# THE Di- $\pi$ -METHANE REARRANGEMENT OF SYSTEMS WITH SIMPLE VINYL MOIETIES

# MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY<sup>1,2</sup>

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Abstract-3,3-Dimethyl-1,1-diphenyl-1,4-pentadiene and two 5-substituted derivatives were synthesized and studied. The regioselectivity, stereochemistry, quantum efficiency, multiplicity, and excited state reaction rates were studied in each case. The parent hydrocarbon, 5-MeO-derivative, and 5-cyano-diene-all rearranged on direct irradiation to give vinylcyclopropanes. The first compound led to 3,3-dimethyl-2,2-diphenyl-1-vinylcyclopropane. The second afforded 3,3-dimethyl-2,2-diphenyl-1-(2'-methoxyvinyl)cyclopropane. The last gave 1-cyano-3,3dimethyl-2-(2',2'-diphenylvinyl)cyclopropane. Thus, the vinyl and methoxyvinyl groups survive in the products intact, while the cyanovinyl group is incorporated in the three-ring. In the two substituted dienes, cis-reactant gave cis-product and trans-reactant gave trans-product, both where the substituent was on the vinyl group of the product and where it became a ring substituent. The substituted di- $\pi$ -methane systems underwent only cis-trans isomerization on sensitization, while the parent, unsubstituted diene led to di- $\pi$ -methane product on sensitized as well as direct photolysis. While the quantum yields for the hydrocarbon diene were the same at room temperature for the direct and sensitized runs, only the sensitized runs showed a temperature dependence of efficiency with a dramatic, 5-fold increase on a 46° temperature increase. Thus, evidence was obtained for a singlet rearrangement in all cases and a triplet process only in the case of the unsubstituted diene. A sizable activation energy was seen for the triplet but not for the singlet. The room temperature quantum yields in the direct irradiations were:  $\phi$  (parent diene) = 0.011,  $\phi$ (trans-methoxydiene) = 0.051,  $\phi$ (cis-methoxy-diene) = 0.050,  $\phi$ (trans-cyanodiene) = 0.36, and  $\phi$ (cis-cyano-diene) = 0.20. A competing side reaction was cis-trans isomerization but these quantum yields were lower. Single photon counting was employed to obtain excited singlet reaction and decay rates at low temperature (i.e.  $77^{\circ}K$ ) and the method of magic multipliers was used to obtain room temperature rates. These were:  $k_r$  (parent diene) =  $4.7 \times 10^8 \text{ sec}^{-1}$ ,  $k_r(trans - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 8.0 \times 10^9 \text{ sec}^{-1}$ , and  $k_r(trans - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene) = 1.5 \times 10^{10} \text{ sec}^{-1}$ ,  $k_r(cis - cyano-diene)$ methoxy-diene) =  $1.9 \times 10^9$  sec<sup>-1</sup>. The results are discussed in terms of excited state molecular structure.

An SCF-CI molecular orbital treatment of the reaction was developed. This used a cyclopropyldicarbinyl diradical species, with Walsh cyclopropane basis orbitals, as representing the half-reacted species. The energy of formation of this species from vertical excited state reactant was calculated for all three dienes and an excellent correlation with observed excited singlet rates was obtained. Similarly, dissection of the excited diradical energy into bond components led to a correlation between regioselectivity and weakness of the three-ring bond broken in the regioselectivity-determining step. Evidence was adduced for localization of the excitation energy in  $S_1$  of reactant in the diphenylvinyl chromophore with migration of electronic excitation into the cyclopropyldicarbinyl diradical moiety during the vinyl-vinyl bridging process. A general method for quantitatively partitioning excitation energy was developed and applied to the case in hand. Finally, there was predicted a greater probability of di- $\pi$ -methane three-ring fission in the excited state compared to the diradical ground state where Grob fragmentation proved energetically more favorable.

A number of di- $\pi$ -methane rearrangements have been studied<sup>3-6</sup> with the intent of relating excited state reaction rate to substitution. We were interested in the situation where the two  $\pi$  moieties consisted of a diphenylvinyl moiety, which would readily be excited to its first singlet state, together with a methoxy- or cyano-substituted vinyl group which would not partake of the excitation. Hitherto, such examples have not been investigated. Therefore we wished to study the importance of placement of substituents relative to the site of electronic excitation. An unsubstituted model was also required for study.

Thus, the systems selected for study were 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene (1), 1 - cyano -

3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (2) and 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 pentadiene (3). In the case of the latter two, both *cis* and *trans*-stereoisomers were desired.

#### RESULTS

# Synthesis of photochemical reactants and potential photoproducts

The starting point for the synthesis of reactants was the known<sup>7</sup> 2,2 - dimethyl - 4,4 - diphenyl - 3 - butenal (4). The parent hydrocarbon 1 was obtained by reaction of aldehyde 4 with methylenetriphenylphosphorane (note Chart 1). To obtain the *trans*-isomer of cyano-diene 2, the same aldehyde (i.e. 4) was reacted with the diethyl





Chart. 1. Synthesis of photochemical reactant dienes.

cyanomethylphosphonate anion.<sup>8</sup> For the *cis*-isomer, trimethylsilylacetonitrile<sup>9</sup> with lithium diisopropylamide at  $-78^{\circ}$  was employed successfully. This has analogy in the behavior of ethyl trimethylsilylacetate.<sup>10</sup> These subsequent reactions are summarized in Chart 1 as well.

In the case of the *cis*- and *trans*-methoxy-dienes, 3c and 3t, methoxymethylenetriphenylphosphorane<sup>11</sup> was used in conjunction with aldehyde 4. The mixture of stereoisomers obtained was separated by spinning band fractionation followed by column and high pressure liquid chromatography. The reaction is depicted in Chart 1.

With the photochemical reactants in hand, it was desirable to develop independent syntheses of as many of the potential photochemical products as possible. A convenient starting point was the known<sup>12</sup> 3,3 - dimethyl - 2,2 - diphenylcyclopropanecarboxaldehyde (5). Reaction with methylenetriphenylphosphorane led to 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane (6). This was a possible product of the di- $\pi$  methane rearrangement of the parent diene 1. Note Chart 2.

The same aldehyde 5 used with sodium diethyl cyanomethylphosphonate<sup>8</sup> afforded a 2:1 cis-trans mixture of 1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane (7c.t) which was separated by preparative gc. This is included in Chart 2. These isomers were potential products of the photolysis of cyano-diene 2.

Similarly, treatment of aldehyde 5 with methoxy-

methylenetriphenylphosphorane led to the *cis*- and *trans*-isomers of 1 - (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane (8c,t) as noted in Chart 2. Liquid chromatography proved most useful for separation of isomers. These were desired since they were*a priori*products of the irradiation of methoxy diene 3.

Also, the other possible photoproduct from parent diene 1 was obtained by reaction of 2,2 - dimethylcyclopropanecarboxaldehyde<sup>13</sup> (9) with the diethyl diphenylmethylphosphonate (10) anion. This led smoothly to 2,2 dimethyl - 1 - (2',2' - diphenylvinyl)cyclopropane (11). This approach is also included in Chart 2.

Finally, the *cis*- and *trans*-isomers of 1 - cyano - 3,3 dimethyl - 2 - (2',2'-diphenylvinyl)cyclopropane (**12c.t**) were desired. Their synthesis is outlined in Chart 3. The *cis*- and *trans*-isomers of 5,5 - diphenyl - 2,4 pentadienenitrile (**13c**,t) were obtained from the Wadsworth-Emmons reaction of diethyl cyanomethylphosphonate with 3,3-diphenylpropenal (**14**).<sup>14</sup> In this case the *trans* product predominated only slightly, and the isomers were separated chromatographically.

With each of these available, it was of some interest to study the reaction of these with diphenylsulfonium isopropylide<sup>15a</sup> which is known <sup>15b</sup> to give cyclopropanes by Michael addition followed by 1,3-elimination. Evidence is available for both  $\alpha,\beta$ -<sup>15b,c</sup> and  $\gamma,\delta$ -addition, <sup>15c</sup> thus offering hope for the desired  $\alpha,\beta$ -reactivity.

In addition, a synthesis of both the cis- and transstereoisomers was required. The literature of cyclo-



Chart 2. Synthesis of potential photoproducts.

propane formation from reaction of Michael systems with sulfur ylides revealed examples exhibiting lack of stereospecificity<sup>16a-i</sup> and cases with stereospecificity.<sup>15b,16j</sup> Interestingly, most of the examples showing varying degrees of stereospecificity<sup>17</sup> utilize diphenylsulfonium ylides while those lacking stereospecificity involve dimethylsulfonium and other ylides.

Starting with cis - 5, 5 - diphenyl - 2,4 - pentadienenitrile (13c), reaction with diphenylsulfonium isopropylide led to a 12.6:1 ratio of cis to trans isomers of 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane (12). conversely, the same reaction with the trans-unsaturated nitrile 13t led to a 10.2:1 ratio of trans to cis stereoisomers of cyclopropane 12. The yields were essentially quantitative and no evidence for  $\gamma,\delta$ -addition was observed. Refer to Chart 3 for a summary of these results.

We note that this is the first example of stereospecificity in which the electron withdrawing group is cyano. Since this example, and the other exhibiting stereospecificity, have diphenylsulfide as the departing moiety in a carbanionic three-ring formation step, it may be that such a non-nucleophilic departing group allows faster cyclization than free rotation about the  $\alpha,\beta$  bond of the Michael system.

### RESULTS

### Exploratory photochemistry

Product isolation and identification. The first compound selected for photolysis was 3,3 - dimethyl - 1,1

- diphenyl - 1,4 - pentadiene (i.e. the "parent hydrocarbon diene" 1). As with the remainder of the preparative runs, irradiation was carried out using the Wisconsin Black Box apparatus.<sup>18</sup> A nickel-cobaltbismuth filter having maximum transmission at 280 nm was employed (Experimental). Irradiation of 300 mg in t-butyl alcohol for 9.5 hr afforded 57 mg of a product (6), m.p. 46°, along with 231 mg of recovered reactant.

The NMR showed two three-hydrogen singlets at 8.83 and 8.97  $\tau$  which seemed ascribable to two isolated methyl groups. Also a doublet (J = 9Hz) at 7.90  $\tau$  was observed. This seemed most likely due to a cyclopropyl methine adjacent to a vicinal hydrogen. Finally, 270 MHz NMR revealed three remaining one-hydrogen absorptions at 4.63, 4.67 and 4.93  $\tau$ . The derived coupling constants (Experimental for details) included a 9 Hz interaction by one of these three; and overall a simple vinyl moiety (i.e. -CH = CH<sub>2</sub>) was indicated.

This information, coupled with the expectation of a di- $\pi$ -methane rearrangement, suggested 3,3 - dimethyl - 2,2 - diphenyl - 1 vinylcyclopropane as the structure of photoproduct 6. This was one of the two possible regioisomers from such a rearrangement, and these had been prepared (vide supra) independently. Indeed photoproduct 6 was found to be identical to the synthetically prepared material described above.

The alternative di- $\pi$ -methane regioisomer 11 also had been synthesized. Thus it was possible using both NMR and gc to establish that this regioisomer was formed to less than 0.1 per cent. Also it was established that the non-observed regioisomer 11 did not afford the observed



Chart 3. Synthesis of potential photoproducts. Reaction stereospecificity of diphenylsulfonium isopropylide with 5,5-diphenyl-2,4-pentadienenitrile.

photoproduct  $\mathbf{6}$  when it itself was irradiated. Note eqn (1) for a summary.

The second compound selected for irradiation was 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (2). Each stereoisomer, *cis* and *trans*, was investigated separately. An independent investigation of the *trans*-isomer of cyano-diene 2 has been reported in preliminary form.<sup>19</sup>

It was found that irradiation of either the *cis*- or *trans*-isomer of cyano-diene 2 under preparative conditions led to formation of two, stereoisomeric cyclo-

propane products. The product structures were suggested by NMR evidence and confirmed rigorously by comparison with the independently synthesized compounds described above. Thus these proved to be the cis- and trans - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' diphenylvinyl)cyclopropanes (12c and 12t).<sup>20</sup> Additionally, it was observed that the reactants were stereoisomerizing under reaction conditions. Beyond this, the photoproducts were also isomerizing. The photochemical behavior of the cyano-dienes under preparative conditions is summarized in eqns (2a) and (2b).



To be certain that the reaction was indeed as regioselective as it thus appeared, the second possible di- $\pi$ -methane photoproducts 7c and 7t had been synthesized. With three different gc columns a search was made for the presence of this regioisomer of product; none was found. An upper limit of 0.1 per cent of this product could be set.

Turning now to the case of 1 - methoxy-3,3 - dimethyl -5,5 - diphenyl - 1,4 - pentadiene (3), we noted that in contrast to the cyano example, the reaction product had the substituent on the vinylcyclopropane double bond. Thus, it was observed that 1 - (2' - methoxyvinyl) - 3,3 dimethyl - 2,2 - diphenylcyclopropane (8) was formed. Both cis and trans products were obtained from transreactant. Also, reactant was observed to stereoisomerize competitive with rearrangement. Again, the photoproducts had been anticipated and were already in hand. Experimental difficulties were posed by the oxygen sensitivity of the cis-reactant and also its tendency to isomerize to the *trans*-isomer so that stereochemistry could not be studied at high conversion. The results of the preparative run are summarized in eqn (3).

Again a search for the non-observed regioisomers of product was made. These would be diphenylvinyl substituted methoxy-cyclopropane derivatives. The NMR spectra showed only peaks due to the major photoproducts. More stringently, high pressure liquid chromatography of the product mixtures (Experimental) revealed no extraneous peaks.

One other reaction was explored, and this involved the photochemistry of the cyano-cyclopropanes 12c and 12t. Under preparative conditions it was found that these *cis*-and *trans*-photoproducts were interconverted. Using the same 280 nm filter a *ca.* 1.6 ratio of *cis* to *trans* cyano-cyclopropane mixture (12c: 12t) was formed independent

of which stereoisomeric cyclopropane was irradiated. Note eqn (4).

In these exploratory efforts sensitized runs were carried out as well. In the substituted diene cases (i.e. 2 and 3), *cis-trans* isomerization was the only observed reaction (eqns 5b, c). Interestingly, the parent hydrocarbon diene 1 underwent the di- $\pi$ -methane rearrangement with facility. Note eqn (5a).

#### RESULTS

Reaction stereochemistry, quantum yield studies, and multiplicity determination

As will become self-evident, our stereochemical studies required very low conversion runs of the same type used for quantum yield determinations. Thus, these two types of results are intertwined.

First, we consider the stereochemistry of the di- $\pi$ methane rearrangement of the *cis*- and *trans*-cyanodienes (2c and 2t). It is apparent from the exploratory runs that both *cis*- and *trans*-cyano-cyclopropanes (12c and 12t) result in runs made to moderately high conversion. In view of the interconversion of the cyanocyclopropane products (12c and 12t) and the concomitant stereoisomerization of cyano-diene reactant, this lack of stereospecificity seemed possibly to be an artifact.

Runs were made to successively shorter conversions. These are listed in Table 1. This gives the product distribution as a function of per cent conversion for each cyanodiene reactant.

It is apparent that the product distribution varies markedly with extent conversion. In order to obtain kinetic product distributions and correct quantum yields it was necessary to carry out low conversion runs and then extrapolate the quantum yields to zero time. In the case of product distributions, the values at lowest con-





Table 1. Product distribution as a function of per cent conversion for cyano dienes 2c and 2t

		Ratio	Totol N		
Compd	Run	Isomerized 2	<u>12t</u>	120	Conversion
2t.	1	0.17	1.00	0.41	14.39
~~	2	0.17	1.00	0.34	9.79
	3	0.25	1.00	0.15	1.78
	4	0.36	1.00	0.08	0.99
	5	0.51	1.00	0.07	0.59
	6	0.51	1.00	0.04	0.42
	7	a	1.00	0.00	0.20
	8	a	1.00	0.00	0.12
2c	1	0.98	0.14	1.00	1.61
~~	2	0.94	0.10	1.00	0.91
	3	1.02	0.09	1.00	0.48
	4	1.12	0.05	1.00	0.34
	5	1.16	0.03	1.00	0.21

### <sup>a</sup>Not determined.

version in Table 1 can be taken as being kinetic. Extrapolated quantum yields are given in Table 2. It is clear that quantum yield and product distribution determinations, in general, need to be made at varying conversions, including those low enough that product light absorption becomes negligible.

In connection with the cyano-diene photochemistry, we note that when observed under kinetic conditions, the reaction is stereospecific. Thus, at zero conversion *cis*-cyano-diene **2c** gives *cis*-cyano-cyclopropane **12c** while *trans*-cyano-diene **2t** affords *trans*-cyano-cyclopropane **12t** (see eqn 6). Loss of stereochemistry results in part from the competitive *cis*-*trans* cyano-diene interconversion which can be seen (note Table 2) to be of the same order of magnitude in efficiencies as the di- $\pi$ -methane rearrangement. Even more important is the similarly efficient (note Table 2) *cis*-*trans* cyano-cyclopropane interconversion which becomes especially dominating due to the high extinction coefficients of these compounds.

Turning now to the methoxy-diene photochemistry, the problem of severe light absorption by product was no longer present. Here extrapolation of the quantum yield data in the Experimental simply led to the observed quantum yields given in Table 2.

Again the reaction proved to be stereospecific.

However, here the stereochemistry was confined to substitution on the double bond of reactant and product. Thus, *cis*-methoxy-diene led to *cis*-vinylcyclopropane and *trans*-methoxy-diene led to *trans*-vinylcyclopropane. The reaction stereochemistry is summarized in eqns (7a) and (7b).

Finally, the parent diene was studied for comparison and the reaction efficiency was determined to be  $\phi =$ 0.011. Note also Table 2 and eqn (8).

With the study of reaction stereochemistry completed and quantum efficiencies determined, we turned to an investigation of the reaction multiplicity.

In the case of the cyano-dienes 2c and 2t, sensitization with acetophenone ( $E_T = 74$  kcal/mole) gave only *cistrans* isomerization, and this proved to be quite efficient. Note Table 3 and eqn (9). No vinylcyclopropanes were detectable, even at high enough conversions that these would be formed in major amounts in counterpart direct irradiations. Hence the cyano-diene triplets, generated by sensitization, do not give the same rearrangement photochemistry as observed on direct irradiation. This means that the direct irradiation rearrangement must involve an excited state other than the triplet. The evidence does not rule out the *cis*-trans isomerization arising from intersystem crossing to the triplet and subsequent stereoisomerization.

Reactant	Temp <sup>0</sup> C	Product	Quantum Yield
1	27	6	0.011
1	73	6	0.011
2t ~~	27	12t	0.356
		2c	0.136
2c	27	12c	0.201
		2t	0.273
3t	27	8t	0.051
		3c	0.032
3c	27	8c	0.050
		3t	0.048
12t	27	12c	0.391
12c	27	12t	0.173

Table 2. Summary of ext	trapolated quantum yield	d results for direct irradiations
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Table 3a. Results of sensitized quantum yield determinations

Reactant	Run	Temp <sup>o</sup> C	Sensitizer	Product	Quantum Yield	% Conv
1 1 27		27	Acetophenone	6	0.010	0.88
-	2	27	Acetophenone	õ	0.011	1.39
	3	27	Benzophenone	õ	0.011	1.24
	1	73	Acetophenone	õ	0.058	6.65
	2	73	Acetophenone	õ	0.058	4.14
2t	1	27	Acetophenone	2c	0.159	2.76
~~	2	27	Acetophenone	2c	0.163	1.40
	3	27	Acetophenone	2c	0.165	0.82
	1	73	Acetophenone	2c	0.225	4.35
2c	1	27	Acetophenone	2t	0.503	5.33
~~	2	27	Acetophenone	2t	0.549	2.89
	3	27	Acetophenone	2t	0.581	1.65
3t	1	27	<u>m</u> -methoxyacetophenone	3c	0.0048	1.41
~~	2	27	m-methoxyacetophenone	3c	0.0047	0.66
	3	27	<u>m</u> -methoxyacetophenone	3c	0.0048	0.40
3c	1	27	m-methoxyacetophenone	3ť	0.028	3.50
~~	2	27	<u>m</u> -methoxyacetophenone	3t	0.028	2.21

	Table 3b. Summar	/ of extra	polated o	uantum	yield re	esults fo	or sensitize	d irradiations
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Reactant	Temp <sup>0</sup> C	Product	Quantum Yield
1	27	6	0.011
ĩ	73	6	0.058
2 t	27	2 c	0.167
2t	73	2c	0.230
2 c	27	2t	0.613
3t	27	3c	0.0048
3c	27	3t	0.028

The case of the methoxy-dienes 3c and 3t was parallel. Sensitization with either acetophenone ( $E_T = 74 \text{ kcal/mole}$ ) or *m*-methoxyacetophenone ( $E_T = 72 \text{ kcal/mole}$ ) led only to *cis-trans* isomerization of reactant dienes and no detectable di- $\pi$ -methane rearrangement (note eqn 10). *m*-Methoxyacetophenone proved more convenient due to its higher extinction coefficient, and this was used in our quantitative studies.



cially important to ascertain that energy transfer in the sensitization experiments was complete. This was done by the benzophenone-benzhydrol test.<sup>22a</sup> Here the effect

of addition of the photochemical reactant, hydrocarbon

diene 1, on the formation of benzopinacol from ben-

zophenone plus benzhydrol was studied. The complete quenching of this triplet reaction<sup>22b</sup> signifies complete



The quantum efficiencies are given in Table 3. It is seen that these are lower than the cyano-diene counterparts. The total absence of di- $\pi$ -methane rearrangement product again means that this reaction in the direct irradiations must originate from the excited singlet.



interception of benzophenone triplet. Additionally, there is the point that both benzophenone ( $E_T = 68.5 \text{ kcal/mole}$ ) and the higher energy acetophenone ( $E_T = 74 \text{ kcal/mole}$ ) sensitizer gave the same di- $\pi$ methane rearrangement and with the same efficiency. If incomplete transfer were involved, it is unlikely that the inefficiency would be the same in the two cases.

At this point the identity of the two quantum yields of di- $\pi$ -methane rearrangement of hydrocarbon diene 1, direct and sensitized, would normally be interpreted as signifying that the direct irradiation proceeded via the triplet. The reasoning here would normally rest on our "fingerprint method"<sup>23</sup> which suggests that when identical product distributions are obtained from an excited state of known (e.g. triplet in a sensitized run) multiplicity and an unknown one (e.g. in a direct run), the same excited state can be taken as responsible for the reaction. However, presently there was only one product, and its quantum yield constituted the "fingerprint".

If the triplet were the responsible species in the direct runs, then the identity of quantum yields cited above would require a unity intersystem crossing efficiency. This seemed unlikely, as styryl systems tend to have intersystem crossing efficiencies below  $0.1^{24}$  and hydrocarbons, in general, but with some exceptions,<sup>25</sup> tend to have low intersystem crossing yields. Thus there was reason for suspicion.

One thought was an attempt to perturb the reaction in some way—by a solvent change, a temperature modification, an extraneous additive—both in the direct and sensitized runs. Then, one could see if both quantum efficiencies were perturbed in a parallel fashion.

An exciting result was derived from a study of the effect of temperature on the reaction quantum yield. When the reaction temperature was raised from 27° to 73°, the quantum yield of di- $\pi$ -methane rearrangement in the direct irradiation was unchanged (Table 2). Dramatically, in the sensitized irradiation the quantum yield increased *ca.* 5.5-fold from  $\phi = 0.011$  to 0.058 (Table 3). Since energy transfer by triplet sensitizers had been shown (*vide supra*) to be perfectly efficient at room temperature, a temperature enhancement could not be rationalized in terms of the energy transfer step. It had to derive from a more efficient rearrangement of the triplet, once formed.

Since the temperature dependence of the reaction efficiencies was different in the direct and sensitized runs, different excited states had to be involved in the two runs.<sup>26</sup> The sensitized runs involved triplets and the logical conclusion was that the direct irradiations proceeded with rearrangement of the singlet excited state.

Finally, since a temperature dependence had been encountered in the case of the parent hydrocarbon triplet diene rearrangement, it was of interest to see if this was more general. Not only would this establish the reality of such an effect, thus supporting the different multiplicities in direct and sensitized runs, but also it would be of intrinsic interest. Acetophenone sensitization of the *trans*-cyano-diene **2t** was investigated at 73° (note Table 3). The *trans*  $\rightarrow$  *cis* isomerization of diene **2t** increased *ca*. 1.5-fold (i.e. from  $\phi = 0.17$  to  $\phi = 0.23$ ). Thus a less dramatic but still real temperature dependence was again found.

### RESULTS

# Excited singlet rate constant determination by single photon counting

It has been noted that one really should correlate excited state reactivity with rate constants for the excited state rather than with quantum yields. The rate at which an excited state reacts is controlled by its inherent tendency to transform itself, while a quantum yield merely gives the ratio of that rate constant to the rate of loss of the excited state by all possible pathways.<sup>27</sup>

For obtaining the desired rate constants, single photon counting has proven particularly reliable and useful.<sup>28</sup> The method<sup>28</sup> utilized an RCA 8850 photomultiplier for photon detection, a pressurized (80 psi) nitrogen flash lamp run at 30 kHz, an entrance and an exit monochromator preceding and following the sample chamber, a 1P28 photomultiplier to detect the beginning of each lamp flash, appropriate amplifiers, a time-to-amplitude converter, an A/D converter and a PDP8/I minicomputer which both performed the function of a multichannel analyzer and also effective deconvolution of the fluorescence emission with lamp flash profile.

The approach has been<sup>28</sup> to determine the total rate of excited singlet decay, that is  ${}^{1}k_{dt}$ . The reaction quantum yield can be determined as well. Hence two of the three quantities in eqns (12) are subject to experimental determination, and one can solve for  ${}^{1}k_{r}$ , the rate of excited singlet rearrangement.

$$\phi_r = ({}^1k_r)/({}^1k_{dt}); \text{ or } {}^1k_r = \phi_r({}^1k_{dt})$$
 (12a,b)

This approach allows determination of reaction rates where the excited singlet has lifetimes as low as ca. 75-100 picoseconds. For shorter lived excited singlets, the method of "magic multipliers"<sup>28</sup> has proven useful. Thus, most often lifetimes which are too fast to measure at room temperature are slowed down enough at 77°K to measure. For molecules with temperature invariant natural rates of fluorescence<sup>29</sup> (i.e.  $k_t$ ), the ratio of fluorescence intensities at 77°K and room temperature gives<sup>28</sup> the ratio of rates of decay at room temperature to decay at 77°K. This ratio is the magic multiplier M.

$$^{1}k_{dt}^{rt} = M(^{1}k_{dt}^{77}).$$
 (13)

Hence the room temperature excited singlet reaction rate is given by

$${}^{1}\mathbf{k}_{r}^{rt} = \phi_{r} \mathbf{M} ({}^{1}\mathbf{k}_{dt}^{77}). \tag{14}$$

This method was used in the present study to give the results described in Table 4. The temperature dependences of the fluorescence intensities (i.e. the M's) are similar for all compounds studied, *ca.* 260. The rates of excited state decay also were similar, being of the order of  $1.6 \times 10^8 \text{ sec}^{-1}$  at 77°K and *ca.*  $4 \times 10^{10} \text{ sec}^{-1}$  at room temperature. Thus the low temperature lifetimes are about 6 nsec and the room temperature lifetimes are about 23-26 psec.

Hence in this case, the reaction quantum yields are seen to give a reasonable indication of the excited singlet

Compd	М	Temp <sup>0</sup> K	τ	<sup>1</sup> kdt' <sup>sec-1</sup>	<sup>1</sup> k <sub>r</sub> , sec <sup>-1</sup>
1	256	300	23.4 ps	4.3 x 10 <sup>10</sup>	$4.7 \times 10^8$
~		77	6.0 ns	$1.7 \times 10^8$	10
2t	260	300	24.5 ps	$4.1 \times 10^{10}$	$1.5 \times 10^{10}$
~~		77	6.4 ns	$1.6 \times 10^8$	0
2c	260	300	25.1 ps	4.0 x 1010	$8.0 \times 10^9$
~~		77	6.5 ns	$1.5 \times 10^8$	0
3t	262	300	26.6 ps	$3.8 \times 10^{10}$	$1.9 \times 10^9$
~~		77	7.0 ns	1.4 x 10 <sup>8</sup>	

Table 4. Summary of singlet lifetimes, decay rates and magic multipliers

rearrangement rates. The most reactive compounds were found to be the stereoisomeric cyano-dienes 2c and 2t with rearrangement rates of  $8.0 \times 10^9 \text{ sec}^{-1}$  and  $1.5 \times 10^{10} \text{ sec}^{-1}$  respectively. The next most reactive compound was the *trans*-methoxy-diene 3t with a rearrangement rate of  $1.9 \times 10^9 \text{ sec}^{-1}$  and the least reactive was the parent hydrocarbon diene 1 which had a rate of  $4.7 \times 10^8 \text{ sec}^{-1}$ . Study of the rate of the *cis*-methoxy-diene 3c proved impractical due to lability of samples of the purity required for single photon counting. The rate data are also included in Table 4.

### INTERPRETATIVE DISCUSSION

# The di- $\pi$ -methane rearrangement and regioselectivity in these systems

The first observation is probably the least surprising, this being the occurrence of the di- $\pi$ -methane rearrangement in dienes 1, 2 and 3. Ever since the initial observation  $^{30a}$  of a di- $\pi$ -methane rearrangment in the case of the transformation of barrelene to semibullvalene $^{30h}$  and the realization $^{30a-d}$  of its generality, this rearrangement has proven to be one of the most general photochemical processes. $^{30e,31}$ 

The next point to be considered is the reaction regioselectivity. We note that parent hydrocarbon diene 1 affords only that vinylcyclopropane product 6 in which the simple vinyl group survives. This has a mechanistic basis. The cyclopropyldicarbinyl diradical 15 has been postulated<sup>30</sup> as a species on the excited state hypersurface leading from vertical excited state to product. A priori, this could have proceeded onward (note Chart 4) to either the observed photoproduct 6, or alternatively to the isomeric vinylcyclopropane 11. Subsequently in this publication we discuss the quantum mechanical treatment of the di- $\pi$ -methane rearrangement including the structure of the cyclopropyldicarbinyl diradical. For the present, we note that the observed photochemical behavior can be understood in qualitative resonance terms.

Thus, Path A in Chart 4 utilizes electron density largely concentrated on the terminal methylene and therefore available for delocalization into the three-ring for opening. This is the three-ring opening which leads to the observed product. In contrast, Path B, utilizes electron density of the benzhydryl system and this is delocalized over the entire moiety. Thus, electron density is not readily available for Path B. Another way of putting this is that there is loss of benzhydryl delocalization energy as demand is increased for electron density in the three-ring opening of Path B.

Hence the regioselectivity observed fits our generalization<sup>32</sup> that three-ring opening utilizes the center with less delocalized electron density.

In the cases of cyano- and the methoxy-dienes 2 and 3,

respectively, it would be difficult to predict *a priori* whether greater stabilization is afforded by benzhydryl delocalization or by the groups in question (i.e. cyano and methoxyl).<sup>33</sup>

However, we have the experimental observation that Path A is preferred where the substituent X (see Chart 4) is hydrogen as in the parent diene or is methoxy as in diene 3. Conversely, we know that Path B is preferred where the substituent X is cyano. This suggests that the carbinyl carbons in the cyclopropyldicarbinyl diradical 15 are electron rich in the excited state and that retention of this stabilization by cyano leads to preference of Path B. The electron rich center is adjacent to the electron donating methoxy in 15c and utilization of Path A becomes preferred.

The above discussion is predicated on the assumption that ground state substituent effects by cyano and methoxy are legitimate when considering the excited diradical species 15a, b and c. This point is considered below in connection with our quantum mechanical calculations.

One intriguing point deals with whether or not there is a relationship between which  $\pi$  moiety is excited and which one migrates in the di- $\pi$ -methane rearrangement. Thus, although the mechanisms in Chart 4 are written stepwise, one might describe Path A as involving a 1,2-shift of the X-CH=CH-moiety and Path B as utilizing a 1,2-shift of a diphenylvinyl group.

Independent of the nature of X, the diphenylvinyl moiety has a lower energy excitation energy (ca. 100 kcal/mole) than any of the vinyl chromophores, all of which absorb below 230 nm. Thus, despite initial heavy localization of the excitation energy in the diphenyl vinyl group, the vinyl moiety migrates (formally) in two of the three cases while diphenylvinyl migrates in the third case.

Hence, we can conclude that initial localization of the excitation in one of the moieties is not a factor in the observed regioselectivity. This point is discussed more quantitatively below.

### INTERPRETATIVE DISCUSSION

The reaction stereochemistry

We turn now to the stereochemistry of the methoxydiene rearrangement. In this example the monosubstituted vinyl moiety survives the reaction and appears in the product. Focussing attention on biradical 15, we might concern ourselves with free rotation and loss of reactant stereochemistry. However, this problem has been studied previously;<sup>32b</sup> the earlier example <sup>32b</sup> was parallel except that the substituent was methyl rather than methoxy. Stereochemistry was retained as in the present example. It was noted that the carbinyl center



Chart 4. Valence bond considerations controlling reaction regioselectivity.

p-orbitals overlapped with the three-ring providing a barrier to free-rotation. This is again the case.

Stereochemistry again is a factor in the photochemistry of cyano-diene 2. However here the substituent providing the stereochemistry ends up on the three-ring. We observe that the reactant stereoisomer having the *cis* cyano group (i.e. 2c) leads to the product isomer with the cyano group *cis* to diphenyl-vinyl on the three-ring. Similarly, the *trans*-cyano-diene 2t affords the di- $\pi$ methane product having the cyano group trans to the diphenyl moiety on the three-ring.

This reaction stereochemistry is less obvious to interpret, since vinyl configurations are converted to cyclopropane configurations. However, again the reaction stereochemistry has precedent.<sup>34a</sup> The earlier example<sup>34a</sup> was one where the present cyano group had instead a phenyl substituent marking the stereochemistry. The stereochemical course was rationalized in terms of a requirement for a six orbital Möbius cyclic array for allowedness.<sup>34c</sup> This aspect will be discussed below in connection with the overall reaction course.

## INTERPRETATIVE DISCUSSION

# A quantum mechanical model

A number of effects now need discussion. These include the effect of substituents on the excited singlet rates of reaction, the mode of radiationless decay, evidence derived from the temperature dependence of decay, the fluorescence emission spectra and similar aspects. In order to better understand the behavior of the excited singlets during reaction, we turned to a molecular orbital treatment of the reaction.

A starting point was the understanding of the cyclopropyldicarbinyl diradical 19 and its substituted derivatives 15a, 15b, and 15c (i.e. X = H, CN, MeO). Parallel studies in our Laboratories<sup>35</sup> have dealt with the quantum mechanical aspects of the di- $\pi$ -methane problem.

Calculations on the basic diradical 19 utilized a Walsh model<sup>36</sup> for the cyclopropane basis orbitals and, additionally, two *p*-orbitals at the carbinyl carbons oriented to overlapping with three-ring p-orbitals. Additionally, calculations were carried out with the added phenyl, methoxy and cyano groups as needed for species 15a, 15b and 15c.<sup>37a</sup> This basis set is not too different from



our usual Möbius model for the reaction.<sup>37b</sup> These calculations were of the SCF-CI variety, utilizing up to 120 singly and doubly excited configurations.

The calculations afforded a number of interesting results. One is that the carbinyl carbons are electron rich in  $S_1$ , the first excited singlet involved in the rearrangement.

A second item of interest is that inspection of the results reveals that the most heavily weighted configuration in the first excited singlet  $S_1$  is that configuration in which excitation is from the highest bonding MO to the lowest antibonding MO of the diradical system. Furthermore, in the diradicals 19, 15a, 15b and 15c these two MO's are split and not degenerate as would be expected in the absence of interaction of p-orbitals 1 and 4 with the Walsh cyclopropane. These two MO's are depicted in Fig. 1.

Inspection of these two MO's indicates that the lower energy of the two has  $\chi_1 - \chi_4$  weighting while the higher energy has a  $\chi_1 + \chi_4$  contribution. This arises from interaction of the two p-orbitals with the three-ring system with consequent splitting.

Moreover, careful analysis (note Table 5 and Figs. 2a and b) of these MO's shows that they differ primarily in the cyclopropyldicarbinyl diradical moiety with only minor variations of quantitative but not qualitative nature in the benzhydryl radical-like moiety. Thus, both the lowest antibonding MO and the highest bonding MO have benzhydryl basis orbital weightings which are reminiscent of the nonbonding MO of the benzhydryl radical. Hence this portion of the molecule is not involved in the excitation to S<sub>1</sub>. This is true of all three substituted diradicals of interest—15a, 15b and 15c.



Fig. 1. Highest bonding and lowest antibonding MO's involved in excitation; the excitation process.

Along similar lines, the electron density on the methoxyl oxygen and the relative sign of the wavefunction compared to the adjacent carbon in the two MO's provide a measure of methoxyl involvement in the excitation process. We find that the relative signs do not change and that the electron density changes but not grossly. We can conclude that excitation does not involve this moiety appreciably. In the case of the cyano diradical **15b**, there is a greater change in the wavefunction at this point in the molecule on excitation. Nevertheless, excitation merely shifts a node down the chain of  $\dot{C}$ -C=N, and again we can conclude that excitation is not introduced heavily in this portion of the molecule.

The nearly total localization of excitation in the cyclopropyldicarbinyl diradical portion of diradicals 15a, 15b and 15c contrasts with the almost total localization of excitation in the diphenylvinyl moiety of the di- $\pi$ -methane reactant. Here the diphenylvinyl group is the lowest energy chromophore and excitation expectedly is confined to this portion of the molecule. Note evidence bearing on this point in our section on excitation distribution (note below).

That initial excitation is indeed localized in the diphenylvinyl moiety is evidenced not only by the quantum mechanical calculations (vide infra) but also by the experimental evidence. Thus, we note the very similar fluorescence emission at 305-325 nm (i.e.  $\pm 10$  nm) for all three di- $\pi$ -methane systems 1, 2 and 3, and that these are the emissions expected for diphenylethylenes since diphenylethylene itself emits at 312 nm. Reference to Table 4 shows that the three compounds have very similar magic multipliers indicating similar temperature dependences of radiationless processes. This is most readily understood if a substantial fraction of the decay derives from simple internal conversion of the diphenylvinyl moiety. Finally, Table 4 reveals that the

Table 5. Cyclopropyldicarbinyl diradical highest bonding and lowest antibonding SCF eigenfunctions for substituted dienes<sup>a</sup>

	PARENT Diene 1		IT Diene 1 CYANO Diene 2			METHOXY Diene 3		
	Ψ7 (Highest Bonding)	<sup>♥</sup> 8 (Lowest Anti- bonding)	4	<sup>ψ</sup> 8 (Highest Bonding)	Ψg (Lowest Anti- bonding)		<sup>∜</sup> 8 (Highest Bonding)	Ψ <mark>9</mark> (Lowest Anti- bonding)
۲	0.5780	0.5926	xı	0.5723	-0.5079	xı	0.4755	0.6317
×2	0.1090	-0.2352	×2	0.1069	0.2620	x2	0.1605	-0.2086
×3	-0.1751	-0.2976	X3	-0.1633	0.2607	x3	-0.1508	-0.2932
×4	-0.5116	0.5196	x <b>4</b>	-0.4799	-0.5460	X4	-0.5614	0.4676
х <sub>5</sub>	0.4193	0.0410	×5	0.3988	0.0107	χ5	0.4030	0.0688
×6	-0.0954	0.0745	×6	-0.0905	-0.0799	Х6	-0.1003	0.0669
×7	-0.0142	-0.1611	×7	-0.0152	0.1540	x7	0.0094	-0.1557
×8	0.1092	0.0870	Хg	0.1057	-0.0747	х8	0.0911	0.0890
χ <sub>9</sub>	0.1352	0.1585	Xg	0.1274	-0.1269	xو	0.1199	0.1567
×10	0.2163	-0.2293	×10	0.1998	0.2307	X10	0.2336	-0.2067
x11	-0.0433	-0.0537	×11	-0.0411	0.0420	×11	-0.0382	-0.0531
×12	-0.2216	0.2406	x <sub>12</sub>	-0.2044	-0.2332	×12	-0.2341	0.2196
×13	-0.0527	-0.0578	X <sub>13</sub>	-0.0484	0.0464	X13	-0.0472	-0.0569
×14	0.2140	-0.2287	X14	0.1985	0.2303	X14	0.2320	-0.2062
			x15	-0.0002	-0.1395	×15	-0.2191	-0.2178
			<sup>X</sup> 16	-0.2899	0.2673			



Fig. 2(a) Basis set orbital array used for quantum mechanical calculations on the starting dienes.  $\chi_7$  sp-hybridized to give methane carbon sp<sup>3</sup> hybridization.



Fig. 2(b). Basis set orbital array used for quantum mechanical calculations on the cyclopropyldicarbinyl diradical.

rates of excited singlet decay also are similar, which again suggests decay derives mainly from internal conversion.

Thus, we have *migration of excitation*, as measured by energy and wavefunction effects, as the excited state transforms itself along the reaction coordinate. This is a new concept in organic photochemistry, and one likely to be of use more generally.

In the specific instance at hand, one might inquire why excitation migrates towards the cyclopropyldicarbinyl diradical<sup>38</sup> moiety. This becomes apparent if one considers that without interaction with the three-ring orbitals, the p-orbitals 1 and 4 would be degenerate. In fact, the diradical is nearly degenerate and thus has minimum excitation energy. Also, our calculations (note below) indicate that the total energy is minimized. In fact, it was noted 16 years ago that photochemical processes occur favorably when excited state species can minimize their energy while still remaining on the excited state hypersurface.<sup>39</sup>

Another point deals with the effect of methoxy and cyano substituents on the electronic energy of the parent hydrocarbon cyclopropyldicarbinyl diradical 15a. Inspection of the wavefunctions for the substituted species reveals that the odd electrons are indeed distributed onto the methoxyl and cyano groups, thus providing additional delocalization stabilization. A discussion of the energetics of bridging is delayed for discussion of the rates. But these, too, support stabilization by these groups.

# INTERPRETATIVE DISCUSSION

The excited singlet rate constants

The excited singlet rearrangement rates are tabulated in Table 4. We note that these are in the order of

$$[PARENT DIENE] < [METHOXY DIENE]4.7 × 108 sec-1 < 1.9 × 109 sec-1 $< [CYANO DIENE]$   
1.5 × 10<sup>10</sup> sec<sup>-1</sup>$$

It is interesting to compare the observed rate constants with the calculated energies of bridging of the three dienes 1, 2 and 3 to give the corresponding cyclopropyldicarbinyl diradicals 15a, 15b and 15c:

'[PARENT DIENE]1	'[METHOXY DIENE] 3
BRIDGING	BRIDGING
– 0.241 eV	-0.418  eV
	<sup>1</sup> [CYANO DIENE] 2
	BRIDGING
	- 0.681 eV

Thus, it is seen that the bridging process is calculated to be exothermic as far as the truncated, delocalized system is concerned.<sup>40</sup> Moreover, the most favorable bridging is of the cyano-diene singlet, with the methoxy-diene singlet next and the parent hydrocarbon diene singlet least favorable. This is the same ordering as observed experimentally above.

The very unfavorable di- $\pi$ -methane rearrangement in the case where a simple -CR=CH<sub>2</sub> vinyl group is one of the two chromophores was encountered previously<sup>27b</sup> in the case of diene 20 which leads to biradical 21\* on bridging. This bridged species (i.e. 21\*) has the unfavorable, relatively localized odd-electron at a primary center in common with the parent hydrocarbon diene 1 example currently described.

A comment is required that all the above calculations and the discussion assume that bridging occurs in the  $S_1$ manifold with formation of the excited singlet cyclopropyldicarbinyl diradicals. We have already pointed out<sup>28a</sup> that the ground state counterparts should undergo fragmentation reverting to diene reactant. We have also commented<sup>28a,41a,b</sup> as has Michl<sup>42</sup> that as points of degeneracy are reached along the reaction coordinate, an excited state has an optimum chance for radiationless decay. Decay of the  $S_1$  diradicals to  $S_0$  then will give species which will revert to diene reactant and account for part of the less than unit efficiencies determined. The parallel between bridging energies and rates supports the idea<sup>28a</sup> that such decay of  $S_1$  diradicals is a relatively constant loss for all reactants.

A final point to be made is that the molecules presently under study all have as the effective reactant a species with the same excited diphenylvinyl chromophore. Thus we are dealing with a comparison of rates where only the transition states (in the S<sub>1</sub> manifold), and not the starting S<sub>1</sub> states, differ in energy. This is not the case in all di- $\pi$ -methane rearrangements;<sup>1b</sup> and, in general, the rate of S<sub>1</sub> di- $\pi$ -methane rearrangement will be controlled by the energy difference between the excited chromophore of the reactant diene and the S<sub>1</sub> state of the cyclopropyldicarbinyldiradical species.

### INTERPRETATIVE DISCUSSION

### Ouantum mechanical basis of the regioselectivity

One other phenomenon which seemed likely to be understood on a quantum mechanical basis is the regioselectivity. Interestingly, a correlation of prediction and observation was found. To begin with, a simple correlation was tried using simple bond orders derived from summation of  $nC_rC_s$  terms, where the C's are the SCF coefficients at atoms r and s, and n is the occupation number for each MO. This did not take into account the much larger overlap of orbitals 6 and 7 and 8 (note Fig. 1); not surprisingly the correlation was not helpful. Bond



orders based on summation of  $nS_{rs}C_{rc}$  terms, were improved and very close in correlating with experiment except that little regioselectivity from the cyano-cyclopropyl-diradical **15b** was predicted, and this was in the wrong direction.

Strikingly, dissection of the energy into local bond contributions by looking at the summation of  $n[(1/2)(H_{rs} + F_{rs})]$  terms, where  $H_{rs}$  and  $F_{rs}$  are the oneelectron and Fock matrix elements, respectively, led to correct prediction of the regioselectivity.

This summation in effect gives the local bond energies including all overlapping orbitals in the two three-ring bonds, A and B, susceptible to opening. Also included is the third three-ring bond C formed on bridging. The results are tabulated in Table 6. Thus it is the weaker bond, A or B, in the cyclopropyldicarbinyl diradical which opens, and the bond strengths are affected by the cyano and methoxyl groups even prior to beginning of ring opening. Bond C is the weakest bond. Opening in the excited or ground state accounts for some of the radiationless decay. Also, the relative energies of this bond for the three diradicals correlate nicely with the rates of rearrangement.

### INTERPRETATIVE DISCUSSION MO determination of excitation distribution

Measurement of excitation drift. It has been noted above in qualitative fashion that the initially formed vertical excited states (i.e.  $S_t$ ) have the electronic excitation primarily localized in the diphenylvinyl moieties while, in contrast, once bridging is complete, excitation has drifted into the cyclopropyldicarbinyl diradical portion of the molecule. This can be seen intuitively or by qualitative inspection of ground state and excited state wavefunctions.

We note that one can define the locus of excitation more quantitatively in the following way. Thus, on excitation of a molecule, the electron densities at certain atoms and the bond orders between selected orbitals tend to remain relatively invariant while these properties do change at other sites in the molecule. Hence a matrix consisting of elements:

$$\Delta P_{rs}^{Excit} = P_{rs}^{S_1} - P_{rs}^{S_0}$$
(16a)

$$\Delta P_{rs}^{Excit} = P_{rs}^{Mot} - P_{rs}^{Mok}$$
(16b)

where  $P_{rs}^{Mok}$  refers to the bond order between orbitals r and s in MO k and  $P_{rs}^{Mol}$  is the same bond order but in MO 1. In the present study k and l would refer to the highest bonding and lowest antibonding MO's. Alternatively, we can use bond orders for entire states. Here S<sub>0</sub> and S<sub>1</sub> refer to ground and excited states respectively. In this case we obtain bond order changes derived from configuration interaction calculations. Either approach, though, gives us a measure of the wave-function change

Table 6. Electronic components of bond energies of the excited state cyclopropyl-dicarbinyl diradical. Correlation to the observed regiospecificity

	Reactant							
	Parent 1	Cyano 2	Methoxy 3					
Overlap <sup>a</sup>	Bond Energy <sup>C</sup>	Bond Energy <sup>C</sup>	Bond Energy <sup>C</sup>					
2,5	-2.9812	-3.1870 -11.6776	-2.9790					
5,6 2,7	-1.6744 -1.2062	-1.6554 -1.2474	-1.6842 -1.2628					
Total Bond A Eñergy <sup>b</sup>	-17.5370	-17.7674	-17.5426					
3,5 8,7 5,8 3,7	-3.0558 -11.6932 -1.6748 -1.2520	-3.1488 -11.6528 -1.6786 -1.2644	-3.1492 -11.6736 -1.6306 -1.2826					
Total Bond B Energy <sup>b</sup>	-17.6758	-17.7446	~17.7360					
2,3 3,6 6,8 2,8	-2.7128 -1.2636 -11.6624 -1.2142	-2.8294 -1.2798 -11.6752 -1.2794	-2.8030 -1.3046 -11.6940 -1.2386					
Total Bond C Energy <sup>b</sup>	-16.8530	-17.0638	-17.0402					

<sup>a</sup>Reference is to orbital basis set defined in Figure 2b.

 $^bBond$  A is the bond broken in Mechanism A (see Chart IV) (i.e. the bond on the -CHX side, Bond B is the bond broken in Mechanism B (next to  $\theta_2 \text{CH.}$ ), and Bond C is the bond formed during bridging.

<sup>C</sup>The energies include only the delocalized electronic energies ascribable to each two-center bond and do not include such terms as nuclear-nuclear repulsion; thus the relative but not absolute values are meaningful. on excitation at each site in the molecule. Where  $\Delta P_{rs}^{\text{Excit}}$  is zero or small, we know excitation has not affected the wavefunction and the nature of the molecule at that site. Where this index is non-zero, we know that excitation has affected the molecule at that site. A negative index for a bond means introduction of antibonding on excitation, a positive index means increased bonding. For an atom, a positive index signifies an increase in electron density on excitation and negative index connotes a decreased density.

Applied to the present reaction, we note in Table 7 and Fig. 2 that excitation in the reactant vertical excited state is indeed localized in the diphenylvinyl moiety since the  $\Delta P$  indices are very small in the rest of the molecule. However, as we move along the reaction coordinate and reach the cyclopropyldicarbinyl diradicals, we find that the indices are large in the three-ring but small in the rest of the system (e.g. the diphenylmethyl radical moiety).

The beauty of the approach is being able to follow the flow of electronic excitation in a photochemical reaction.

### INTERPRETATIVE DISCUSSION

## The triplet photochemistry

Most commonly in our past studies, the triplet excited states of acyclic di- $\pi$ -methane systems have been relatively unreactive towards rearrangement, 12,30d,32b and cis-trans isomerization has dominated the triplet chemistry.<sup>32b</sup> We have noted that the "free rotor effect", <sup>12,24,30d,32b</sup> involving twisting about an excited  $\pi$ -bond, leads to energy dissipation at a rate which very often competes effectively with the rates of typical triplet reactions. This is seen again in the present study as evidenced by cis-trans isomerization. These efficiencies vary from 0.61 for the cyano-diene 2 to 0.0048 (note Table 4) for the methoxy-diene 3. In the methoxy case, we note that triplet excitation should be heavily localized in the diphenvlvinvl chromophore  $(E_{T} =$ 62<sup>12.32b</sup> kcal/mole) as was the case for the singlet, and yet it is the vinyl moiety which *cis-trans* isomerizes. This may be interpreted as an endothermic energy transfer, a non-vertical energy transfer to a twisted double bond, or as a cyclopropyldicarbinyl diradical (15b or 15c)

	PARENT 1				CYANO 2		METHOXY 3				
	Bond Density			Bond D	Bond Density			Bond Density			
Bond <sup>a</sup>	s <sub>0</sub>	s <sub>1</sub>	ΔP	<sup>s</sup> 0	<sup>s</sup> 1	ΔP	<sup>s</sup> 0	۶۱	Δ <b>P</b>		
1,15				0.2764	0.2701	-0.0064	0.2963	0.2935	-0.0028		
1,2	0.9651	0.9990	0.0348	0.9433	0.9616	0.0183	0.9252	0.9557	0.0305		
2,5	0	0	0	0	0	0	0	0	0		
2,7	0	0	0	0	0	0	0	0	0		
2,3	0	-0	0	0	0	0	0	0	0		
2,8	0	0	0	0	0	0	0	0	0		
3,4	0.9339	0.7649	-0.1690	0.9336	0.7645	-0.1691	0.9293	0.7580	-0.1713		
3,5	0	0	0	0	0	0	0	0	0		
3,7	0	0	0	0	0	0	0	0	0		
3,6	0	0	0	0	0	0	0	0	0		
4,9	0.2835	0.4043	0.1207	0.2835	0.4043	0.1208	0.2827	0.389 <b>9</b>	0.1072		
6,7	0.7042	0.7042	0	0.7019	0.7019	0	0.7068	0.7068	0		
6,8	-0.1520	-0.1520	0	-0.1535	-0.1535	0	-0.1495	-0.1495	0		
7,8	0.7039	0.7039	0	0.7064	0.7064	0	0.7011	0.7011	0		
5,8	0.6913	0.6913	0	0.6890	0.6890	0	0.6938	0.6938	0		
5,6	0.6911	0.6911	0	0.6918	0.6918	0	0.6902	0.6902	0		
15,16				0.9359	0.9431	0.0072					
1,1	1.0159	1.0165	0.0006	1.0335	1.0368	0.0033	0.9853	0.9785	-0.0068		
2,2	0.9841	0.9835	-0.0006	0.9347	0.9354	0.0007	1.1033	1.1059	0.0026		
3,3	0.9801	0.9768	-0.0033	0.9932	1.0107	0.0175	0.9604	0.9424	-0.0180		
4,4	1.0161	1.0039	-0.0122	1.0073	1.0136	0.0063	1.0301	0.9995	-0.0306		
5,5	0.7891	0.7891	0	0.7841	0.7841	0	0.7948	0.7948	0		
6,6	1.0583	1.0583	0	1.0725	1.0725	0	1.0424	1.0424	0		
7,7	1.0930	1.0930	0	1.0913	1.0913	0	1.0940	1.0940	0		
8,8	1.0596	1.0596	0	1.0522	1.0522	0	1.0688	1.0688	0		
9,9	0.9947	0.9927	-0.0020	0.9990	1.0015	0.0025	0.9902	0.9943	0.0041		
10,10	1.0024	1.0049	0.0025	1.0007	0.9938	-0.0069	1.0053	1.0136	0.0083		
11,11	1.0008	1.0074	0.0066	0.9996	0.9898	-0.0098	1.0021	1.0174	0.0153		
12,12	1.0030	1.0025	-0.0005	0.9997	1.0066	0.0069	1.0068	1.0053	-0.0015		
13,13	1.0012	1.0069	0.0057	1.0002	0.9917	-0.0085	1.0019	1.0145	0.0126		
14,14	1.0017	1.0050	0.0033	1.0003	0.9923	-0.0080	1.0032	1.0131	0.0099		
15,15				0.8233	0.8191	-0.0042	1.9115	1.9157	0.0042		
16,16		-		1.2085	1.2087	0.0002					

Table 7(a). Change in bond density between ground and excited state of starting diene

a. See Figure 2a for basis set definition.

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Table 7(b). Change in bond densities between ground and excited state 1,4-cyclopropyldicarbinyl diradicals

PARENT Radical 15a			Ra	CYANO Radical 15b			METHOXY Radical 15c			
Bond Density				Bond	Density		Bond Density			
Bond <sup>a</sup>	s <sub>0</sub>	s 1	Δ₽	s <sub>0</sub>	۶ <sub>1</sub>	ΔP	s <sub>o</sub>	<sup>s</sup> 1	ΔΡ	
1,15			~~-	0.3546	0.4136	0.0590	0.3413	0.3163	-0.0250	
1,2	0.6621	0.5111	-0.1510	0.6155	0.4487	-0.1668	0.6202	0.4374	-0.1828	
2,5	0.4575	0.4890	0.0315	0.4833	0.5140	0.0307	0.4385	0.4960	0.0575	
2,7	0.2452	0.2739	0.0287	0.2475	0.2827	0.0352	0.2583	0.2830	0.0247	
2,3	0.4013	0.4627	0.0614	0.4104	0.4795	0.0691	0.4122	0.4745	0.0633	
2,8	0.2507	0.2740	0.0233	0.2598	0.2863	0.0265	0.2518	0.2793	0.0275	
3,4	0.6151	0.4336	-0.1815	0.6170	0.4234	-0.1936	0.6006	0.4072	-0.1934	
3,5	0.4660	0.4992	0.0332	0.4633	0.5155	0.0522	0.4812	0.5084	0.0272	
3,7	0.2504	0.2833	0.0329	0.2527	0.2850	0.0323	0.2518	0.2900	0.0382	
3,6	0.2568	0.2840	0.0272	0.2567	0.2873	0.0306	0.2623	0.2916	0.0293	
4,9	0.3883	0.4966	0.1083	0.3901	0.5009	0.1108	0.3927	0.5098	0.1171	
6,7	0.6186	0.6090	-0.0096	0.6205	0.6089	-0.0116	0.6145	0.6066	-0.0079	
6,8	0.5996	0.6118	0.0122	0.5990	0.6125	0.0135	0.6011	0.6132	0.0121	
7,8	0.6191	0.6099	-0.0092	0.6167	0.6082	-0,0085	0.6207	0.6086	-0.0121	
5,8	0.3709	0.3373	-0.0336	0.3751	0.3373	-0.0378	0.3610	6.3317	-0.0293	
5,6	0.3716	0.3370	0.0346	0.3671	0.3351	0.0320	0.3783	0.3372	0.0411	
15,16				0.9061	0.8679	-0.0382				
1,1	1.0192	1.0359	0.0167	1.0503	0.9890	-0.0613	0.9783	1.1190	0.1407	
2,2	1.1309	1.1662	0.0353	1.1183	1.1697	0.0514	1.2000	1.2153	0.0153	
3,3	1.1411	1.1854	0.0443	1.1491	1.1863	0.0372	1.1245	1.1797	0.0552	
4,4	1.0166	1.0253	0.0087	0.9718	1.0295	0.0577	1.0941	1.0078	-0.0863	
5,5	1.3596	1.2308	-0.1288	1.3470	1.2111	-0.1359	1.3657	1.2312	-0.1345	
6,6	0.8060	0.8034	-0.0026	0.8019	0.8001	-0.0018	0.8157	0.8115	-0.0042	
7,7	0.7142	0.7329	0.0187	0.7160	0.7361	0.0201	0.7182	0.7381	0.0199	
8,8	0.8033	0.8003	-0.0030	0.8078	0.8029	-0.0049	0.7916	0.7916	0	
9,9	1.0070	1.0079	0.0009	1.0193	1.0157	-0.0036	0.9856	0.9996	0.0140	
10,10	0.9982	1.0023	0.0041	0.9906	1.0011	0.0105	1.0091	0.9975	-0.0116	
11,11	0.9900	0.9983	-0.0007	0.9972	0.9962	-0.0010	1.0014	1.0042	0.0028	
12,12	1.0013	1.0042	0.0029	0.9882	0.9956	0.0074	1.0158	1.0159	0.0001	
13,13	0.9990	0.9983	-0.0007	0.9981	0.9970	-0.0011	1.0010	1.0035	0.0025	
14,14	1.0045	1.0087	0.0042	0.9943	1.0048	0.0105	1.0156	1.0044	-0.0112	
15,15		-		0.8392	0.8622	0.0230	1.8834	1.8805	-0.0029	
16,16				1.2108	1.2027	-0.0081				

a. See Figure 2b for basis set definition.

which is formed and then reverts to stereoisomerized diene.

Nevertheless, the di- $\pi$ -methane rearrangement does occur to some extent from the triplet of the parent hydrocarbon diene 1. The efficiency of 0.011, while small, is still appreciable and comparable to the triplet di- $\pi$ methane rearrangement quantum efficiencies for 3,3 dimethyl - 1,1,5,5 - tetraphenyl - 1,4 - pentadiene (22) and 1,1 - diphenyl - 3,3,5 - trimethyl - 1,4 - hexadiene (23), these having efficiencies of 0.01 and 0.008, respectively.

With this triplet reactivity of the parent hydrocarbon in hand, we note that the direct and sensitized quantum



yields are the same within experimental error (i.e.  $\phi = 0.011$ ). This then leads to the concern that the direct irradiations might be giving triplet reactivity as a result of intersystem crossing; this intersystem crossing would have to be perfectly efficient to account for the same direct and sensitized quantum yields and this seems unlikely. Since obtaining similar reactivity from a species of known multiplicity (as in a sensitized run) as from one of unknown multiplicity ordinarily leads one to then identify the unknown with the known species, further evidence was needed.

We turned to the temperature dependence of the quantum yields. Strikingly, the triplet quantum yield of di- $\pi$ -methane proved to be markedly temperature dependent; note Table 4. At 73° the efficiency rose to  $\phi = 0.058$ . In contrast, the direct irradiation was temperature independent. Thus, the equivalent quantum yields at room temperature proved to be accidental and not meaningful.

A similar temperature dependence was encountered in the *cis-trans* isomerization efficiency of the *trans*cyano-diene 2. Here the quantum yield (note Table 3b again) rose from  $\phi = 0.16$  to 0.23.

The use of elevated temperatures to assess reactivity and for practical purposes has not been appreciably explored in photochemistry and these results suggest the likely importance of such studies.

The temperature dependence of the di- $\pi$ -methane rearrangement above (i.e. of 1) leads to an Arrhenius activation energy of 7.5 kcal/mole if we assume that the rate of radiationless decay from the triplet is temperature independent. To the extent that radiationless decay increases with temperature, the activation energy for the di- $\pi$ -methane rearrangement must be still greater. The calculated activation energy for the *cis-trans* isomerization of *trans*-cyano-diene is 1.7 kcal/mole.

Appreciable thermal barriers in the excited state for the triplet reactions has precedent. Thus, for example, the rearrangement of 4 - p - cyanophenyl - 4 - phenylcyclohexenone<sup>43</sup> was found to be 10.5 kcal/mole.

It is interesting to compare the lack of temperature dependence of the singlet excited state di- $\pi$ -methane rearrangement, and its essentially zero activation energy with the 7.5 kcal/mole barrier for the triplet. Since somewhere along the reaction coordinate a multiplicity change is required for the triplet, and since a totally concerted process is not available, this difference is reasonable. It seems likely that in general triplet activation barriers will be larger than singlet ones. Also, in the present case, the singlet temperature dependence may be small enough so that it was not observed and a small but real barrier is probably present. Assuming a 5.0 per cent quantum yield change could not be observed, an estimate of this upper limit is a 0.22 kcal/mole singlet barrier.

### CONCLUSION

We note that correlation of excited state reactivity with structure in the di- $\pi$ -methane rearrangement is possible using a cyclopropyldicarbinyl diradical model with quantum mechanical detail. Both methoxyl and cyano terminal groups stabilize this species on the excited hypersurface. Bridging leads to migration of excitation from the low energy diphenylvinyl chromophore to the three-ring moiety. Finally, our treatment of excitation localization and redistribution seems likely to be of general utility and interest.

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#### **EXPERIMENTAL<sup>44</sup>**

2,2 - Dimethyl - 4,4 - diphenyl - 3 - butenal. The synthesis of this aldehyde previously described by Julia and Baillarge<sup>7</sup> was closely followed except for the modification of two steps published by Zimmerman and Pratt.<sup>32a</sup>

3,3 - Dimethyl - 1,1 - diphenyl - 1,4 - pentadiene. To a stirred suspension of 6.25 g (17.5 mmol) of methyltriphenylphosphonium bromide in 100 ml anhyd ether at room temp under N<sub>2</sub> was added 11.5 ml of 1.45 M n-BuLi in hexane (16.7 mmol). The soln was stirred for 1.0 hr and then 3.50 g (14.0 mmol) of 2.2 - dimethyl - 4,4 - diphenyl - 3 - butenal in 50 ml of anhyd ether was added. The mixture was stirred overnight, ether added, and the soln filtered through Celite. The combined filtrate and washings were concentrated *in vacuo* to yield 3.90 g of a yellow oil which was passed through a 35 cm × 4.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane and eluted with hexane. After elution with 500 ml, 2500 ml were collected. Solvent removal *in vacuo* yielded 2.69 g of an oil which upon microdistillation at 70° (0.03 mm) yielded 2.30 g (66%) of analytically pure diene as a clear, colorless oil.

The spectral data were: IR (thin film) 3.24, 3.26, 3.29, 3.36, 3.40, 3.47, 5.12, 5.30, 5.53, 6.11, 6.25, 6.35, 6.67, 6.78, 6.83, 6.90, 7.07, 7.22, 7.29, 7.33, 8.18, 8.44, 8.48, 8.65, 9.57, 9.65, 9.98, 10.96, 11.29, 12.82, 13.09, 13.42, 13.97, 14.20, 14.39  $\mu$ ; NMR (CCl<sub>4</sub>)  $\tau$  2.84 (m, 10 H, arom), 3.97 (s, 1 H, vinyl), 4.23 (d of d, 1 H, J<sub>1</sub> = 18.0, J<sub>2</sub> = 12.0 Hz, vinyl), 5.17 (d of d, 1 H, J<sub>1</sub> = 18.0, J<sub>2</sub> = 1.5 Hz, vinyl), 5.31 (d of d, 1H, J<sub>2</sub> = 1.0, J<sub>2</sub> = 1.5 Hz, vinyl), 5.31 (d of d, 1H, J<sub>2</sub> = 1.0, J<sub>2</sub> = 1.5 Hz, vinyl), 8.94 (s, 6 H, C(CH<sub>3</sub>)<sub>2</sub>); UV (95% EtOH) 248 nm (e 14,200); mass spectrum (Cale. for C<sub>19</sub>H<sub>20</sub>, 248.15650) *m/e* 248.15610. (Found: C, 91.94; H, 8.15. Cale. for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12%).

trans - 1 - Cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 pentadiene. To a stirred suspension of 0.65 g (15.3 mmol) of a 56.3% sodium hydride dispersion (prewashed with dry ether) in 30 ml of dry dimethoxyethane at room temp. under N2 was added 2.13 g (12.0 mmol) of diethyl cyanomethylphosphonate8 in 5.0 ml of dry dimethoxyethane dropwise. The reaction was exothermic and the resulting grey soln was stirred until it returned to ambient temp. Then 2.30 g (9.20 mmol) of 2.2 - dimethyl - 4.4 - diphenyl - 3 butenal in 10 ml of dry dimethoxyethane was added dropwise over a period of 15 min. This reaction was also exothermic and the orange soln was stirred until it returned to ambient temp., then poured onto water, ether extracted and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and solvent removal in vacuo yielded 2.85 g of a 7:1 mixture of trans: cis-isomers by NMR analysis as a yellow oil. This oil was chromatographed on a 185 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-180, 0.25% ether in hexane, nil; fractions 181-385, 0.25% ether in hexane, 82.0 mg of impurity; fractions 386-510, 0.25% ether in hexane, 317 mg of pure cis-diene; fractions 511-560, 0.25% ether in hexane, 194 mg of a mixture of cis- and trans-dienes; fractions 561-720, 0.25% ether in hexane, 1.14 g of pure trans-diene; fractions 721-820, 1.0% ether in hexane, 630 mg of pure trans-diene. Fractions 561-820 were combined to yield 1.77 g (70%) of the trans-diene, m.p. 43-45°, that crystallized in 95% ethanol. Recrystallization from 95% ethanol gave 1.62 g (64%) of a white crystalline solid, m.p. 48°.

The spectral data were: IR (KBr) 3.25, 3.27, 3.31, 3,38, 3.42, 3.49, 4.49, 6.14, 6.15, 6.27, 6.71, 6.85, 6.87, 6.94, 7.23, 7.30, 7.35, 7.63, 7.75, 7.84, 8.71, 9.33, 9.73, 10.12, 10.31, 10.59, 10.81, 11.01, 11.19, 11.31, 11.57, 11.78, 12.02, 12.95, 13.21, 13.77, 14.25, 14.49, 15.53  $\mu$ ; NMR (CCl<sub>4</sub>)  $\tau$  2.78 (m, 10 H, arom), 3.64 (d, 1 H, J = 17.0 Hz, vinyl), 4.08 (s, 1 H, vinyl), 5.20 (d, 1 H, J = 17.0 Hz, vinyl), 8.82 (s, 6 H, C(CH<sub>3</sub>)<sub>2</sub>); UV (95% EtOH) 251 nm (e15,100); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N, 273.15175) *m/e* 273.15163. (Found: C, 87.96; H, 7.05. Calc. for C<sub>20</sub>H<sub>19</sub>N: C, 87.87; H, 7.01%).

cis - 1 - Cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 pentadiene. To a stirred soln of lithium diisopropylamide (reagent freshly prepared by stirring 0.91 ml (6.50 mmol) of diisopropylamine and 3.25 ml of 2.0 M n-BuLi (6.50 mmol) in 10 ml of dry THF under  $N_2$  at  $-78^\circ$  for 0.5 hr) was added 0.68 g (6.00 mmol) of trimethylsilylacetonitrile9 in 15 ml of THF dropwise slowly to yield a pale yellow soln. After 10 min at -78°, 1.25 g (5.00 mmol) of 2,2 - dimethyl - 4,4 - diphenyl - 3 - butenal in 15 ml of THF was added dropwise slowly to yield a clear yellow soln. After stirring 1.0 hr at -78°, 2.0 ml of conc H<sub>2</sub>SO<sub>4</sub> in 8.0 ml of THF<sup>45</sup> was added and the mixture warmed to room temp, over a period of 0.5 hr. The mixture was then poured onto water, ether extracted and dried over MgSO4. Filtration and solvent removal in vacuo yielded 1.52 g of a yellow oil which was a 15:1 mixture of cis trans-isomers by NMR analysis. This oil was chromatographed on a 190 cm × 3.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-115, 0.5% ether in hexane, nil; fractions 116-210, 0.5% ether in hexane, 157 mg of unidentified impurities; fractions 211-307, 0.5% ether in hexane, 843 mg of pure cis-diene; fractions 308-347, 1.0% ether in hexane, 138 mg of pure cis-diene; fractions 348-397, 1.0% ether in hexane, 57.0 mg of a mixture of cis- and trans-dienes; fractions 398-450, 10.0% ether in hexane. 88.0 mg of *trans*-diene and impurities. Fractions 211-347 were combined to yield 981 mg (72%) of *cis*-diene, m.p. 36-39°, which crystallized upon trituration with pentane at 0°. Recrystallization from pentane gave 810 mg (59%) of a white crystalline solid, m.p. 43°.

Spectral data. IR (KBr) 3.24, 3.27, 3.31, 3.37, 3.41, 3.48, 4.52, 6.16, 6.27, 6.37, 6.71, 6.85, 6.94, 7.28, 7.34, 7.79, 8.00, 8.23, 8.54, 8.66, 8.73, 8.89, 9.35, 9.71, 10.05, 10.31, 10.53, 10.66, 11.01, 11.39, 11.49, 12.85, 13.16, 13.79, 14.08, 14.29, 14.41, 14.49,  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.82 (m, 10 H, arom), 3.94 (s, 1 H, vinyl), 3.96 (d, 1 H, j = 12.0 Hz, vinyl), 5.25 (d, 1 H, J = 12.0 Hz, vinyl), 8.64 (s, 6 H, C(CH<sub>3</sub>)<sub>2</sub>); UV (95% EtOH) 249 nm ( $\epsilon$  13,700); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N; C, 87.87; H, 7.01%).

cis- and trans - 1 - Methoxy - 3.3 - dimethyl - 5.5 - diphenyl -1,4 - pentadiene. To a stirred suspension of 43.9 g (128 mmol) of methoxymethylenetriphenylphosphonium chloride11 in 500 ml of anhyd ether at 0° under N2 was added 115 ml of 1.00 M PhLi in ether (115 mmol). The mixture was stirred for 1 hr at room temp. and then 16.0 g (64.0 mmol) of 2.2 - dimethyl - 4,4 - diphenyl - 3 butenal in 100 ml of anhyd ether was added. After 1.0 hr ether was added, the mixture water extracted, washed with sat. NaCl aq and dried over MgSO<sub>4</sub>. Filtration and solvent removal in vacuo yielded a yellow oil which was diluted with 500 ml of pentane and cooled to 0°. The precipitated triphenylphosphine oxide was filtered off and washed with pentane. The combined filtrate and washings were concentrated to 50 ml and this soln was passed through a 85 cm × 5.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution with 5.0% ether in hexane yielded 17.2 g of a clear, colorless oil which was a 4:1 mixture of cis: trans-isomers plus an impurity by NMR analysis. Spinning band distillation (0.06 mm) of this oil gave the following results: fraction 1, b.p. 105-109°, 2.02 g of a 12:1 mixture of cis: trans; fraction 2, b.p. 109-115°, 2.89 g of a 1:1 mixture of cis: trans; fraction 3, b.p. 115-115.5°, 2.33 g of a 1:5 mixture of cis:trans; fraction 4, 115.5-118°, 1.47 g of a 1:10 mixture of cis: trans (49%).

Pure trans-diene was obtained by two-fold chromatography of fractions 3 and 4 on a 85 cm  $\times$  5.0 cm silica gel (Grace, grade 62, 60–200 mesh) column slurry packed in hexane. Elution with 0.25% ether in hexane completely separated the isomeric dienes. The resulting trans-diene, however, was contaminated with the homologated aldehyde due to acid catalysis on the column. Fast rechromatography on a 35 cm  $\times$  4.0 cm silica gel (Grace, grade 62, 60–200 mesh) column slurry packed in hexane and eluted with 1.0% ether in hexane yielded the trans-diene. Low temperature recrystallization (3  $\times$ ) from pentane at  $-78^{\circ}$  followed by micro-distillation at 80° (0.03 mm) yielded analytically pure material as a clear, colorless oil.

Spectral data. IR (thin film) 3.25, 3.26, 3.28, 3.34, 3.38, 3.44, 3.49, 3.53, 6.06, 6.27, 6.70, 6.83, 6.93, 7.23, 7.31, 7.36, 7.50, 8.22, 8.35, 8.61, 8.72, 8.97, 9.24, 9.72, 10.69, 12.48, 13.18, 13.75, 14.32  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.79 (m, 10 H, arom), 3.89 (d, 1 H, J = 14.0 Hz, vinyl), 3.92 (s, 1 H, vinyl), 5.36 (d, 1 H, J = 14.0 Hz, vinyl), 6.76 (s, 3 H, OCH<sub>3</sub>), 8.90 (s, 6 H, C(CH<sub>3</sub>)<sub>2</sub>); UV (95% EtOH) 248 nm ( $\epsilon$  15,400); mass spectrum (Calc. for C<sub>20</sub>H<sub>22</sub>O, 278.16706) *m/e* 278.16709. (Found: C, 86.17; H, 7.90. Calc. for C<sub>20</sub>H<sub>22</sub>O; C. 86.29; H, 7.97%).

The air and acid sensitive, thermally labile *cis*-diene could only be obtained by high-pressure liquid chromatography of fraction 1 on a  $50 \text{ cm} \times 0.96 \text{ cm}$  silica microsphere column (particle size  $10-30 \mu$ ) by elution with 0.25% ether and 0.05% methanol in hexane. Rechromatography under these conditions yielded pure *cis*-diene as a clear colorless oil.

Spectral data. IR (thin film) 3.14, 3.25, 3.29, 3.33, 3.37, 3.40, 3.43, 3.48, 3.52, 6.04, 6.27, 6.36, 6.69, 6.80, 6.85, 6.92, 7.17, 7.30, 7.35, 7.81, 7.92, 8.13, 8.68, 8.81, 9.07, 9.31, 9.69, 10.15, 11.24, 12.66, 13.13, 13.64, 14.25  $\mu$ ; NMR (CCl<sub>4</sub>) $\pi$  2.84 (m, 10 H, arom), 3.85 (s, 1 H, vinyl), 4.62 (d, 1 H, J = 7.5 Hz, vinyl), 5.93 (d, 1 H, J = 7.5 Hz, vinyl), 5.93 (d, 1 H, J = 7.5 Hz, vinyl), 5.52 (s, 3 H, OCH<sub>3</sub>), 8.88 (s, 6 H, C(CH<sub>3</sub>)<sub>2</sub>); UV (95% EtOH) 250 nm ( $\epsilon$  15.200); mass spectrum (Calc. for C<sub>20</sub>H<sub>22</sub>O, 278.16706) m/e 278.16736. (Found: C, 86.22; H, 7.88. Calc. for C<sub>20</sub>H<sub>22</sub>O; C, 86.29; H, 7.97%).

Diphenyldiazomethane. This material was prepared by the

method of Miller $^{46}$  from benzophenone hydrazone and mercuric oxide.

3,3 - Dimethyl - 2,2 - diphenyl - 1 - cyclopropylcarboxylic acid. The synthesis of this acid previously described by Zimmerman and Mariano<sup>12</sup> was slightly modified. A solution of 102 g (0.527 mol) of the diphenyldiazomethane in 353 g (2.76 mol) of ethyl 3 - methyl - 2 - butenoate in a 21, acid-washed<sup>47</sup> flask, was heated at 65-70° for 9 days. Unreacted ester was distilled, the remaining material was taken up in ether, and crystalline dimeric material was filtered. The filtrate was concentrated in vacuo and taken up in 500 ml of EtOH, 50.0 g (0.891 mol) of NaOH in 100 ml of water added, and the mixture was refluxed for 5.0 hr, poured onto 11. of ice water and extracted with CH2Cl2. The water layer was acidified (Congo Red) with HCl and CH2Cl2 extracted. The organic layer was water washed, dried over MgSO4, and the solvent removed in vacuo to yield 24.6 g (18%) of 3.3 - dimethyl -2,2 - diphenyl - 1 - cyclopropylcarboxylic acid, m.p. 232-234°, as a crystalline solid which was identical to the previously described acid 1

3,3 Dimethyl - 2,2 - diphenylcyclopropylmethanol. A soln of 4.99 g (18.8 mmol) of 3,3 - dimethyl - 2,2 - diphenyl - 1 - cyclopropylcarboxylic acid in 80 ml of dry THF was added to a stirred suspension of 1.15 g (30.3 mmol) of LAH in 50 ml of THF at 0°. Stirring was continued for 12.0 hr at room temp. followed by refluxing for 30 min. After cooling an excess of a 1:1 mixture of sodium sulfate decahydrate-celite was added to destroy unreacted LAH. The mixture was stirred until the grey solid turned white, then the granular ppt was filtered off. Solvent removal *in vacuo* yielded 4.18 g (100%) of crystalline 3,3 - dimethyl - 2,2 diphenylcyclopropylmethanol, m.p. 97°. Recrystallization from hexane gave 4.08 g (98%) of product as a white crystalline solid, m.p. 99°.

Spectral data. IR (CHCl<sub>3</sub>) 2.74. 2.87, 3.21, 3.23, 3.32, 3.38, 3.46, 6.26, 6.68, 6.91, 7.25, 7.60, 8.15, 8.86, 9.24, 9.89, 14.39  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.79 (m, 10 H, arom), 6.14 (d of d, 1 H, J = 12.0, 7.5 Hz, diastereotopic CH<sub>2</sub>), 6.47 (d of d, 1 H, J = 12.0, 7.5 Hz, diastereotopic CH<sub>2</sub>), 8.37 (t, 1 H, J = 7.5 Hz, cyclopropyl), 8.39 (br s, 1 H, OH), 8.80 (s, 3 H, CH<sub>3</sub>), 8.99 (s, 3 H, CH<sub>3</sub>); mass spectrum (Calc. for C<sub>18</sub>H<sub>20</sub>O, 252.1514) *m/e* 252.15150. (Found: C. 85.80; H, 8.08. Calc. for C<sub>18</sub>H<sub>20</sub>O; C, 85.67; H, 7.99%).

3,3 - Dimethyl - 2,2 - diphenylcyclopropanecarboxaldehyde. A soln of pyridine and CrO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> was prepared according to the method of Ratcliffe and Rodehorst<sup>48</sup> by slowly adding 7.00 g (69.9 mmol) of CrO<sub>3</sub> to a soln of 12.1 ml (150 mmol) of pyridine in 160 ml of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 15 min and then 2.52 g (10.0 mmol) of 3.3 - dimethyl - 2,2 - diphenyl - cyclopropylmethanol was added to yield a black tarry ppt. After stirring for 15 min the mixture was decanted and the residues washed with ether. The combined organic solns were washed consecutively with 10% NaOH, 10% HCl, 10% NaHCO<sub>3</sub> aq, sat. NaCl aq and dried over MgSO<sub>4</sub>. Solvent removal *in racwo* yielded 2.49 g (99%) of essentially pure white crystalline solid product, m.p. 203–205°. Recrystallization from hexane gave 2.30 g of solid product (91%), m.p. 205–208° which was identical to the previously described aldehyde.<sup>12</sup>

3,3 - Dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane. To a stirred suspension of 900 mg (2.52 mmol) of methyltriphenylphosphonium bromide in 25 ml of anhyd ether at 0° under N- was added 1.60 ml of 1.45 M n-BuLi in hexane (2.32 mmol). The soln was stirred for 0.5 hr and then 500 mg (2.00 mmol) of 3,3 dimethyl - 2,2 - diphenylcyclopropanecarboxaldehyde in 30 ml of anhyd ether was added. The mixture was stirred for 0.5 hr at 0°, pentane added, and the soln filtered through Celite. The combined filtrate and washings were concentrated in vacuo to yield 505 mg of a yellow oil which was passed through a 40 cm  $\times$ 1.2 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane and eluted with hexane. After elution with 250 ml, 1000 ml were collected. Solvent removal in vacuo yielded 390 mg of a clear, colorless oil which crystallized upon trituration with pentane at -78°. Recrystallization from pentane yielded 370 mg (75%) of a white crystalline solid. m.p. 46°.

Spectral data. IR (KBr) 3.24, 3.26, 3.29, 3.32, 3.34, 3.38, 3.39, 3.42, 3.48, 5.06, 5.12, 5.48, 5.53, 6.12, 6.15, 6.25, 6.33, 6.70, 6.86, 6.90, 7.00, 7.20, 7.27, 7.60, 8.21, 8.62, 8.94, 9.23, 9.33, 9.62, 9.74,

9.93, 10.00, 10.07, 10.29, 10.63, 10.86, 10.99, 11.24, 11.59, 11.74, 12.90, 13.21, 13.48, 14.03, 14.22, 14.84  $\mu$ ; NMR<sup>49</sup> (CDCl<sub>3</sub>)  $\tau$  2.74 (m, 10 H, arom), 4.63 (m, 1 H, J = 16.8, J = 10.5, J = 9.0 Hz, vinyl), 4.67 (m, 1 H, J = 16.8, J = 2.1 Hz, vinyl), 4.93 (m, 1 H, J = 10.5, J = 2.1 Hz, vinyl), 7.90 (d, 1 H, J = 9.0 Hz, cyclopropyl), 8.83 (s, 3 H, CH<sub>3</sub>), 8.97 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 226 nm ( $\epsilon$  16,800), (Calc. for C<sub>19</sub>H<sub>20</sub>, 248.15650) *m*/*e* 248.15654. (Found: C, 91.76; H, 8.26. Calc. for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12%).

cis- and trans - 1 - (2' - Cyanovinyl) - 3,3 - dimethyl - 2,2 diphenylcyclopropane. To a stirred suspension of 0.50 g (11.7 mmol) of a 56.3% sodium hydride dispersion (prewashed with dry ether) in 40 ml of dry dimethoxyethane at room temp. under N<sub>2</sub> was added 1.24 g (7.00 mmol) of diethyl cyanomethylphosphonate<sup>8</sup> in 5.0 ml of dry dimethoxyethane dropwise. The reaction was exothermic and the resulting grey soln was stirred until it returned to ambient temp. Then 1.17 g (4.68 mmol) of 3,3 dimethyl - 2,2 - diphenylcyclopropanecarboxaldehyde in 40 ml of dry dimethoxyethane was added dropwise over a period of 15 min. This reaction was also exothermic and the soln was stirred until it returned to ambient temp., then poured onto water, ether extracted and dried over MgSO<sub>4</sub>. Filtration and solvent removal in vacuo yielded 1.22 g (95%) of a 2:1 mixture (analysis by NMR and GC) of cis: trans-isomers as a yellow oil. The isomers were separated at 155° on a Prepmaster 776 gas chromatograph fitted with a 2 m × 2.0 cm column of 10% QF-1 on 60-80 Chromosorb W. The cis-isomer eluted first (44 min), followed by the trans-isomer (60 min). The cis-isomer so prepared was analytically pure and crystallized in 95% EtOH. Recrystallization from 95% EtOH gave 450 mg (35%) of a white crystalline solid, m.p. 101°.

Spectral data for cis - 1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. IR (KBr) 3.26, 3.27, 3.29, 3.30, 3.31, 3.33, 3.35, 3.40, 3.42, 3.48, 4.51, 6.25, 6.30, 6.72, 6.87, 6.93, 7.20, 7.28, 7.63, 8.10, 8.12, 8.37, 8.66, 8.93, 8.99, 9.28, 9.35, 9.71, 9.79, 9.82, 10.08, 10.15, 10.70, 10.92, 11.26, 11.48, 11.85, 12.82, 13.07, 13.16, 13.44, 14.10, 14.35, 14.71, 15.67  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.81 (m, 10 H, arom), 4.00 (d of d, 1 H, J = 11.5, J = 11.0 Hz, vinyl), 4.86 (d, 1 H, J = 11.0 Hz, vinyl), 7.35 (d, 1 H, J = 11.5 Hz, cyclopropyl), 8.76 (s, 3 H, CH<sub>3</sub>), 8.92 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 224 nm ( $\epsilon$  19,100), 246 nm ( $\epsilon$  12.800); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N, 273.15175) m/e 273.15189. (Found: C, 87.71; H, 7.16. Calc. for C<sub>20</sub>H<sub>19</sub>N; C, 87.87; H, 7.01%).

The *trans*-isomer so prepared, however, had some *cis*-isomer as an impurity and was rechromatographed by GC. The *trans*isomer so obtained was analytically pure and crystallized in 95% EtOH. Recrystallization from 95% EtOH gave 190 mg (15%) of a white crystalline solid, m.p. 160°.

Spectral data for trans - 1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. IR (KBr) 3.25, 3.26, 3.27, 3.30, 3.34, 3.36, 3.39, 3.42, 3.47, 4.50, 6.18, 6.26, 6.71, 6.93, 7.27, 7.61, 8.53, 8.62, 8.68, 8.99, 9.26, 9.33, 9.48, 9.70, 9.78, 9.84, 10.06, 10.18, 10.34, 10.94, 11.25, 11.49, 12.20, 12.99, 13.25, 13.66, 14.08, 14.33, 15.72  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.77 (m, 10 H, arom), 3.72 (d of d, 1 H, J = 16.0, J = 11.0 Hz, vinyl), 4.49 (d, 1 H, J = 16.0 Hz, vinyl), 7.73 (d, 1 H, J = 11.0 Hz, cyclopropyl), 8.77 (s, 3 H, CH<sub>3</sub>), 8.93 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 227 ( $\epsilon$  19,500), 245 ( $\epsilon$  16,400); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N; C, 87.87; H, 7.01%).

cis- and trans - 1 - (2' - Methoxyvinyl) - 3,3 - dimethyl - 2,2 diphenylcyclopropane. To a stirred soln of dimsyl sodium (freshly prepared by heating 0.55 g (12.9 mmol) of a 56.3% sodium hydride dispersion in 10 ml of anhyd dimethyl sulfoxide at 65° under N<sub>2</sub> for 1.0 hr) was added 3.50 g (10.2 mmol) of methoxymethylenetriphenylphosphonium chloride<sup>11</sup> in 15 ml of THF at 0°. The soln was stirred for 30 min and warmed to room temp. Then 1.25 g (5.00 mmol) of 3.3-dimethyl - 2,2 - diphenylcyclopropanecarboxaldehyde in 20 ml of THF was added. After 15 min the mixture was poured onto water and pentane extracted. The extract was washed with sat. NH<sub>4</sub>Cl aq, sat. NaCl aq and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration through Celite and solvent removal *in vacuo* yielded 1.88 g of a yellow oil. This oil was filtered through a 30 cm × 1.2 cm neutral alumina (Fisher, Brockman Activity 1, 80-200 mesh) column packed in hexane. Elution with 10.0% ether in hexane yielded 1.25 g of a light yellow oil. This oil was chromatographed on a 15 cm  $\times$  2.2 cm neutral alumina (Fisher, Brockman Activity 1, 80-200 mesh) column packed in hexane. Fast elution with hexane yielded 342 mg of the *cis*-enol ether containing two impurities followed immediately by elution with 4.0% ether in hexane to yield 326 mg of the *trans*-enol ether containing an impurity. The fraction containing the *cis*-isomer was rechromatographed on a 60 cm  $\times$  2.2 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution with hexane yielded 138 mg (10%) of the *cis*-enol ether as a colorless oil which crystallized upon trituration with pentane at  $-78^{\circ}$ . Recrystallization from pentane gave 110 mg (8.0%) a white solid, m.p. 212°.

Spectral data for the cis-isomer. IR (KBr) 3.25, 3.27, 3.31, 3.34, 3.35, 3.36, 3.40, 3.42, 3.43, 3.50, 3.55, 6.07, 6.27, 6.35, 6.71, 6.85, 6.93, 7.24, 7.30, 7.51, 7.61, 7.66, 7.94, 8.26, 8.66, 8.77, 8.98, 9.29, 9.35, 9.49, 9.80, 9.85, 10.08, 10.60, 10.79, 10.89, 12.41, 13.02, 13.28, 13.53, 14.14, 14.41, 15.36  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.80 (m, 10 H, arom), 3.92 (d, 1 H, J = 6.5 Hz, vinyl), 6.07 (d of d, 1 H, J = 10.0, 6.5 Hz, vinyl), 6.31 (s, 3 H, OCH<sub>3</sub>), 7.56 (d, 1 H, J = 10.0 Hz, cyclo-propyl), 8.88 (s, 3 H, CH<sub>3</sub>), 8.98 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 223 nm ( $\epsilon$  20,300); mass spectrum (Calc. for C<sub>20</sub>H<sub>22</sub>O, 278.16706) m/e 278.16709. (Found: C, 86.11; H, 7.91. Calc. for C<sub>20</sub>H<sub>22</sub>O; C, 86.29; H, 7.97%).

The fraction containing the *trans*-isomer was also rechromatographed on a  $60 \text{ cm} \times 2.2 \text{ cm}$  silica gel (Grace, grade 62, 60-200mesh) column slurry packed in hexane. Elution with hexane yielded 242 mg (17%) of essentially pure *trans*-enol ether as a colorless oil which crystallized upon trituration with pentane at -78°. Recrystallization from pentane gave 215 mg (15%) of a white solid, m.p. 79°.

Spectral data for the trans-isomer: IR (KBr) 3.28, 3.31, 3.34, 3.36, 3.37, 3.41, 3.55, 6.08, 6.28, 6.72, 6.86, 6.94, 7.25, 7.30, 7.52, 7.63, 7.95, 8.29, 8.70, 8.79, 8.99, 9.29, 9.51, 9.74, 10.62, 10.80, 11.01, 12.42, 13.04, 13.33, 13.55, 14.12, 14.43, 15.41  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.80 (m, 10 H, arom), 3.44 (d, 1 H, J = 13.0 Hz, vinyl), 5.72 (d of d, 1 H, J = 13.0, 10.0 Hz, vinyl), 6.56 (s, 3 H, OCH<sub>3</sub>), 8.05 (d, 1 H, J = 10.0 Hz, cyclopropyl), 8.91 (s, 3 H, CH<sub>3</sub>), 9.00 (s, 3 H, CH<sub>3</sub>); UV (95% EIOH) 225 nm ( $\epsilon$  17.800); mass spectrum (Calc. for C<sub>20</sub>H<sub>22</sub>O, 278.16706) m/e 278.16683. (Found: C, 86.38; H, 7.92. Calc. for C<sub>20</sub>H<sub>22</sub>O; C, 86.29; H, 7.97%).

Diethyl diphenylmethylphosphonate. A mixture of 24.5 g (99.2 mmol) of benzhydryl bromide and 17.1 ml (100 mmol) of triethyl phosphite was slowly heated to  $185^{\circ}$  and stirred for 1.0 hr. The resulting brown oil was then quickly distilled at 0.8 mm to avoid decomposition. Collecting three fractions gave: fraction 1, b.p. less than  $55^{\circ}$ , 2.00 g of triethyl phosphite; fraction 2, b.p.  $55-137^{\circ}$ , 2.54 g of unidentified impurities; fraction 3, b.p.  $138-170^{\circ}$ , 42.2 g (70%) of a clear, colorless oil which crystallized upon cooling at 0° to yield diethyl diphenylmethylphosphonate as a white crystalline solid, m.p.  $22-25^{\circ}$ .

Spectral data. IR (thin film) 3.20, 3.23, 3.26, 3.31, 3.37, 3.40, 6.25, 6.31, 6.64, 6.72, 6.83, 7.12, 7.25, 7.65, 7.90, 8.47, 8.96, 9.30, 9.60, 10.18, 11.29, 11.47, 12.47, 13.16, 13.85, 13.99  $\mu$ ; NMR (CCl<sub>4</sub>)  $\tau$  2.60 (m, 10 H, arom), 5.70 (d, 1 H, J = 25.0 Hz, methine), 6.19 (m, 4 H, CH<sub>2</sub>-O), 8.96 (t, 6 H, J = 7.0 Hz, CH<sub>3</sub>); mass spectrum (Calc. for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>P, 304.12283) *m/e* 304.12319. (Found: C, 66.84; H, 7.05. Calc. for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>P: C, 67.07; H, 6.96%).

Methyl 2,2-dimethylcyclopropylcarboxylate. Methyl 2,2-dimethylcyclopropylcarboxylate was prepared by the method of Corey and Jautelat<sup>15a,b</sup> from methyl acrylate and diphenyl-sulfonium isopropylide.

2,2-Dimethylcyclopropylmethanol. This known<sup>50,51</sup> compound was prepared most conveniently by the following procedure. 2.00 g (15.6 mmol) of methyl 2.2soln of dimethylcyclopropylcarboxylate in 25 ml of anhyd ether was added to a stirred suspension of 0.70 g (18.5 mmol) of LAH in 30 ml of ether at 0°. The mixture was stirred at 1.0 hr at 0° and then an excess of a 1:1 mixture of sodium sulfate decahydratecelite was added to destroy unreacted LAH. The mixture was stirred until the grey solid turned white, then the granular ppt was filtered off. Solvent removal in vacuo at -20° yielded 1.58 g of a light yellow oil which was microdistilled at 78° to give 1.47 g (94%) of the desired alcohol as a clear, colorless oil. This was

characterized as the known<sup>50,51</sup> 2,2-dimethylcyclopropylmethanol by infrared and NMR spectral data.

Spectral data. IR (thin film) 2.99 (br OH), 3.26, 3.33, 3.38, 3.47, 6.85, 7.22, 9.69, 9.93  $\mu$ , NMR (CCl<sub>4</sub>)  $\tau$  6.49 (multiplet, 2 H, -CH<sub>2</sub>O-), 6.98 (s, 1 H, OH), 8.90 (s, 3 H, CH<sub>3</sub>), 8.93 (s, 3 H, CH<sub>3</sub>), 8.90-10.05 (complex multiplet, 3 H. cyclopropyl).

2,2-Dimethylcyclopropylcarboxaldehyde. This known<sup>13</sup> compound was best prepared by the following procedure. A solution of pyridine and CrO<sub>3</sub> in dichloromethane<sup>48</sup> was prepared by slowly adding 7.71 g (77.0 mmol) of CrO<sub>3</sub> to a soln of 12.4 ml (154 mmol) of pyridine in 160 ml of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 15 min and then 1.10 g (11.0 mmol) of 2,2-dimethyl-cyclopropylmethanol was added to yield a black tarry ppt. After stirring for 15 min, the mixture was decanted and the residues washed with ether. The combined organic fractions were washed consecutively with 10% NaOH, 10% HCl, 10% NaHCO<sub>3</sub> aq, sat. NaCl aq and dried over MgSO<sub>4</sub>. Solvent removal *in vacuo* at  $-20^{\circ}$  yielded 0.623 g of a light yellow oil which was microdistilled at 78° to give 0.593 g (55%) of the known<sup>13</sup> aldehyde as a clear.

Its spectral data agreed with those of the literature; IR (thin film) 3.38, 3.48, 3.53, 3.65, 5.88, 6.90, 7.25, 8.50, 8.94, 10.20  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  0.62 (d. 1 H, J = 5.0 Hz, aldehyde H), 8.72 (s, 3 H, CH<sub>3</sub>), 8.80 (s, 3 H, CH<sub>3</sub>), 8.20–9.20 (complex multiplet, 3 H, cyclopropyl).

2.2 - Dimethyl - 1 - (2',2' - diphenylvinyl)cyclopropane. To a soln of 2.50 g (8.22 mmol) of diethyl diphenylmethylphosphonate in 35 ml of anhyd dimethoxyethane was added 5.70 ml of 1.45 M n-BuLi in hexane (8.27 mmol) at  $0^{\circ}$  under N<sub>2</sub> to yield an orange soln. After stirring for 0.5 hr, 500 mg (5.10 mmol) of 2,2-dimethylcyclopropanecarboxaldehyde in 10 ml of dry dimethoxyethane was added. The mixture was stirred for 0.5 hr at 0° then poured into water, ether extracted and dried over MgSO<sub>4</sub>. Filtration and solvent removal in vacuo yielded 3.27 g of a light yellow oil which was chromatographed on a  $30\,\mathrm{cm} \times$ 3.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 100 ml fractions gave: fractions 1-8, hexane, nil; fractions 9-20, hexane, 896 mg of cyclopropane and an impurity; fractions 21-25, hexane, nil. The colorless oil crystallized upon trituration with pentane at -78°. Recrystallization from 1:2 benzene: methanol afforded 684 mg (54%) of 2,2 dimethyl - 1 - (2',2' - diphenylvinyl)cyclopropane as a white crystalline solid, m.p. 70°.

Spectral data. IR (KBr) 3.25, 3.27, 3.30, 3.34, 3.37, 3.39, 3.43, 3.49, 5.06, 5.12, 6.20, 6.27, 6.36, 6.68, 6.69, 6.93, 7.20, 7.26, 7.46, 7.67, 7.92, 8.08, 8.43, 8.52, 8.67, 8.98, 9.31, 9.60, 9.71, 9.78, 9.96, 10.50, 10.85, 11.24, 11.56, 12.47, 12.90, 13.02, 13.72, 14.29  $\mu$ : NMR<sup>49</sup> (CDCl<sub>3</sub>)  $\tau$  2.73 (m, 10 H, arom), 4.27 (d, 1 H, J = 9.6 Hz, vinyl), 8.68 (d of d of d, 1 H, J = 9.6, J = 8.3, J = 5.4 Hz, cyclopropyl), 8.81 (s, 3 H, CH<sub>3</sub>), 8.97 (s, 3 H, CH<sub>3</sub>), 9.26 (d of d, 1 H, J = 5.4, J = 4.2 Hz, cyclopropyl), 9.51 (pseudo triplet, 1 H, J = 5.4, J = 4.2 Hz, cyclopropyl), 9.57 (s, 248.15650) m/e 248.15632. (Found: C, 91.84; H, 8.15, Calc. for C<sub>19</sub>H<sub>20</sub>; C, 91.88; H, 8.12%), 3,3-Diphenylacrolein. The synthesis of 3.3-diphenylacrolein

was performed by the method of Wittig and Hesse.<sup>14</sup>

cis- and trans - 5.5 - Diphenvl - 2.4 - pentadienenitrile. To a stirred suspension of 0.90 g (21.1 mmol) of a 56.3% sodium hydride dispersion (prewashed with dry ether) in 30 ml of N,Ndimethylformamide at room temp, under N2 was added 2.97 g (16.8 mmol) of diethyl cyanomethylphosphonate<sup>8</sup> dropwise slowly to yield a brown soln. After 15 min, 2.50 g (12.0 mmol) of 3,3-diphenylacrolein in 20 ml of N,N-dimethylformamide was added. The mixture was stirred for 20 min after which the resulting dark brown soln was poured onto water, ether extracted and dried over MgSO4. Filtration and solvent removal in vacuo yielded 5.03 g of a 3:2 mixture of trans : cis-isomers by NMR analysis as a brown oil. This oil was chromatographed on a 240 cm × 3.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-283, 0.5% ether in hexane, nil; fractions 284-394, 0.5% ether in hexane, 1.09 g (39%) of essentially pure cis-diene as a yellow oil; fractions 395-437, 1.0% ether in hexane, 0.075 g of a mixture of cis- and trans-dienes; fractions 438-575, 2.0% ether in hexane, 1.55 g (56%) of essentially pure *trans*-diene as a yellow oil; fractions 576-625, 2.0% ether in hexane, nil. The fractions containing the *cis*-diene crystallized upon trituration with pentane at 0°. Recrystallization from pentane yielded 951 mg (34%) of white crystalline product, m.p. 70°.

Spectral data for cis - 5.5 - diphenyl - 2.4 - pentadienenitrile. IR (KBr) 3.24, 3.26, 3.27, 3.29, 4.05, 6.22, 6.35, 6.36, 6.69, 6.72, 6.92, 7.17, 7.40, 7.62, 7.81, 7.94, 8.00, 8.21, 8.44, 8.66, 8.97, 9.27, 9.71, 9.95, 10.31, 10.63, 10.72, 10.78, 11.25, 11.71, 11.82, 12.59, 12.84, 13.18, 13.33, 14.18, 15.20, 15.87  $\mu$ ; NMR (CCl<sub>4</sub>)  $\tau$  2.76 (m, 11 H, arom and 1 vinyl), 3.24 (pseudo triplet, 1 H, J = 11.0, J = 10.0 Hz, vinyl), 4.93 (d, 1 H, J = 10.0 Hz, vinyl); masss spectrum (Calc. for C<sub>17H 13</sub>N, 231, 10480) m/e 231, 10497. (Found: C. 88.11; H, 5.71. Calc. for C<sub>17</sub>H<sub>13</sub>N; C, 88.32; H, 5.62%).

The fractions containing the *trans*-diene also crystallized upon trituration with pentane at 0°. Recrystallization from pentane yielded 1.40 g (51%) of white crystalline product, m.p. 75°.

Spectral data for trans - 5,5 - diphenyl - 2,4 - pentadienenitrile. IR (KBr) 3.25, 3.26, 3.27, 3.30, 3.31, 3.42, 4.52, 6.23, 6.27, 6.36, 6.73, 6.91, 6.94, 7.36, 7.63, 7.72, 7.76, 7.82, 8.22, 8.47, 8.53, 8.65, 8.83, 9.31, 9.73, 10.02, 10.05, 10.27, 10.33, 10.37, 10.75, 10.82, 11.10, 11.24, 12.52, 12.80, 12.84, 13.02, 13.70, 14.20, 14.33, 15.60  $\mu$ ; NMR (CCl<sub>4</sub>)  $\tau$  2.79 (m, 10 H, arom), 3.04 (d of d, 1 H, J = 16.0, J = 11.0 Hz, vinyl), 3.34 (d, 1 H, J = 11.0 Hz, vinyl), 4.60 (d, 1 H, J = 16.0 Hz, vinyl); mass spectrum (Calc. for  $C_{17}H_{13}N$ , 231, 10480) m/e 231,10431, (Found: C, 88.60; H, 5.58, Calc. for  $C_{17}H_{13}N$ ; C, 8.32; H, 5.62%).

trans - 1 - Cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

Stereospecificity of reaction of diphenylsulfonium isopropylide with trans - 5,5 - diphenyl - 2,4 - pentadienenitrile. A suspension of diphenylisopropylsulfonium iodide in 50 ml of dry dimethoxyethane was prepared according to the method of Corey <sup>15a,b</sup> from 1.31 g (4.32 mmol) of diphenylethylsulfonium fluoroborate, 4.32 mmol of lithium diisopropylamide (from 0.61 ml of diisopropylamine and 2.20 ml of 2.0 M soln of n-BuLi in hexane) dissolved in 15 ml of dimethoxyethane, 0.28 ml (4.32 mmol) of CH<sub>3</sub>Cl<sub>2</sub>, and 0.28 ml (4.32 mmol) MeI. To this another 4.32 mmol of lithium diisopropylamide in 15 ml of dry dimethoxyethane was added. The entire procedure was carried on at -78° under N<sub>2</sub>. To the soln of diphenylsulfonium isopropylide at -78° was added 500 mg (2.16 mmol) of pure trans - 5,5 diphenyl - 2,4 - pentadienenitrile in 20 ml of dimethoxyethane dropwise slowly with vigorous stirring. After addition the mixture was stirred for 5.0 hr at -78° and subsequently warmed to room temp. overnight. The mixture was then poured into water, ether extracted and dried over MgSO4. Filtration and solvent removal in vacuo yielded a dark brown oil which was chromatographed on a 32 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 250 ml fractions gave: fractions 1-4, hexane, 1.11 g of diphenylsulfide; fractions 5-7, 2.0% ether in hexane, nil; fractions 8-10. 4.0% ether in hexane, 0.611 g (quantitative) of a mixture of cyclopropanes in the ratio of 10.2:1.0 trans : cis as a yellow solid (91% stereospecific). Product separation and isolation is described in a succeeding section.

#### cis - 1 - Cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

Stereospecificity of reaction of diphenylsulfonium isopropylide with cis-5,5-diphenyl-2,4-pentadienenitrile. A soln of 4.32 mmol of diphenylsulfonium isopropylide was prepared by the method of Corey<sup>15a,b</sup> as described previously (vide supra). To the soln of diphenylsulfonium isopropylide at  $-78^{\circ}$  was added 500 mg (2.16 mmol) of pure cis - 5.5 - diphenyl - 2.4 - pentadienenitrile in 20 ml of dimethoxyethane dropwise slowly with vigorous stirring. After addition the mixture was stirred for 5.0 hr at  $-78^{\circ}$  and warmed to room temp. overnight. The mixture was then poured into water, ether extracted. and dried over MgSO<sub>4</sub>. Filtration and solvent removal in vacuo yielded a dark brown oil which was chromatographed on a 32 cm  $\times$  3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 250 ml fractions gave: fractions 1-4, hexane, 1.09 g of diphenylsulfide; fractions 5-6, 2.0% ether in hexane, nil; fractions 7-10, 4.0% ether in hexane, 0.604 g (quantitative) of a mixture of cyclopropanes in the ratio of 12.6:1.0 *cis: trans* as a yellow solid (93% stereospecific). Separation and isolation is described in the following section.

#### Separation and characterization of cis- and trans - 1 - cyano -3.3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

The following typifies the separations in the two preceding preparations. An approximately equimolar mixture (1.63 g) of *cis*- and *trans*-cyclopropanes was chromatographed on a 240 cm  $\times$  3.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-675, 0.5% ether in hexane, 20.0 mg of an impurity; fractions 676-985, 0.5% ether in hexane, 520 mg of *cis*-cyclopropane; fractions 986-1044, 0.5% ether in hexane, 73.0 mg of a mixture of *cis*- and *trans*-cyclopropane; fractions 1306-1350, 1.0% ether in hexane, ml. The fractions containing the *cis*-isomer crystallized upon trituration with pentane at 0°. Recrystallization from pentane gave 450 mg of *cis*-product as a white solid, m.p. 104°.

Spectral data for the cis-isomer. IR (KBr) 3.25, 3.27, 3.30, 3.36, 3.38, 3.39, 3.41, 3.43, 4.47, 6.27, 6.31, 6.37, 6.71, 6.93, 6.94, 7.19, 7.25, 7.36, 7.41, 8.98, 9.34, 9.52, 9.73, 10.00, 10.15, 10.31, 10.32, 10.68, 10.80, 10.92, 11.22, 11.42, 11.86, 12.05, 12.50, 12.92, 13.05, 13.70, 14.25, 14.37, 14.53, 15.92  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.76 (m, 10 H, arom), 4.11 (d, 1 H, J = 9.0 Hz, vinyl), 8.21 (pseudo triplet, 1 H, J = 9.0, J = 8.5 Hz, cyclopropyl), 8.56 (d, 1 H, J = 8.5 Hz, cyclopropyl), 8.64 (s, 3 H, CH<sub>3</sub>) 8.89 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 227 nm ( $\epsilon$  14,300), 263 nm ( $\epsilon$  15,600); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N, 273.15175) *m/e* 273.15163. (Found: C, 87.63; H, 6.99. Calc. for C<sub>20</sub>H<sub>19</sub>N: C, 87.87; H, 7.01%).

The fractions containing the *trans*-cyclopropane also crystallized upon trituration with pentane at 0°. Recrystallization from pentane gave 850 mg of *trans*-product as a white solid, m.p. 98°.

Spectral data for the trans-isomer. IR (KBr) 3.25, 3.27, 3.28, 3.31, 3.34, 3.36, 3.38, 3.39, 3.42, 3.49, 4.47, 6.27, 6.37, 6.70, 6.72, 6.83, 6.90, 6.94, 7.20, 7.25, 7.37, 7.87, 8.26, 8.58, 8.67, 8.97, 9.34, 9.57, 9.71, 9.76, 10.55, 10.88, 11.33, 11.38, 11.51, 12.50, 12.66, 12.89, 13.02, 13.74, 14.16, 14.29, 14.49, 15.82  $\mu$ ; NMR (CDCl<sub>3</sub>)  $\tau$  2.78 (m, 10 H, arom), 4.39 (d, 1 H, J = 9.0 Hz, vinyl), 8.12 (d of d, 1 H, J = 9.0, J = 5.0 Hz, cyclopropyl), 8.73–8.76 (1 H, cyclopropyl) buried under methyls), 8.73 (s, 3 H, CH<sub>3</sub>), 8.76 (s, 3 H, CH<sub>3</sub>); UV (95% EtOH) 227 nm ( $\epsilon$  14.900), 263 nm ( $\epsilon$  16.900); mass spectrum (Calc. for C<sub>20</sub>H<sub>19</sub>N, 273.15175) *m/e* 273.15163. (Found: C, 87.61; H, 6.87. Calc. for C<sub>20</sub>H<sub>19</sub>N: C, 87.87; H, 7.01%).

# Photolysis equipment for preparative irradiations and quantum yield determinations

All direct and sensitized preparative irradiations were performed on the black box apparatus<sup>18</sup> at 27° unless otherwise specified. Direct and sensitized quantum yield irradiations were performed at 27° on the black box or on the microoptical bench<sup>18</sup> using a Model 33-86-79 Bausch and Lomb monochromator. Light output was monitored with an electronic actinometer<sup>52</sup> that utilized two IP28 photomultipliers, a multiplexed voltage to frequency converter and two digital counters. This was calibrated with ferrioxalate actionometry<sup>53</sup> prior to each run and for each wavelength used. The light absorbed in the reaction cell was determined by the splitting ratio technique previously described.<sup>18</sup>

For direct photolyses in the black box apparatus, the band pass was controlled by the following filter solution: Filter A (a) 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid, (b) 2.0 M cobalt sulfate heptahydrate in 5% sulfuric acid, (c) 0.0002 M bismuth trichloride in 10% hydrochloric acid. This combination gave an 18% transmission maximum at 280 nm and was opaque above 305 nm and below 255 nm. For sensitized photolyses, the band pass was controlled by the following filter solutions: Filter B (a) 0.23 M nickel sulfate hexahydrate in 10% sulfuric acid, (b) 2.0 M cobalt sulfate heptahydrate in 5% sulfuric acid, (c) 0.2 M stannous chloride dihydrate in 15% hydrochloric acid. This combination gave a 31% transmission maximum at 342 nm and was opaque above 370 nm and below 320 nm. Filter C (a) 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid, (b) 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid, (c) 0.022 M stannous chloride dihydrate in 15% hydrochloric acid. This combination gave a 20% transmission maximum at 327 nm and was opaque above 355 nm and below 310 nm.

For the direct irradiations performed on the microoptical bench at a wavelength of 280 nm a 5.3 mm monochromator entrance slit and 3.0 mm exit slit was used, giving a 22 nm theoretical band width. In addition a 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid solution filter was employed to exclude dominant 360 nm light. For the sensitized irradiations wavelengths of 330 nm and 340 nm with a 5.4 mm entrance slit and 3.0 mm exit slit were employed, giving a band pass of 22 nm at half-peak height.

Exploratory direct photolysis of 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene

Product isolation. A soln of 300 mg (1.21 mmol) of 3,3 dimethyl - 1,1 - diphenyl - 1,4 - pentadiene in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln A for 9.5 hr. The photolysate was then concentrated in vacuo at 40° to yield 346 mg of a yellow oil which was chromatographed on a 185 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-49, hexane, nil; fractions 50-95, hexane, 231 mg of pure starting diene; fractions 96-135, hexane, 57.0 mg of pure 3,3dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane; fractions 136-160, 3% MeOH in hexane, nil. The reactant diene as well as the vinylcyclopropane photoproduct were identical to the independently synthesized compounds as demonstrated by GC, NMR and m.p.

# Exploratory sensitized photolysis of 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene

Product isolation. A soln of 250 mg (1.01 mmol) of 3,3 dimethyl - 1,1 - diphenyl - 1,4 - pentadiene and 5.09 g (27.9 mmol) of benzophenone in 750 ml of t-BuOH was purged with purified  $N_2$  for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter solution B for 10.0 hr. The photolysate was then concentrated in vacuo at 40° to yield 5.44g of a clear, colorless oil which was chromatographed on a 100 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 100 ml fractions gave: fractions 1-8, hexane, nil; fractions 9-23, hexane, 263 mg of a hydrocarbon mixture; fractions 24-29, 10.0% ether in hexane, nil; fractions 30-40, 10.0% ether in hexane, 5.06 g of benzophenone (99.4%). The 263 mg of the hydrocarbon mixture was rechromatographed on a 185 cm × 2.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-29, hexane, nil; fractions 30-59, hexane, 208 mg of pure starting diene; fractions 60-64, hexane, 1.0 mg of a mixture of starting diene and vinylcyclopane; fractions 65-100, hexane, 41.0 mg of pure 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane; fractions 101-110, hexane, nil. The reactant diene as well as the vinylcyclopropane photoproduct were identical to the independently synthesized materials as demonstrated by GC, NMR and m.p.

Exploratory direct photolysis of trans - 1 - cyano - 3,3 - dimethyl' - 5,5 - diphenyl - 1,4 - pentadiene.

Product isolation. A solution of 500 mg (1.83 mmol) of trans - 1

- cvano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln A for 8.0 hr. The photolysate was then concentrated in vacuo to yield 546 mg of a yellow oil which was chromatographed on a 185 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-455, 0.25% ether in hexane, nil; fractions 456-540, 0.25% ether in hexane, 17.3 mg of pure cis - 1 cvano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene; fractions 541-710, 0.25% ether in hexane, 28.0 mg of a mixture of cisdiene, trans-diene and cis-cyclopropane; fractions 711-860, 0.25% ether in hexane, 313 mg of a mixture of trans - 1 - cyano -3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene and cis - 1 cvano - 3,3 - dimethyl - 2 - (2',2'-diphenylvinyl)cyclopropane; fractions 861-975, 0.25% ether in hexane, 31.1 mg of a mixture of trans-diene, cis-cyclopropane and secondary products; fractions 976-1115, 0.25% ether in hexane, 23.7 mg of trans-diene, transcyclopropane and secondary products; fractions 1116-1240, 1.0% ether in hexane, 63.0 mg of pure trans - 1 - cyano - 3.3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane.

Fractions 711-860 were combined and an aliquot portion (15.0 mg) was chromatographed by high pressure liquid chromatography on a 100 cm  $\times$  0.96 cm cyanopropyl-coated silica microsphere column (particle size 10-30  $\mu$ ) by elution with 12% THF and 0.05% MeOH in hexane. The mixture was recycled seven times and the appropriate cuts were made on each recycling mode. The results were: fraction 1, 5.0 mg of a mixture of *trans*-diene; fraction 3, 1.4 mg of pure *cis*-cyclopropane. All compounds isolated were identical by GC, NMR and m.p. to independently synthesized materials.

# Exploratory direct photolysis of cis - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

Product isolation. A soln of 500 mg (1.83 mmol) of cis - 1 cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln A for 7.5 hr. The photolysate was then concentrated in vacuo to yield 536 mg of a yellow oil which was chromatographed on a 185 cm × 3.0 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-440, 0.25% ether in hexane, nil; fractions 441-610, 0.25% ether in hexane, 240 mg of pure cis - 1 - cyano - 3,3 dimethyl - 5,5 - diphenyl - 1,4 - pentadiene; fractions 611-720, 0.25% ether in hexane, 22.0 mg of a mixture of cis-diene and secondary products; fractions 721-880, 0.25% ether in hexane, 158 mg of a mixture of trans-diene and cis-cyclopropane; fractions 881-950, 0.25% ether in hexane, 17.1 mg of a mixture of trans-diene and trans-cyclopropane; fractions 951-1035, 1.0% ether in hexane, 29.3 mg of a mixture of trans-cyclopropane and secondary photoproducts; fractions 1036-1080, 10.0% ether in hexane, 21.5 mg of pure trans - 1 - cyano - 3,3 - dimethyl - 2 -(2'.2' - diphenvlvinvl)cvclopropane.

Fractions 721-880 were combined and an aliquot portion (30.0 mg) was chromatographed by high pressure liquid chromatography on a 100 cm  $\times$  0.96 cm cyanopropyl-coated silica microsphere column (particle size 10-30  $\mu$ ) by elution with 12% tetrahydrofuran and 0.05% methanol in hexane. The mixture was recycled five times and the appropriate cuts were made on each recycling mode. The results were: fraction 1, 6.0 mg of a 1:1 mixture of *trans*-diene and *cis*-cyclopropane; fraction 2, 8.7 mg of pure *cis*-cyclopropane; fraction 3, 4.9 mg of a 10:1 mixture of *cis*-cyclopropane and *trans*-diene. Fraction 4 was recycled twice to yield 4.4 mg of a mixture of *cis*-cyclopropane and *trans*-diene. All compounds isolated were identical to independently synthesized materials as demonstrated by GC, NMR and m.p. Exploratory sensitized photolysis of trans - 1 - cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene

Product isolation. A soln of 507 mg (1.86 mmol) of trans - 1 cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene and 5.67 g (47.2 mmol) of acetophenone in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln B for 5.0 hr. The photolysate was then concentrated in vacuo to yield a clear, colorless oil from which the remaining acetophenone was removed at 50° (1.0 mm). The residual light yellow oil (545 mg) was subsequently chromatographed on a 185 cm × 2.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-250, 0.25% ether in hexane, nil; fractions 251-340, 0.25% ether in hexane. 72.1 mg of pure cis - 1 - cyano - 3,3 - dimethyl - 5.5 - diphenyl - 1.4 pentadiene; fractions 341-375, 0.25% ether in hexane, 2.3 mg of a mixture of cis- and trans-dienes: fractions 376-540, 0.5% ether in hexane, 424 mg of pure trans - 1 - cyano - 3,3 - dimethyl - 5,5 diphenyl - 1,4 - pentadiene. All compounds isolated were identical to independently synthesized materials as demonstrated by GC, NMR and m.p.

Exploratory sensitized photolysis of cis - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

Product isolation. A soln of 300 mg (1.10 mmol) of cis - 1 cvano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene and 5.15 g (42.9 mmol) of acetophenone in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln B for 3.0 hr. The photolysate was then concentrated in vacuo to yield a clear, colorless oil from which the remaining acetophenone was removed at 55° (1.0 mm). The residual light yellow oil (320 mg) was subsequently chromatographed on a 185 cm × 2.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-130, 0.5% ether in hexane, nil; fractions 131-210, 0.5% ether in hexane, 132 mg of pure cis -1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene; fractions 211-230, 0.5% ether in hexane, 4.8 mg of a mixture of cis- and trans-dienes; fractions 231-350, 0.5% ether in hexane, 146 mg of pure trans - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl -1,4 - pentadiene. All compounds isolated were identical to independently synthesized materials as demonstrated by GC, NMR and m.n.

Exploratory direct photolysis of trans - 1 - cyano - 3.3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

Product isolation. A soln of 284 mg (1.04 mmol) of trans - 1 cyano - 3.3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter solution A for 9.5 hr. The photolysate was then concentrated in vacuo to yield 305 mg of a vellow oil which was chromatographed on a 185 cm × 2.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-230, 0.5% ether in hexane, nil; fractions 231-389, 0.5% ether in hexane, 13.5 mg of a mixture of several secondary photoproducts; fractions 390-439, 0.5% ether in hexane, 20.6 mg of a mixture of cis-cyclopropane and secondary photoproducts; fractions 440-569, 0.5% ether in hexane, 138 mg of pure cis - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane; fractions 570-664, 0.5% ether in hexane, 18.2 mg of a mixture of cis- and trans-cyclopropanes; fractions 665-820, 1.0% ether in hexane, 82.0 mg of pure trans - 1 - cyano -3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane. All compounds isolated were identical to independently synthesized materials as demonstrated by GC. NMR and m.p.

Exploratory direct photolysis of cis - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

Product isolation. A solution of 284 mg (1.04 mmol) of cis - 1 cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln A for 11.0 hr. The photolysate was then concentrated in vacuo to yield 310 mg of a yellow oil which was chromatographed on a  $185 \text{ cm} \times 2.5 \text{ cm}$ silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-409, 0.25% ether in hexane, 5.5 mg of several secondary photoproducts; fractions 410-430, 0.25% ether in hexane, 9.2 mg of a mixture of cis-cyclopropane and several secondary photoproducts; fractions 431-540, 0.25% ether in hexane, 155 mg of pure cis - 1 - cyano - 3,3 - dimethyl - 2 - (2'.2' diphenylvinyl)cyclopropane; fractions 5.41-640, 0.25% ether in hexane, 29.5 mg of a mixture of cis- and trans-cyclopropanes: fractions 641-900, 2.0% ether in hexane, 51.8 mg of pure trans - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane. All compounds isolated were identical to independently synthesized materials as demonstrated by GC, NMR and m.p.

# Exploratory direct photolysis of trans - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

Product isolation. A soln of 300 mg (1.08 mmol) of trans - 1 methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter solution A. After irradiation the photolysate was concentrated in vacuo at 40° to yield 362 mg of a yellow oil which was chromatographed by high pressure liquid chromatography on a 50 cm × 0.96 cm silica microsphere column (particle size 10-30  $\mu$ ) by elution with 0.25% ether and 0.5% methanol in hexane. The results were: fraction 1, 14.4 mg of cis - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 pentadiene; fraction 2, 99.7 mg of starting trans-diene; fraction 3, 50.2 mg of a mixture of trans-diene, trans - 1 - (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane and several secondary photoproducts; fraction 4, 93.4 mg of an 8:1 mixture of trans: cis-cyclopropyl-enol ethers. Fraction 4 was further chromatographed on a 55 cm × 1.0 cm neutral alumina (Fisher, Brockman Activity 2, 80-200 mesh) column packed in hexane. The results were: fraction 1, hexane, 10.7 mg of pure cis - 1 - (2' methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane; fraction 2, 4.0% ether in hexane, 10.0 mg of a mixture of cis- and trans-cyclopropylenol ethers; fraction 3, 4.0% ether in hexane, 63.7 mg of pure trans - 1 - (2' - methoxyvinyl) - 3,3 - dimethyl -2,2 - diphenylcyclopropane. All compounds isolated were identical to independently synthesized materials as demonstrated by GC, NMR and m.p.

# Exploratory sensitized photolysis of trans - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

Product isolation. A solution of 250 mg (0.899 mmol) of trans -1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene and 400 mg (2.66 mmol) of *m*-methoxyacetophenone in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus through filter soln C. After irradiation the photolysate was concentrated in vacuo at 40° to yield 665 mg of a yellow oil which was chromatographed by high pressure liquid chromatography on a 50 cm × 0.96 cm silica microsphere column (particle size  $10-30 \mu$ ) by elution with 0.25% ether and 0.05% methanol in hexane. The results were: fraction 1, 11.2 mg of cis-diene; fraction 2, 35.4 mg of a mixture of cis- and trans-dienes; fraction 3, 190 mg of trans-diene. Elution with ether yielded 430 mg of material identified as m-methoxyacetophenone with several minor impurities. All compounds isolated were identical to independently synthesized materials by GC and NMR.

Summary of quantum yield results for the direct irradiation of 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene

Direct runs 1-5 were performed on the black box apparatus using filter solution A. In each case 750 ml of t-BuOH, freshly distilled from calcium hydride, was used as solvent. Solns were purged with purified nitrogen for 1.0 hr before and during photolysis. Direct run 6 was performed on the microoptical bench using 280 nm as the irradiation wavelength. Again t-BuOH (40 ml) was used as solvent. Solutions were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Analysis was by vapor phase chromatography using a 6 ft  $\times$  0.25 in. column packed with 5% Apiezon N on 100-120 Varaport 30 at 170°. Phenanthrene was used as an internal standard.

The data are listed as follows: starting 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene (mmol); light absorbed; 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane (mmol); quantum yield; per cent conversion.

*Run* 1. Diene (0.460 mmol); 2.54 mEinstein; cyclopropane (2.72 × 10<sup>-2</sup> mmol);  $\Phi = 1.07 \times 10^{-2}$ ; 5.90%.

*Run* 2. Diene (0.506 mmol); 1.05 mEinstein; cyclopropane ( $1.16 \times 10^{-2}$  mmol);  $\Phi = 1.10 \times 10^{-2}$ ; 2.29%.

Run 3. Diene (0.497 mmol); 0.625 mEinstein; cyclopropane (6.56 × 10<sup>-3</sup> mmol);  $\Phi = 1.05 \times 10^{-2}$ ; 1.32%. Run 4. Diene (0.401 mmol); 1.06 mEinstein; cyclopropane

*Run* 4. Diene (0.401 mmol); 1.06 mEinstein; cyclopropane  $(1.11 \times 10^{-2} \text{ mmol}); \Phi = 1.05 \times 10^{-2}; 2.63\%.$ 

*Run* 5. Diene (0.420 mmol): 2.12 mEinstein; cyclopropane (2.24 × 10<sup>-2</sup> mmol);  $\Phi = 1.06 \times 10^{-2}$ ; 5.33%.

**Run** 6. Diene  $(5.12 \times 10^{-2} \text{ mmol}); 8.32 \times 10^{-3} \text{ mEinstein}; cyclopropane (9.14 × 10^{-5} \text{ mmol}); <math>\Phi = 1.10 \times 10^{-2}; 0.179\%.$ 

Summary of quantum yield results for the sensitized irradiation of 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene

The sensitized runs were performed on the microoptical bench using 340 nm  $\pm$  22 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solns were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Acetophenone and benzophenone were used as sensitizers. Analysis was by vapor phase chromatography using a 6ft  $\times$  0.25 in. column packed with 5% Apiezon N on 100-120 Varaport 30 at 170°. Phenanthrene was used as an internal standard.

The data are listed as follows: starting 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene (mmol); sensitizer (mmol); mEinsteins of light absorbed by the sensitizer; 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane (mmol); quantum yield; per cent conversion.

**Run** 1. Diene  $(6.45 \times 10^{-2} \text{ mmol})$ ; acetophenone (9.44 mmol);  $5.62 \times 10^{-2} \text{ mEinstein}$ ; cyclopropane  $(5.64 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 1.01 \times 10^{-2}$ ; 0.875%.

*Run* 2. Diene  $(5.96 \times 10^{-2} \text{ mmol})$ ; acetophenone (8.37 mmol); 7.51×10<sup>-2</sup> mEinstein; cyclopropane  $(8.29 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 1.10 \times 10^{-2}$ ; 1.39%.

*Run* 3. Diene  $(5.56 \times 10^{-2} \text{ mmol})$ ; benzophenone (2.77 mmol); 5.98 × 10<sup>-2</sup> mEinstein; cyclopropane  $(6.89 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 1.15 \times 10^{-2}$ ; 1.24%.

Summary of quantum yield results for the high temperature direct irradiation of 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene

The high temp. direct runs were performed on the microoptical bench at  $73^{\circ}$  using 280 nm as the irradiation wavelength. Again t-BuOH (40 ml) was used as solvent. Solns were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis.

The data are listed as follows: starting 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene (mmol); light absorbed; 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane (mmol); quantum yield; per cent conversion.

*Run* 1. Diene  $(5.16 \times 10^{-2} \text{ mmol})$ ;  $9.66 \times 10^{-3} \text{ mEinstein}$ ; cyclopropane  $(1.08 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 1.18 \times 10^{-2}$ ; 0.209%.

*Run* 2. Diene  $(5.68 \times 10^{-2} \text{ mmol}); 7.48 \times 10^{-3} \text{ mEinstein}; cyclopropane <math>(7.98 \times 10^{-5} \text{ mmol}); \Phi = 1.07 \times 10^{-2}; 0.141\%.$ 

Summary of quantum yield results for the high temperature sensitized irradiation of 3.3 - dimethyl - 1.1 - diphenyl - 1.4 - pentadiene

The high temp. sensitized runs were performed on the microoptical bench at  $73^{\circ}$  using  $340 \text{ nm} \pm 22 \text{ nm}$  as the irradiation wavelength. Again t-BuOH (40 ml) was used as the solvent. Solns were purged with purified nitrogen for 0.5 hr before and during photolysis. Acetophenone was used as the sensitizer.

The data are listed as follows: starting 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene (mmol); sensitizer (mmol); mEinsteins of light absorbed by the sensitizer; 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane (mmol); quantum yield; per cent conversion.

*Run* 1. Diene  $(4.96 \times 10^{-2} \text{ mmol})$ ; acetophenone (8.43 mmol); 5.69×10<sup>-2</sup> mEinstein; cyclopropane  $(3.30 \times 10^{-3} \text{ mmol})$ ;  $\Phi = 5.79 \times 10^{-2}$ ; 6.65%.

*Run* 2. Diene  $(5.22 \times 10^{-2} \text{ mmol})$ ; acetophenone (8.68 mmol); 3.74 × 10<sup>-2</sup> mEinstein; cyclopropane (2.17 × 10<sup>-3</sup> mmol);  $\Phi = 5.80 \times 10^{-2}$ ; 4.14%.

# Energy transfer test<sup>22</sup>

Quenching of benzophenone triplets by 3.3 - dimethyl - 1.1 diphenyl - 1,4 - pentadiene. A soln of 220 mg (0.886 mmol) of 3.3 dimethyl - 1,1 - diphenyl - 1,4 - pentadiene, 5.05 g (27.7 mmol) of benzophenone and 2.02 g (10.9 mmol) of benzhydrol in 750 ml of t-BuOH was purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. The irradiation was performed on the black box apparatus at 27° through filter soln B until 6.66 mEinstein was absorbed. The photolysate was then concentrated in vacuo at 40° to yield 7.29 g of a colorless oil which was chromatographed on a 190 cm × 3.5 cm silica gel (Grace, grade 62, 60-200 mesh) column slurry packed in hexane. Elution in 40 ml fractions and monitoring by UV at 254 nm gave: fractions 1-40, 0.25% ether in hexane, nil; fractions 41-105, 0.25% ether in hexane, 217 mg of starting diene and cyclopropane photoproduct; fractions 106-150, 0.25% ether in hexane, nil; fractions 151-420, 1.0% ether in hexane. 5.05 g of benzophenone, m.p. 47-48°; fractions 421-570, 2.0% ether in hexane, nil; fractions 571-690, 6.0% ether in hexane, 1.98 g of benzhydrol, m.p. 80-81°; fractions 691-750, 10.0% ether in hexane, nil: No benzopinacol was isolated.

# Summary of quantum yield results for the direct irradiation of trans - 1 - cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene

Direct runs 1-2 were performed on the black box apparatus using filter soln A. In each case 750 ml of t-BuOH freshly distilled from calcium hydride, was used as solvent. Solutions were purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. Direct runs 3-8 were performed on the microoptical bench using 280 nm as the irradiation wavelength. Again t-BuOH (40 ml) was used as solvent. Solns were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Analysis was by vapor phase chromatography using a 6 ft  $\times$  0.25 in. column packed with 7% DEGS on 70-80 Varaport 30 and a 6 ft  $\times$  0.25 in. column packed with 10% QF-1 on 100-120 Varaport 30 at 180°. p-Terphenyl was used as an internal standard.

The data are listed as follows: starting *trans* - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (mmol); light absorbed; *trans* - 1 - cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl-vinyl)cyclopropane (mmol), quantum yield, per cent conversion; *cis* - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (mmol), quantum yield, per cent conversion; *cis* - 1 cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl - 1,4 - pentadiene (mmol), quantum yield, per cent conversion; *cis* - 1 cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl - 1,4 - pentadiene (mmol), quantum yield, per cent conversion; *cis* - 1 cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl - 1,4 - pentadiene (mmol), quantum yield, per cent conversion; *cis* - 1 cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl - 1,4 - pentadiene (mmol), quantum yield, per cent conversion; *cis* - 1 cyano - 3,3 - dimethyl - 2 - (2',2') - diphenyl - 2 -

*Run* 1. *trans*-Diene (0.561 mmol); 1.06 mEinstein; *trans*cyclopropane (4.87 × 10<sup>-2</sup> mmol);  $\Phi = 4.58 \times 10^{-2}$ , 8.69%; *cis*-diene (8.29 × 10<sup>-3</sup> mmol),  $\Phi = 7.79 \times 10^{-3}$ , 2.13%; *cis*-cyclopropane (2.00 × 10<sup>-2</sup> mmol),  $\Phi = 1.88 \times 10^{-2}$ , 3.57%.

*Run* 2. *trans*-Diene (0.476 mmol); 0.585 mEinstein; *trans*-cyclopropane ( $3.11 \times 10^{-2}$  mmol),  $\Phi = 5.31 \times 10^{-2}$ , 6.54%, *cis*-diene ( $4.95 \times 10^{-3}$  mmol),  $\Phi = 8.80 \times 10^{-3}$ , 1.08%; *cis*-cyclo-propane ( $1.03 \times 10^{-2}$  mmol),  $\Phi = 1.77 \times 10^{-2}$ , 2.17%.

Run 3. trans-Diene (0.112 mmol):  $1.52 \times 10^{-2}$  mEinstein; trans-

cyclopropane  $(1.43 \times 10^{-3} \text{ mmol}), \Phi = 9.38 \times 10^{-2}, 1.28\%$ ; *cis*diene  $(3.46 \times 10^{-4} \text{ mmol}), \Phi = 2.28 \times 10^{-2}, 0.309\%$ ; *cis*-cyclopropane  $(2.11 \times 10^{-4} \text{ mmol}), \Phi = 1.39 \times 10^{-2}, 0.189\%$ .

*Run 4. trans*-Diene (0.111 mmol);  $7.08 \times 10^{-3}$  mEinstein; *trans*cyclopropane ( $7.60 \times 10^{-4}$  mmol),  $\Phi = 0.107$ , 0.683%; *cis*-diene ( $2.72 \times 10^{-4}$  mmol),  $\Phi = 3.85 \times 10^{-2}$ , 0.254% *cis*-cyclopropane ( $6.30 \times 10^{-5}$  mmol),  $\Phi = 8.91 \times 10^{-3}$ , 0.057%.

*Run* 5. *trans*-Diene (0.107 mmoł);  $3.61 \times 10^{-3}$  mEinstein; *trans*cyclopropane ( $4.04 \times 10^{-4}$  mmoł),  $\Phi = 0.112$ , 0.376%; *cis*-diene ( $2.04 \times 10^{-4}$  mmoł),  $\Phi = 5.65 \times 10^{-2}$ , 0.190%; *cis*-cyclopropane ( $2.85 \times 10^{-5}$  mmol),  $\Phi = 0.0079$ , 0.027%.

*Run* 6. *trans*-Diene (0.109 mmol);  $1.87 \times 10^{-3}$  mEinstein; *trans*-cyclopropane (2.99 × 10<sup>-4</sup> mmol),  $\Phi = 0.160$ , 0.273%; *cis*-diene (1.52 × 10<sup>-4</sup> mmol),  $\Phi = 8.14 \times 10^{-2}$ , 0.139%; *cis*-cyclopropane (1.11 × 10<sup>-5</sup> mmol),  $\Phi = 0.0059$ , 0.010%.

*Run* 7. *trans*-Diene (0.105 mmol);  $1.04 \times 10^{-3}$  mEinstein; *trans*-cyclopropane (2.16 × 10<sup>-4</sup> mmol),  $\Phi = 0.208$ , 0.204%.

*Run* 8. *trans*-Diene (0.108 mmol);  $4.92 \times 10^{-4}$  mEinstein; *trans*-cyclopropane ( $1.32 \times 10^{-4}$  mmol),  $\Phi = 0.269$ , 0.122%.

A plot of quantum yield vs per cent conversion yielded the following quantum yields of appearance: *trans*-cyclopropane,  $\Phi = 0.356$ ; *cis*-diene,  $\Phi = 0.136$ ; *cis*-cyclopropane,  $\Phi \approx 0$  (secondary photoproduct).

Summary of quantum yield results for the direct irradiation of cis - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

The direct runs were performed on the microoptical bench using 280 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solns were purged with purified  $N_2$  for 0.5 Hr before and during photolysis. Analysis was by vapor phase chromatography using a 6 ft × 0.25 in. column packed with 10% QF-1 on 100-120 Varaport 30 at 180°. p-Terphenyl was used as an internal standard.

The data are listed as follows: starting cis - 1 - cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol); light absorbed; <math>cis - 1 - cyano - 3.3 - dimethyl - 2 - (2'.2' - diphenyl-vinyl)cyclopropane (mmol), quantum yield, per cent conversion; trans - 1 - cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol), quantum yield, per cent conversion; trans - 1 - cyano - 3.3 - dimethyl - 2 - (2'.2' - diphenyl - 1.4 - pentadiene (mmol), quantum yield, per cent conversion; trans - 1 - cyano - 3.3 - dimethyl - 2 - (2'.2' - diphenyl - 1.4 - pentadiene (mmol), quantum yield, per cent conversion; trans - 1 - cyano - 3.3 - dimethyl - 2 - (2'.2' - diphenyl - 2

**Run** 1. cis-Diene (0.0988 mmol);  $9.56 \times 10^{-3}$  mEinstein; ciscyclopropane (7.56 × 10<sup>-4</sup> mmol).  $\Phi = 0.0790$ , 0.764%; trans-diene (7.35 × 10<sup>-4</sup> mmol),  $\Phi = 0.0769$ , 0.744%; trans-cyclopropane (1.01 × 10<sup>-4</sup> mmol),  $\Phi = 0.0105$ , 0.102%.

*Run* 2. *cis*-Diene (0.0992 mmol):  $4.58 \times 10^{-3}$  mEinstein; *cis*cyclopropane ( $4.37 \times 10^{-4}$  mmol),  $\Phi = 0.0955$ , 0.441%; *trans*-diene ( $4.14 \times 10^{-4}$  mmol),  $\Phi = 0.0903$ . 0.417%; *trans*-cyclopropane ( $4.77 \times 10^{-5}$  mmol),  $\Phi = 0.0104$ , 0.048%.

*Run* 3. *cis*-Diene (0.0996 mmoł);  $2.15 \times 10^{-3}$  mEinstein; *cis*-cyclopropane (2.26 × 10<sup>-4</sup> mmol),  $\Phi = 0.105$ , 0.227%; *trans*-diene (2.30 × 10<sup>-4</sup> mmol),  $\Phi = 0.107$ , 0.231%; *trans*-cyclopropane (2.01 × 10<sup>-5</sup> mmol),  $\Phi = 0.0094$ , 0.020%.

*Run* 4. *cis*-Diene (0.0985 mmol);  $1.21 \times 10^{-3}$  mEinstein; *cis*-cyclopropane ( $1.53 \times 10^{-4}$  mmol),  $\Phi = 0.126$ , 0.155%; *trans*-diene ( $1.72 \times 10^{-4}$  mmol),  $\Phi = 0.141$ , 0.174%; *trans*-cyclopropane ( $7.64 \times 10^{-6}$  mmol),  $\Phi 0.0063$ , 0.0078%.

*Run* 5. *cis*-Diene (0.0966 mmol);  $5.82 \times 10^{-4}$  mEinstein; *cis*-cyclopropane (9.60 × 10<sup>-5</sup> mmol),  $\Phi = 0.165$ , 0.093%; *trans*-diene (1.11 × 10<sup>-4</sup> mmol),  $\Phi 0.191$ , 0.115%; *trans*-cyclopropane (2.83 × 10<sup>-6</sup> mmol),  $\Phi = 0.0049$ , 0.0029%.

A plot of quantum yield vs per cent conversion yielded the following quantum yields of appearance: *cis*-cyclopropane  $\Phi = 0.201$ ; *trans*-diene,  $\Phi = 0.273$ ; *trans*-cyclopropane.  $\Phi \approx 0$  (secondary photoproduct).

Summary of quantum yield results for sensitized irradiation of trans - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene The sensitized runs were performed on the microoptical bench using 340 nm  $\pm$  22 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solutions were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Aceto-phenone was used as the sensitizer. Analysis was by vapor phase chromatography using a 6 ft  $\times$  0.25 in. column packed with 10% QF-1 on 100-120 Varaport 30 at 180°. *p*-Terphenyl was used as an internal standard.

The data are listed as follows: starting trans - 1 - cyano - 3, 3 - dimethyl - 5, 5 - diphenyl - 1, 4 - pentadiene (mmol); acetophenone (mmol); mEinsteins of light absorbed by the sensitizer; <math>cis - 1 - cyano - 3, 3 - dimethyl - 5, 5 - diphenyl - 1, 4 - pentadiene (mmol); quantum yield; per cent conversion.

**Run** 1. trans-Diene (9.45 × 10<sup>-2</sup> mmol); acetophenone (9.26 mmol); 1.64 × 10<sup>-2</sup> mEinstein; cis-diene (2.61 × 10<sup>-3</sup> mmol);  $\Phi \approx 0.159$ ; 2.76%.

**Run** 2. trans-Diene  $(9.23 \times 10^{-2} \text{ mmol})$ ; acetophenone (9.17 mmol); 7.92 × 10<sup>-3</sup> mEinstein; *cis*-diene (1.29 × 10<sup>-3</sup> mmol);  $\Phi \approx 0.163$ ; 1.40%.

*Run* 3. *trans*-Diene (9.15×10<sup>-2</sup> mmol); acetophenone (9.20 mmol);  $4.54 \times 10^{-3}$  mEinstein; *cis*-diene (7.48×10<sup>-4</sup> mmol);  $\Phi \approx 0.165$ ; 0.818%.

A plot of quantum yield vs per cent conversion yielded the following quantum yield of appearance at zero per cent conversion upon least squares analysis: cis- 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene,  $\Phi = 0.167$ .

Summary of quantum yield results for the sensitized irradiation of cis - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

The sensitized runs were performed on the microoptical bench using 340 nm  $\pm$  22 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solutions were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Acetophenone was used as the sensitizer.

The data are listed as follows: starting cis - 1 - cyano - 3, 3 - dimethyl - 5, 5 - diphenyl - 1, 4 - pentadiene (mmol); acetophenone (mmol); mEinsteins of light absorbed by the sensitizer;*trans*- 1 - cyano - 3, 3 - dimethyl - 5, 5 - diphenyl - 1, 4 - pentadiene (mmol); quantum yield; per cent conversion.

**Run** 1. cis-Diene  $(9.04 \times 10^{-2} \text{ mmol})$ ; acetophenone (9.07 mmol);  $9.59 \times 10^{-3} \text{ mEinstein}$ ; trans-diene (4.82 ×  $10^{-3} \text{ mmol}$ );  $\Phi = 0.503$ ; 5.33%.

**Run** 2. cis-Diene (9.15 × 10<sup>-2</sup> mmol); acetophenone (9.71 mmol);  $4.82 \times 10^{-3}$  mEinstein; trans-diene (2.65 × 10<sup>-3</sup> mmol);  $\Phi = 0.549$ ; 2.89%.

**Run** 3. cis-Diene  $(8.93 \times 10^{-2} \text{ mmol})$ ; acetophenone (9.32 mmol);  $2.54 \times 10^{-3} \text{ mEinstein}$ ; trans-diene (1.48 ×  $10^{-3} \text{ mmol}$ );  $\Phi = 0.581$ ; 1.65%.

A plot of quantum yield vs per cent conversion yielded the following quantum yield of appearance at zero per cent conversion upon least squares analysis: *trans* - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene,  $\Phi = 0.613$ .

Summary of quantum yield results for the high temperature sensitized irradiation of trans - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

High temp. sensitized runs were performed on the microoptical bench at 73° using 340 nm  $\pm$  22 nm as the irradiation wavelength. t-BuOH (40 ml) was used as the solvent and solns were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Acetophenone was used as the sensitizer.

The data are listed as follows: starting *trans* - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (mmol); acetophenone (mmol); mEinsteins of light absorbed by the sensitizer; *cis* - 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (mmol); quantum yield; per cent conversion.

**Run** 1. trans-Diene  $(8.53 \times 10^{-2} \text{ mmol})$ ; acetophonone (8.51 mmol);  $1.64 \times 10^{-2} \text{ mEinstein}$ ; cis-diene  $(3.71 \times 10^{-3} \text{ mmol})$ ;  $\Phi = 0.225$ ; 4.35%.

Summary of quantum yield results for the direct irradiation of trans - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclo-propane

The direct runs were performed on the microoptical bench using 280 nm as the irradiation wavelength. In each case t-BuOH alcohol (40 ml) was used as the solvent. Solutions were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Analysis was by vapor phase chromatography using a 6 ft  $\times$  0.25 in. column packed with 10% QF-1 on 100-120 Varaport 30 at 180°. p-Terphenyl was used as an internal standard.

The data are listed as follows: starting *trans* - 1 - cyano - 3,3 - dimethyl - 2 - (2',2') - diphenylvinyl)cyclopropane (mmol); light absorbed; *cis* - 1 - cyano - 3,3 - dimethyl - 2 - (2',2') - diphenylvinyl)cyclopropane (mmol); quantum yield; percent conversion.

*Run* 1. *trans*-Cyclopropane  $(8.97 \times 10^{-2} \text{ mmol});$  7.70 ×  $10^{-3}$  mEinstein; *cis*-cyclopropane  $(1.46 \times 10^{-3} \text{ mmol});$   $\Phi = 0.190;$  1.63%.

*Run* 2. *trans*-Cyclopropane  $(9.08 \times 10^{-2} \text{ mmol}); 3.90 \times 10^{-3} \text{ mEinstein};$ *cis* $-cyclopropane <math>(9.88 \times 10^{-4} \text{ mmol}); \Phi = 0.254; 1.09\%.$ 

*Run* 3. *trans*-Cyclopropane ( $8.86 \times 10^{-2}$  mmol); 2.01 ×  $10^{-3}$  mEinstein; *cis*-cyclopropane ( $6.16 \times 10^{-4}$  mmol);  $\Phi = 0.306$ ; 0.695%.

A plot of quantum yield vs percent conversion yielded the following quantum yield of appearance at zero percent conversion upon least squares analysis:  $cis - 1 - cyano - 3, 3 - dimethyl - 2 - (2', 2' - diphenylvinyl)cyclopropane, <math>\Phi \approx 0.391$ .

Summary of quantum yield results for the direct irradiation of cis-1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane

The direct runs were performed on the microoptical bench using 280 nm as the irradiation wavelength. In each case *tert*-butyl alcohol (40 ml) was used as the solvent. Solutions were purged with purified nitrogen for 0.5 h before and during photolysis.

The data are listed as follows: starting cis - 1 - cyano - 3, 3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane (mmol); light absorbed; trans - 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane (mmol); quantum yield; per cent conversion.

**Run** 1. cis-Cyclopropane  $(8.93 \times 10^{-2} \text{ mmol});$  7.78 ×  $10^{-3}$  mEinstein; trans-cyclopropane  $(8.27 \times 10^{-4} \text{ mmol});$   $\Phi = 0.106; 0.925\%.$ 

Run 2. cis-Cyclopropane  $(9.01 \times 10^{-2} \text{ mmol});$  3.93 × 10<sup>-3</sup> mEinstein; trans-cyclopropane  $(5.27 \times 10^{-4} \text{ mmol});$  Φ = 0.134; 0.585%.

*Run* 3. *cis*-Cyclopropane  $(9.01 \times 10^{-2} \text{ mmol}); 1.79 \times 10^{-3}$ mEinstein; *trans*-cyclopropane  $(2.69 \times 10^{-4} \text{ mmol}); \Phi = 0.150; 0.299\%.$ 

A plot of quantum yield vs per cent conversion yielded the following quantum yield of appearance at zero per cent conversion upon least squares analysis: *trans* - 1 - cyano - 3,3 - dimethyl - 2 - (2',2') - diphenylvinyl)cyclopropane,  $\Phi = 0.173$ .

Summary of quantum yield results for the direct irradiation of trans - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

The direct runs were performed on the black box apparatus using filter solution A. In each case 750 ml of t-BuOH, freshly distilled from calcium hydride, was used as solvent. Solutions were purged with purified N<sub>2</sub> for 1.0 hr before and during photolysis. Analysis was by vapor phase chromatography using a  $5 \text{ ft} \times 0.25$  in. column packed with 10% SE-30 on 100-120 Varaport 30 at 165°. 4,4'-Dimethylbenzophenone was used as an internal standard.

The data are listed as follows: starting *trans*-1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene (mmol); light absorbed; *cis* - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 pentadiene (mmol), quantum yield, per cent conversion; *trans* - 1 - (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane (mmol), quantum yield, per cent conversion.

Run 1. trans-Diene (0.368 mmol); 0.859 mEinstein; cis-diene

 $(1.68 \times 10^{-2} \text{ mmol}), \Phi = 0.0196, 4.58\%$ ; *trans*-enol ether  $(2.08 \times 10^{-2} \text{ mmol}), \Phi = 0.0242, 5.64\%$ .

*Run* 2. *trans*-Diene (0.422 mmol); 0.314 mEinstein; *cis*-diene (8.04 × 10<sup>-2</sup> mmol),  $\Phi = 0.0253$ , 1.90% *trans*-enol ether (1.15 × 10<sup>-2</sup> mmol),  $\Phi = 0.0367$ , 2.73%.

*Run* 3. *trans*-Diene (0.612 mmol); 0.206 mEinstein; *cis*-diene (6.31 × 10<sup>-3</sup> mmol),  $\Phi = 0.0305$ , 1.03%; *trans*-enol ether (9.17 × 10<sup>-3</sup> mmol),  $\Phi = 0.0444$ , 1.50%.

A plot of quantum yield vs per cent conversion yielded the following quantum yields of appearance: *cis*-diene,  $\Phi = 0.0323$ ; *trans*-enol ether,  $\Phi = 0.0508$ .

Summary of quantum yield results for the direct irradiation of cis - 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene

The direct runs were performed on the microoptical bench using 280 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solns were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. Analysis was by vapor phase chromatography using a 6 ft  $\times$  0.25 in. column packed with 7% DEGS on 70-80 Varaport 30 at 150°. 4.4'-Dimethylbenzophenone was used as an internal standard.

The data are listed as follows: starting cis - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol); light absorbed; *trans* - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol), quantum yield, per cent conversion; cis - 1 - (2' - methoxyvinyl) - 3.3 - dimethyl - 2.2 - diphenylcyclopropane (mmol), quantum yield, per cent conversion.

*Run* 1. *cis*-Diene (8.74×10<sup>-2</sup> mmol);  $1.19 \times 10^{-2}$  mEinstein; *trans*-diene (5.56×10<sup>-4</sup> mmol),  $\Phi = 0.0469$ , 0.636%; *cis*-enol ether (5.92×10<sup>-4</sup> mmol),  $\Phi = 0.0499$ , 0.677%.

Run 2. cis-Diene ( $1.00 \times 10^{-1}$  mmol);  $5.32 \times 10^{-3}$  mEinstein; trans-diene ( $2.52 \times 10^{-4}$  mmol),  $\Phi = 0.0473$ , 0.251% cis-enol ether ( $2.75 \times 10^{-4}$  mmol),  $\Phi = 0.0516$ , 0.274%.

*Run* 3. *cis*-Diene ( $9.28 \times 10^{-2}$  mmol);  $2.58 \times 10^{-3}$  mEinstein; *trans*-diene ( $1.27 \times 10^{-4}$  mmol),  $\Phi = 0.0492$ , 0.137%; *cis*-enol ether ( $1.27 \times 10^{-4}$  mmol),  $\Phi = 0.0492$ , 0.137%.

Summary of quantum yield results for the sensitized irradiation of trans - 1 - methoxy - 3,3 - dimethyl - 5.5 - diphenyl - 1,4 - pentadiene

The sensitized runs were performed on the microoptical bench using 330 nm  $\pm$  22 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solutions were purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. *m*-Methoxyacetophenone was used as the sensitizer. Analysis was by vapor phase chromatography using a 6 ft × 0.25 in. column packed with 7% DEGS on 70-80 Varaport 30 at 150°. 4.4'-Dimethylbenzophenone was used as an internal standard.

The data are listed as follows: starting trans - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol); mmethoxyacetophenone (mmol); mEinsteins of light absorbed by the sensitizer; cis - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl -1.4 - pentadiene (mmol); quantum yield; per cent conversion. Run 1. trans-Diene ( $4.06 \times 10^{-2}$  mmol); m-methoxy-

*Run* 1. *trans*-Diene  $(4.06 \times 10^{-2} \text{ mmol})$ ; *m*-methoxy-acetophenone (0.237 mmol);  $1.19 \times 10^{-1} \text{ mEinstein}$ ; *cis*-diene  $(5.73 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 4.81 \times 10^{-3}$ ; 1.41%

Run 2. trans-Diene  $(4.28 \times 10^{-5} \text{ mmol})$ ; *m*-methoxy-acetophenone (0.258 mmol);  $6.00 \times 10^{-2}$  mEinstein; *cis*-diene  $(2.84 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 4.73 \times 10^{-3}$ ; 0.663%.

*Run* 3. *trans*-Diene  $(3.70 \times 10^{-2} \text{ mmol})$ ; *m*-methoxy-acetophenone (0.270 mmol);  $3.15 \times 10^{-2} \text{ mEinstein}$ ; *cis*-diene  $(1.49 \times 10^{-4} \text{ mmol})$ ;  $\Phi = 4.74 \times 10^{-3}$ ; 0.404%.

using 330 nm  $\pm$  22 nm as the irradiation wavelength. In each case t-BuOH (40 ml) was used as the solvent. Solutions were purged with purified nitrogen for 0.5 hr before and during photolysis. *m*-Methoxyacetophenone was used as the sensitizer.

The data are listed as follows: starting cis - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol); *m*-methoxy-acetophenone (mmol); mEinsteins of light absorbed by the sensitizer; *trans* - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene (mmol); quantum yield; per cent conversion.

**Run 1.** cis-Diene  $(4.06 \times 10^{-2} \text{ mmol})$ ; *m*-methoxyacetophenone (0.237 mmol);  $5.11 \times 10^{-2} \text{ mEinstein}$ ; trans-diene  $(1.42 \times 10^{-3} \text{ mmol})$ ;  $\Phi = 2.79 \times 10^{-2}$ ; 3.50%.

*Run* 2. *cis*-Diene  $(3.99 \times 10^{-2} \text{ mmol})$ ; *m*-methoxyacetophenone (0.261 mmol);  $3.15 \times 10^{-2} \text{ mEinstein}$ : *trans*-diene (8.84 ×  $10^{-4} \text{ mmol})$ ;  $\Phi = 2.81 \times 10^{-2}$ ; 2.21%.

#### Emission studies

Purification of solvent. Isopentane and methylcyclohexane were purified by repeated washing with 10% fuming sulfuric acid until the washings were colorless, then with water, 5% potassium hydroxide, drying over calcium chloride, and distillation. The solvent was then passed through a  $80 \times 2.5$  cm alumina column containing 10% of silver nitrate.<sup>54</sup> The early and late fractions were discarded, and the solvent was redistilled. Solvents treated in this fashion were transparent in the ultraviolet and fluorescence free.

Magic multipliers. For each compound, the fluorescence spectrum was recorded in 4:1 methylcyclohexane:isopentane solution at 77°K and 295°K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901 C-1 150 W Xenon lamp. Concentrations were adjusted to give an optical density in the range of 0.8-2.0. The magic multipliers<sup>24,28,28,28</sup> were obtained from a single sample by integrating the emission intensities obtained at the two temperatures. The average value obtained for each compound was as follows:

1. 3,3 - Dimethyl - 1,1 - diphenyl - 1,4 - pentadiene, M = 256 (3 runs)

2. trans - 1 - Cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene, M = 260 (5 runs)

3. cis - 1 - Cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene, M = 260 (3 runs).

4. trans - 1 - Methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene, M = 262 (3 runs).

Single photon counting. The apparatus and procedure have been described previously.<sup>24,28a</sup> The experiments were run for a time sufficient to collect a minimum of 2000 counts in the highest channel when collecting at 3% of the lamp frequency. The 3% factor assures that few double photons are collected. Excitation was at 265 and 275 nm, and emission was monitored by an RCA 8850 photomultiplier at 310 and 325 nm. Optical densities were adjusted to 0.8-2.0 at the excitation wavelength. Different choices of excitation and emission wavelength produced no significant change in the observed decay rate of all the compounds investigated. All runs were performed at 77°K. The data are reported as follows: compound, average lifetime. average rate of decay, number of runs, average A value.<sup>24</sup>

1. 3.3 - Dimethyl - 1.1 - diphenyl - 1.4 - pentadiene, 6.0 nsec,  $1.7 \times 10^8 \text{ sec}^{-1}$ , six runs, 0.039.

2. trans - 1 - Cyano - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene, 6.4 nsec,  $1.6 \times 10^8 \text{ sec}^{-1}$ , six runs, 0.048.

3. cis - 1 - Cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene, 6.5 nsec,  $1.5 \times 10^8 \text{ sec}^{-1}$ , six runs, 0.038.

4. trans - 1 - Methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene, 7.0 nsec,  $1.4 \times 10^8 \text{ sec}^{-1}$ , six runs, 0.039.

Summary of quantum yield results for the sensitized irradiation of cis - 1 - methoxy - 3.3 - dimethyl - 5.5 - diphenyl - 1.4 - pentadiene

The sensitized runs were performed on the microoptical bench

#### Control experiments

(a) Photolysis of 2,2-dimethyl-1-(2',2'-diphenylvinyl)cyclopropane. A soln of 101 mg (0.41 mmol) of 2,2 - dimethyl - 1 - (2',2' - diphenylvinyl)cyclopropane in 125 ml of t-BuOH was purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. The irradiation was performed for 0.5 hr using a 450-W Hanovia medium pressure lamp equipped with a 1 mm Corex glass filter. Examination of the crude photolysate by GC (5% Apiezon N) and NMR showed the absence of both 3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene and 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane with a detectability level of 0.1%.

(b) Photolysis of 3,3 - dimethyl - 2,2 - diphenyl - 1 - vinyl - cyclopropane. Similar irradiation and analysis of 60.0 mg (0.24 mmol) of <math>3,3 - dimethyl - 2,2 - diphenyl - 1 - vinylcyclopropane in 125 ml of t-BuOH showed the absence of both <math>3,3 - dimethyl - 1,1 - diphenyl - 1,4 - pentadiene and <math>2,2 - dimethyl - 1 (2',2' - diphenylvinyl)cyclopropane.

(c) Photolysis of cis -1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. A soln of 40.0 mg (0.15 mmol) of cis - 1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane in 125 ml of t-BuOH was purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. The irradiation was performed for 20 min using a 450-W Hanovia medium pressure lamp equipped with a 1 mm Corex glass filter. Examination of the crude photolysate by GC (10% QF-1) and NMR showed the absence of both 1 - cyano - 3,3 - dimethyl - 2, 5 - diphenyl - 1,4 - pentadiene and 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenylvinyl)cyclopropane with a detectability level of 0.1%.

(d) Photolysis of trans -1 - (2' - cyanovinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. Similar irradiation and analysis of 40.0 mg (0.15 mmol) of trans <math>-1 - (2' - cyanovinyl) 3,3 - dimethyl - 2,2 - diphenylcyclopropane in 125 ml of t-BuOH showed the absence of both 1 - cyano - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene and 1 - cyano - 3,3 - dimethyl - 2 - (2',2' - diphenyl-vinyl)cyclopropane.

(e) Photolysis of cis - 1 - (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. A soln of 40.0 mg (0.14 mmol) of cis - <math>1 - (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane in 125 ml of t-BuOH was purged with purified N<sub>2</sub> for 0.5 hr before and during photolysis. The irradiation was performed for 0.5 hr using a 450-W Hanovia medium pressure lamp equipped with a 1 mm Corex glass filter. Examination of the crude photolysate by GC (7% DEGS) and NMR showed cistrans isomerization of the reactant in addition to the total absence of 1 - methoxy - 3,3 - dimethyl - 5,5 - diphenyl - 1,4 - pentadiene.

(f) Photolysis of trans  $-1 \cdot (2' - methoxyvinyl) - 3,3 - dimethyl - 2,2 - diphenylcyclopropane. Similar irradiation and analysis of 60.0 mg (0.22 mmol) of trans <math>-1$  (2' - methoxyvinyl) -3,3 - dimethyl -2,2 - diphenylcyclopropane in 125 ml of t-BuOH showed trans-cis isomerization of the reactant in addition to the total absence of 1 - methoxy -3,3 - dimethyl -5,5 - diphenyl -1,4 - pentadiene with a detectability level of 0.1%.

Calculations. The Pople semi empirical SCF method<sup>55,56</sup> (complete neglect of differential overlap) was used for closed shell SCF calculations. The SCF molecular orbitals were then used in a configuration interaction treatment including both single and double excitations to obtain states. For single excitations, the highest six occupied and lowest six unoccupied MO's (36 configurations) were used; double excitations were selected by a first order perturbation approach <sup>35,57</sup> from the 325 possible configurations obtained by promoting from the highest 5 occupied to the lowest 5 unoccupied MO's. Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of spin operator S<sup>2</sup> as given by Murrell and McEwen.<sup>58</sup> Standard techniques for the reduction of many electron integrals then gave general formulas used to calculate matrix elements between configurations.55.36,38 Matrix elements between doubly excited configurations were derived.35

Standard geometries for starting styryl vinyl methanes were assumed. Geometries for 1,4-biradical species were extrapolated from a reported INDO calculation with geometry optimization for the ground state 2-vinyl-cyclopropyldicarbinyl diradical.<sup>59</sup>

Two-electron integrals were calculated by the Pariser-Parr approach.<sup>60</sup> Those for heteroatoms were obtained as suggested by Dewar<sup>61</sup> except that the Pariser-Parr parameterization was retained. Resonance integrals were calculated by the Mulliken approximation as employed by Hoffmann,<sup>62</sup> but with K scaled according to the CNDO/S convention reported by Boyd and Whitehead.<sup>63,64</sup> Only "nearest neighbor" resonance integrals were used. Valence state ionization potentials were taken from Hinze and Jaffe<sup>65</sup> except for the case of oxygen having a + 2 core charge. For oxygen, Dewar's parameterization was used.<sup>61,66</sup>

Calculations were performed with programs<sup>35</sup> that utilized a PDP-11/T55 computer having 32K words memory and 16 bit words. Direct access to and from disc allowed usage of large matrices encountered in the CI calculations.

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- <sup>336</sup> However, ESR evidence <sup>336</sup> reveals that the odd electron delocalization in the cumyl radical is greater than in the 2-cyanoisopropyl radical. This means that one phenyl stabilizes more than one cyano group and two phenyls would be still more effective; <sup>b</sup>S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.* **91**, 986 (1969). Note also evidence for methoxy and cyano stabilization by J. W. Timberlake, A. W. Garner and M. L. Hodges, *Tetrahedron Letters* **309** (1973), J. W. Timberlake and M. L. Hodges, *Ibid.* **4147** (1970).
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