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DI-π-METHANE HYPERSURFACES AND REACTIVITY; MULTIPLICITY AND REGIOSELECTIVITY; RELATIONSHIP BETWEEN THE DI-π-METHANE AND BICYCLE REARRANGEMENTS

MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY[1,2]†

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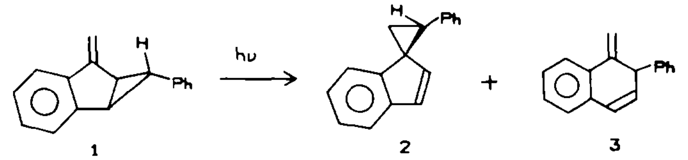
Abstract The photochemistry of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene and 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene was investigated. Both direct and sensitized photolyses of the 3,3-diester afforded 1,1-dicarbomethoxy-2,2-diphenyl-3-(2',2'-diphenylvinyl)cyclopropane with quantum yields of 0.42 and 0.32, respectively. Direct irradiation of the 1,1-dicarbomethoxy-pentadiene gave this same diphenylvinyl-cyclopropane product (Ø = 0.39), while acetophenone sensitization of the 1,1-dicarbomethoxy-pentadiene led to the regioisomeric 1,1,2,2-tetraphenyl-3-(2',2'-dicarbomethoxyvinyl) cyclopropane (Ø = 0.92). Thus the unsymmetrically substituted cyclopropyldicarbinyl diradical opened one or the other of two three-ring bonds depending on multiplicity. Direct irradiation of the dicarbomethoxyvinylcyclopropane resulted in a bicycle rearrangement affording the diphenylvinyl-cyclopropane (Ø = 0.10); additionally, the 1,1-dicarbomethoxy-pentadiene was formed (Ø = 0.069) in this photolysis. The second product can be viewed as arising from a reverse di-π-methane rearrangement or, alternatively, as deriving from partial bicycling of the diphenylcarbon moiety. To confirm that the bicycling process was intramolecular rather then by disengagement of a diphenylcarbene followed by readdition, a crossover experiment was run using 1,1-dicarbomethoxy-4,4-di-*p*-tolylbutadiene. However, no diphenylcarbene transfer was seen. Single photon counting was employed to obtain unimolecular rate constants for the S_1 excited states undergoing the di-π-methane rearrangements. A plot of the log of the S_1 rates for centrally disubstituted 1,1,5,5-tetraphenyl-1,4-pentadienes— having central carbomethoxy, cyano or methyl groups vs Hammett ground state sigma constants proved linear with a rho value of −2.53. The various excited states, intermediate species and the related hypersurfaces were subjected to SCF and SCF-CI calculations. The delta-P treatment showed that excitation is concentrated in the cyclopropyldicarbinyl diradical moiety as the di-π-methane rearrangement proceeds. The calculations also suggest that for a successful bicycle rearrangement excitation energy needs to be distributed into the three-ring bond not conjugated with the vinyl group. Triptych correlation diagrams were constructed using SCF and SCF-CI energies and are used to interpret the photochemistry. The differing singlet versus triplet regiochemistry was found to follow the "small K vs large K" generalization used previously.

One of the basic aims of organic photochemistry is to uncover new and general reactions as well as to study their mechanisms. The photochemical bicycle rearrangement is an intriguing reaction whose generality we have been investigating. Two illustrative examples are depicted in eqns (1) and (2). The reaction in eqn(1)[3] is more typical. Here a divalent carbon moves along the surface of a benzofulvene system with stereospecificity. Several similar examples have been studied in our previous investigations.[4,5]



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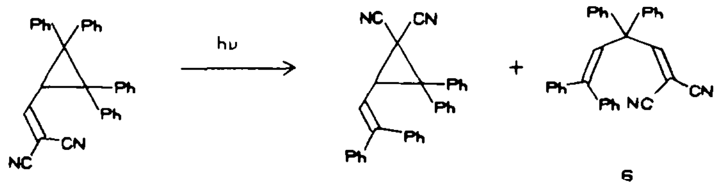

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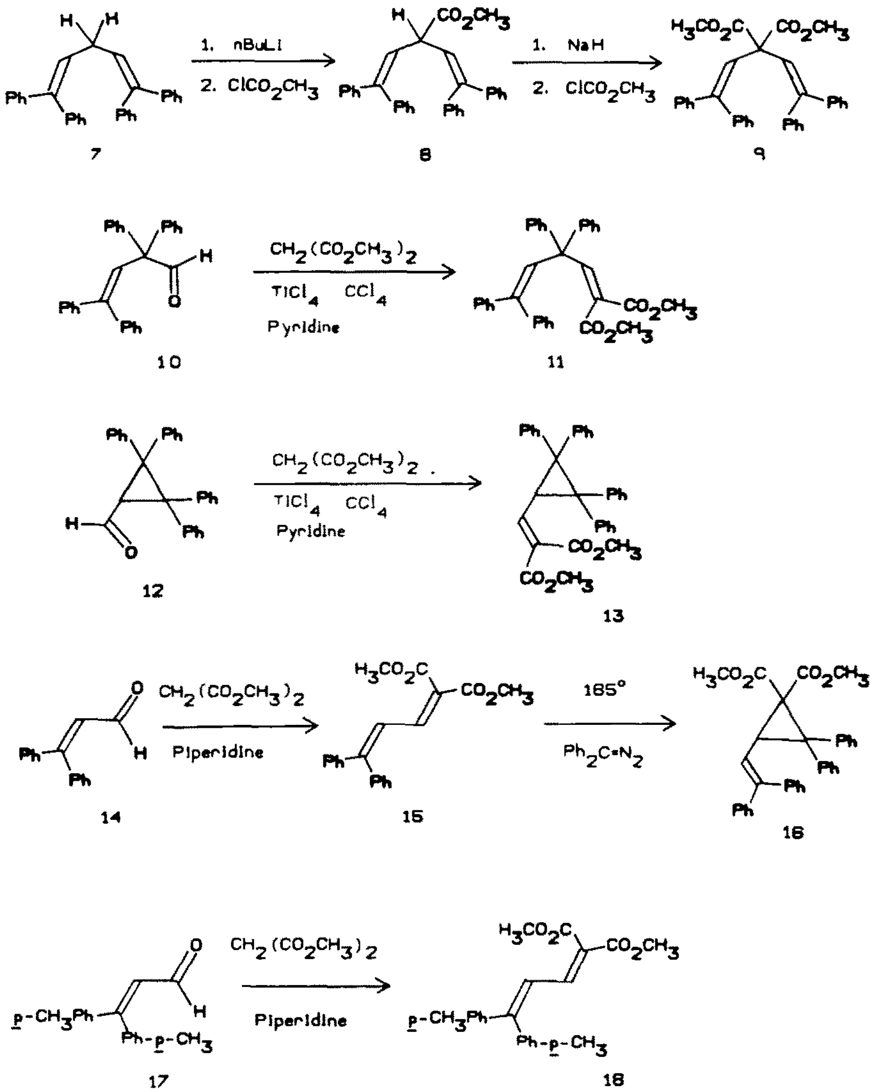
†This paper pays tribute to Robert B. Woodward and his chemistry.



Scheme 1. Synthesis of photochemical reactants and photoproducts.

The reaction in eqn (2)[2] provides the first example of an acyclic bicycle rearrangement wherein the bicycling C atom, here diphenylmethylene, moves along the surface of an acyclic system.

The present investigation had the goal of broadening the scope of the acyclic bicycle rearrangement as well as studying related di-π-methane rearrangement photochemistry. The compounds of interest for photochemical study were parallel to those in eqn (2) with carbomethoxy substitution rather than cyano. Additionally, it was of interest to investigate a di-π-methane system having both diphenylvinyl and dicarbomethoxyvinyl moieties as well as central phenyl substitution.

Synthesis of compounds of photochemical interest

Results. These syntheses are depicted in Scheme 1 and detailed in the Experimental. The synthesis of 3,3-dicarbomethoxy-diene **9** was one developed earlier in our laboratories.[6] The philosophy paralleled that of the synthesis of the corresponding dicyano-diene of our earlier study.[2b] The regioselective central carbethoxylation and cyanation of the 1,1,5,5-tetraphenylpentadienyl carbanion derives from the central carbon (i.e. C-3) having the highest electron density, a situation characteristic of such conjugated anions.[7]

Exploratory photochemistry of the dienes

Results. The photochemistry of the 3,3-dicarbomethoxy diene **9** was investigated first. A remarkably facile rearrangement was observed. The product proved to be the diphenylvinyl cyclopropane **16** synthesized earlier (note above). This photoproduct (i.e. **16**) is that expected from a typical di-π-methane rearrangement.[8] Surprisingly however, the rearrangement proceeded not only on direct irradiation, as is characteristic of acyclic diene photoreactivity in the di-π-methane rearrangement but also afforded the same product, with comparable facility on sensitization with acetophenone. These reactions are summarized in Scheme 2 eqn (3). Commonly, the di-π-methane rearrangement proceeds only inefficiently when sensitized in examples which are structurally very similar, for example where carbomethoxyl groups **9** are replaced by methyls.[8b,9,10]

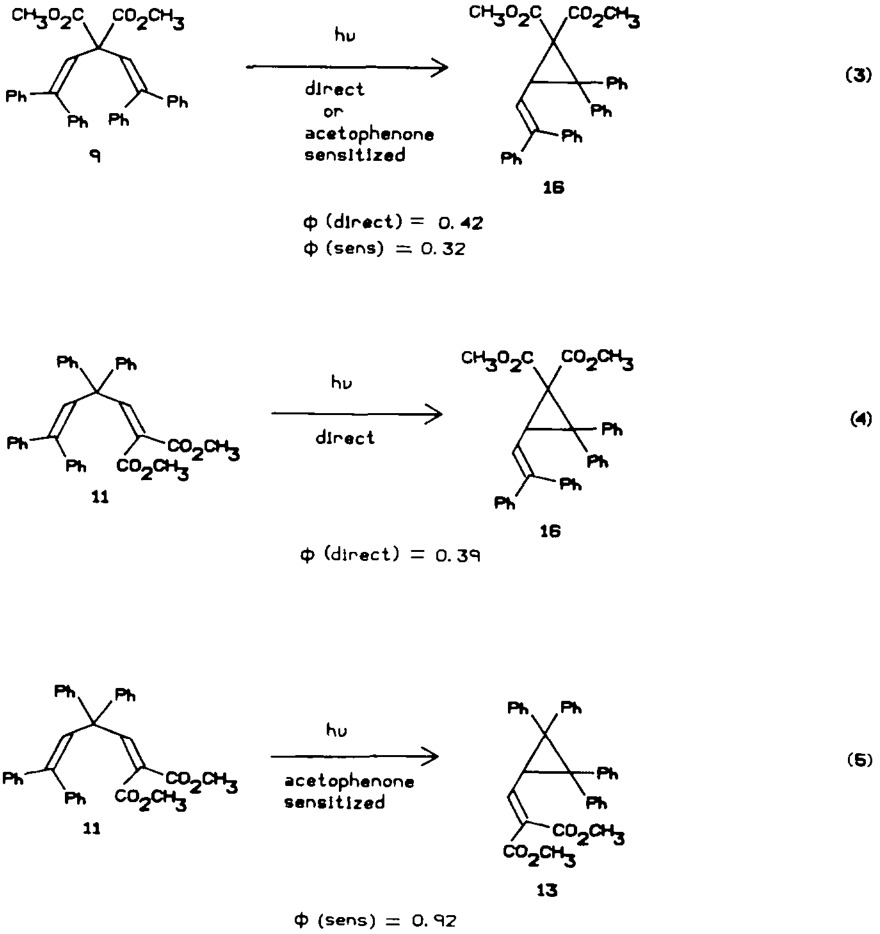
Attention was next turned to the photochemistry of the 1,1-dicarbomethoxy diene **11**. Direct irradiation afforded the same photoproduct, **16**, as encountered in the photochemistry of the 3,3-dicarbomethoxy isomer (*cf* eqn (4), Scheme 2). Formation of this product was not surprising, since it was one of two mechanistically possible regioisomeric di-π-methane photoproducts deriving from the 1,1-dicarbomethoxydiene **11**. Strikingly, however, acetophenone sensitized irradiation of **11** afforded the other possible regioisomer, **13**, from di-π-methane rearrangement of diene **11** (*cf* eqn (5), Scheme 2). The structure of this product, (i.e. **13**) was established by its identity with the previously synthesized material (note above in the synthetic section).

Thus, in the photochemistry of 1,1-dicarbomethoxy diene **11** one regioisomeric product (i.e. **16**) is formed on direct irradiation and the other regioisomeric product (i.e. **13**) results from the sensitized photolysis.

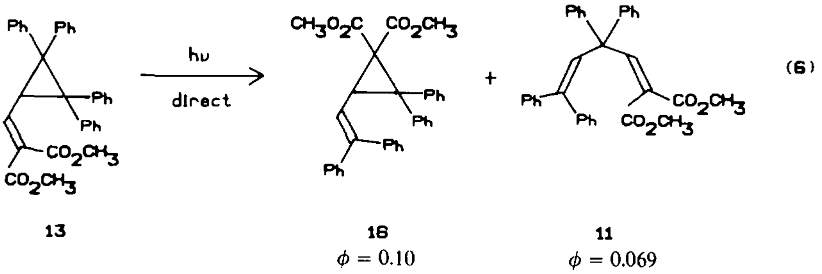
In the case of the 1,1-dicarbomethoxy diene photochemistry, two questions arise in each of the types of irradiation, direct and sensitized. One question is whether the regioisomer not observed was merely destroyed under reaction conditions. The second question is whether the regioisomer not encountered was an unobserved reaction intermediate.

In the direct irradiation, the first question was answered by a control run in which 0.2 percent of dicarbomethoxyvinyl cyclopropane **13** was added to the diene **11** being photolyzed. After 12% conversion it was found that 76% of the added cyclopropane **13** was still present and thus would have been observed in ordinary runs if it had been formed. This also answers the second question, for had cyclopropane **13** been an intermediate in the photochemistry it would have survived and been observed.

In the case of the sensitized irradiation of **11** a control was run. This revealed that the sensitized irradiation of diphenylvinyl cyclopropane **16** did not lead to formation of the sensitized di-π-methane product deriving from the 1,1-dicarbomethoxy diene **11**. Therefore isomer **16** could not be an intermediate in the rearrangement. Further evidence derived from the very high, nearly unity quantum yield for the di-π-methane rearrangement (note below). With such a high quantum yield, a two-step, two-photon mechanism is precluded. Similarly, the other possibility accounting for high observed regioselectivity,[11] namely destruction of the non-observed diphenylvinylcyclopropane **16**, is also precluded by the high quantum efficiency which permits no appreciable



Scheme 2 Photochemical transformations of dienes.



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side reactions. Finally, the 95–96% mass balances add weight to the reality of the observed regioselectivity.

Hence, the striking conclusion is that the singlet of diene **11** affords the diphenylvinyl regioisomer (i.e. **16**) while the triplet of **11** leads to the dicarbomethoxyvinyl counterpart (i.e. **13**).

Observation of a bicycle rearrangement and reverse di-π-methane rearrangement by one of the vinylcyclopropanes

Results. For a thorough understanding of the diene photochemistry, it was necessary to investigate the behavior of their photoproducts. Of the two vinylcyclopropanes, **13** was unreactive under sensitized conditions and **16** was only very slightly reactive (note Experimental).

In contrast, direct irradiation of the dicarbomethoxyvinyl cyclopropane **13** led to a modestly facile rearrangement. The two products observed were the diphenylvinyl cyclopropane **16** and the 1,1-dicarbomethoxy diene **11** in a 1.5:1 ratio. Note eqn (6). The formation of diphenylvinyl cyclopropane **16** from its regioisomer **13** provides still another example of the bicycle rearrangement.[2b,3–5] Interestingly, the bicycling was unidirectional and not reversible, since irradiation of the diphenylvinyl photoproduct **16** gave no reaction. Finally, it is seen that the formation of the 1,1-dicarbomethoxyvinyl diene **11** from vinylcyclopropane **13** represents a "reverse di-π-methane rearrangement".

One mechanism for formation of the photoproducts **11** and **16** (note eqn 6) involves the disengagement of diphenylmethylene leaving 1,1-dicarbomethoxy-4,4-diphenylbutadiene and then readdition of the carbene to the diene, however at different sites to lead to **11** and **16**. Thus a crossover experiment was designed in which the photolysis of dicarbomethoxyvinyl cyclopropane **13** was run in a three-fold excess of 1,1-dicarbomethoxy-4,4-di-p-tolylbutadiene. At 47 percent conversion a 99% mass balance was observed and only the normal photochemical products were isolated in addition to essentially quantitative recovery (99%) of the di-*p*-tolyl diene. No crossover photoproducts were detectable.

This result is shown in eqn (7):

Quantum yield and excited singlet rate determinations

Results. For quantum yield determinations both the Black Box apparatus[12] and the semimicro optical bench[12] previously described were used. Additionally, the electronic actinometer[13] used in our photochemistry generally was calibrated with ferrioxalate[14] for each run; but for each wavelength the calibration was essentially invariant with time. The quantum yield results are given in Scheme 2 and also eqn (6). Details are given in the Experimental.

Since reactivity is better correlated to excited state rate constants than to quantum efficiencies as we have noted earlier[15,16] we turned to the method of single photon counting used in our earlier studies[2b,3,15,17–19]

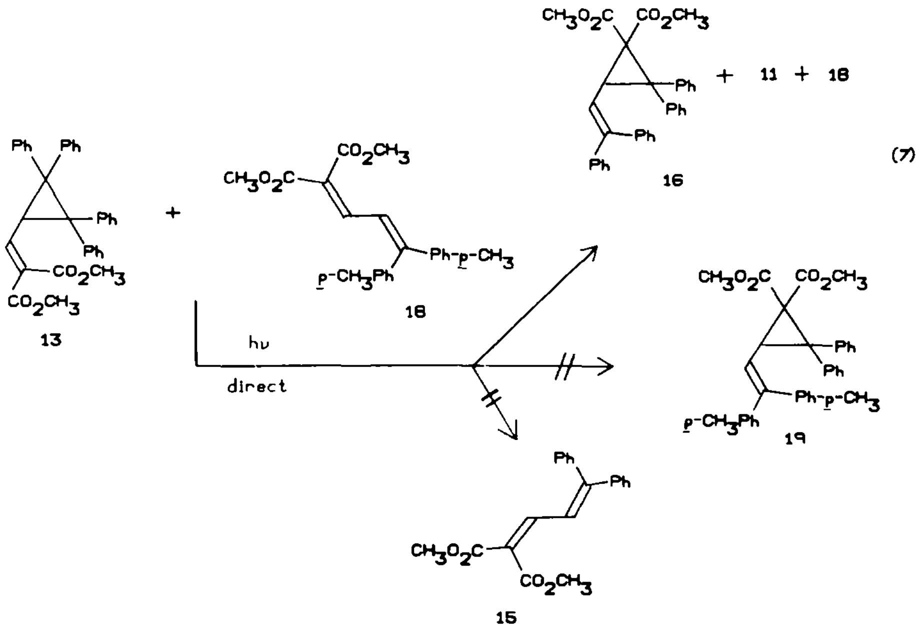

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Table 1. Summary of singlet rates and lifetimes[a,b,c]

Compound	Temp, K	M[d]	τ, ps	$^1k_{d(tot)}$, s^{-1}	k_r, s^{-1}
3,3-Dicarbomethoxydiene, **9**	293	21	39.4	2.63×10^{10}	1.10×10^{10}
	77		827.	1.25×10^{9}	----------
1,1-Dicarbomethoxydiene, **11**	293	197	1.66	6.01×10^{11}	2.34×10^{11}
	77		330.	3.05×10^{9}	----------

[a] See Experimental Section for full details. [b] All runs were made in methylcyclohexane-isopentane (4:1). [c] Estimated probable error limits ± 10%. [d] Average value of several runs.

to determine the rates of S_1 decay and rearrangement. The modification originally described in 1974 uses an on-line minicomputer to serve as a multichannel analyzer and to perform an iterative simulated deconvolution. The method assumes a decay function which is the sum of negative exponentials with variable pre-exponential constants and variable rate constants as the exponentials. With the profile of the lamp flash collected and an initially assumed sum of exponentials as the decay function, the minicomputer calculates the predicted profile of the fluorescence emission. The deviation of the prediction from the observed sample emission profile is used by an efficient algorithm[15] to determine the optimum choice of exponentials for the next iteration. The process is repeated until the experimental curve is reproduced. Our most recent results were obtained on a PDP-11/55 and with improved programming[20] so that printout of the rate constants is complete within two minutes of completion of the experiment, thus making single photon counting a routine tool.

The results of single photon counting measurements are given in Table 1. As in our past studies where exceptionally rapid rates of decay are involved, we made use of the inhibition of decay and reaction rates by temperature lowering. With the 77K decay rates available, the multiplier M converting these to room temperature rates is defined as $\text{Ø}_f^{77}/\text{Ø}_f^{RT} = M$.[15] These values are also included in Table 1.

Due to very weak emission single photon counting studies were not carried out on the dicarbomethoxyvinyl cyclopropane **13**.

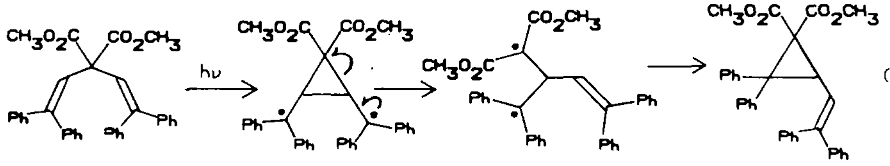
The overall reaction mechanism of the di-π-methane rearrangement of the 3,3-dicarbomethoxy diene 9

Interpretative discussion. The rearrangement of the 3,3-dicarbomethoxy diene **9** follows a typical di-π-methane mechanism as depicted in eqn (8). A number of aspects involving the reaction efficiency and the excited state rates are of special interest, but discussion is deferred for consideration of the quantitative aspects of the photochemistry of all the systems under study. For the moment it is sufficient to note that in contrast to most examples of the di-π-methane rearrangement not only the singlet but also the triplet reacts with facility. In the closely related example of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**20**)[8b] the triplet was found to rearrange only with extreme reluctance.[8b]

Inspection of the mechanism in eqn (8) reveals that ring opening of the cyclopropyldicarbinyl diradical **21*** leads to an especially stabilized triplet 1,3-diradical **22**. The success of the di-π-methane rearrangement of the triplet presently discussed may derive from the ring opening process competing more successfully with intersystem crossing to ground state cyclopropyldicarbinyl diradical **21**. It has been our general observation[5,15,22,23] that ground state cyclopropyldicarbinyl diradicals tend to undergo 1,4-diradical-2,3-fragmentation. Hence, intersystem crossing to ground state leads back to di-π-methane reactant, and the more rapid three-ring opening thus prevents reversion to reactant. Interestingly, central cyano substitution[2b] and also central phenyl substitution[2b,24] afforded di-π-methane systems with reactive triplets. Hence the evidence is accumulating that it is the increased rate of three-ring opening resulting from stabilization of the triplet 1,3-diradicals which is the common feature in all of these cases.

Consideration of the reaction pathways of the 1,1-*dicarbomethoxy diene* 11

Interpretative discussion. The most striking observation in the photochemistry of the 1,1-dicarbomethoxy diene **11** is the different regiochemistry observed in the direct and the sensitized runs, this reflecting the different reactivity of the singlet and the triplet excited states of the diene (i.e. **11**). The overall mechanisms involved are outlined in Scheme 3. It is again seen that the triplet is reactive, here as a result of the central phenyl substitution. This has precedent.[22] In Scheme 3 the partition between the singlet and triplet pathways begins with three-ring opening of the cyclopropyldicarbinyl diradical species.



9 21 22 16

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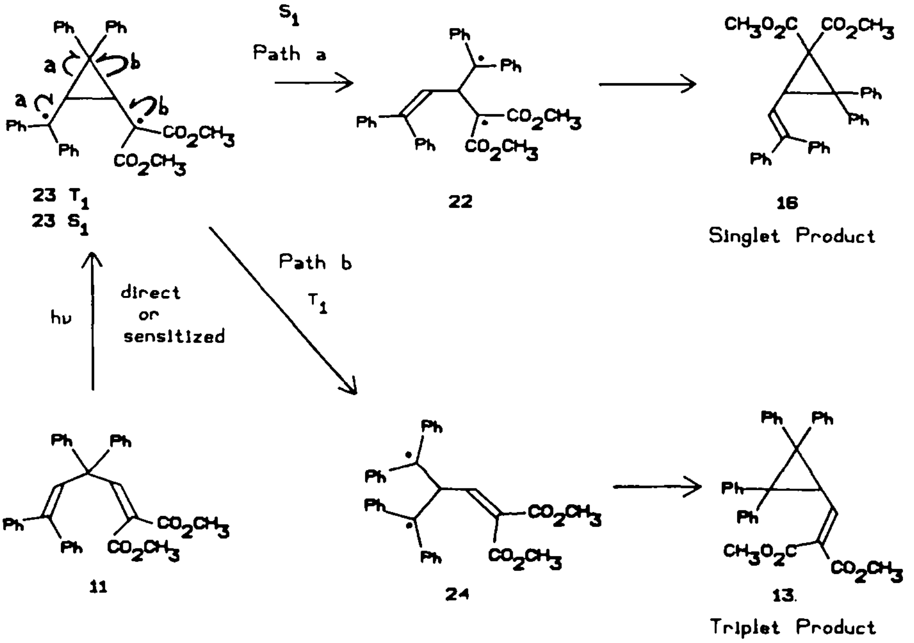


Scheme 3. Overall reaction mechanisms of the 1,1-dicarbomethoxy diene **11**

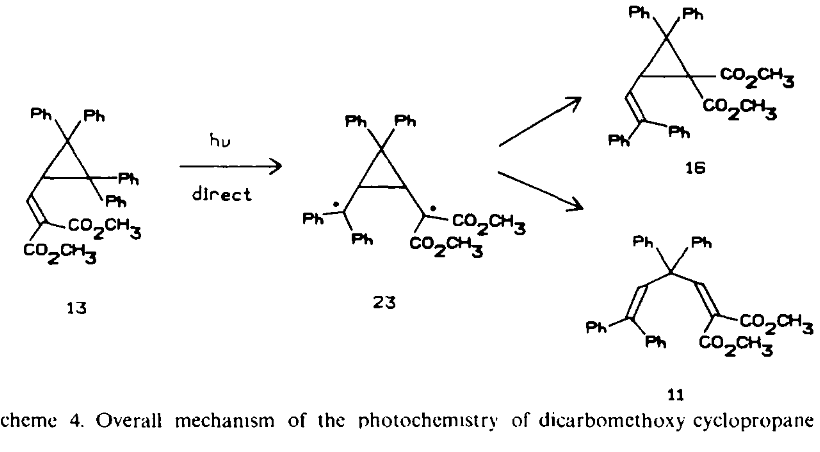
This multiplicity dependence on the regioselectivity[11] of the di-π-methane rearrangement also has precedent. To begin with, the reaction of the excited singlets of dienes bearing electron withdrawing moieties at one end of the di-π-methane system tends to prefer formation of that regioisomer having the electron withdrawing group on the product cyclopropyl ring rather than on the double bond.[16b,17,18,25] Conversely, electron donors tend to appear on the product vinyl group.[17,18,26] This generalization has been noted by us previously.[17,27]

Furthermore, in two instances the triplet excited states of di-π-methane type dienes bearing cyano[2h] or carbomethoxy[28] terminal substituents have been observed to give regioselectivity which is unusual in that the electron withdrawing moiety is found on the product double bond rather than the three-ring. Additionally, in both the cyano and carbomethoxy examples[2h,28] direct irradiation was observed to give partially reversed regioselectivity in which the product with the electron withdrawing cyano or carbomethoxy group on the three ring constituted approximately half of the di-π-methane product. That the above generalization regarding the regioselectivity of singlets does not apply exactly to the direct irradiations may derive[2h] from intersystem crossing in part in these cases.

It is seen that the presently investigated example of 1,1-dicarbomethoxy diene **11** exhibits a very pretty and unambiguous dependence of its regioselectivity on the reaction multiplicity. The source of this phenomenon has been considered in our earlier studies[2h] and is analyzed in detail below in the theoretical section.

General mechanisms in the photochemistry of dicarbomethoxyvinyl cyclopropane **13**

Interpretative discussion. The intriguing bicycling rearrangement and reverse di-π-methane reaction observed for the singlet of the 1,1-dicarbomethoxyvinyl cyclopropane **13** are qualitatively understood in terms of the mechanisms outlined in Scheme 4. The two processes can be seen to be related



Scheme 4. Overall mechanism of the photochemistry of dicarbomethoxy cyclopropane **13**.

Table 2.

Compd	Central Substitution	σ	Φ	k_r^{RT}, s^{-1}	k_r^{RT}/k_0 ᵃ	log k_r^{RT}/k_0
26	CN	0.66	0.11	0.92×10^9	8.42×10^{-2}	-1.08
9	CO_2CH_3	0.39	0.42	1.1×10^{10}	1.00	0.00
20	CH_3	-0.17	0.080	1.4×10^{11}	12.7	1.10

[a] $k_0 = k_r^{RT}$ for cmpd **9**.

Table 3. Rates and efficiencies for terminally substituted dienes

Compd	Temp,K	M	$^1k_{d(tot)}$, s^{-1}	Φ	k_r, s^{-1}	k_d, s^{-1} ᶜ
1,1-Dimethyl-diene **25**ᵃ	293 77	216	1.13×10^{11} 5.3×10^8	0.076	8.5×10^9	1.05×10^{11} (ref 24)
1,1-Dicyano-diene **6**ᵇ	293 77	247	1.11×10^{12} 4.49×10^9	0.044	4.93×10^{10}	1.06×10^{12} (ref 2b)
1,1-Dicarbo-methoxy diene **11**	293 77	197	6.01×10^{11} 3.05×10^9	0.39	2.34×10^{11}	3.67×10^{11} (this study)

[a] Data from ref 24. [b] Data from ref 2b [c] $k_d = k_{d(tot)} - k_r - k_f$.

with the first bicycling step leading to the common cyclopropyldicarbinyl diradical structure **23**. The diphenylvinyl cyclopropane product **16** arises from a second bicycling step while the 1,1-dicarbomethoxy diene **11** derives from a 1,4-diradical-2,3-fragmentation.[29] One aspect worthy of comment is that species **23** is a general one which, in principle, might represent any of several electronic states of this cyclopropyldicarbinyl diradical- S_0, S_1 or T_1. As noted before S_0 is the configuration which most commonly undergoes the 1,4-diradical-2,3-fragmentation while the continued bicycling of **23** is more characteristic of S_1.[5,15,22,23]

Excited state rates of reaction and quantum efficiencies

Interpretative Discussion. One of the most interesting features of the rate data derives from comparison of the rates at which the singlets of 3,3-disubstituted-1,1,5,5-tetraphenyl dienes rearrange as a function of central substitution. Referring to Table 2 we note that the fastest rearranging system has central methyl substitution (i.e. diene **20**[8b,15]). The centrally cyano-substituted diene has a slower reacting singlet.[2b] The presently investigated 3,3-dicarbomethoxy diene **9** is intermediate in reactivity. An interesting correlation between the log of these unimolecular rate constants and the Hammett sigma values[31] was found and is illustrated in Fig. 1.

We note with interest that this linear relationship is between ground state (i.e. Hammett) constants and excited state rates.

This suggests that the portion of the molecule bearing the cyano, carbomethoxy or methyl group must be unexcited both in the vertical excited state reactant (i.e. reactant S_1) and also at the rate limiting stage along the excited state hypersurface. This point is

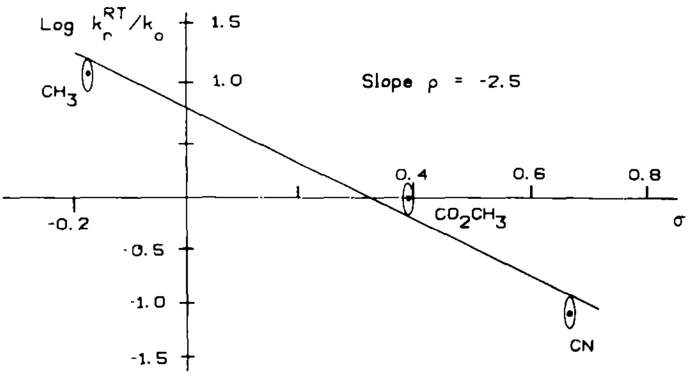


Fig. 1. Plot of log(k_r/k_0) versus the Hammett sigma constants. Here k_0 is the rate for carbomethoxy substitution. Correlation coefficient, 0.98.

considered below in connection with our delta-P partition of excited state energies.

It is interesting to compare the S_1 rate for the 1,1-dicarbomethoxy diene **11** with that for the corresponding analog **25**[15,24] in which the carbomethoxy groups are replaced by methyls. The rate for the dicarbomethoxy diene **11** is 2.3×10^{11} while that for the dimethyl analog **25** is $8.5 \times 10^{9}\ \mathrm{sec}^{-1}$. The dicyano diene **6** also has a high S_1 rate but smaller than that of the presently studied dicarbomethoxy diene (i.e. **11**). These comparisons are seen by reference to Table III.

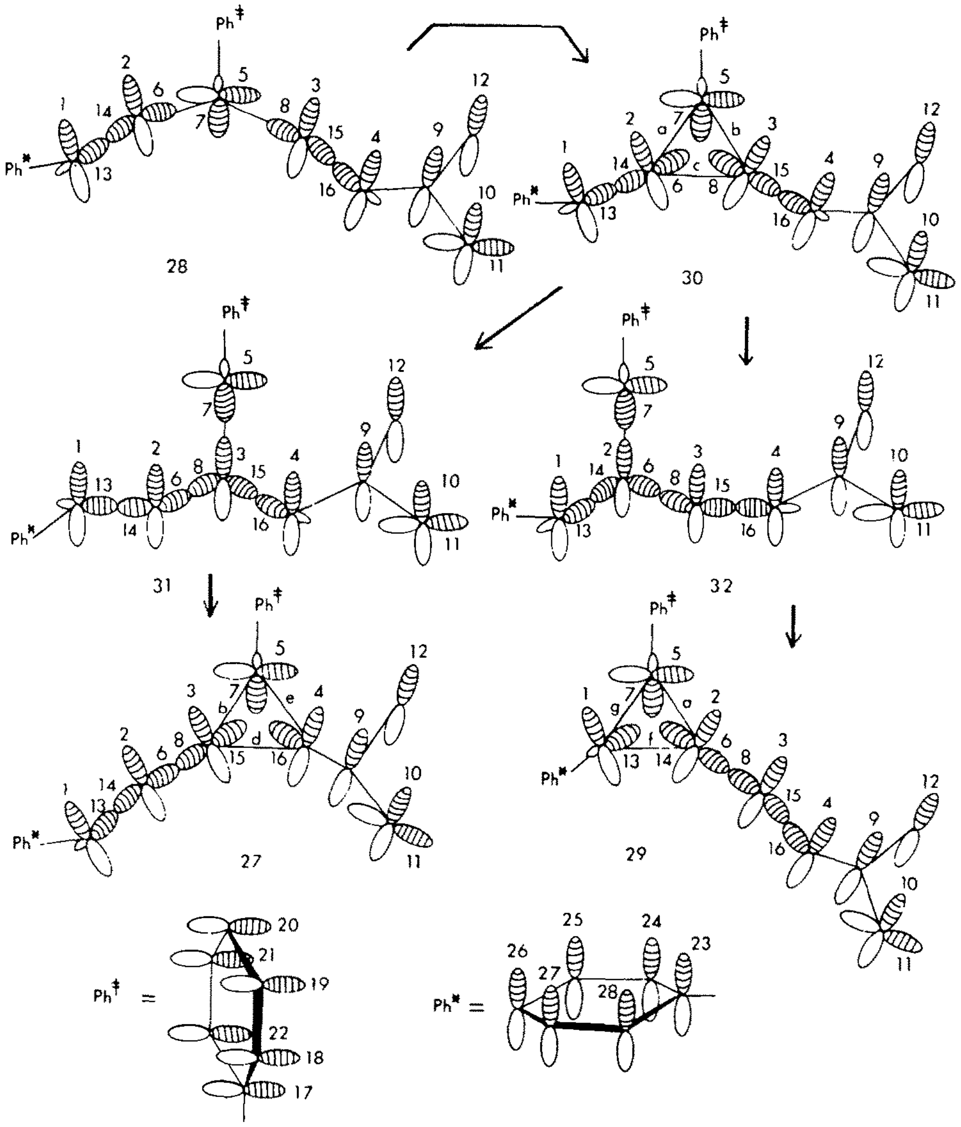
A summary of the situation is that the dicarbomethoxy diene has both a faster k_r and k_d, but the enhancement in k_r is greater than that in k_d with the result of a very high quantum efficiency for the dicarbomethoxy diene **11**.

Theoretical considerations

Calculations. SCF and SCF-CI calculations were carried out on a truncated set of basis orbitals. The orbitals selected were those involved in electronic excitation as chromophores and also those orbitals involved in bonding changes along the reaction coordinate for the di-π-methane and bicycle processes. Where carbomethoxy substituents were present, one of these was introduced rather than two. Phenyl substitution was similarly provided by one phenyl group at each site bearing two. For interest's sake, the calculations were also carried out without phenyl substitution. The reactions of interest, with basis orbitals defined, are outlined in Scheme 5. Details are given in the Section on calculations.

Correlation diagrams and hypersurfaces

Interpretative discussion. SCF calculations were used to construct MO correlation diagrams for the di-π-methane and bicycle rearrangements. Inspection of Schemes 3 and 4 reveals that the 1,1-dicarbomethoxy diene **11**, the diphenylvinyl cyclopropane **16**, and the dicarbomethoxyvinyl cyclopropane **13** are interconverted via the common structure, the



Scheme 5. Reactions with basis orbitals defined

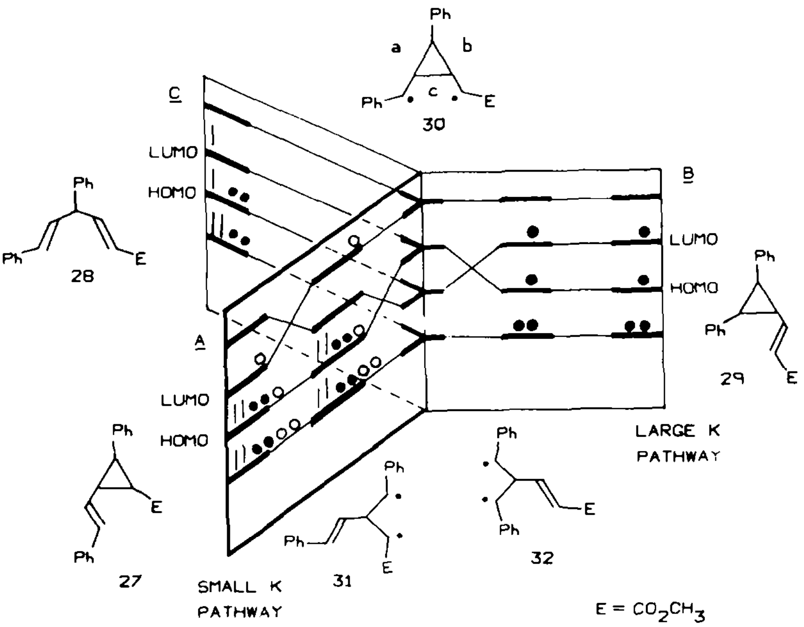
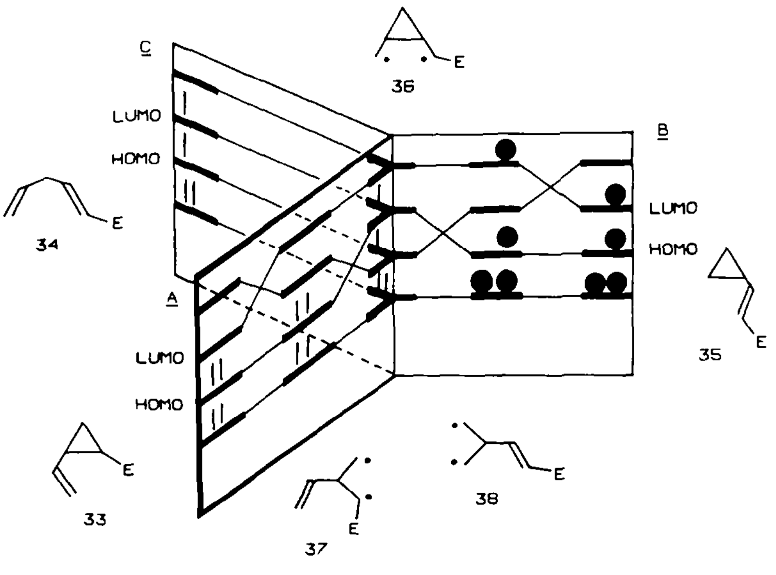


Fig. 2(a). SCF Correlation diagram for di-π-methane rearrangement of the 1-carbomethoxy diene and for bicycling (phenyl groups included). ○ Electron configuration in reactions from bridge A, ● from bridge B, from bridge C

cyclopropyldicarbinyl diradical **23**, although different electronic configurations of **23** seem involved in the different reactions. With three compounds and one interposed structure, we turned to the triptych representation for the correlation diagrams as used in our earlier study on the cyano substituted systems.[2h] This is shown in Figs. 2(a) and 2(b).

The two correlation diagrams are similar in many respects but do differ as a result of phenyl substitution (in the case of Fig. 2a) being introduced. Thus, the HOMO-LUMO crossings in bridges *A* and *B* are found for both phenylated and non-phenyl substituted systems. Additionally, there is a LUMO-LUMO + 1 crossing in bridge *A* of both triptych's. However, phenyl substitution removes the LUMO-LUMO + 1 crossing in bridge *B*.

We now need to refer individually to the three excited states, each one corresponding to one excited reactant of interest. If we focus attention on the excited state in bridge *A* it is seen that this quickly leads to an upper, and very high energy, configuration. This corresponds to a bicycle process which does not occur.



E = CO_2CH_3

Fig. 2(b) SCF correlation diagram without phenyl groups.

Turning now to the di-π-methane reactant **28** in bridge *C*, we find that the cyclopropyldicarbinyl diradical **30** is formed in its excited state (note the triptych central axis approached from *C*) and that crossing points,[32] or bifunnels,[5,33] affording a possible leakage to ground state products are found in each of bridges *A* and *B*. Indeed, both vinylcyclopropanes **27** and **29** are found experimentally as products, one (i.e. **27**) from the singlet and the other (i.e. **29**) from the triplet.

Lastly in connection with the correlation diagrams, we consider the carbomethoxyvinyl cyclopropane reactant in bridge *B*. Here, Figure 2a reveals the excited state configuration shown arrives at the central triptych axis after passing a HOMO-LUMO crossing point (i.e. a bifunnel) and thus the cyclopropyldicarbinyl diradical is likely to be partitioned between ground and excited state configurations. The excited state configuration of diradical **30** is forced, by the usual disinclination for formation of upper configurations, to proceed into bridge *A*. The ground state configuration of the diradical is forced to proceed into bridge *C*. Experimentally, starting with the carbomethoxyvinyl cyclopropane both bicycling and reverse di-π-methane rearrangements are observed (*vide supra*).

Interestingly, without phenyl substitution, the LUMO-LUMO + 1 crossing in bridge *B* would be expected to inhibit both bicycling and reverse di-π-methane rearrangements. This, too, accords with fact, since with diminished phenyl substitution (i.e. no benzylic-benzylic bond remote from the vinyl group), di-π-methane products do not exhibit a reverse reaction.[9,8h,18] All the examples which do show this reactivity have PhC-CPh substitution on the three ring remote from the vinyl group.

SCF-CI calculations were also carried out. While the advantage of the SCF one-electron calculations is that these show MO correlations and thus intended state crossings, the CI allows us to determine where crossings are avoided. These SCF-CI calculations are depicted in a triptych representation in Fig. 3. The reaction coordinates are the same as for the SCF diagrams in Figs. 2(a) and 2(b).

One important result is that at each HOMO-LUMO crossing point of the SCF treatment (note Fig. 2a) there is a corresponding approach of S_0 and S_1, that is, a bifunnel.[5,32,33]

Furthermore, perusal of the CI-triptych in Fig. 3 provides an interesting understanding of the experimentally observed photochemistry. Thus, starting with the di-π-methane reactant (note bridge *C* of the triptych) and the S_1 vertical excited state of **28** we find a hypersurface leading to the cyclopropylidicarbinyl diradical **30**, at the central triptych axis, in its S_1 (i.e. singly excited) state. This species can be seen to select bridge *A* over bridge *B* since the bridge *A* S_1 hypersurface leads downward in energy to a bifunnel whereas the bridge *B* surface has a maximum interposed between the central axis and a less efficient (more widely spaced S_0 S_1 gap) bifunnel. The bifunnel in bridge *A* leads to the observed singlet di-π-methane product, the regioisomer bearing a carbomethoxy group on the three-ring (note **27** in bridge *A*).

The reactivity of the carbomethoxyvinyl cyclopropane **29**, represented in bridge *B*, can be accounted for in either of two ways; and both may be operative. A bifunnel is encountered in bridge *B* before reaching the central axis and the cyclopropyldicarbinyl diradical. Either total or partial funneling to ground state occurs here. If total conversion to S_0 occurs here, then the ground state diradical just partitions itself between the reverse di-π-methane process leading to bridge *C* and the bicycling process requiring surmounting a small (<0.4 eV) S_0 barrier leading to bridge *A*.

Alternatively, if internal conversion in the bridge *B*

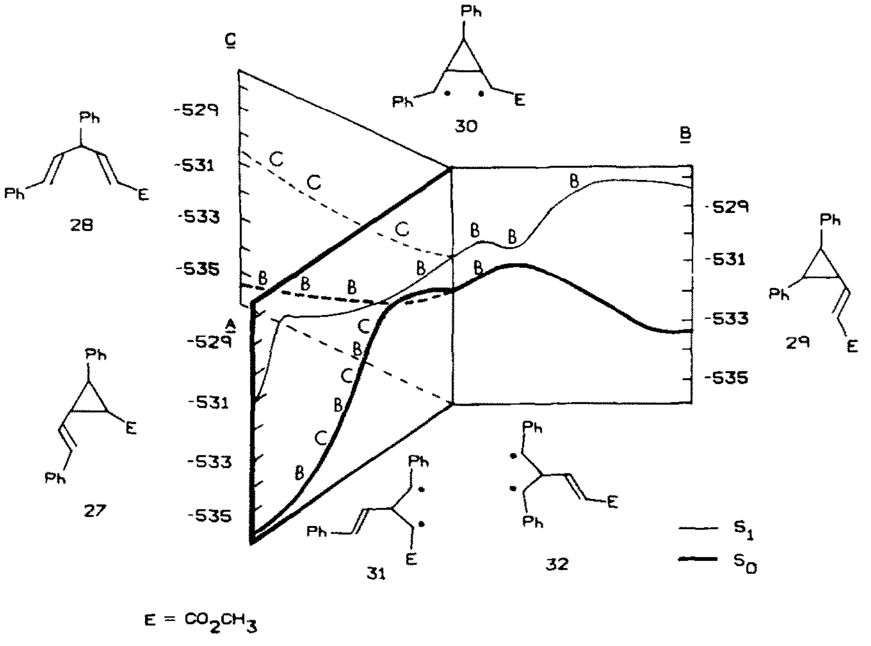


Fig. 3. SCF-CI reaction hypersurfaces.

bifunnel is not totally efficient, then the cyclopropyldicarbinyl diradical at the central axis is formed in two states, S_1 and S_0. S_0 can proceed into bridge *C* without encountering a barrier and this affords reverse di-π-methane product **28**. S_1 diradical, following the downward curvature of the excited surface, arrives at the efficient bifunnel in bridge *A* and internal coversion to S_0 leads to phenylvinyl cyclopropane **27** in an overall bicycling process.

Lastly, reaction of the phenylvinyl cyclopropane involves formation of an S_1 state (note bridge *A*) confronted with a large energy barrier. No reaction is encountered experimentally.

The nature of bifunnels

Interpretative discussion. The role of HOMO-LUMO crossings in enhancing conversion of excited state reactant to ground state product was suggested in 1966.[8a,32a,34] Since that time the point has received considerable attention.[2b,5,33,35,36] One interesting point has been made by Oosterhoff[35] who pointed out that the S_0–S_2 approach (a bifunnel) is perhaps adventitiously intersected by S_1 which is the surface actually involved in the photochemistry. Thus the application of the Woodward–Hoffmann[37] and the Zimmerman Möbius–Hückel[32,34] concepts to photochemistry seems to derive from this apparently accidental crossing of S_1 and S_2. Similar findings derive from the work by Devaquet.[36]

However, the purity of S_0 and S_2, relative to S_1 weighting, derives from S_1 having different symmetry in the model systems (e.g. cyclobutene–butadiene) studied.[38] Inspection of the CI wavefunctions throughout the regions of the two bifunnels in the present study (of Fig. 3) reveals that the lower state in each bifunnel, having an energy maximum is weighted most heavily in S_0 but contains contributions from both S_1 and S_2 configurations. The first excited state (i.e. the bifunnel upper surface) is weighted most heavily in the S_1 (i.e. HUMO-LUMO) configuration and also quite heavily in S_0 and S_2 configurations. The weighting of S_2 and S_0 in the first excited state diminishes as one proceeds away from the bifunnel.

The very heavy inclusion of S_1 in the upper portion of a bifunnel thus comes from its ability to admix with S_2 which, in turn, admixes with S_0. The absence of S_1 in completely symmetrical cases is artificial since it is not likely that a symmetrical geometry will correspond to the optimum energy pathway.

Interestingly, the admixture of these configurations can be understood as analogous to the admixture of three contiguous atomic orbitals of unequal energy in an "allyl-like" array except that here the matrix elements are positive MO repulsion integrals and nodal characteristics should approximate an "energetically inverted allyl" species. To the extent that upper configurations are included and important, the pattern expected for the inverted allyl-like species will be affected. For a pure "inverted allyl" species $\mathbf{S}_0$ would be weighted as $S_0 - S_2 + S_1$. Here the italicized symbols are configurations prior to configuration interaction and the boldfaced symbols are final state functions resulting from CI. The $\mathbf{S}_1$ state should contain $S_0 + S_2 - S_1$. Also the ground state should have S_0 and S_2 weighted with opposite signs while $\mathbf{S}_1$ and $\mathbf{S}_2$ should have S_0 and S_2 weighted with the same sign. This last expectation is found throughout while the "allyl-like" pattern is found to be approximated in the actual calculations and of help in understanding the CI wavefunctions; deviations from the pattern seem to come from admixture of higher energy configurations.

While upper configurations are found to be admixed to some extent, the preceding analysis focuses attention on just three configurations of particular interest and most involved.

The important conclusion, however is that the first excited singlet does lead directly to the upper surface of the photochemical bifunnel.

Exchange integral control of regioselectivity and reactivity

Interpretative discussion. Previously[2b] we have noted that where there is a marked difference in singlet–triplet splitting for the surfaces corresponding to two reaction pathways available to an excited state, the reaction pathway with the smaller singlet–triplet splitting will be preferred by the singlet while the pathway with the larger singlet–triplet splitting will be preferred by the triplet. This assumes that there are not extraneous factors (e.g. steric, energy dissipation mechanisms) to favor one reaction pathway or inhibit another. Note Fig. 4.

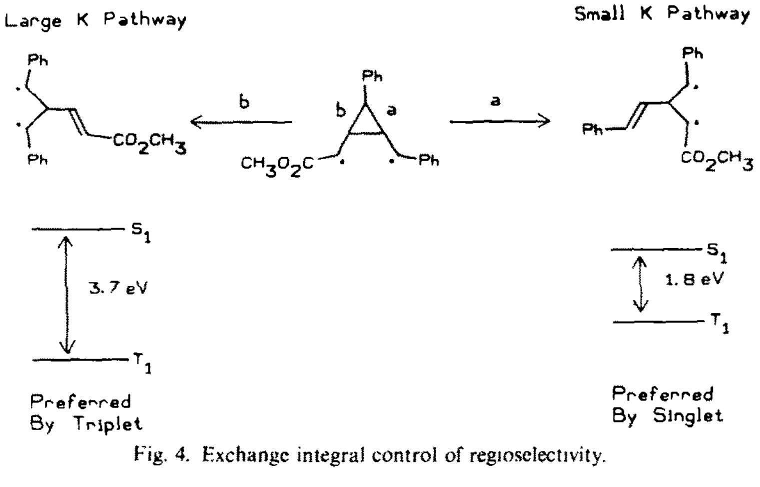


Fig. 4. Exchange integral control of regioselectivity.

For a single (singly excited) configuration the singlet–triplet splitting is given by 2K (e.g. with K being the exchange integral between HOMO and LUMO). Where an electronegative group, or other group polarizing the system, is placed on one of two diradicaloid centers, one can expect a small exchange integral. This results since the atomic orbitals weighted heavily in HOMO are not in LUMO and vice versa. More details have been discussed earlier.[2b] Thus, having carbomethoxy groups on a diradical center of the 1,3-diradical, resulting from di-π-methane three-ring opening, lowers the value of the exchange integral K and leads to a preference for pathway by the singlet. Without carbomethoxy substitution on a diradicaloid center, a larger K results and this pathway is the one preferred by the triplet. This is schematically shown in Fig. 4 using CI energies as an approximation.

Thus, had complete surfaces been determined for the triplet species in analogy to the triptych representation for the singlets, one would expect a lower barrier in bridge *B* compared with bridge *A* in contrast to the singlet situation.

Delta-P determination of excitation energy distribution

Interpretative discussion. A useful technique in considering photochemical reactivity is determination of delta-P and delta-E matrices.[3,5,17,18,27,39] The delta-P matrix has at its elements the difference in corresponding bond orders and electron densities in proceeding from the ground to the excited state of interest. In those portions of the molecule, where the differences are near zero, there is no appreciable electronic excitation. In other portions where there is a large difference, the molecule has been excited. A negative change means that the given site has become more antibonding while a positive change corresponds to increased bonding. This provides a simple way of comparing ground and excited state wavefunctions. The delta-E matrix is the counterpart in which local bond orders have been converted to local energy contributions. This has an advantage where hybrid orbitals are included since changes in overlap populations between s-weighted orbitals have a larger energetic effect than changes involving just p-orbitals.

Table 4 lists some delta-P and delta-E values of particular interest for the vertical excited state, for the cyclopropyldicarbinyl diradical, and for the two vinylcyclopropane products.

As expected, the excitation energy of the di-π-methane reactant is seen to be localized very heavily in the styryl moiety and much less so in the carbomethoxyvinyl group. The C-3 phenyl group is seen to be devoid of excitation. These conclusions are apparent in both the delta-P and the delta-E versions.

In looking at the cyclopropyldicarbinyl diradical species we find that the large delta-P and delta-E

Table 4. Use of delta-P and delta-E to identify sites of electronic excitation

Orbitals	1,4-Diradical 30	
r,t	ΔP_{rt}	ΔE_{rt},ev
2,5	-0.0779	0.4659
6,7	-0.0102	0.1944
5,6	-0.0769	0.3636
2,7	0.0206	-0.0860
Bond a		0.9379
3,5	-0.0119	0.0731
7,8	-0.0014	0.0271
5,8	-0.0499	0.2318
3,7	0.0238	-0.0994
Bond b		0.2326
2,3	0.0732	-0.4333
3,6	-0.0413	0.1934
6,8	0.0189	-0.3605
2,8	-0.0147	0.0555
Bond c		-0.5449
1,2	-0.1868	1.345
1,23	0.0588	-0.3759
23,24	-0.0295	0.2219
24,25	-0.0047	0.0371
25,26	-0.0020	0.0154
Carbinyl Phenyl		0.1729
3,4	-0.1457	1.0199
5,17	0.0569	-0.3366
17,18	-0.0283	0.2175
18,19	0.0112	-0.0875
19,20	-0.0163	0.1269
Cyclopropyl Phenyl		0.1772

Orbitals	Vinylcyclopropane 27	
r,t	ΔP_{rt}	ΔE_{rt},ev
4,5	-0.0512	0.3583
4,7	-0.0054	0.0308
5,16	-0.0133	0.0759
7,16	0.0053	-0.1009
Bond e		0.3641
3,4	-0.0806	0.5685
3,16	-0.0087	0.0494
15,16	0.0008	0.0152
4,15	-0.0043	0.0243
Bond d		0.6574
3,5	-0.0832	0.5925
7,15	-0.0019	0.0362
3,7	-0.0096	0.0542
5,15	-0.0050	0.0782
Bond b		0.7611

Orbitals	Vinylcyclopropane 29	
r,t	ΔP_{rt}	ΔE_{rt},ev
1,5	-0.0814	0.5766
1,7	-0.0070	0.0396
5,13	-0.0081	0.0459
7,13	0.0016	-0.0305
Bond g		0.6316
1,2	-0.0612	0.4315
1,14	-0.0157	0.0892
2,13	-0.0181	0.1026
13,14	0.0039	-0.0742
Bond f		0.5491
2,5	-0.0584	0.4110
2,7	-0.0191	0.1084
5,14	-0.0180	0.1024
7,14	0.0036	-0.0685
Bond a		0.5533

Orbitals	Di-π-methane Diene 28	
r,t	ΔP_{rt}	ΔE_{rt},ev
1,2	-0.1999	1.833
1,23	0.1017	-0.06053
23,24	-0.0398	0.3025
24,25	0.0031	-0.0244
25,26	-0.1356	1.0348
Styryl[a]		2.5406
3,4	0.0003	-0.6053
4,9	0.0020	-0.0116
9,10	-0.0012	0.0109
9,12	-0.0011	0.0105
Carbomethoxy Vinyl		0.0070
5,17	0.0000	0.0000
17,18	0.0000	0.0000
18,19	0.0000	0.0000
19,20	0.0000	0.0000
Central Phenyl[a]		0.0000

[a] All phenyl bonds are included in the total ΔE.

values are largely in the cyclopropyldicarbinyl moiety itself with comparable values only in the C-1 and ortho locations of the phenyl substituent on the carbinyl carbon. This migration of energy of excitation from the vertically excited chromophore into the cyclopropyldicarbinyl diradical moiety has been noted before[23,39] and seems to be general in the di-π-methane rearrangement.

The same treatment applied to the bicycle rearrangement requires the delta-P and delta-E values for the vinylcyclopropanes (note Table 4 again). The reactive vinylcyclopropane (i.e. the carbomethoxyvinylcyclopropane **29**) is the one having a benzylic benzylic three-ring bond g. This isomer has its excitation energy heavily weighted in this three-ring sigma bond remote from the vinyl group, and it is this remote sigma bond which opens in the bicycling process. In contrast for the unreactive vinylcyclopropane **27** the bond e which needs to break is considerably less energy rich than the other two bonds b and d. Reversible opening at these bonds affords a mechanism for energy dissipation and does not lead to bicycling (note Scheme 5 for labeling).

Finally, the delta-P treatment leads to an understanding of why ground state sigma constants correlate well with the log of the S_1 rates for centrally substituted di-π-methane systems. We note that a central phenyl group (Table 4) has much lower delta-E values than found in the three ring (here delta-P's are less helpful). This is true both for the vertical excited state and for the cyclopropyl dicarbinyl diradical whose formation is thought to be rate limiting. To the extent that this is general for the groups presently under discussion— CN, Me, COOMe—one is indeed dealing with ground state moieties and ground state sigma constants are applicable.

Conclusion

The bicycle rearrangement is seen to be a reaction of ever increasing generality and intimately tied to the di-π-methane rearrangement in mechanism. Regioselectivity dependence on multiplicity is a phenomenon which also requires more attention in the future.

EXPERIMENTAL[40]

3-*Carbomethoxy*-1,1,5,5-*tetraphenyl*-1,4-*pentadiene*. A soln of 5.04 g (13.6 mmol) of 1,1,5,5-tetraphenyl-1,4-pentadiene[41] in 100 ml anhyd THF was cooled to 0° and 9.03 mL (13.6 mmol 1.5 M hexane soln) of n-BuLi was added dropwise. The soln was stirred 25 min and transferred under N_2 via canula to a stirred soln of 3.12 mL (40.3 mmol) methyl chloroformate in 100 mL THF. After the addition, the mixture was stirred for 30 min, poured into 500 mL sat NH_4Cl aq and ether extracted. The extracts were washed with water, brine, dried over Na_2SO_4 and concentrated *in vacuo* to give 4.79 g (82.9%) of 3-carbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene, m.p. 163–165°. Recrystallization from CH_2Cl_2 and hexane yielded 4.57 g (79%) of the 3-carbomethoxy diene, m.p. 164–165°.

The spectral data were: NMR ($CDCl_3$) δ 7.4–6.8 (m, 20 H, arom), 6.16 (d, 2 H, J = 10 Hz, vinyl), 4.21 (t, 1 H, J = 10 Hz, methine), 3.68 (s, 3 H, $CO_2C\underline{H}_3$); IR (KBr) 3086, 3058, 3021, 2959, 1733, (s, C = 0) cm^{-1}; MS *m/e* 430.19329 (Calc. for $C_{31}H_{26}O_2$, *m/e* 430.19199). (Found: C, 86.44; H, 6.26 Calc. for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09%).

3,3-*Dicarbomethoxy*-1,1,5,5-*tetraphenyl*-1,4-*pentadiene*. Sodium hydride (0.576 g, 0.012 mmol, 50% in mineral oil) was washed free of mineral oil with hexane. A soln of 4.30 g (0.010 mmol) of 3-carbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene in 60 mL anhyd THF was added to the sodium hydride under N_2 and the mixture was refluxed for 12 hr. The mixture was allowed to cool to room temp and 1.55 mL (0.020 mmol) methyl chloroformate was added. The mixture was refluxed for 25 min, cooled, poured into sat NH_4Cl aq and extracted with CH_2Cl_2. The organic extracts were washed with water, brine, dried over Na_2SO_4 and concentrated *in vacuo*. The yellow solid obtained was recrystallized from CH_2Cl_2 and hexane to yield 2.98 g (61.1%) of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene, m.p 139–140°.

The spectral data were: NMR ($CDCl_3$) δ 7.4–6.96 (m, 20 H, arom), 6.63 (s, 2 H, vinyl), 3.39 (s, 6 H, CO_2CH_3); IR (KBr) 3086, 3058, 3030, 2994, 2950, 2841, 1736 (s, C=O); UV (Et_2O) λ_{max} 257.5 nm (ε 24.300), 295 (ε 3310): MS *m/e* 488.19949 (Calc. for $C_{33}H_{28}O_4$, *m/e* 488.19876). (Found: C, 81.31; H, 5.61. Calc. for $C_{33}H_{28}O_4$: C, 81.13; H, 5.78%).

1,1-*Dicarbomethoxy*-3,3,5,5-*tetraphenyl*-1,4-*pentadiene*. The titanium tetrachloride method described by Lehnert[42] was applied. To a soln of 100 mL dry THF at 0° under N_2 was added 5.70 mL (51.9 mmol) titanium tetrachloride in 13 mL CCl_4. To this mixture was added 1.50 mL (13.1 mmol) dimethyl malonate and 5.02 g (13.4 mmol) 2,2,4,4-tetraphenyl-3-butenal.[24] The mixture was allowed to stir at 0° for 20 min followed by addition of 8.30 ml (103 mmol) dry pyridine in 17.0 mL THF. The soln was allowed to warm to room temp and stirred under N_2 an additional 24 hr, diluted with 30 mL water and poured into 100 mL ether. The aqueous layer was ether extracted and the combined extracts washed with water, $NaHCO_3$, brine, dried and concentrated *in vacuo* leaving 6.27 g of a yellow oil. Chromatography on a 2.5 × 95 cm silica gel column slurry packed in 2% ether in hexane with elution in 250 mL fractions gave: fractions 1–5, 2% ether in hexane, nil; 6–7, 4% ether in hexane, 696 mg dimethyl malonate; 8, a mixture of 131 mg of dimethyl malonate and 326 mg (4.98%) 1,1-dicarbomethoxy-3,3,5.5-tetraphenyl-1,4-pentadiene, 9–10, 3.15 g (49.1%) 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene, m.p. 122–124°. Recrystallization from EtOH gave 2.87 g (43.8%) colorless crystals, m.p. 123–125°.

The spectral data were: NMR ($CDCl_3$) δ 7.62 (s, 1 H, $-C\underline{H}{=}C(COOCH_3)_2$, 7.40–6.80 (m, 21 H, arom and $Ph_2C{=}C\underline{H}-$) 3.67 (s, 3 H, $-CO_2C\underline{H_3}$), 3.16 (s, 3 H, $-CO_2C\underline{H_3}$); IR ($CHCl_3$) 3060, 3020, 2955, 1725 (s, C=O), 1630, 1598, 1492, 1445, 1438, 1372, 1252, 1215, 1070, 1030, 1025, 1002, 985, 700 cm^{-1}; UV (EtOH) λ_{max} 250 nm (ε 19,866); MS *m/e* 488.1986 (Calc. for $C_{33}H_{28}O_4$, *m/e* 488.1988. (Found: C, 81.29; H, 5.90. Calc. for $C_{33}H_{28}O_4$: C, 81.13; H, 5.78%).

1,1,2,2-*Tetraphenyl*-3-(2,2-*dicarbomethoxyvinyl*) *cyclopropane*. Using the titanium tetrachloride procedure described above,[42] a mixture of 10 mL THF, 0.570 mL (5.19 mmol) titanium tetrachloride in 1.30 mL CCl_4, 0.150 mL (1.31 mmol) dimethyl malonate, 500 mg (1.34 mmol) 2,2,3,3-tetraphenylcyclopropane-1-carboxaldehyde[2h] and 0.830 mL (10.3 mmol) pyridine in 1.70 ml THF was reacted for 24 hr to yield 636 mg yellow oil. Chromatography on a 2.5 × 30 cm silica gel column slurry packed in 2% ether in hexane with elution in 100 mL fractions gave: fractions 1–5, 2% ether in hexane, nil; 6–8, 3% ether in hexane, 45.0 mg dimethyl malonate; 9, nil; 10–11, 0.431 g (65.9%) 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl) cyclopropane, m.p. 216–218°. Recrystallization from EtOH gave 409 mg (62.5%) of colorless crystals, m.p. 217–218°.

The spectral data were: NMR ($CDCl_3$) δ 7.60–6.84 (m, 21 H, arom and vinyl), 4.01 (s, 3 H, $CO_2C\underline{H_3}$), 3.95 (d, 1 H, J = 6 Hz, cyclopropyl), 3.71 (s, 3 H, $-CO_2C\underline{H_3}$); IR ($CHCl_3$) 3055, 3020, 2950, 1720 (s, C=O), 1622, 1595, 1490, 1442, 1435, 1350, 1258, 1230, 1152, 1100, 1065, 1030, 985, 700 cm^{-1}; UV (EtOH) λ_{max} 223 nm (ε 20,333), 250 (ε 10,167); MS *m/e* 488.1963 (Calc. for $C_{33}H_{28}O_4$, *m/e* 488.1988). (Found: C, 81.29; H, 5.90). Calc. for $C_{33}H_{28}O_4$: C, 81.13; H, 5.78%).

1,1-*Dicarbomethoxy*-4,4-*diphenyl*-1,3-*butadiene*. To a soln of 1.49 g (7.16 mmol) 3,3-diphenylacrolein[43] in 15 mL dioxane was added 1.08 mL (9.45 mmol) dimethyl malonate and 0.85 mL (8.59 mmol) piperidine. The mixture was stirred under N_2 for 24 hr, poured into 100 mL water and ether extracted. The extract was washed with 10% HCl, $NaHCO_3$, brine, dried and concentrated *in vacuo*. The solid residue obtained (2.21 g) was recrystallized from 95% EtOH, yielding 1.20 g (52.0%) 1,1-dicarbomethoxy-4,4-diphenyl-1,3-butadiene, m.p. 85–85.5°.

The spectral data were: NMR ($CDCl_3$) δ7.57–7.03 (m, 12h, arom and vinyls), 3.82 (s, 3H, $-CO_2\underline{CH_3}$), 3.69 (s, 3H, $-CO_2\underline{CH_3}$); IR ($CHCl_3$) 3010, 2945, 1715, 1605, 1590, 1445, 1435, 1375, 1345, 1270, 1250, 1190, 1175, 1145, 1070, 700 cm^{-1}; MS *m/e* 322.1210 (Calc. for $C_{20}H_{18}O_4$, *m/e* 322.1205). (Found: C, 80.91; H, 5.79. Calc. for $C_{33}H_{28}O_4$: C, 81.13; H, 5.78%).

1,1-*Dicarbomethoxy-4,4-di-*p*-tolyl-2,3-butadiene.* To a soln of 2.20 g (9.32 mmol) 3,3-di-*p*-tolylacrolein[2h] in 11.4 mL dioxane was added 1.41 mL (12.3 mmol) dimethyl malonate and 1.10 mL (11.1 mmol) piperidine. The mixture was stirred under N_2 for 15 hr, poured into water, ether extracted, the ether extract was washed with 10% HCl, $NaHCO_3$, brine, dried and concentrated *in vacuo*. The solid residue obtained (3.55 g) was recrystallized from 95% EtOH, yielding 2.33 g (71.4%) 1,1-dicarbomethoxy-4,4-di-*p*-tolyl-1,3-butadiene, m.p. 120–121°.

The spectral data were: NMR ($CDCl_3$) δ7.48–6.82 (m, 10H, arom and vinyl), 3.80 (s, 3H, $-CO_2\underline{CH_3}$), 3.66 (s, 3H, $-CO_2\underline{CH_3}$), 2.36 (s, 3H, p-$\underline{CH_3}$Ph), 2.30 (s, 3H, p-$\underline{CH_3}$Ph); IR ($CHCl_3$), 3010, 2950, 1718 (s, C=O), 1592, 1435, 1375, 1270, 1250, 1225, 1190, 1175, 1140, 1070, 825; UV (EtOH) λ_{max} 236 nm (ε 15,641), 255 (ε 13,235); MS *m/e* 350.1523 (Calc. for $C_{22}H_{22}O_4$, *m/e* 350.1518. (Found: C, 75.60; H, 6.34. Calc. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33%).

General procedure for exploratory photolyses. All direct and sensitized exploratory irradiations used a 450-W medium pressure mercury lamp immersion apparatus or the Black Box apparatus[12] as specified for each run. For Black Box photolyses the band-pass was controlled by filter solutions in a three compartment quartz faced cell.[12] The solns employed were: Filter A–Cell 1, 2.0 M nickel sulfate in 10% H_2SO_4, Cell 2, 0.8 M cobalt sulfate in 10% H_2SO_4, Cell 3, 2.46 × 10^{-4} M bismuth trichloride in 40% HCl. The transmission was 0% below 254 nm, 26% at 285 nm and 0% above 307 nm.

All quantum yield photolyses were purged with purified N_2 for 1 hr before and during each run.

Exploratory direct photolysis of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene.[6] A soln of 500 mg (1.02 mmol) 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene in 480 mL t-BuOH was irradiated for 1.5 hr with the 450-W lamp through a Corex filter and then concentrated *in vacuo*. The crude photolysate was chromatographed on a 3 × 57 cm silica gel column with elution in 40 mL fractions using 2% CH_2Cl_2 in hexane: 196–256, 220 mg (44.2%) of starting diene; 257–340, 274 mg (55%) of 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane as colorless crystals, m.p. 135–136°. The spectral data were identical to independently synthesized material.

Exploratory senitized photolysis of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene. A soln of 101 mg (0.207 mmol) 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene and 4.60 g (38.3 mmol) acetophenone in 101 mL benzene was irradiated for 0.31 hr through filter A using the Black Box apparatus. The light absorbed was 0.183 mEinsteins. Concentration *in vacuo* left 4.78 g of a yellow oil. Bulb to bulb distillation (0.015 Torr, 30°) removed the acetophenone leaving 100 mg solid residue. The NMR showed this to be a 3:1 mixture of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene and 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane.

The crude photolysate was chromatographed on a 1.5 × 90 cm silica gel column slurry packed in 3% ether in hexane with elution in 150 mL fractions: 16, 71.8 mg (71.1%) 3,3-dicarbomethoxy diene; 17, 23.8 mg (23.6%) diphenylvinyl cyclopropane. The overall mass balance was 94.7%.

Exploratory direct photolysis of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene. A soln of 121 mg (0.248 mmol) 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene in 120 mL *t*-BuOH was irradiated 2 hr through Pyrex using the 450 watt immersion apparatus and then concentrated *in vacuo* leaving 124 mg solid. The NMR spectrum showed total conversion to 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl) cyclopropane. Recrystallization from 95% EtOH gave 78.3 mg colorless crystals, m.p. 136–137°. Concentration of the mother liquors and chromatography on a 1.5 × 60 cm silica gel column slurry packed in 5% ether in hexane in 250 ml fractions gave in 13 and 14 an additional 36.2 mg diphenylvinyl cyclopropane, m.p. 135–137° (total 114.5 mg, 94.6%). The spectral data were identical to that of independently synthesized material.

Exploratory sensitized photolysis of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene. A soln of 200 mg (0.410 mmol) 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene and 8.03 g (66.9 mmol) acetophenone in 200 ml benzene was irradiated for 30 min through a Pyrex filter and then concentrated *in vacuo* leaving a yellow oil. Subsequent bulb to bulb distillation (0.015 Torr, 30°) was used to remove the acetophenone leaving 202 mg white crystals. The NMR showed total conversion to 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl) cyclopropane. Recrystallization from ether/hexane gave 161 mg of colorless crystals, m.p. 216–217°. Concentration of the mother liquor and chromatography of the residue on a 1.5 × 60 cm silica gel column slurry packed in 5% ether in hexane with elution in 250 mL fractions gave in 17 and 18 an additional 30.2 mg tetraphenyl cyclopropane, m.p. 217–218°, (total 191.2 mg, 95.6%). The spectral data were identical to that of independently synthesized material. The same results were obtained when the photolysis was performed in *t*-BuOH.

Exploratory direct photolysis of 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane. A soln of 205 mg (0.420 mmol) 1,1,2,2-tetraphenyl-2-(2,2,-dicarbomethoxyvinyl)cyclopropane in 200 mL-*t*-BuOH was irradiated 30 min through Pyrex and concentrated *in vacuo* leaving 210 mg solid residue. Analysis by 270 MHz NMR showed a mixture of starting material, 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene and 1,1-dicarbomethoxy-2,2-diphenylvinylcyclopropane in a ratio of *ca* 4.2:1:1.5.

The crude photolysate was chromatographed on a 1.5 × 90 cm silica gel column slurry packed in 3% ether in hexane with elution in 150 mL fractions gave: fractions 17, 18, 43.6 mg (21.3%) diphenylvinyl cyclopropane; 19–20, 29.3 mg (14.7%) 1,1-dicarbomethoxy diene; 21, 128 mg (62.4%) dicarbomethoxyvinyl cyclopropane. The overall mass balance was 98%.

Prolonged irradiation (10 hr) for a 102 mg soln of dicarbomethoxyvinyl cyclopropane in 102 mL of t-BuOH under the same conditions yielded 91 mg (89.2%) diphenylvinyl cyclopropane as the only photoproduct.

Control experiment

Direct photolysis of 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane. A soln of 98 mg (0.201 mmol) 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane in 100 mL t-BuOH was irradiated 2 hr through Pyrex and concentrated *in vacuo* leaving 95.6 mg (97.5%) white crystals, m.p. 135–136°, identical with starting material.

Control experiment

Sensitized photolysis of 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane. A soln of 101 mg (0.207 mmol) 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane and 3.94 g (32.8 mmol) acetophenone in 100 mL benzene was irradiated 45 min through Pyrex and concentrated *in vacuo* leaving a yellow oil. Bulb to bulb distillation (0.010 Torr, 30°) removed acetophenone leaving 99.0 mg (98.0%) white crystals, m p. 216–217°, identical with starting material.

Control experiment

Direct photolysis of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene and 1,1,2,2-tetraphenyl-3-(2,2-dicarbo-

methoxyvinyl) cyclopropane. A soln of 502 mg (1.03 mmol) 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene and 1.03 mg (2.11×10^{-3} mmol) 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)-cyclopropane in 750 mL t-BuOH was irradiated 4.26 hr through filter A on the Black Box apparatus using 2.66 mEinsteins. Analysis, under identical conditions to quantum yield determinations described above, detected 86% of starting 1,1-2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane. Therefore conversion to the tetraphenyl cyclopropane was $\Phi < 7.93 \times 10^{-4}$.

Control experiment

Direct photolysis of a mixture of 1,1,2,2-*tetraphenyl*-3-(2,2-*dicarbomethoxyvinyl)cyclopropane and* 1,1-*dicarbomethoxy*-4,4-p-*tolyl*-1,3-*butadiene.* A soln of 75 mg (0.154 mmol) 1,1,2,2,-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane- and 168 (0.0480 mmol) 1,1-dicarbomethoxy-4,4-*p*-tolyl-1,3-butadiene in 250 mL t-BuOH was irradiated 45 min through Pyrex and concentrated *in vacuo* leaving 248 mg yellow oil. Chromatography on a 1.5 × 90 cm silica gel column slurry packed in 2% ether in hexane with elution in 150 mL fractions gave: fractions 14–15, 166 mg (98.8%) dicarbomethoxy-di-*p*-tolyl-butadiene; 18–19, 3% ether in hexane, 21.2 mg (28.3%) diphenylvinyl cyclopropane; 20–21, 13.9 mg (18.5%) 1,1-dicarbomethoxy diene; 22, 38.4 mg (51.2%) dicarbomethoxyvinyl cyclopropane. The overall mass balance was 98 6%.

Control experiment

Sensitized photolysis of 1,1-*dicarbomethoxy*-2,2-*diphenyl*-3-(2,2-*diphenylvinyl)cyclopropane.* A soln of 250 mg (0.512 mmol) 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane and 9.1 g (75.8 mmol) acetophenone in 250 mL benzene was irradiated 2.31 hr through filter A on the Black Box apparatus with 1.44 m Einsteins. Bulb to bulb distillation (0.010 Torr, 30°) removed acetophenone and analysis under identical conditions to quantum yield determinations described was performed. No dicarbomethoxyvinyl cyclopropane was detected. A control mixture containing 0.654% dicarbomethoxyvinyl cyclopropane was examined under identical conditions and this conversion would have been measurable. Therefore conversion was <0.654%, $\Phi < 1.42 \times 10^{-3}$.

Photolysis apparatus for quantum yield determinations. All quantum yield determinations were run on either the Black Box apparatus[12] or semimicroptical bench.[12] Light output was measured using a digital actinometer[13] calibrated by ferrioxalate actinometry.[14] Microoptical bench photolyses employed an Osram HBO 200-W high-pressure mercury lamp and Bausch and Lomb Model 33-86-79 monochromator with a 5.4-mm entrance slit and 3.0-mm exit slit giving a band-pass of 22 nm a half-peak height. For Black Box photolyses the band pass was controlled by the filter solutions described above.

Summary of quantum yield results. All runs were analyzed by high-pressure liquid chromatography using a 4.0 × 270 mm column packed with 5-10 μ silica beads[44] eluted with 15% anhyd ether in anhyd hexane. The internal standard used was *p*-cyanoanisole. The data are reported in Tables 5 9.

Emission studies magic multipliers.[15] The fluorescence spectrum of each compound was measured in a 4:1 methylcyclohexane isopentane soln at 77 K and 295 K using an Aminco-Keirs spectrofluorometer equipped with a Hanovia 901C-1 150-W Xenon arc lamp. Concentrations of solns were adjusted to give optical densities of 0.8 0.9. All solns were thoroughly degassed immediately before the spectra were obtained. Emission wavelength maxima were found to be independent of excitation wavelength over a 50 nm range. Magic Multiplers were calculated by dividing the integrated intensity of fluorescence at 77 K by the integrated intensity of fluorescence at 295°K. The average value obtained for each compound was: 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene, M = 21.0 (3 runs); 1,1-dicarbo-methoxy-3,3,5,5-tetraphenyl-1,4-pentadiene, M = 197 (3 runs).

Single photon counting. The apparatus and procedure have been described previously.[15,20] Individual samples were prepared in 4:1 methylcyclohexane-isopentane to give an optical density in the range of 0.8–0.9, thoroughly degassed immediately before counting, and counted at 77 K. Data was collected at less than 5% lamp flash frequency to insure exclusion of double photon counting. Excitation wavelength was varied over the range 275 and 310 nm and emission was monitored over the range 305 to 360 nm with an RCA 8850 photomultiplier. The decay range was found to be independent of excitation wavelength, emission wavelength and optical density to within 5% using the "A" value[15] as a measure of the fit of calculated to experimentally observed decay rate. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, A-value.

(1) 3,3-Dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene, 0.827 ns, $1.25 \times 10^{9}\,s^{-1}$, 7, 0.037.

Table 5. Photolysis of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene to afford 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl) cyclopropane

Run	Reactant, mmol	light absorbed mEinstein	% convn	photoproduct mmol	Φ
1[a]	1.11×10^{-1}	2.40×10^{-1}	7.20	8.00×10^{-3}	0.34
2[a]	1.04×10^{-1}	4.40×10^{-1}	15.4	1.60×10^{-2}	0.23
3[a]	1.04×10^{-1}	1.70×10^{-1}	23.7	2.50×10^{-2}	0.14

[a] Black Box, 80 mL of cyclohexane, filter A.

Table 6. Sensitized photolysis of 3,3-dicarbomethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene to afford 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl) cyclopropane

Run	Reactant, mmol	added sens, mmol	light absorbed, mEinstein	% convn	photoproduct mmol	Φ
1[a]	7.05×10^{-2}	29.2	2.14×10^{-3}	0.912	6.43×10^{-4}	0.30
2[a]	6.39×10^{-2}	26.7	4.26×10^{-3}	1.93	1.23×10^{-3}	0.29
3[a]	6.52 x 10-2	26.7	6.66×10^{-3}	2.79	1.82×10^{-3}	0.27

[a] microoptical bench, 40 mL of benzene, 340 nm.

Table 7. Photolysis of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene to afford 1,1-dicarbomethoxy-2, 2-diphenyl-3-(2,2-diphenylvinyl) cyclopropane

Run	Reactant, mmol	light absorbed mEinstein	% convn	photoproduct mmol	Φ
1[a]	5.97×10^{-1}	1.50×10^{-2}	0.985	5.38×10^{-3}	0.39
2[a]	1.83×10^{-1}	2.12×10^{-2}	4.11	7.52×10^{-3}	0.36
3[a]	2.30×10^{-1}	7.32×10^{-2}	11.2	2.57×10^{-2}	0.35
4[a]	3.85×10^{-1}	1.26×10^{-1}	17.4	6.68×10^{-2}	0.30

[a]Black Box, 250 mL of tert-butyl alcohol, filter A.

Table 8. Sensitized photolysis of 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene to afford 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl) cyclopropane

Run	Reactant, mmol	added sens, mmol	light absorbed mEinstein	% convn	photoproduct mmol	Φ
1[a]	6.91×10^{-2}	28.3	1.45×10^{-3}	1.91	1.32×10^{-3}	0.91
2[a]	7.66×10^{-2}	30.0	6.88×10^{-3}	7.86	6.02×10^{-3}	0.88
3[a]	6.45×10^{-2}	25.7	1.01×10^{-2}	13.1	8.46×10^{-3}	0.84

[a]microoptical bench, 40 mL of benzene, 340 nm.

Table 9. Photolysis of 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl) cyclopropane to afford 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl) cyclopropane and 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene

Run	Reactant, mmol	light absorbed mEinstein	% convn	photoproduct mmol	Φ
1[a]	7.76×10^{-2}	9.52×10^{-3}	2.00	9.24×10^{-4}[b] 6.29×10^{-4}[c]	9.7×10^{-2} 6.6×10^{-2}
2[a]	4.00×10^{-2}	1.18×10^{-2}	4.50	1.06×10^{-3}[b] 7.33×10^{-4}[c]	9.0×10^{-2} 6.2×10^{-2}
3[a]	6.66×10^{-2}	3.36×10^{-2}	6.87	2.75×10^{-3}[b] 1.84×10^{-3}[c]	8.2×10^{-2} 5.5×10^{-2}

[a]microoptical bench, 40 mL of tert-butyl alcohol, 285 nm. [b]1,1-Dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane. [c]1,1-Dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene.

(2) 1,1-Dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene, 0.330 ns, $3.05 \times 10^9 s^{-1}$, 6, 0.031.

Calculations. The method employed was described previously.[3,5,17,19] Standard geometries for styryl vinyl methanes, vinyl cyclopropanes and 1,3-biradicals were established using a geometry program[45] with standard[46] bond lengths and angles. Geometries for 1,4-biradical species were taken from a reported INDO calculation with geometry optimization for the ground state 2-vinylcyclopropylcarbinyl radical.[47]

Calculations were performed with Fortran IV programs[48] on a PDP-11/T55 computer having 32 K words of memory. Direct access to and from two disks of 1.2×10^6 words per disk allowed storage and use of the large matrices encountered in configuration interaction calculations.

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