropane (7.77×10^{-3} mmol would have been detected); the mass balance was 96.5%. The quantum yield would be less than 0.001 35.

Summary of Quantum Yield Results for the Direct Irradiation of 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. The Black Box apparatus and filter solution A as described above were used. After workup, 1,2-diphenylethane was added an an internal standard and assay was performed by HPLC using column C. The retention times follow: 1,2-diphenylethane, 55 min; 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane, 88 min; 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene, 108 min. The data are listed as follows: 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene (mmol), light absorbed, 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane (mmol), quantum yield, % conversion.

Run 1. 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene (0.790 mmol), 0.473 mEinsteins, 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane (0.0291 mmol), $\Phi = 0.0615$, 3.69%.

Run 2. 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene (0.805 mmol), 0.245 mEinsteins, 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane (0.0133 mmol), $\Phi = 0.0544$, 1.67%.

Run 3. 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene (0.901 mmol), 1.47 mEinsteins, 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane (0.0860 mmol), $\Phi = 0.0588$, 9.54%.

Quantum Yield for the Sensitized Irradiation of 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. The Black Box apparatus and filter solution B were used as described above. A solution of 348 mg (1.06 mmol) of 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene and 916 mg (6.11 mmol) of *m*-methoxyacetophenone in 250 mL of *tert*-butyl alcohol absorbed 5.27 mEinsteins of light. The photolysate was concentrated in vacuo and chromatographed on a 90 × 2.0 cm silica gel column slurry packed in hexane. Elution with 1.5% ether in hexane and taking 500-mL fractions gave 347 mg (1.06 mmol) of recovered starting material. The mass balance was 99.7%. Analysis of fractions 8–10 by 270-MHz NMR showed no observable 1,1-diphenyl-2-(*p*-methoxyphenyl)-3,3-dimethylcyclopropane (1.03×10^{-2} mmol would have been detected). The limit of detection was determined by doping the residue after NMR analysis with the cyclopropane and reanalyzing. The quantum yield for cyclopropane formation is less than 0.001 95.

Summary of Quantum Yields for 1,1-Diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene. The direct quantum yield photolyses employed the Black Box apparatus and filter solution A.

Analysis involved concentration of the photolysate in vacuo, addition of a weighed amount of bibenzyl as an internal standard, and assay on column C by HPLC. The retention times follow: bibenzyl, 47 min; 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane, 93 min; 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene, 120 min. Run 3 was analyzed by 270-MHz NMR using the relative integration of the benzylic protons of the bibenzyl standard at τ 7.263 (in benzene-d_6) and the cyclopropyl proton of the photoproduct at τ 7.350. The variation in relaxation times was compensated for by comparison to a known mixture of standard and photoproduct.

The data for the direct quantum yield runs are as follows: starting 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene (mmol), light absorbed, 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane, quantum yield of formation, per cent conversion.

Run 1. Starting olefin, 0.815 mmol; 0.535 mEinsteins absorbed; cyclopropane formed, 0.0131 mmol; $\Phi = 0.0244$; 1.6% conversion.

Run 2. Starting olefin, 0.816 mmol; 1.020 mEinsteins absorbed; cyclopropane formed, 0.0257 mmol; $\Phi = 0.0252$; 3.1% conversion.

Run 3. Starting olefin, 0.774 mmol; 1.560 mEinsteins absorbed; cyclopropane formed, 0.0364 mmol; $\Phi = 0.0233$; 4.7% conversion.

Quantum Yield Procedure for Sensitized Irradiation of 1,1-Diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene. Sensitized quantum yields were run on the Black Box apparatus as described above using filter solution B. *m*-Methoxyacetophenone was used as sensitizer and absorbed over 99% of the light incident on the solution.

In the determination, 331 mg (1.01 mmol) of 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene was irradiated in the presence of 1.01 g (6.77 mmol) of *m*-methoxyacetophenone for 10 h absorbing 10.86 mEinsteins of light. The photolysate was concentrated in vacuo, and the sensitizer separated from the mixture by chromatography on a 2.8 × 88 cm silica gel (Grace 62, 60–200 mesh) column containing 2% no. 2282 green Sylvania phosphor, slurry packed in hexane. Elution with 1% ether in hexane gave the following 500-mL fractions: fractions 1–2, nil; 3–4, 319 mg of starting olefin and any cyclopropane photoproduct. Fractions 3–4 were analyzed by 270-MHz NMR. No cyclopropyl proton at τ 7.350 (in benzene-d_6) could be observed. Ad-

dition of 1% (by weight) of 1,1-diphenyl-2-(*m*-methoxyphenyl)-3,3-dimethylcyclopropane to the NMR solution gave a detectable peak at τ 7.350. Thus, the limit of detection of the expected photoproduct was 1% or better. Using this detection limit as a lower bound, the following results were obtained:

Sensitized Run. Starting olefin, 1.01 mmol; 10.86 mEinsteins absorbed; cyclopropane formed, <0.0101 mmol; $\phi < 0.000\ 93$.

Summary of Quantum Yield Results for the Direct Irradiation of 1,1,3-Triphenyl-1-propene. The Black Box apparatus and filter solution A as described above were used. After workup, 1,1,1-triphenylethane was added as internal standard and analysis was performed by VPC on column D. The retention times follow: triphenylethane, 9.5 min; 1,1,2-triphenylcyclopropane, 14.5 min; 1,1,3-triphenyl-1-propene, 21.0 min; and 1,1-diphenylindan, 23.0 min. The data are reported as follows: starting 1,1,3-triphenyl-1-propene (mmol), light absorbed, 1,1,2-triphenylcyclopropane formed (mmol), quantum yield, 1,1-diphenylindan (mmol), quantum yield, % conversion.

Run 1. 1,1,3-Triphenyl-1-propene (1.83 mmol), 3.80 mEinsteins, 1,1,2-triphenylcyclopropane (0.0277 mmol), $\Phi = 0.007\ 29$, 1,1-diphenylindan (5.26×10^{-3} mmol), $\Phi = 0.001\ 38$, 1.8% conversion.

Run 2. 1,1,3-Triphenyl-1-propene (0.948 mmol), 3.32 mEinsteins, 1,1,2-triphenylcyclopropane (0.0252 mmol), $\Phi = 0.007\ 60$, 1,1-diphenylindan (4.68×10^{-3} mmol), $\Phi = 0.001\ 41$, 3.12% conversion.

Quantum Yield for the Sensitized Irradiation of 1,1,3-Triphenyl-1-propene. The Black Box apparatus and filter solution B were used as described above. A solution of 332 mg (1.23 mmol) of 1,1,3-triphenyl-1-propene and 519 mg (3.46 mmol) of *m*-methoxyacetophenone in 250 mL of *tert*-butyl alcohol absorbed 11.7 mEinsteins of light. The photolysate was concentrated in vacuo and chromatographed on a 90 × 2.7 cm silica gel column eluting with hexane taking 500-mL fractions. Fractions 4–8 afforded 327 mg (98.5% mass balance) of 1,1,3-triphenyl-1-propene and no observable 1,1,2-triphenylcyclopropane or 1,1-diphenylindan by VPC analysis on column D. The limits of detection were 0.005 mmol for both the cyclopropane and the indan each. Thus, quantum yields for each are less than 4.2×10^{-4}.

Summary of Quantum Yield Results for the Direct Irradiation of *trans*-1,3-Diphenyl-3-methyl-1-butene. The optical bench apparatus as described above was used. Workup consisted of concentration in vacuo and addition of bibenzyl as internal standard. Assay was by VPC on column E. The retention times follow: bibenzyl, 14.3 min; *cis*-1,3-diphenyl-3-methyl-1-butene, 22.6 min; *cis*-1,2-diphenyl-3,3-dimethylcyclopropane, 28.2 min; *trans*-1,2-diphenyl-3,3-dimethylcyclopropane, 31.0 min; and *trans*-1,3-diphenyl-3-methyl-1-butene, 59.0 min. The data are listed as follows: *trans*-1,3-diphenyl-3-methyl-1-butene starting material (mmol), mEinsteins absorbed, *cis*-1,3-diphenyl-3-methyl-1-butene formed (mmol), quantum yield, *cis*-1,2-diphenyl-3,3-dimethylcyclopropane (limit of detection in mmol), *trans*-1,2-diphenyl-3,3-dimethylcyclopropane (mmol), quantum yield, % conversion.

Run 1. *trans*-Styryl starting material (0.325 mmol), 6.54×10^{-3} mEinsteins, *cis*-styryl product not analyzed, *cis*-cyclopropane not observed (2.0×10^{-5} mmol would have been detected), *trans*-cyclopropane formed (2.44×10^{-3} mmol), $\Phi = 0.373$, ca. 0.75%.

Run 2. *trans*-Styryl starting material (0.112 mmol), 3.85×10^{-3} mEinsteins, *cis*-styryl product (2.57×10^{-4} mmol), $\Phi = 0.0667$, *cis*-cyclopropane not observed (2×10^{-5} mmol would have been detected), *trans*-cyclopropane formed (1.65×10^{-3} mmol), $\Phi = 0.428$, 1.71%.

Run 3. *trans*-Styryl starting material (0.159 mmol), 2.08×10^{-3} mEinsteins, *cis*-styryl product (1.30×10^{-4} mmol), $\Phi = 0.0630$, *cis*-cyclopropane not observed (2×10^{-5} mmol would have been detected), *trans*-cyclopropane formed (7.44×10^{-4} mmol), $\Phi = 0.357$, 0.55%

The following run was determined using the Black Box apparatus with filter solution A as described above.

Run 4. *trans*-Styryl starting material (1.04 mmol), 0.0991 mEinsteins, *cis*-styryl product not analyzed, *cis*-cyclopropane not observed (5 × 10−4 mmol would have been detected), *trans*-cyclopropane formed (0.0451 mmol), $\Phi = 0.455$, *ca.* 4.34%

Summary of Quantum Yield Results for the Sensitized Irradiation of *trans*-1,3-Diphenyl-3-methyl-1-butene. The optical bench apparatus at a wavelength of 325 nm was used as described above. Assay was by VPC on column E as with the direct runs. The data are listed as follows: *trans*-1,3-diphenyl-3-methyl-1-butene starting material (mmol), *m*-methoxyacetophenone (mmol), light absorbed, *cis*-1,3-diphenyl-3-methyl-1-butene formed (mmol), quantum yield, *cis*-1,2-diphenyl-3,3-dimethylcyclopropane (limit of detection in mmol), *trans*-1,2-diphenyl-3,3-dimethylcyclopropane (limit of detection in mmol), % conversion.

Run 1. *trans*-Styryl starting material (0.271 mmol), *m*-methoxyacetophenone (0.659 mmol), 0.0283 mEinsteins, *cis*-styryl product (0.0114 mmol), $\Phi = 0.401$, *cis*-cyclopropane not observed (1×10^{-4} mmol would have been detected), *trans*-cyclopropane not observed (1×10^{-4} mmol would have been detected), 4.19%

Run 2. *trans*-Styryl starting material (0.291 mmol), *m*-methoxyacetophenone (0.595 mmol), 6.28×10^{-3} mEinsteins, *cis*-styryl product (2.97×10^{-3} mmol), $\Phi = 0.473$, *cis*-cyclopropane not observed (2×10^{-5} mmol would have been detected), *trans*-cyclopropane not observed (2×10^{-5} mmol would have been detected), 1.02%.

Run 3. *trans*-Styryl starting material (0.105 mmol), *m*-methoxyacetophenone (0.523 mmol), 1.14×10^{-3} mEinsteins, *cis*-styryl formed (5.54×10^{-4} mmol), $\Phi = 0.486$, no *cis*-cyclopropane was observed (2×10^{-5} mmol would have been detected), *trans*-cyclopropane not observed (2×10^{-5} mmol would have been detected), 0.527%.

Summary of Quantum Yield Results for the Direct Irradiation of *cis*-1,3-Diphenyl-3-methyl-1-butene. The optical bench apparatus as described above was used. The wavelength was 280 nm. Workup consisted of concentration in vacuo and addition of *o*-terphenyl as internal standard. Assay was by VPC on column E as described above for the *trans*-styryl compound. The retention time for *o*-terphenyl was 51 min. The data are listed as follows: *cis*-1,3-diphenyl-3-methyl-1-butene starting material (mmol), light absorbed, *trans*-1,3-diphenyl-3-methyl-1-butene formed (mmol), quantum yield, % conversion. Neither *cis*-1,2-diphenyl-3,3-dimethylcyclopropane nor *trans*-1,2-diphenyl-3,3-dimethylcyclopropane was observed (2×10^{-5} mmol would have been detected).

Run 1. *cis*-Styryl starting material (0.116 mmol), 1.83×10^{-3} mEinsteins, *trans*-styryl product (7.25×10^{-4} mmol), $\Phi = 0.396$, 0.626%.

Run 2. *cis*-Styryl starting material (0.249 mmol), 1.98×10^{-3} mEinsteins, *trans*-styryl product (8.32×10^{-4} mmol), $\Phi = 0.419$, 0.334%.

Summary of Quantum Yield Results for the Sensitized Irradiation of *cis*-1,3-Diphenyl-3-methyl-1-butene. The optical bench apparatus with a wavelength of 325 nm was used as described above. Assay was by VPC on column E as described for the direct irradiations. The data are listed as follows: *cis*-1,3-diphenyl-3-methyl-1-butene starting material (mmol), *m*-methoxyacetophenone (mmol), light absorbed, *trans*-1,3-diphenyl-3-methyl-1-butene formed (mmol), quantum yield, % conversion. Neither *cis*- nor *trans*-1,2-diphenyl-3,3-dimethylcyclopropane was observed (1×10^{-5} mmol limit of detection for each).

Run 1. *cis*-Styryl starting material (0.0788 mmol), *m*-methoxyacetophenone (0.460 mmol), 2.58×10^{-3} mEinsteins, *trans*-styryl product (1.16×10^{-3} mmol), $\Phi = 0.448$, 1.47%.

Run 2. *cis*-Styryl starting material (0.0851 mmol), *m*-methoxyacetophenone (0.3127 mmol), 7.94×10^{-4} mEinsteins, *trans*-styryl product (3.58×10^{-4} mmol), $\Phi = 0.451$, 0.421%.

Run 3. *cis*-Styryl starting material (0.111 mmol), *m*-methoxyacetophenone (0.275 mmol), 1.86×10^{-3} mEinsteins, *trans*-styryl product (8.35×10^{-4} mmol), $\Phi = 0.449$, 0.754%.

Control Run. Quantum Yield for the Direct Irradiation of *trans*-1,3-Diphenyl-3-methyl-1-butene with Added *cis*-1,2-Diphenyl-3,3-dimethylcyclopropane. The procedure employed the microbench apparatus with a wavelength of 280 nm as for the direct irradiation of *trans*-1,3-diphenyl-3-methyl-1-butene above. A solution of 0.114 mmol of *trans*-1,3-diphenyl-3-methyl-1-butene and 4.71×10^{-3} mmol of *cis*-1,2-diphenyl-3,3-dimethylcyclopropane in 40 mL of dry *tert*-butyl alcohol was degassed for 0.75 h and irradiated until 3.57×10^{-3} mEinsteins were absorbed. VPC analysis on column E with added bibenzyl as an internal standard gave *cis*-1,3-diphenyl-3-methyl-1-butene (2.14×10^{-4} mmol), $\Phi = 0.0600$; *cis*-1,2-diphenyl-3,3-dimethylcyclopropane recovered (4.71×10^{-3} mmol), 100%; and *trans*-1,2-diphenyl-3,3-dimethylcyclopropane (1.40×10^{-3} mmol), $\Phi = 0.391$, 1.41% conversion with no disappearance of *cis*-cyclopropane additive.

Energy Transfer Tests. Quenching of Benzophenone Triplets by 1,1,3-Triphenyl-3-methyl-1-butene. The irradiations were carried out on the Black Box apparatus with filter solution combination C as

described above. A solution of 1.10 g (6.04 mmol) of benzophenone and 541 mg (2.94 mmol) of benzhydrol in 250 mL of *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.0 h before and during the irradiation. Similarly, a solution of 998 mg (5.48 mmol) of benzophenone, 494 mg (2.68 mmol) of benzhydrol, and 141 mg (0.473 mmol) of 1,1,3-triphenyl-3-methyl-1-butene in 250 mL of *tert*-butyl alcohol was purged with nitrogen and irradiated. Each photomixture was chromatographed on a 100 × 3 cm silica gel column (MCB, grade 62, 60–200 mesh) slurry packed in hexane taking 250-mL fractions. The chromatograms follow: fractions 1–4, hexane, nil; 5–12, 1% ether in hexane, 1,1,3-triphenyl-3-methyl-1-propene (when present in photolysate); 13–22, 1% ether in hexane, benzophenone; 23–26, 2% ether in hexane, nil; 27–32, 4% ether in hexane, benzpinacol; 33–38, 8% ether in hexane, nil; 39–50, 8% ether in hexane, benzhydrol. The data are reported as follows: 1,1,3-triphenyl-3-methyl-1-butene quencher recovered, light absorbed, benzophenone recovered (mmol), benzpinacol formed (mmol), quantum yield, benzhydrol recovered (mmol), mass balance (%), percent quenching.

Run 1. No quencher, 4.70 mEinsteins, benzophenone recovered (5.40 mmol), benzpinacol (0.677 mmol), $\Phi = 0.144$, benzhydrol recovered (2.12 mmol), 99% mass balance, 0% quenching.

Run 2. Quencher, 1,1,3-triphenyl-3-methyl-1-butene recovered (0.473 mmol), 4.20 mEinsteins, benzophenone recovered (5.40 mmol), benzpinacol (0.0439 mmol), $\Phi = 0.0105$, benzhydrol recovered (2.33 mmol), mass balance 96%, 93% quenching. No 1,2-diphenyl-3,3-dimethylcyclopropane photoproduct was detected.

Sample Preparation for Fluorescence Measurements and Single Photon Counting. For UV fluorescence and rate studies, purified[12,43] methylcyclohexane and isopentane, transparent by UV and emission free, were used. 1,1,3-Triphenyl-3-methyl-1-butene was recrystallized alternating between 95% ethanol and UV pure methylcyclohexane as solvents. 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene was recrystallized similarly from 95% ethanol and UV pure isopentane. 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene was recrystallized from 95% ethanol, UV pure isopentane, and UV pure methylcyclohexane. 1,1,3-Triphenyl-1-propene was purified by silica gel chromatography and molecular distillation to afford analytically pure material by VPC (vide supra). *trans*-1,3-Diphenyl-3-methyl-1-butene was purified by repetitive silica gel column chromatography and molecular distillation as described above.

The studies employed 4:1 methylcyclohexane–isopentane as solvent; samples were prepared in 1-cm quartz cells and degassed by five freeze–pump–thaw cycles. Samples were suspended in a quartz Dewar for low-temperature measurements using liquid nitrogen as coolant (77 K).

Fluorescence Spectroscopy. Fluorescence measurements employed an Aminco-Kiers spectrofluorimeter with a Hanovia 901C-1 150-W xenon lamp. All compounds studied exhibited fluorescence at 310 ± 2 nm both at room temperature and low temperature (77 K). Emission maxima and intensities were independent of excitation wavelength (255–270 nm) for optical densities of 0.80–1.00 at the excitation wavelength employed. The ratio of the integrated emissions at low temperature (77 K) to that at room temperature gave the "magic multiplier", M[12,43] (determinations made with a sample suspended in a quartz Dewar at both temperatures). The data were as follows: 1,1,3-triphenyl-3-methyl-1-butene, 202 ± 17 (4 runs); 1,1-diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene, 281 ± 3 (3 runs); 1,1-diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene, 289 ± 12 (3 runs); 1,1,3-triphenyl-1-propene, 202 ± 8 (3 runs); 1,1-diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene, 132 ± 13 (9 runs).

Rate Measurements by Single Photon Counting. The method used for determination of fluorescence decay rates has been described by Zimmerman, Kamm, and Werthemann.[12,43] Samples were prepared as noted above. The sampling rate was 5% of the nitrogen flash lamp frequency (25–30 kHz) to avoid counting double photon pulses and the maximum number of counts collected in any one of 512 channels was ca. 2000. The deconvolution technique using an on-line PDP-8I minicomputer gave the decay rate obtained from the measured intensity vs. time curves for flash and experiment.[12,43]

Rates measured at 77 K were converted to room temperature rates by multiplying by the "magic multiplier". Optical densities were from 1.5 to 2.0 for 77 K runs; for *trans*-1,3-diphenyl-3-methyl-1-butene, which was the only case where measurements were made at room temperature, optical densities of 1.0–1.3 were required to minimize fluorescence quenching. Variation in wavelength of excitation (250–270 nm) and wavelength of emission (310–325 nm) for each case produced changes in lifetime well within experimental error. The ratio of the area mismatch between experimental and computer-calculated intensity vs. time curves to the area under the experimental curve[43] was 5% or less in all cases. The data are listed as follows: temperature at which the measurements were made, average rate of decay (s^{-1}), average lifetime, and the number of runs. Error limits reported are average deviations.

1. 1,1,3-Triphenyl-3-methyl-1-butene. 77 K, $2.6 \pm 0.2 \times 10^8$ s^{-1}, 3.9 ± 0.4 ns, 7 runs.
2. 1,1-Diphenyl-3-(*p*-cyanophenyl)-3-methyl-1-butene. 77 K, $1.69 \pm 0.02 \times 10^8$ s^{-1}, 5.93 ± 0.05 ns, 4 runs.
3. 1,1-Diphenyl-3-(*p*-methoxyphenyl)-3-methyl-1-butene. 77 K, $5.7 \pm 0.5 \times 10^8$ s^{-1}, 1.8 ± 0.1 ns, 4 runs.
4. 1,1-Diphenyl-3-(*m*-methoxyphenyl)-3-methyl-1-butene. 77 K, $3.84 \pm 0.05 \times 10^8$ s^{-1}, 2.61 ± 0.03 ns, 4 runs.
5. 1,1,3-Triphenyl-1-propene. 77 K, $2.55 \pm 0.03 \times 10^8$ s^{-1}, 3.92 ± 0.05 ns, 3 runs.
6. *trans*-1,3-Diphenyl-3-methyl-1-butene. 295 K, 1.02×10^9 s^{-1}, 0.978 ± 0.003 ns, 3 runs.

Calculations. The Pople semiempirical SCF method[14] (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. An initial set of up to 100 singly excited and 5050 doubly excited configurations was generated. Important configurations were selected from this set, as determined by the extent of the perturbations[15] on the first two excited states by a representative set of up to 26 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.[44] Standard techniques[20] for the reduction of many electron integrals then gave general formulas used to calculate matrix elements between configurations.[45]

Valence state ionization potentials were taken from Hinze and Jaffe,[46] except for heteroatoms, where values compiled by Nishimoto[47] were used. The Pariser–Parr method[14b] was used to calculate atomic orbital repulsion integrals.

Resonance integrals were evaluated using[48] $\beta_{ij} = \{S_{ij}/(1 + S_{ij})\}(I_i + I_j)K$ where S_{ij} is the overlap integral,[49] and I_i and I_j are the respective valence state ionization potentials for 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 model compounds.

Standard geometries for starting distyryl methanes were assumed based on model compounds reported.[50] Geometries for 1,4-biradical species were extrapolated from a reported INDO calculation with geometry optimization for the ground state 2-vinylcyclopropylcarbinyl radical.[51]

Calculations were performed with programs[45] 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.

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References and Notes

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Photochemical Electron-Transfer and Triplet Reactions of 1,2-Diphenylcyclopropene-3-carboxylate[1]

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Abstract: In nonpolar solvents singlet-excited 9,10-dicyanoanthracene (^{1}DCA*) and methyl 1,2-diphenylcyclopropene-3-carboxylate (CP) form an emitting exciplex and yield the exo Diels-Alder adduct **1**. In polar solvents ^{1}DCA* reacts with CP at a diffusion-controlled rate leading to the formation of the radical ions $CP^{+}\cdot$ and $DCA^{-}\cdot$. Recombination of this radical ion pair partially gives ^{3}CP*, which reacts with CP to give the dimer **3**. The triplet yield in this reaction is increased by more than an order of magnitude when 1,2,4,5-tetracyanobenzene (TCNB) is added in small amounts. This effect is due to a secondary electron transfer from $DCA^{-}\cdot$ to TCNB, followed by recombination of $TCNB^{-}\cdot$ and $CP^{+}\cdot$, which leads to a higher triplet yield than that from the corresponding reaction with $DCA^{-}\cdot$. Further support for this electron-transfer/triplet mechanism is obtained from quenching of $CP^{+}\cdot$ by compounds having low oxidation potentials and from quenching and chemical trapping of ^{3}CP*. In connection with the latter experiments the preparative and kinetic aspects of the triplet reactions of CP with dimethyl fumarate (F) and *p*-cyanocinnamate esters (CNC) are investigated. The main products of these reactions are the bicyclopentane derivatives **4-6** and **11-13**, respectively. The radical cation $CP^{+}\cdot$, formed in polar solvents, tautomerizes to the enol radical cation ($E^{+}\cdot$), which adds to $DCA^{-}\cdot$ and, upon reketonization of the product, the endo Diels-Alder adduct **2** is obtained. This mechanism is supported by a deuterium isotope effect, incorporation of deuterium in the product on irradiation in the presence of *t*-BuOD, and other experiments. The intermediate $E^{+}\cdot$ can be trapped with F and CNC giving different products (**8-10** and **14**, respectively) from those obtained from the reaction of ^{3}CP* with these reactants. Irradiation of DCA and CP in polar solvents in the presence of O_2 leads, in a chain process, to several oxidation products. This oxidation probably proceeds via reaction of $CP^{+}\cdot$ with oxygen.

Introduction

Reactions of exciplexes and electron transfer are currently attracting considerable interest in organic photochemistry. Photochemical charge-transfer (exciplex) and electron-transfer (radical ions) reactions are controlled by redox potentials, excitation energy, and solvent polarity.[2] Whereas excited complexes and exciplexes are usually formed in nonpolar sol-

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