

Unusual Organic Photochemistry Effected by Cyano and Methoxy Substitution. Exploratory and Mechanistic Organic Photochemistry^{1,2}

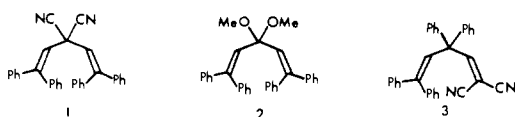
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Abstract: The photochemistry of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene, 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene, and 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene was investigated. The 1,1-dicyanodiene led to a mixture of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane, 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane, and 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. Quantum yields for direct irradiation in benzene were $\Phi = 0.044$, $\Phi = 0.059$, and $\Phi = 0.051$, respectively. In contrast, acetophenone sensitized irradiation afforded just 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane with a quantum yield of $\Phi = 0.79$. Singlet excited state reaction rates for formation of the first two products were determined by single photon counting to be $k_r = 4.9 \times 10^{10} \text{ s}^{-1}$ and $k_r = 6.5 \times 10^{10} \text{ s}^{-1}$, respectively. Synthesis of the 3,3-dicyanodiene proved nontrivial and a novel approach was devised. Both direct and acetophenone sensitized irradiations led to 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane in quantum yields of $\Phi = 0.11$ and $\Phi = 0.53$, respectively. The S_1 rate of reaction was $k_r = 9.24 \times 10^8 \text{ s}^{-1}$. This is severely inhibited (ca. 150 times slower) compared with the 3,3-dimethyl analogue. The triplet efficiency contrasts with the lack of reactivity of the dimethyl analogue as well. Direct irradiation of 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene led to 1,1-dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane, along with 1,1,4,4-tetraphenylbutadiene as a minor product. The quantum yields were $\Phi = 0.15$ and $\Phi = 0.018$, respectively. No reaction was observed on sensitization. Direct irradiation of 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane led to isomeric 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene, with quantum yields of $\Phi = 0.12$ and $\Phi = 0.34$, respectively. These formally derive from a unique acyclic bicycle reaction and reverse di- π -methane rearrangement, respectively. Finally, new photochemical theory was developed to deal with singlet vs. triplet reaction preferences and to treat the di- π -methane rearrangement. In the former, the role of the exchange integral K between electrons in HOMO and LUMO is shown to be often dominant.

The present investigation was initiated with the idea of studying the role of substitution on the methane carbon of acyclic di- π -methane systems where these substituents were either exceptionally effective electron withdrawing or donating groups. This interest was prompted by previous studies in our laboratory³ which suggested that the rate-limiting step of the rearrangement led to a cyclopropyldicarbonyl diradical whose carbonyl carbons are electron rich and where the original "methane carbon" has become electron deficient.

The systems chosen for study were 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene (**1**) and 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene (**2**). Additionally, a study of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (**3**) was undertaken both because of its intrinsic interest and because it quickly became apparent that the photochemistry of this compound was closely intertwined with that of 3,3-dicyanodiene **1** and therefore pertinent.

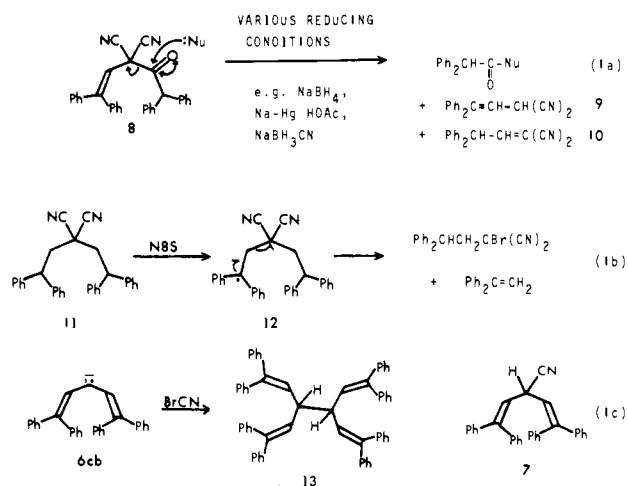


Results

Synthesis of Photochemical Reactants. The simplest synthesis was that of dimethoxydiene **2** which was obtained as noted in Chart I by the reaction of methyl orthoformate with 1,1,5,5-tetraphenyl-1,4-pentadien-3-one (**4**). Almost equally straightforward was the preparation of 1,1-dicyanodiene **3**. The condensation of malononitrile with 2,2,4,4-tetraphenyl-3-butenal (**5**) to give diene **3** is depicted in Chart I. Also, both of these syntheses are detailed in the Experimental Section.

More difficult was the preparation of 3,3-dicyanodiene **1**. Three approaches which were not successful, but which are of intrinsic interest, are depicted in eq 1a-c. The utilization of the keto precursor **8** in the synthesis of 3,3-dicyanodiene **1** fell prey

to the exceptional susceptibility of this ketone to nucleophilic deacylation; note eq 1a. The benzylic bromination of tetraphenyl precursor **11** failed due to the facile radical elimination shown in eq 1b.



The synthesis of the monocyanodiene **7**, an intermediate leading to the desired 3,3-dicyanodiene **1**, initially seemed successfully attained from the treatment of the conjugate base of tetraphenyldiene **6** with cyanogen bromide. The recrystallized product of the reaction gave an NMR spectrum with aryl, vinyl, and methine hydrogens in a ratio of 20:2:1 as anticipated for the desired monocyanodiene **7**. The vinyl peak was the expected doublet and the methine peak was the expected triplet; the methine peak at τ 6.5 was at higher field than might have been expected. Still, the mass spectrum of the compound revealed a parent peak, albeit weak, at m/e 397 (theory 397). Also, there was a strong mass peak at 371, as expected for the $(\text{Ph}_2\text{CH}=\text{CH}-)_2\text{CH}$ fragment which would result from the loss of the cyano moiety. However, elemental analysis, which

Chart I. Syntheses of Photochemical Reactants

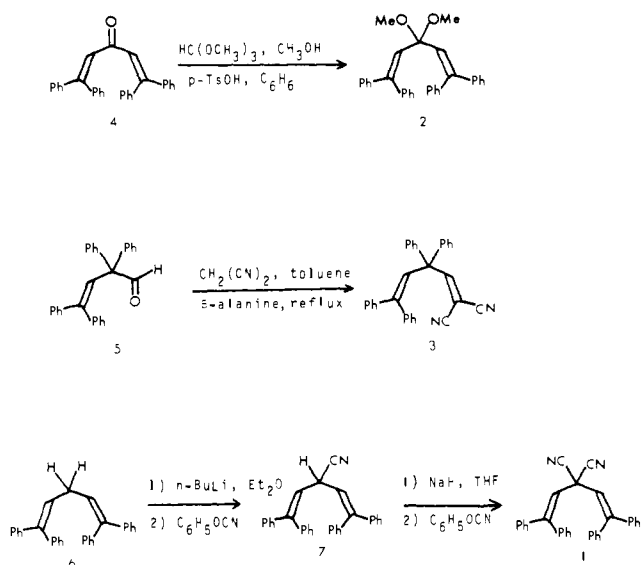
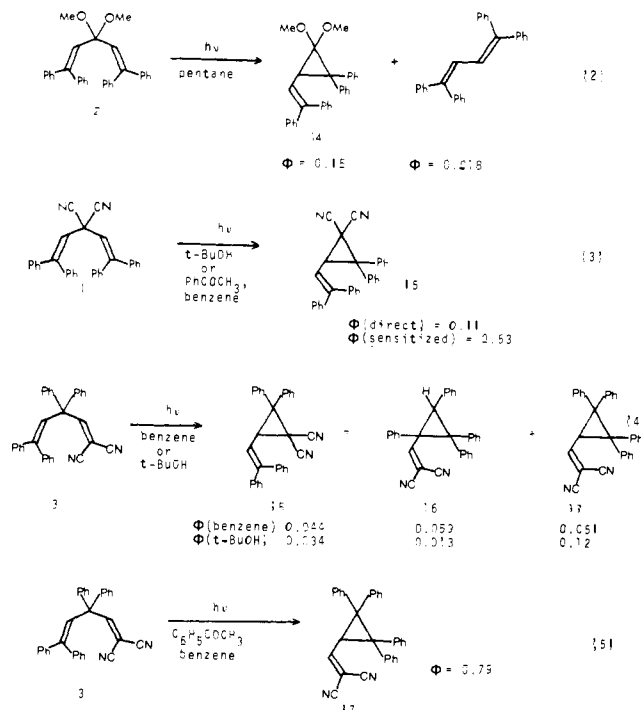


Chart II. Photochemical Transformations of Dienes

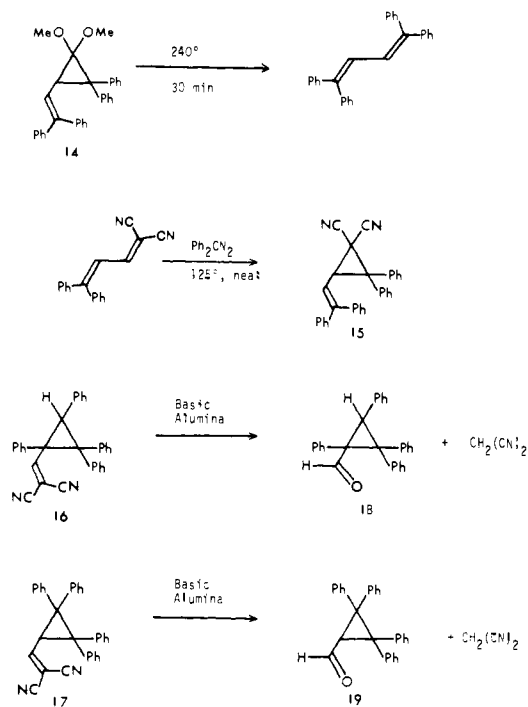


revealed the total absence of nitrogen with carbon and hydrogen totalling 100%, was not in agreement with structure **7** but rather dimeric **13**. The deceptive mass spectral analysis derived from a minute amount of more volatile monocyanodiene **7** present, while the NMR support derived from the structural similarity of the two compounds.

The moral derived is that elemental analysis provides evidence of purity and composition of the entirety of a sample, as well as a safety factor, while mass spectral analysis alone would suggest a 99.9% sand sample contaminated with a desired material to be the desired material.

Since the basic synthetic concept involving cyanation of anion **6cb** seemed sound, an alternative reagent, namely, phenyl cyanate,⁴ was tried. As noted in Chart I, this approach was successful, leading to monocyanodiene **7** which proved to be readily convertible to the desired 3,3-dicyanodiene **1** via the conjugate base of monocyanodiene **7** and further cyanation.

Exploratory Diene Photochemistry. Exploratory runs were

Chart III. Structure Proofs for Di- π -methane Photoproducts

made by using a 450-W immersion apparatus and also the "Black Box"⁵ apparatus. In the case of dimethoxy diene **2**, preparative runs revealed the formation of two photoproducts. One proved to be 1,1,4,4-tetraphenylbutadiene. Also formed was a product, mp 133.0–134.5 °C, shown by high resolution mass spectrometry to be an isomer of the starting dimethoxydiene **2**. The NMR spectrum revealed the presence of two, nonequivalent methoxy groups. Additionally, an AB quartet characteristic of the CH—CH= moiety of a vinylcyclopropane system was noted. Also, the ultraviolet spectrum possessed the intense Ph₂C=C absorption at 269 nm characteristic of diphenylvinylcyclopropanes. Finally, pyrolysis of the photoproduct at 240 °C afforded 1,1,4,4-tetraphenylbutadiene.

This information indicated that the unknown photoproduct has the structure of 1,1-dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**). The photochemical transformation is depicted in Chart II, and the thermolysis of the photoproduct is shown in Chart III.

Exploratory photolyses of 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene (**1**) led to one photochemical product, mp 185.0–186.0 °C. The NMR spectrum of the photoproduct again revealed the vinylmethine AB quartet characteristic of vinylcyclopropanes of the type obtained as di- π -methane photoproducts.

The structure of this photoproduct was shown to be that of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**) by independent synthesis. This involved the slow addition of diphenyldiazomethane to 1,1-dicyano-4,4-diphenyl-1,3-butadiene at 125 °C. Note Chart III, eq 2.

Thus the photolysis of 3,3-dicyanodiene **1** proceeds as shown in eq 3 in Chart II.

At this point, attention was turned to sensitized photolyses of the dimethoxydiene **2** and the dicyanodiene **1**. Not surprisingly, the dimethoxydiene **2** proved unreactive on sensitization, as is the case for a majority of acyclic di- π -methanes.^{6,11}

Interestingly and in contrast, sensitization of 3,3-dicyanodiene **1** led to a facile di- π -methane rearrangement, affording diphenylvinylidicyanocyclopropane **15**. Note Chart II, eq 3 again.

The last compound studied was 1,1-dicyanodiene **3**. The photochemistry of this compound proved more complex than that of the preceding dienes. Photolysis in either benzene or *tert*-butyl alcohol led to three photoproducts. The ratio of products, however, proved to be a function of both solvent and extent of conversion (*vide infra*). The first photoproduct was found to be the same diphenylvinylidicyanocyclopropane **15** encountered in the photochemistry of 3,3-dicyanodiene **1**. The two remaining photoproducts also proved isomeric with reactant and had mp's of 161–162 and 224–225 °C.

The 162 °C photoproduct had a 20-hydrogen multiplet in the aryl region of the NMR, a single unsplit resonance at τ 4.6 and a low field (τ 2.4) vinyl singlet, ascribable to the $-\text{CH}=\text{C}(\text{CN})_2$ moiety. This structural assignment was supported by an intense infrared peak at μ 6.3. The 1,1,2,3-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane structure suggested by the NMR and IR data was confirmed by alumina catalyzed reverse Knoevenagel reaction to the known¹² 1,2,2,3-tetraphenylcarboxaldehyde (**18**); this degradation is included in Chart III.

The last photoproduct, mp 225 °C, possessed a methine hydrogen in the NMR which was split into a doublet. The lower field half of the AB quartet, however, was obscured by aryl absorption. The infrared again indicated the presence of a polarized double bond, and a $\text{CH}-\text{CH}=\text{C}(\text{CN})_2$ moiety was deduced. Alumina-catalyzed hydrolysis in this case led to the known¹² 2,2,3,3-tetraphenylcyclopropanecarboxaldehyde (**19**). This degradation is also included in Chart III.

Hence, the direct photolysis of 1,1-dicyanodiene **3** can be depicted as in eq 4 of Chart II.

Dramatically, sensitization of 1,1-dicyanodiene **3** with acetophenone in benzene led exclusively to the dicyanovinyl-tetraphenylcyclopropane **17** which was one of three direct irradiation products.

Also of interest was the finding that irradiation of 1,1-dicyanodiene **3** in *tert*-butyl alcohol led to marked inhibition of the formation of the phenyl migrated dicyanovinylcyclopropane **16**. This can be seen from the quantum yield distributions in Chart II, eq 4.

Attention was next turned to a dependence of the product distribution on extent of irradiation of 1,1-dicyanodiene **3**. From these efforts, a remarkable result arose. Thus it was found that, at low conversions, the direct irradiation of 1,1-dicyanodiene **3** led to the three photoproducts **15**, **16**, and **17** in a 1:1.3:1.2 ratio. However, in high conversion runs (>60%), dicyanovinyltetraphenylcyclopropane **17** was essentially absent from the product mixture. Careful monitoring of aliquots taken at increasing extents of conversion showed clearly that the proportion of diphenylvinylidicyanocyclopropane **15** increased at the expense of dicyanovinylcyclopropane **17**.

Thus, in high conversion photolyses only two of the cyclopropanes result, these being the phenyl migrated cyclopropane **16** and the diphenylvinylcyclopropane **15**. Such high conversion runs give the erroneous appearance of kinetic regioselectivity which really derives from an approach to a steady state. The results above also suggest the existence of conversion of the dicyanovinylcyclopropane **17** into the diphenylvinylcyclopropane isomer **15**. This reaction is discussed below.

From the above, we note a multiplicity dependence in the regioselectivity of the irradiation of the 1,1-dicyanodiene **3**, in which the direct photolysis leads kinetically to a roughly equal distribution of three cyclopropanes, the phenyl migrated product **16**, the diphenylvinyl isomer **15**, and the dicyanovinyl product **17**. This contrasts with the sensitized runs where only the dicyanovinyl isomer **17** is obtained.

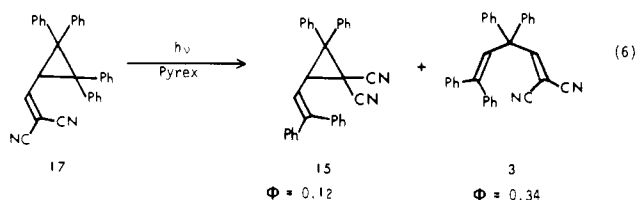
The formation of even 50% of the dicyanovinyl isomer **17** in direct irradiations was surprising, since generally (*vide infra*) electron-withdrawing substituents appear on the three-ring of photoproduct in such irradiations. Therefore, attempts were

made to determine if the triplet of 1,1-dicyanodiene **3** was being formed by some adventitious sensitizer (e.g., benzophenone, some aromatic hydrocarbon present, etc.) or by intersystem crossing. Runs were carried out with added quenchers at varying concentrations, these ranging high enough that even some reactant singlet was being quenched. However, no change in the low conversion (i.e., initial) product distribution was observable.

Representative runs are detailed in the Experimental Section, as are runs with added quencher.

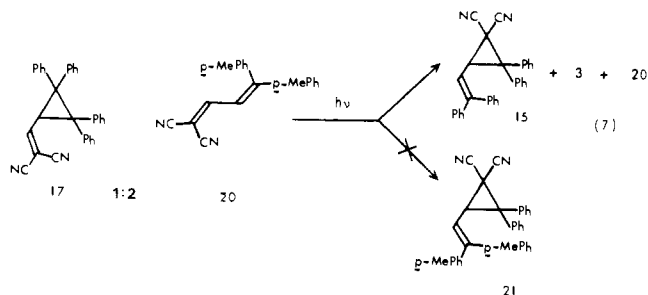
Vinylcyclopropane Photochemistry. In view of the unusual photochemistry of the 1,1-dicyanodiene **3** in which the ratio of the diphenylvinylcyclopropane **15** to the dicyanovinylcyclopropane **17** increased with extent of conversion, it was important to investigate the photochemistry of these two cyclopropanes (i.e., **15** and **17**). For completeness, phenyl migrated cyclopropane **16** was also studied.

Neither the phenyl migrated cyclopropane **16** nor the diphenylvinylcyclopropane **15** reacted on direct irradiation. However, a remarkably facile reaction of the dicyanovinylcyclopropane **17** occurred on direct irradiation, with formation of the 1,1-dicyanodiene **3** and the diphenylvinylcyclopropane **15**. This reaction is depicted in eq 6. This photochemistry is



seen to involve, at least formally, a bicycle reaction¹³ and a reverse di- π -methane rearrangement.

Test of Intramolecularity of the Bicycle Rearrangement. The rearrangement in eq 6 formally requires the migration (i.e., "bicycling") of a diphenylcarbene moiety along a 1,1-dicyano-4,4-diphenyl-1,3-butadiene system. One alternative mechanism was intermolecular, with disengagement of diphenylcarbene and readdition to the dicyanovinyl end of the butadiene. Hence, a test of intramolecularity seemed necessary. This experiment involved the irradiation of the dicyanovinylcyclopropane **17** with an excess of 1,1-dicyano-4,4-di-*p*-tolylbutadiene (**20**). It was observed that the reaction proceeded, as in the absence of the added diene, to give the diphenylvinylcyclopropane **15** with no crossover to form any ditolyl-substituted cyclopropane (i.e., **21**). No complicating photochemistry was observed from the tolyl-substituted butadiene **20**. This then demonstrates the intramolecularity of the rearrangement. The result is illustrated in eq 7.



Quantum Yield Determinations. Quantum yields were determined by using the microbench apparatus⁵ and the electronic actinometer^{14a} we described earlier. The actinometer calibration was checked with ferrioxalate^{14b} during each run for safety, although this remained essentially constant for each given wavelength and bandwidth. Assays were performed by high pressure liquid chromatography except where 270-MHz NMR was required (note Experimental Section). All quantum

Table I. Quantum Yield Determinations

reactant	solvent	sensitizer	14	tetraphenylbutadiene	15	16	17	3
3,3-dicyanodiene 1	<i>t</i> -BuOH	none			0.11	0	0	0
	benzene	C ₆ H ₅ COCH ₃			0.53	0	0	0
dimethoxydiene 2	pentane	none	0.15	0.018				
	benzene	xanthone	0	0				
1,1-dicyanodiene 3	benzene	none			0.044	0.059	0.051	
	<i>t</i> -BuOH	none			0.033	0.012	0.12	
	benzene	C ₆ H ₅ COCH ₃			0	0	0	0
vinylcyclopropane 17	benzene	none			0.12	0	0	0.34

Table II. Single Photon Counting and Rate Data

compd	τ_{77}^a (ns)	τ_{295}^b (ps)	k_{dr}^{77b} (s ⁻¹)	k_{dr}^{295} (s ⁻¹)	magic multiplier	ϕ_r^c	k_r^{295} (s ⁻¹)	photoproduct
3,3-dicyanodiene 1 ^d	1.82	114	5.50×10^8	8.80×10^9	16	0.11	9.24×10^8	diphenylvinylcyclopropane 15
1,1-dicyanodiene 3 ^e	0.228	0.92	4.49×10^9	1.11×10^{12}	247	0.044 ^f	4.93×10^{10}	diphenylvinylcyclopropane 15
tetraphenyldiene 29 ^h	0.124	0.55	8.1×10^9	1.8×10^{12}	225	0.08	1.40×10^{11}	vinylcyclopropane 30
<i>trans</i> -monocyanodiene 33t	6.4	24.5	1.6×10^8	4.1×10^{10}	260	0.36	1.50×10^{10}	vinylcyclopropane ⁱ
<i>cis</i> -monocyanodiene 33c	6.5	25.1	1.5×10^8	4.0×10^{10}	260	0.20	8.00×10^9	vinylcyclopropane ^j
1,1-dimethoxydiene 25 ^k	1.90	9.0	5.3×10^8	1.13×10^{11}	216	0.076	8.5×10^9	vinylcyclopropane 26
						0.051	5.8×10^9	vinylcyclopropane 27

^a All measurements in methylcyclohexane-isopentane, 4:1. ^b Estimated errors for decay rates and lifetimes are 20%. ^c Subscript r refers to the S₁ unimolecular rate of rearrangement. ^d 7 runs. ^e 12 runs. ^f For vinyl-vinyl bridging and diphenylvinyl migration to vinylcyclopropane 15. ^g For phenyl-vinyl bridging and rearrangement to vinylcyclopropane 16. ^h See reference 17a. ⁱ *trans*-1-Cyano-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane; see ref 11c. ^j *cis*-1-Cyano-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane; see ref 11c. ^k See ref 12.

yields were extrapolated to zero percent conversion; these extrapolations included runs below 3% in almost all cases; all were below 6%. This proved necessary since the quantum yields were especially sensitive to extent of conversion.

Quantum yields for the three di- π -methane rearrangements and the one bicycle rearrangement are collected in Table I.

Single Photon Counting Determination of S₁ Rates. Since photochemical reactivity is best related to the excited state reaction rate rather than just the quantum yield, we proceeded to use the previously described method¹⁵ for obtaining these S₁ rates. Due to the very rapid S₁ decay observed for the compounds under study, this required single photon counting measurement of singlet lifetimes at 77 K. The usual reiterative simulated deconvolution was necessary and an on-line mini-computer was again utilized. The 77 K decay rate was converted to a room temperature value ($^1k_{dr}^{RT}$) by use of the expression in eq 8a and this was converted to the reaction rate k_r by use of the expression in eq 8b.

$$^1k_{dr}^{RT} = M(^1k_{dr}^{77}) \quad (8a)$$

$$^1k_r = \phi_r(^1k_{dr}^{RT}) \quad (8b)$$

Here M is the magic multiplier¹⁵ derived experimentally as the ratio of low temperature to room temperature fluorescence emission intensities. Inspection of the fluorescence and absorption spectra revealed no problem with intramolecular charge-transfer effects; note difficulties encountered in our earlier studies^{3a,16a} and those of Salisbury et al.^{16b}

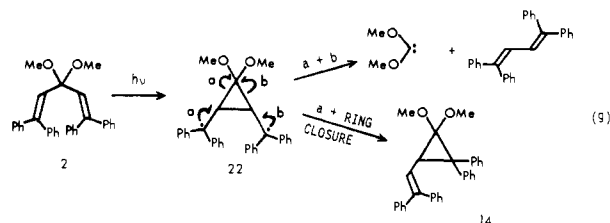
The rate constants obtained are listed in Table II.

It is noted that rates are not given for the dimethoxydiene 2. In these experiments, rapid formation of a tetraphenylbutadiene impurity, which then emitted strongly, led to erroneous data.

Interpretative Discussion

Gross Course of the Rearrangements. In our previous studies, we have shown that 1,1,5,5-tetraaryl-1,4-pentadienes have rearranged via the di- π -methane mechanism only when the central carbon (i.e., the methane carbon, C-3) has been substituted with alkyl or phenyl; with hydrogen substitution, for example, the normal di- π -methane rearrangement does not occur.¹⁷ Thus there was some question whether or not a di- π -methane process would occur with central methoxy or cyano substitution.

The first molecule studied was the methoxydiene 2. As noted above, this did indeed rearrange by way of a di- π -methane process, thus providing further information on the scope of the reaction and also a route to an otherwise difficultly accessible compound. Equally interesting was the observation of expulsion of the dimethoxymethylene moiety and generation of 1,1,4-tetraphenylbutadiene which can be considered as a diversion of the cyclopropyldicarbonyl diradical species 22 involved in the di- π -methane rearrangement. Note eq 9. Ex-

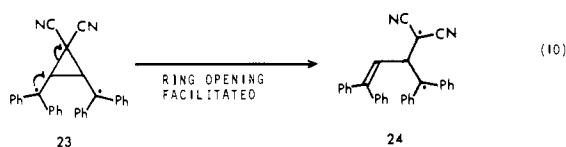


pulsion of dimethoxycarbene has analogy in the expulsion of diphenylcarbene from tetraphenylmethane as reported by Walsh and Powers.¹⁸ Also it has analogy in the carbene expulsion observed in the elegant studies by Iwamura¹⁹ in which

a formal di- π -methane rearrangement of trypticenes derives from aryl-aryl bridging, carbene expulsion, and then readdition of the carbenoid carbon to the π system.

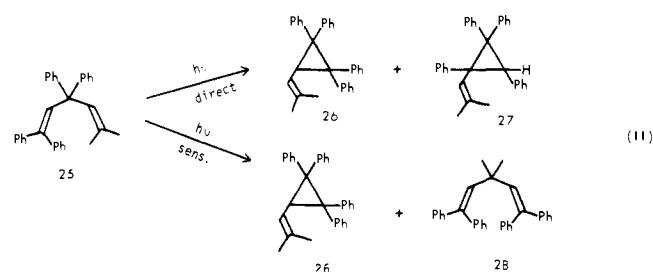
The rearrangement of the 3,3-dicyanodiene **1** also proceeded by a normal di- π -methane mechanism, again extending the scope of the reaction. Also, this reactant was exceptional in rearranging on sensitization. In our previous studies the triplets of tetraaryl 1,4-pentadienes have undergone the di- π -methane rearrangement only when the methane carbon (i.e., C-3) was substituted with phenyl groups.

It seems likely that two factors are operative to effect a triplet di- π -methane rearrangement which successfully competes with radiationless decay by a free rotor effect.¹¹ One factor is the expectation that vinyl-vinyl bridging will be facilitated by the cyano substitution stabilizing the three-ring structure engendered; this is very much like the effect favoring the norcaradiene valence tautomer when cyano substitution is introduced on the methylene group, while the cycloheptatriene tautomer is favored without electron-withdrawing substituents.²⁰ A second factor seems likely to be odd-electron stabilization aiding the three-ring opening of the cyclopropyldicarbonyl diradical species involved in the di- π -methane rearrangement. Note eq 10.



We turn now to the last of the three systems, namely, the 1,1-dicyanodiene **3**. In the direct irradiation, two features are of particular interest. The first is the intervention of phenyl-vinyl bridging along with vinyl-vinyl bridging in the first step of the di- π -methane mechanism for this reactant (note eq 4 and structure **35**).¹² This contrasts with the triplet (i.e., sensitized) behavior where only vinyl-vinyl bridging product **17** is obtained.

This effect has precedent. Thus in our earlier study of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (**25**) phenyl migration competed with vinyl-vinyl bridging to give the products shown in eq 11.¹² Here, as in the present study, sensitized runs



afforded vinyl-vinyl bridging product but no phenyl migrated product.

Regioselectivity of π - π Bridging. One approach to prediction of preferred modes of π - π interaction and bonding merely considers the question of excitation energy distribution. Energy localization as a controlling factor in the di- π -methane rearrangement appears to have been first considered by Zimmerman et al.²¹⁻²³ The suggestion was made that the lowest energy chromophores were the ones which preferentially bonded and that multiplicity differences arose from changes in the locus of electronic excitation. Here, both theoretical and empirical^{21,22,24} (i.e., spectroscopic) determination of chromophore energies were used. A second approach which has been used by the same workers²⁴ involves consideration of the locus of excitation energy as the chromophores are perturbed toward one another and as the molecule moves along the reaction

coordinate; the lowest energy choice is selected by each multiplicity species. The second approach appears more justified than the first. Again, both theoretical²³ and empirical²⁴ approaches were used. The empirical approach requires simulation of two interacting chromophores by a single compound. This is termed reacting chromophore simulation.

For the presently studied systems, we first consider static energy localization. The lowest energy S_1 chromophore is diphenylvinyl ($E_{S_1} = 100$ kcal/mol²⁵). The remaining two chromophores are phenyl ($E_{S_1} = 107$ kcal/mol²⁵) and dicyanovinyl ($E_{S_1} = 106$ kcal/mol^{26a,b}). Thus, based on energy localization alone, an equal competition between phenyl and dicyanovinyl bridging with the diphenylvinyl moiety is reasonable. The third possibility of dicyanovinyl-phenyl bridging involves the two highest energy chromophores; experimentally, this is not observed.

Considering next reacting chromophore simulation, we need to know the energy of the excited singlet as it traverses the three competitive reaction pathways. Thus, we need to estimate the energy of (a) diphenylvinyl-dicyanovinyl, (b) diphenylvinyl-phenyl, and (c) dicyanovinyl-phenyl coupled moieties. An approximation to the first (i.e., a) is 1,1-dicyano-4,4-diphenyl-1,3-butadiene for which we estimate $E_{S_1} = 69$ kcal/mol, based on the UV spectrum (λ_{max} 356 nm, 0-0 transition at ca. 414 nm^{26c,d}). The second (i.e., b) is approximated by triphenylethylene with $S_1 = 76$ kcal/mol (λ_{max} 299 nm, estimated 0-0 band at 377 nm^{26e}). These two are relatively close energetically and can be understood to compete. The third, but experimentally unobserved, alternative of phenyl-dicyanovinyl bridging (i.e., c) can be approximated by cinnamitrile, which is of much higher energy (0-0 band estimated at 300-310 nm, $E_{S_1} = 92-95$ kcal/mol²⁷).

Hence the bridging selectivity of π moieties seems to follow simple energetic control in the case of the reacting singlet.

Turning now to the bridging regioselectivity of the triplet, we note that only vinyl-vinyl bridging is observed. The static approach now uses the triplet energies of the three chromophores present: namely, diphenylvinyl ($E_T = 53-62$ kcal/mol^{28a,b}), dicyanovinyl ($E_T \approx 60$ kcal/mol^{28d}), and phenyl ($E_T = 83$ kcal/mol²⁹). Again, interaction of the two lowest energy chromophores leads to prediction of the reaction course, this involving diphenylvinyl-dicyanovinyl bridging.

The reacting chromophore approach requires the same three model systems a-c, discussed above for the singlet reaction. All of the required triplet energies are not available; however, the observed reaction course would require that the triplet energy of 1,1-dicyano-4,4-diphenyl-1,3-butadiene be lower than that of either triphenylethylene or cinnamitrile, which is quite reasonable.

Excited Singlet Reaction Rates. One of the purposes of investigating the excited singlet rates of the diene rearrangements was to determine the effect of central cyano substitution and also terminal cyano substitution on the di- π -methane rearrangement.

Central cyano substitution is seen (note Table II) to lead to a rate inhibition of ca. 150-fold relative to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene **29**, where the methane carbon bears methyls rather than cyano. However, the quantum yields for the two compounds, **1** and **29**, do not differ appreciably (i.e., $\Phi = 0.11$ vs. $\Phi = 0.080$). Thus quantum yield assessment of reactivity would lead one in error. The advantage of using excited state rate constants, rather than just quantum yields, to correlate with structural effects has been noted by us earlier.¹⁶

We note that the difference in S_1 rates of rearrangement deriving from central cyano substitution comes from an inhibition of k_{dr} , the total rate of disappearance of S_1 which includes both reaction and radiationless decay. We can interpret the inhibited rates of reaction and decay as an inhibition of

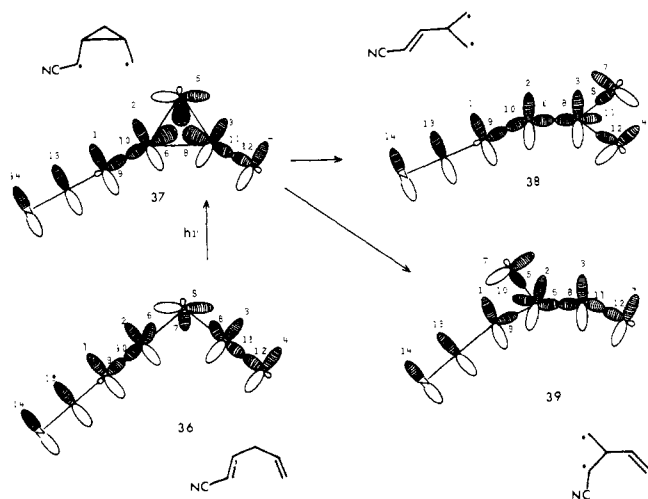
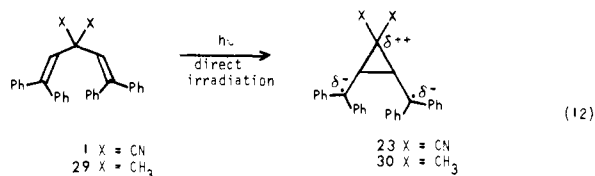


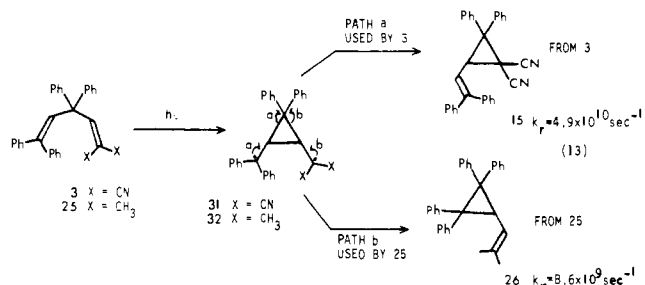
Figure 1. Basis orbitals used in SCF-CI calculations.

vinyl-vinyl bridging on introduction of the central cyano substitution. This accords with our previous calculations of the singlet bridging process of di- π -methane systems which revealed that the methane carbon becomes electron deficient as bridging occurs to form the S_1 cyclopropyldicarbonyl diradical.³ Note eq 12. However, the inhibition of S_1 reactivity



contrasts with the observed (vide supra) facility of T_1 rearrangement.

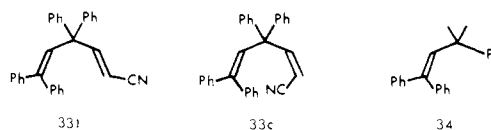
The second rate of interest is that of the 1,1-dicyanodiene singlet (i.e., S_1 of **3**) to form diphenylvinylcyclopropane **15** (note Table II). This is ca. fivefold faster than the singlet of the corresponding analogue **25** where methyl replaces cyano. Note eq 11 and 13. Here the different regioselectivity in the



two cases compared does not detract from the comparison since it is the bridging step to give cyclopropyldicarbonyl diradical which is believed¹⁵ to be rate limiting. Hence, there is a real but not dramatic enhancement by terminal cyano substitution. This is in accord with our previous finding wherein electron-withdrawing groups stabilize the diradical which has electron-rich carbonyl centers.³ Interestingly, similar rates were obtained for the *cis*- and *trans*-monocyanodienes **33c** and **33t** (Table II).

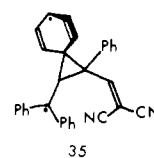
Another S_1 rate is that of aryl migration to afford phenyl migrated vinylcyclopropane **16** ($k_r = 6.5 \times 10^{10} \text{s}^{-1}$; note Table II). This is faster than the S_1 rate for phenyl migration ($1.9 \times 10^9 \text{s}^{-1}$) we have observed^{3b} for 1,1,3-triphenyl-3-methyl-1-butene (**34**) and the rate ($5.8 \times 10^9 \text{s}^{-1}$) encountered¹² for phenyl migration in 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (**25**). Again, we see that conjugating

groups on the methane carbon affect the di- π -methane rearrangement rate.



Solvent Effects on the Photochemistry of the 1,1-Dicyanodiene 3. The effect of solvent polarity on the photochemistry of the 1,1-dicyanodiene **3** can be summarized as leading to an inhibition of phenyl migration with increased solvent polarity (*tert*-butyl alcohol vs. benzene) and an increase in the ratio of dicyanovinylcyclopropane **17** to diphenylvinylcyclopropane **15**. This was depicted in Chart 11, eq 4, giving kinetic product distributions; further information is to be found in Table I. Thus, the results indicate that the ratio of the two types of π - π bridging as well as the regioselectivity of cyclopropyldicarbonyl diradical opening (note species **31** in eq 13) are affected by solvent polarity.

This suggests that the two possible 1,4-diradicals, that formed by vinyl-vinyl bridging (i.e. **31**) and that formed by phenyl-vinyl bridging (i.e., **35**), are polarized to different ex-



tents. It can be seen that the diradical **35** formed by phenyl-vinyl bridging has no diradical valence at the cyano-substituted center and that cyano plays no role in contributing to polarization. In contrast, the diradical **31** formed in vinyl-vinyl bridging has cyano substitution at a diradical center. We have shown in earlier work^{3a,b} that this center is electron rich even in the absence of cyano substitution. Thus, formation of this species with cyano substitution on the diradical center (as in **31**) is favored in polar solvent.

The regioselectivity of the three-ring opening reaction and the role of polarity of the system is discussed in connection with multiplicity effects and in relation to our theoretical calculations.

Theoretical Considerations. In order to understand the electronic factors controlling the photochemistry, we performed SCF-CI calculations on the basic di- π -methane system bearing one vinyl and one cyanovinyl group. The method considered only those basis orbitals involved in the rearrangement and has been described by us in detail in previous studies.^{3a,b} The transformation of the truncated set of orbitals is shown in Figure 1. This leads the diene **36** to the 1,4-diradical **37** and thence to the two possible 1,3-diradicals **38** and **39**.

The first observation deriving from the calculations is that the cyclopropyldicarbonyl diradical **37** is electron rich at the carbonyl carbons; this has been noted in several other systems^{3,11c} we have studied. Similarly, the methane carbon (i.e., carbon 3) is again found to be electron deficient. Note Table III.

The most interesting and useful aspect of the calculations is in understanding the control of regioselectivity by multiplicity. Thus, Table IV gives the energies of the singlet and triplet diradicals, and the energy differences between these two. The two alternative 1,3-diradicals are of special interest. It is seen that the lower energy 1,3-diradical of singlet multiplicity is the one in which cyano is substituted on one of the two diradical centers. Conversely, the more stable diradical of triplet multiplicity is the one in which the cyano moiety is on the developing vinyl group. Additionally, these energy differences for the two pathways, as a function of multiplicity, were calculated by interpolation between the 1,4-diradical **37** and the

Table III. Electron Densities at Selected Atoms in the S_1 Cyclopropyldicarbonyl Diradical **37**

atom	orbital ^a	single-orbital electron density	one-center two-orbital electron density
carbinyl	1	1.0261	
with cyano	9	0.9510	1.9771
cyano carbon	13	0.8542	
cyano nitrogen	14	1.1921	2.0463 ^b
unsubstituted carbinyl	4	1.0520	
	12	0.9845	2.0365
methane carbon	5	1.2109	
	7	0.7416	1.9525

^a See Figure 1, structure **37**, for the basis set of atomic orbitals.^b Total electron density in the cyano group.

1,3-diradicals **38** and **39**. The absolute energies obtained by interpolation techniques probably are too high; however, the energy differences seem likely to be reasonably valid. These are included in Table IV.

Rather than calculating the differences in energy for the two pathways for each multiplicity species, it is interesting to derive the singlet-triplet splittings for the two regioisomeric modes of reaction. This is also included in Table IV.

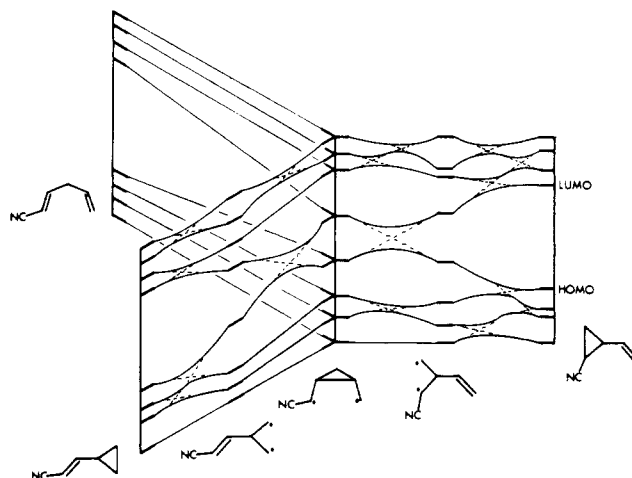
There is one final aspect of the calculations to be mentioned. This is an approach of the S_0 , S_1 , S_2 , and T_1 surfaces calculated for the regioisomeric path in which the cyano group remains on a diradical center; the near-crossing occurs approximately 70% of the way from 1,4- to 1,3-diradical. This state approach corresponds to a near-crossing at the MO level which occurs for both regioisomeric pathways. The MO crossing situation is shown in Figure 2. The situation is that calculated previously¹³ with a somewhat smaller basis set of orbitals. The present situation is that this crossing is avoided but can be detected most easily by noting correspondence in MO's before and after the crossing wherein HOMO becomes LUMO and vice versa. It can be seen that S_1 of each reactant does lead to S_0 of each product if one assumes that each crossing provides a means of state interconversion. For T_1 the same is true but intersystem crossing is also required.

Regioselectivity Control by Multiplicity. Reactivity Control by the Exchange Integral. One of the most dramatic observations is the multiplicity dependence of the regioselectivity of the di- π -methane rearrangement. This can be viewed as multiplicity control of the direction of opening of the cyclopropyldicarbonyl diradical **31**.

Preferential formation of the vinylcyclopropane isomer having the electron-withdrawing group on the cyclopropane ring is the normal reaction course from S_1 . Thus, di- π -methane systems having cyano or *p*-cyanophenyl groups on a π -bond generally^{3a,9,11c,30,31} afford the product having this moiety on the three ring. This follows the generalization we proposed for unsymmetrical di- π -methane systems bearing electron donors or acceptors.^{3a,c}

However, in the system presently studied, direct irradiation afforded both regioisomeric vinylcyclopropane products **15** and **17**. Either this example is a total anomaly in view of the large number of completely regioselective known examples, or another factor is involved. It does seem that the latter is the case and that intersystem crossing of the singlet of the reacting 1,1-dicyanodiene **3** is competing effectively with the rate of S_1 rearrangement.

This rationale is consistent with the observation that the triplet, generated by sensitization, does indeed rearrange with high efficiency to give the regioisomeric product **17** having the

**Figure 2.** MO correlation diagram for regioisomeric di- π -methane routes.**Table IV.** State Energies for Selected Species along the Di- π -methane Reaction Coordinate: SCF-CI Values

species	E_{S_1} (eV)	E_{T_1} (eV)	$E_{S_1} - E_{T_1}$
1,4-diene 36	-267.69	-269.61	1.92
cyclopropyldicarbonyl diradical 37	-267.50	-269.76	2.26
1,3-diradical 38	-259.97	-263.44	3.47
1,3-diradical 39	-260.60	-262.98	2.38
55% opened diradical (37 → 38) ^a	-257.27	-258.48	1.21
70% opened diradical (37 → 39) ^b	-257.67	-257.70	0.03
70% opened diradical (37 → 38) ^c	-257.40	-257.52	0.13
55% opened diradical (37 → 39) ^d	-257.60	-258.36	0.76

^a These energies arise from an interpolation between species **37** and **38**. The interpolation represents a species near the crossing point and is 55% along the reaction coordinate between **37** and **38**. ^b An interpolation 70% along the reaction coordinate between **37** and **39**. This is also near the crossing point. ^c An interpolation 7% along the reaction coordinate between **37** and **38**. ^d An interpolation 55% along the reaction coordinate between **37** and **39**.

electron-withdrawing group (i.e., cyano) on the residual π bond. The failure to quench the triplet selectively seems ascribable to an exceedingly rapid rate of triplet rearrangement which competes effectively with the rate of triplet quenching. Actually, the margin of effectiveness of triplet quenching vs. singlet quenching is sometimes only a factor of ten greater,³² with the result that it is difficult to quench a hydrocarbon triplet without some singlet quenching.

The multiplicity dependent regioselectivity of the reaction of the 1,1-dicyanodiene **3**, determined in the opening of cyclopropyldicarbonyl diradical **31**, is depicted in eq 14.

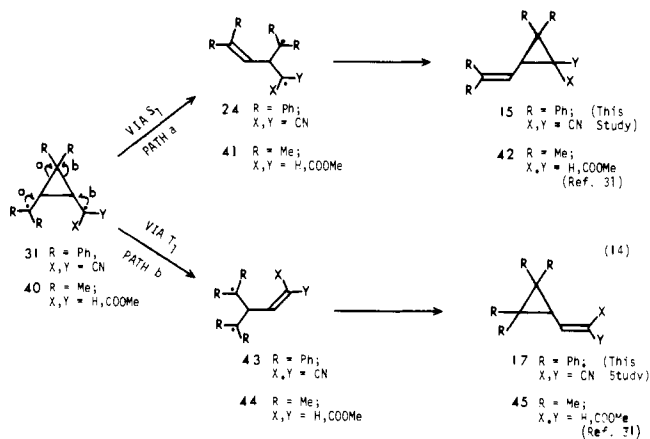
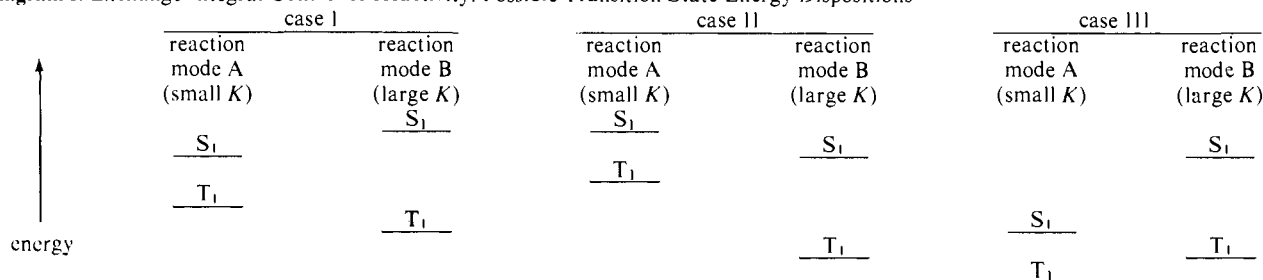


Diagram I. Exchange Integral Control of Reactivity: Possible Transition State Energy Dispositions



Unfortunately, in most of the cases studied with electron-withdrawing groups on one vinyl moiety, the triplet has been unreactive due to a free-rotor decay and only the concordance of the singlet reactivity with the above scheme can be assured.

In one example, however, Baeckstrom³¹ has reported a multiplicity dependence of the di- π -methane rearrangement. Again, the singlet followed the pattern in which an electronegative group, here carbomethoxyl, appeared on the three-ring of product of the singlet process. The triplet led, instead, to product with carbomethoxy on the product π bond. This example is included in eq 14.

The observations of eq 14 can be summarized energetically as in Diagram I, case I. It can be seen in Diagram I, case I, that on energetic grounds, reaction mode A is favored for the singlet reaction, while reaction mode B is favored for the triplet. Modes A and B, in principle, might be any two kinds of reactivity but apply presently to the two regioisomeric modes (i.e., paths a and b) of opening of cyclopropyldicarbinyl diradicals. Mode A, where the singlet is preferred, involves generation of a diradical center bearing an electron-withdrawing group, while mode B, where the triplet is preferred, has the electron-withdrawing group remaining on the developing π bond.

The basic energetic difference between mode A and mode B is reflected in the singlet-triplet splitting. Often in diradicals the S_1 and T_1 states are weighted very heavily in one (HOMO \rightarrow LUMO) configuration. In such a case the singlet-triplet splitting is simply given by twice a single exchange integral (i.e., $2K$). One can treat the quantity K empirically, or instead explicitly recognize it as the exchange integral $G_{kl/lk}$ where k and l are the HOMO and LUMO.³³ The reaction mode having the electron-withdrawing group on a diradical center tends to have the smaller K . Small K reactions are preferred by the singlet, while large K reactions are preferred by the triplet.

Of course such multiplicity control by the exchange integral K as shown in Diagram I, case I, depends on placement of the centers of gravity of the excited states for the two potential reaction pathways (i.e., modes A and B) such that the energy levels for mode A are bracketed by those of mode B. With placement as in Diagram I, case II, both singlet and triplet would select reaction mode B, while with placement as in Diagram I, case III, both states would react by mode A.

Placement of energy levels as in case I depends on the two possible reaction pathways (i.e., modes A and B) having similar energetics except for differing singlet-triplet splittings. Extraneous energetic effects might derive from strikingly different steric requirements for the two potential pathways (A and B), electrostatic effects favoring one pathway over the other, or very unfavorable electron delocalization for one pathway. Hence, control by singlet-triplet splitting (i.e., the exchange effect) can be expected to occur in cases where two possible pathways are quite similar energetically except for interaction of the two odd electrons.

Analysis and Generalization of Reaction Multiplicity Control by the Exchange Integral K . It would be exceptionally useful to ascertain if there is a way to predict the magnitude of K by qualitative means and to determine what factors influence this

integral. A starting point is found in our calculations for the regioisomeric openings of the cyclopropyldicarbinyl diradical **37**. We can then attempt to explore the generality of the factors involved. Inspection of Table IV shows a much larger (3.47 eV) S_1 - T_1 splitting ($2K$) for the reaction mode having the cyano group on the developing π bond than for the mode (2.38 eV) with a cyano group on a diradical center in the diradicals **38** and **39**.

These numbers derive from computer calculation, and we need to dissect the source of the S_1 - T_1 splitting differences for general understanding. We assume zero differential overlap for simplicity. The singlet-triplet splitting for a single configuration is given by $2K$ and eq 15a, where H and L refer to HOMO and LUMO

$$K = \sum_{rs} C_{rH} C_{rL} C_{sH} C_{sL} \gamma_{rs} \quad (15a)$$

or in equivalent matrix notation as in eq 15b. For simplicity

$$K = [(C_{1H}C_{1L})(C_{2H}C_{2L})(C_{3H}C_{3L})(C_{4H}C_{4L})] \times \begin{bmatrix} \gamma_{11} & \gamma_{12} & \gamma_{13} & \gamma_{14} \\ \gamma_{21} & \gamma_{22} & \gamma_{23} & \gamma_{24} \\ \gamma_{31} & \gamma_{32} & \gamma_{33} & \gamma_{34} \\ \gamma_{41} & \gamma_{42} & \gamma_{43} & \gamma_{44} \end{bmatrix} \begin{bmatrix} (C_{1H}C_{1L}) \\ (C_{2H}C_{2L}) \\ (C_{3H}C_{3L}) \\ (C_{4H}C_{4L}) \end{bmatrix} \quad (15b)$$

$$\begin{matrix} C_{1H}C_{1L} & C_{2H}C_{2L} & C_{3H}C_{3L} & C_{4H}C_{4L} \\ C_{1H}C_{1L} & \begin{bmatrix} a & b & c & (d) \\ b & a & b & c \\ c & b & a & b \\ (d) & c & b & a \end{bmatrix} & & \end{matrix} \quad (15c)$$

mnemonic: each column and row is multiplied by its heading and the result is summed

we use a four center case as an example. Thus, K is given by the triple vector-matrix-vector product $\tilde{\omega} \Gamma \omega$. Each of the ω vectors has as its elements the product of two Hückel or SCF coefficients weighting one atomic (basis) orbital; one coefficient is for HOMO and the other for LUMO. The Γ matrix is composed of atomic orbital repulsion integrals (i.e., the γ 's). The diagonal elements (i.e., γ_{11} , γ_{22} , γ_{33} , etc.) represent the mutual repulsion between two electrons in one basis orbital. The off-diagonal elements (i.e., γ_{12} , γ_{23} , etc.) give the repulsion between two electrons, one in each of two atomic orbitals. Since the diagonal elements are all equal for carbon 2p orbitals, we can simply designate these one-center integrals by a 's. For adjacent interactions, we can designate the integrals by b 's. More distantly related orbitals interact with repulsion integrals designated as c (for γ_{13} , γ_{24} , etc.), d , etc. The a 's are taken as 10.53 eV, the b 's as 7.1 eV for parallel vicinal p orbitals.

Premultiplication by the $\tilde{\omega}$ vector is equivalent to multiplying each row of the Γ matrix by the corresponding vector element. Postmultiplication by the vector is equivalent to multiplying the columns of the Γ matrix by the succeeding elements of the ω vector. The result is added to give a final value of K . This is indicated as a simple mnemonic in expression 15c.

All the diagonal a elements are seen to be weighted with squares of two coefficients, one deriving from HOMO and one from LUMO at center r (i.e., $C_{rH}^2 C_{rL}^2 a$); we note that these weightings are positive. All of the off-diagonal elements b are weighted by a product of pairs of one-center HOMO-LUMO coefficients (i.e., $(C_{rH} C_{rL})(C_{sH} C_{sL})$) for atoms r and s . The preceding can be seen in the mnemonic in expression 15c. Where orbitals r and s are adjacent, 1,4-related, 1,6-related, etc., these products tend to be negative as will be the case for strictly alternant systems.

In comparing potential reaction pathways, we need to consider both how the repulsion integrals (i.e., a , b , etc.) compare for the different alternatives and, additionally, how their weightings differ.

Relative to weightings, geometry affects both the weightings of a and weightings of b . Electronegative substituents primarily affect the weightings of a terms.

In the case of the magnitude of the integrals, twisting of parallel adjacent p orbitals diminishes the value of b . Juxtaposition of distant centers introduces a new b term into the 1,4 and 4,1 matrix elements.

It can be seen that, where HOMO and LUMO are heavily weighted at the same sites, a large positive weighting of a and a large K will result. The a element in the \mathbf{T} matrix is multiplied by a large vector element (eq 15c). Where a very polar substituent is present, HOMO and LUMO will be very heavily weighted at different centers and the product of HOMO and LUMO coefficients will be small with a resulting small weighting of a and thus K .

In the present example of the di- π -methane rearrangement, where cyano is not on the diradical centers the only two orbitals weighted appreciably in HOMO and LUMO are the diradical center orbitals 4 and 5, and the weightings are similar. Thus the weightings in HOMO and LUMO do match. This is seen in Figure 3 (cf. 46 and 47) where a large K is accounted for qualitatively. Conversely, with cyano on a diradical center, the HOMO and LUMO weightings are still mainly at the diradical centers but, whereas orbital 4 is more heavily weighted in HOMO, orbital 5 is more heavily weighted in LUMO. This mismatch leads to a smaller K as is seen in Figure 3 (cf. 48 and 49).

The same approach accounts for multiplicity dependent reactions in general. For example, one can consider the behavior of butadiene singlets and triplets. The singlet generally affords cyclobutenes,³⁴ while the triplet undergoes twisting of the terminal π bond,³⁵ which is really an example of the free-rotor effect,¹¹ as well as dimerization. For simplicity, let us consider electrocyclic closure vs. terminal twisting as a function of multiplicity.

The electrocyclic closure is Hückel cyclobutadienoid³⁶ with a preference for disrotatory closure. Figure 3 gives the HOMO and LUMO coefficients for a square array of four orbitals (cf. 50 and 51). The calculated K is shown. Also included is the situation where terminal double bond twisting is proceeding. Here, a larger K is derived. The smaller K reaction (electrocyclic closure) correlates with a preference for singlet reactivity, while the larger K reaction (free rotor twisting) correlates with triplet reactivity (cf. 52 and 53). Finally, we note that the linear combinations for the MO's under discussion were selected as most closely conforming to the MO's of their precursors.

In pericyclic reactions in general, there tends to be a spreading out of the wavefunction in the transition state with the result of decreased weighting of the contribution of the one-center integrals (i.e. the a 's). Also, in pericyclic examples new b interactions are introduced and these are negatively weighted. The net result is a low K for pericyclic reactions.

More generally, treatment of electrocyclic processes vs. diradical processes where a bond is weakened by twisting or

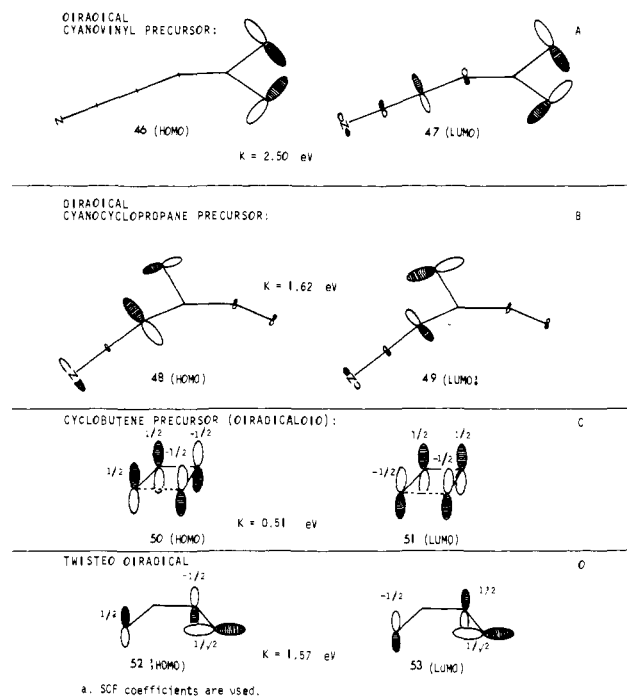


Figure 3. (A, B) HOMO and LUMO for the di- π -methane rearrangement; (C) cyclobutadiene electrocyclic closure; (D) butadiene twisting.

stretching reveals that the electrocyclic processes have smaller K values and prefer the singlet, while the diradical processes have larger K values and occur from the triplet. The preference for compact transition states in S_1 reactions contrasted with the preference for extended geometries for T_1 reactions has been noted earlier by us,³⁷ by Michl,³⁸ and in somewhat related form by Fukui.³⁹

The Bicycle Process and Reverse Di- π -methane Reaction. In our previous studies of the bicycle reaction,^{1,3} a correlation diagram of the type shown in Figure 2 was derived. Presently we have used the structures of the current study. Our present study reveals that, in the bicycling process, only part of the vinylcyclopropane reactant **17** succeeds in reaching vinylcyclopropane product **15**. Part of the reactant is converted to divinylmethane **3**. As we have noted earlier,^{40a} ground-state cyclopropyldicarbonyl diradicals, such as **37**, undergo 1,4-diradical 2,3-fragmentation^{40b} to afford divinylmethanes in contrast to the excited diradicals which lead to vinylcyclopropanes. Hence, the present experimental observations can be interpreted as signifying that during the bicycling process some of the reacting excited singlets internally convert to S_0 of the cyclopropyldicarbonyl diradical and thus form divinylmethane in a formal reversal of the di- π -methane rearrangement. The internal conversion (i.e., $S_1 \rightarrow S_0$) is facilitated by the near-crossing of HOMO and LUMO as seen in Figure 2.

The present example is the first acyclic bicycle reaction observed for a hydrocarbon and the first involving conversion of a simple vinylcyclopropane into an isomeric vinylcyclopropane; previously encountered examples^{1,3} possess additional conjugation. In one case a reverse di- π -methane rearrangement has been observed¹² but no bicycle reaction was encountered. In the present instance it appears that substitution by the electronegative cyano group inhibits internal conversion of S_1 .

Conclusion

The present investigation has revealed the intricate relationship between the di- π -methane rearrangement and the bicycle process; and it has shown the subtle nature of the fac-

tors controlling the di- π -methane rearrangement. It has also emphasized the important role of singlet-triplet splitting in multiplicity control of photochemical processes.

Experimental Section⁴¹

1,1-Dicyano-3,3-diphenyl-1-propene and 1,1-Dicyano-3,3-diphenyl-3-propene. To a solution of 5.89 g (30.0 mmol) of diphenylacetaldehyde in 60 mL of dry dimethylformamide (from BaO) and 90 mL of dry ethylene glycol (stirred over MgSO₄, filtered, and distilled at reduced pressure) were added 2.97 g (37.5 mmol) of malononitrile and 2 g of potassium fluoride. The dark orange reaction mixture was stirred under nitrogen for 1 h and then poured into 1 L of water and ether extracted. The extract was dried over magnesium sulfate and the solvent removed in vacuo. The dark residue was chromatographed on a 4.5 × 47.5 cm silica gel (Matheson, Coleman and Bell, grade 62, 60–200 mesh) column and eluted with 5% ether in hexane. The first UV active⁴¹ band was collected and the red orange oil obtained was crystallized from chloroform and hexane to yield 4.1 g (56%) of a mixture of 1,1-dicyano-3,3-diphenyl-1-propene and 1,1-dicyano-3,3-diphenyl-3-propene as heavy yellow needles, mp 109–112 °C. An analytical sample of 1,1-dicyano-3,3-diphenyl-1-propene was prepared by recrystallizing three times from 95% ethanol to give colorless plates, mp 107.5–113 °C, which turned light violet after 24 h.

The spectral data were: NMR (CDCl₃) τ 2.34 (d, 0.77 H, dicyanovinyl proton, $J = 11$ Hz), 2.44–2.92 (m, 10 H, arom), 3.96 (d, 0.23 H, Ph₂C=CH-, $J = 9$ Hz), 4.68 (d, 0.77 H, Ph₂CH-, $J = 11$ Hz), 5.53 (d, 0.23 H, (NC)₂CH-, $J = 9$ Hz); IR (KBr, for the 1-propene isomer) 3.28, 3.31, 3.42, 4.47 (C≡N), 6.21, 6.26, 6.68, 6.88, 7.58, 7.69, 9.36, 9.71, 10.00, 10.36, 10.87, 10.99, 11.93, 12.09, 13.50 (s), and 14.39 (s) μ ; MS m/e 244.0996 (calcd for C₁₇H₁₂N₂, m/e 244.10005).

Anal. Calcd for C₁₇H₁₂N₂: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.32; H, 5.10; N, 11.36.

3,3-Dicyano-1,1,5,5-tetraphenyl-1-penten-4-one. The conjugate base of the 1,1-dicyano-3,3-diphenylpropenes (1.22 g, 5.0 mmol) was prepared by reaction with potassium *tert*-butoxide in 25 mL of anhydrous dimethoxyethane at 0 °C; formation of the anion was complete after 15 min. Diphenylacetyl chloride^{42a} (1.33 g, 5.75 mmol) was added in a single portion as a solid and the mixture stirred for 0.5 h at 0 °C, then poured into saturated aqueous ammonium chloride, and extracted with chloroform. The extract was dried over MgSO₄ and concentrated in vacuo. The residual dark red oil was triturated with ether, filtered, and recrystallized from chloroform and hexane to give 1.05 g (48%) of the 3,3-dicyano-1,1,5,5-tetraphenyl-1-penten-4-one as yellow orange cubes, mp 160–164 °C. An analytical sample was prepared by recrystallizing once from dichloromethane and hexane and twice from ether and dichloromethane, colorless cubes, mp 165–168.5 °C.

The spectral data were: NMR (CDCl₃) τ 2.60–3.28 (m, 20 H, arom), 4.28 and 4.36 (two s, 2 H, vinyl and benzhydryl protons); IR (KBr) 3.23, 3.26, 3.31, 3.33, 3.42, 4.45 (w, C≡N), 5.69 (s, C=O), 6.10, 6.26, 6.68, 6.89, 6.92, 7.30, 7.43, 7.66, 7.84, 7.95, 8.62, 8.95, 9.16, 9.29, 9.68, 9.89, 10.02, 10.64, 10.86, 11.00, 11.24, 11.86, 12.95 (s), 13.62 (s), and 14.39 (s) μ ; MS m/e 438.1722 (calcd for C₃₁H₂₂N₂O, m/e 438.17321).

Anal. Calcd for C₃₁H₂₂N₂O: C, 84.91; H, 5.06; N, 6.39. Found: C, 84.77; H, 5.18; N, 6.37.

3,3-Dicyano-1,1,5,5-tetraphenylpentane from 1,5-Dibromo-3,3-dicyano-1,5-diphenylpentane. A mechanically stirred slurry of aluminum chloride (12 g, 90 mmol) in 600 mL of dry benzene (from calcium hydride) was cooled to 6 °C with an ice-salt bath. To this was added 9.39 g (21.7 mmol) of 1,5-dibromo-3,3-dicyano-1,5-diphenylpentane^{42b} in 0.5-g portions as a loose powder over a 15-min period. The resulting mixture was stirred for 0.5 h and at the end of this time 100 mL of concentrated hydrochloric acid was added at a rate such that the temperature did not rise above 8 °C. At this point, 100 mL of water was added and then the entire reaction mixture poured into 500 mL of 6 N hydrochloric acid and ether extracted. The extract was washed twice with saturated aqueous sodium carbonate, once with saturated aqueous sodium chloride, dried over magnesium sulfate and the solvent removed in vacuo. The 3,3-dicyano-1,1,5,5-tetraphenylpentane was thus obtained as a colorless oil which was triturated with ether to yield 7.83 g (84.5%) of a white amorphous powder, mp 132–134 °C. An analytical sample was prepared by recrystallization from ether, mp 134–135 °C.

The spectral data were: NMR (CDCl₃) τ 2.70 (s, 10 H, arom), 5.63 (t, 1 H, Ph₂CH-, $J = 7$ Hz), 7.34 (d, 2 H, Ph₂CHCH₂-, $J = 7$ Hz); IR (KBr) 3.23, 3.27, 3.30, 3.33, 3.26, 3.45, 3.48, 4.44 (w, C≡N), 5.09, 5.29, 5.51, 6.25, 6.31, 6.68 (s), 6.86 (s), 6.90 (s), 6.94 (s), 7.35, 7.74, 7.92, 8.21, 8.35, 8.47, 8.66, 9.28, 9.41, 9.69, 9.98, 10.11, 10.22, 10.76, 10.93, 11.11, 11.76, 11.90, 12.63, 13.11 (s), 13.30 (s), 13.46 (s), 14.25 (vs), 15.13, and 16.08 μ ; MS m/e 426.20975 (calcd for C₃₁H₂₆N₂, m/e 426.20960).

Anal. Calcd for C₃₁H₂₆N₂: C, 87.29; H, 6.14. Found: C, 87.23; H, 6.26.

Preparation of 1,1,2,2-Tetrakis(2,2-diphenylvinyl)ethane by Oxidative Coupling of Lithium 1,1,5,5-Tetraphenylpentadienide. Lithium 1,1,5,5-tetraphenylpentadienide (20.0 mmol) was prepared by the addition of 13.3 mL (1.5 M in hexane, 20.0 mmol) of *n*-butyllithium to a solution of 1,1,5,5-tetraphenyl-1,4-pentadiene⁴³ (7.44 g, 20.0 mmol) in 150 mL of anhydrous ether. The deep red slurry of the anion (vide supra) was transferred via canula over 0.5 h to a well stirred solution of cyanogen bromide in 100 mL of anhydrous ether. After stirring 15 min the mixture was poured into 500 mL of saturated aqueous ammonium chloride and the ether layer separated. The aqueous layer was extracted once with ether and the combined organic phases were dried over magnesium sulfate. After solvent removal in vacuo, the remaining oil was triturated with ether and filtered to yield 4.56 g (57.4%) of the 1,1,2,2-tetrakis(2,2-diphenylvinyl)ethane as an amorphous colorless powder. An analytical sample was prepared by recrystallization from ether, mp 169–171 °C (with slight decomposition).

The spectral data were: NMR (CDCl₃) τ 2.6–3.4 (m, 20 H, arom), 3.95 (d, 2 H, vinyl, $J = 10$ Hz), 6.50 (t, 1 H, methine, $J = 10$ Hz); IR (KBr) 3.23, 3.25, 3.27, 3.31, 3.36, 3.42, 5.12, 5.29, 5.53, 5.71, 5.97, 6.25, 6.68, 6.91, 7.30, 8.47, 8.66, 9.32, 9.71, 10.00, 10.18, 10.34, 10.78, 11.09, 11.33, 11.88, 13.09, 13.46, 13.66, 13.91, 14.39, 14.99, and 15.75 μ ; MS m/e 371.1803 (calcd for C₂₉H₂₃, m/e 371.1800).

Anal. Calcd for C₂₉H₂₃: C, 93.76; H, 6.24. Found: C, 93.25; H, 6.38.

This compound was reported^{43b} to have been made by oxidation of 1,1,5,5-tetraphenyl-1,4-pentadiene with potassium permanganate in acetone (lit.^{43b} mp 169–171.5 °C, with decomposition). Material prepared in this fashion had mp 169–171 °C and gave an undepressed melting point. The spectral properties were identical with those of 1,1,2,2-tetrakis(2,2-diphenylvinyl)ethane prepared by oxidative coupling of lithium 1,1,5,5-tetraphenylpentadienide with cyanogen bromide.

Phenyl Cyanate. The method of Grigat and Putter⁴⁴ was generally followed except that cyanogen bromide was used in place of cyanogen chloride.

Phenyl cyanate, 43.65 g (91%, lit.⁴⁴ 94% using cyanogen chloride), was prepared from 45.0 g (42.4 mmol) of cyanogen bromide, 38.0 g (40.4 mmol) of phenol, and 40.9 g (56.2 mL, 40.4 mmol) of anhydrous triethylamine in 100 mL of acetone. The product was distilled at 72–75 °C, 7 Torr (lit.⁴⁴ 82–83 °C, 16 Torr), into a receiver cooled to –78 °C. This material should be prepared shortly before use as it readily trimerizes to triphenyl cyanurate even during storage at –15 °C.

3-Cyano-1,1,5,5-tetraphenyl-1,4-pentadiene. In 400 mL of anhydrous ether, the conjugate base of 1,1,5,5-tetraphenyl-1,4-pentadiene (18.6 g, 0.05 mol) was prepared by the dropwise addition of 50.0 mmol (1.5 M in hexane, 33.3 mL) of *n*-butyllithium over a period of 15 min. The slurry of the anion was transferred under nitrogen via canula to a mechanically stirred solution of 17.86 g (14.4 mL, 0.15 mol) of phenyl cyanate in 400 mL of anhydrous ether; the addition required 1 h. The reaction mixture was then poured into 1 L of water and the organic phase separated. The aqueous layer was treated with a cold 15% solution of calcium hypochlorite to destroy any residual phenyl cyanate present. The ether layer was dried over magnesium sulfate and the solvent removed in vacuo. The residue was chromatographed on a 4.5 × 50 cm silica gel (Matheson, Coleman and Bell, grade 62, 60–200 mesh) column. Unreacted starting diene and phenyl cyanate eluted together in a single band with 5% ether in hexane. The 3-cyano-1,1,5,5-tetraphenylpentadiene eluted as the only other UV active band with 10% ether in hexane. After solvent removal, the product remained as a light yellow glassy oil (16.8 g, 84.6%).

The spectral data were: NMR (CCl₄) τ 2.6–3.2 (m, 20 H, arom), 4.00 (d, 2 H, vinyl, $J = 10$ Hz), 5.84 (t, 1 H, methine, $J = 10$ Hz); IR (CCl₄) 3.26, 3.28, 3.32, 3.43, 4.52 (C≡N), 5.15, 5.32, 5.53, 5.68, 5.95, 6.28, 6.37, 6.71 (s), 6.81, 6.93 (s), 7.35, 7.67, 7.81, 8.10, 8.42, 8.67, 9.36, 9.54, 9.77, 10.07, 10.31, 10.43, 10.86, 11.00, 11.17, 11.47, 11.75,

14.04 (s), 14.45 (vs), 15.92, and 16.31 μ ; MS *m/e* 397.18434 (calcd for C₃₀H₂₃N, *m/e* 397.18305).

3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene. The 3-cyano-1,1,5,5-tetraphenyl-1,4-pentadiene from above (16.8 g, 42.3 mmol) was dissolved in 200 mL of anhydrous tetrahydrofuran and added over 0.5 h to a mechanically stirred mixture of 1.02 g (42.3 mmol, 50% dispersion in mineral oil) of sodium hydride and a few crystals of phenol in 200 mL of anhydrous tetrahydrofuran. The dark red mixture was stirred for 1 h and then 5.04 g (4.10 mL, 42.3 mmol) of phenyl cyanate was added dropwise in 5 min. The reaction mixture was then poured into 1200 mL of saturated aqueous ammonium chloride and ether extracted. The extract was dried over magnesium sulfate, the solvent removed in vacuo, and the oily product chromatographed on a 4.5 \times 50 cm silica gel column. Excess phenyl cyanate eluted with 5% ether in hexane and the product 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene eluted as the only other UV active band with 15% chloroform in hexane. After solvent removal in vacuo, the oily residue was triturated with ether and filtered to give 14.1 g (79%) of a bright yellow powder. Recrystallization from dichloromethane and hexane gave 11.9 g (66.8%) of colorless prisms, mp 154–156 °C. An analytical sample was prepared by a single recrystallization from methylene chloride and hexane, mp 155–156 °C.

The spectral data were: NMR (CDCl₃) τ 2.4–3.0 (m, 20 H, arom), 4.00 (s, 2 H, vinyl); IR (KBr) 3.24, 3.27, 3.30, 4.47 (C \equiv N), 5.08, 5.28, 5.49, 5.78, 6.17, 6.21, 6.26, 6.35, 6.70, 7.30, 7.35, 7.83, 7.94, 8.44, 8.64, 9.29, 9.71, 9.99, 10.62, 10.70, 11.64, 12.02, 12.84, 13.04, 13.14, 13.33, 13.66, 14.01, 14.29 (s), 14.60, 15.43 and 16.08 μ ; UV (ether) λ_{\max} 261 (ϵ 24 240); MS *m/e* 422.17843 (calcd for C₃₁H₂₂N₂, *m/e* 422.17830).

Anal. Calcd for C₃₁H₂₂N₂: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.10; H, 5.28; N, 6.65.

3,3-Dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene. This material was prepared from 1,1,5,5-tetraphenyl-1,4-pentadiene-3-one. The dienone was prepared with slight modification of literature procedures.^{45,46} Propargyl alcohol was converted to propargyl bromide as described by Lauger and Prost.⁴⁵ This bromide was condensed with benzophenone using aluminum to give 4,4-diphenyl-1-butyn-4-ol and this was condensed with a second molecule of benzophenone using the method of Marin⁴⁶ but replacing potassium hydroxide with potassium *tert*-butoxide. The resultant 1,1,5,5-tetraphenyl-2-pentyne-1,5-diol was converted to the dienone with H₂SO₄ using the method of Marin.⁴⁶ The dienone (3.86 g, 10.0 mmol) was dissolved in 2 mL of methanol and 12 mL of benzene containing 6.4 mL (58 mmol) of trimethyl orthoformate and 50 mg of *p*-toluenesulfonic acid. The reaction mixture was heated to 50 °C for 6 h and then quenched with an excess of sodium methoxide in methanol. The residue left after concentration in vacuo was chromatographed on a 50 \times 4 cm slurry packed alumina (activity IV) column. Elution with 800 mL of 40% benzene-hexane gave 3.50 g (81%) of crystalline 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene, mp 140–141 °C. Elution with an additional 3 L of the same eluent gave 50 mg of unreacted starting material.

The spectral data for the dimethoxydiene were: NMR (C₆D₆) τ 2.84 (m, 20 H, arom), 4.00 (s, 2 H, vinyl), 6.84 (s, 6 H, OCH₃); IR (KBr) 3.27, 3.40, 3.54, 6.71, 6.95, 9.10, 9.60, 9.75, 10.30, 11.30, 13.20, 13.70 and 14.40 μ ; UV (cyclohexane) λ_{\max} 251 nm (ϵ 21 000); MS *m/e* 432.20913 (calcd for C₃₁H₂₈O₂, *m/e* 432.20893).

1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. A mixture of 2.10 g (5.61 mmol) of 2,2,4,4-tetraphenyl-3-butenal,¹² 400 mg (60.6 mmol) of malononitrile, 160 mg of β -alanine, and 3 mL of acetic acid in 85 mL of toluene was refluxed for 15 h. The water generated during the condensation was azeotropically removed by using a Dean Stark trap. The mixture was then cooled, diluted with ether, and washed with water. The organic layer was dried and concentrated in vacuo to give 2.25 g of the crude 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. Recrystallization from ethanol gave 1.96 g (83%) of colorless crystals, mp 174–175 °C.

The spectral data were: NMR (CDCl₃) τ 2.54 (s, 1 H, (NC)₂C=CH-), 2.76 (m, 20 H, arom), 3.24 (s, 1 H, Ph₂C=CH-); IR (KBr) 3.26, 2.38, 4.48, 6.25, 6.70, 6.95, 13.00, 13.30, 13.75 and 14.45 μ ; UV (cyclohexane) λ_{\max} 253 nm (ϵ 16 000); MS (70 eV) *m/e* (rel intensity) 345.164 (100), M – C₄H₂N₂ (calcd for C₂₇H₂₀N₂, *m/e* 345.164), 268 (11), 267 (38), 252 (6), 167 (14), 165 (14), 91 (7), 77 (1); the molecular ion was not observed, even at low ionization voltages.

Anal. Calcd for C₃₁H₂₂N₂: C, 88.15; H, 5.21. Found: C, 88.38; H,

5.49.

Exploratory Direct Photolysis of 3,3-Dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene. The photolysis was performed in the “Black Box”⁵ apparatus. The light was filtered using a triple compartment cell containing (a) 2 M nickel sulfate hexahydrate in 10% sulfuric acid, (b) 0.8 M cobalt sulfate heptahydrate in 10% sulfuric acid, and (c) 0.0002 M bismuth trichloride in 10% hydrochloric acid. This combination gave a transmission maximum (40%) at 283 nm and was opaque below 250 and above 310. A solution of 760 mg of 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene in 750 mL of *n*-pentane was degassed for 1 h with purified nitrogen⁴⁷ and then irradiated for 8.5 h. The pentane was removed in vacuo and the residual solid chromatographed on a 2.5 \times 72 cm slurry packed silica gel (Matheson, Coleman and Bell, grade 62, 60–200 mesh) column; 250-mL fractions were collected, fractions 1–10 were eluted with 3% ether in hexane, and fractions 11–15 were eluted with ether. Fractions 3–8 contained 367 mg of a mixture of 1,1,4,4-tetraphenyl-1,3-butadiene and 1,1-diphenyl-2,2-dimethoxy-3-(2,2-diphenylvinyl)cyclopropane, fractions 9–10 contained 45 mg of an unidentified material, and fractions 13–15 contained 338 mg of 1,1,5,5-tetraphenyl-1,4-pentadiene-3-one.

Fractions 3–8 were rechromatographed on a 2.5 \times 68 cm slurry packed alumina (activity II) column. Elution was with 4.5 L of hexane and 2.5 L of 5% ether in hexane; 250-mL fractions were collected. Fractions 4–16 contained 65 mg of 1,1,4,4-tetraphenyl-1,3-butadiene and fractions 20–26 contained 294 mg of the vinylcyclopropane, mp 133–134.5 °C.

The spectral data for the 1,1-dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane were: NMR (CCl₄) τ 2.9 (m, 20 H, arom), 4.62 (d, 1 H, vinyl), 6.60 (s, 3 H, OCH₃), 6.98 (s, 3 H, OCH₃), 7.18 (d, 1 H, cyclopropyl); IR (C₆H₆) 3.28, 3.30, 3.52, 6.25, 6.68, 6.90, 7.20, 7.39, 8.10, 8.84, 8.75, 8.93, 9.52, 9.58, 13.10, 13.30, 14.30 and 15.2 μ ; MS *m/e* 432.20893 (calcd for C₃₁H₂₈O₂, *m/e* 432.20954).

Exploratory Direct Photolysis of 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene. The photolysis was carried out on the “Black Box”⁵ apparatus with light filtered through a triple compartment cell containing (a) 2.0 M nickel sulfate, (b) 2.0 M cobalt sulfate, both in 5% sulfuric acid; and (c) 0.0002 M bismuth trichloride in 10% hydrochloric acid. This combination gave a maximum transmission at 272 nm (20%) and was opaque above 312 nm and below 240 nm. The light output was monitored using a digital actinometer^{14a} calibrated by ferrioxalate actinometry.^{14b} A solution of 502 mg (1.19 mmol) of the 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene in 5 mL of methylene chloride was prepared and to this was added 750 mL of anhydrous *tert*-butyl alcohol. This solution was purged with purified nitrogen⁴⁷ for 0.5 h and then photolyzed until 10.7 mEinsteins of light had been absorbed (ca. 7 h). The solvent was removed in vacuo and the residue chromatographed on a 3 \times 56.5 cm silica gel column. The column was eluted with 0.5% ether in hexane and 40-mL fractions were collected. Fractions 50–86 gave 140 mg of 5-cyano-1,1,5,5-tetraphenyl-1,3-pentadiene (the sole product formed when the starting diene is heated in *tert*-butyl alcohol), 185–255 gave 152 mg of starting diene, and 256–340 gave 201 mg of a 85:15 mixture of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and the starting diene respectively (mass balance 100%).

Fractions 256–340 were recrystallized from ethanol to yield 150 mg of the vinylcyclopropane as colorless plates, mp 182–184 °C. An analytical sample was prepared by recrystallization from ethanol, mp 185–186 °C.

The spectral data were: NMR (CDCl₃) τ 2.3–2.8 (m, 20 H, arom), 4.33 (d, 1 H, vinyl, *J* = 10 Hz), 6.47 (d, 1 H, cyclopropyl, *J* = 10 Hz); IR (KBr) 3.22, 3.24, 3.27, 3.30, 3.32, 4.46 (C \equiv N), 5.10, 5.29, 5.52, 5.75, 6.24, 6.67, 6.89, 7.46, 8.42, 8.63, 9.29, 9.72, 9.99, 10.28, 10.76, 11.10, 11.49, 12.84, 13.07, 13.35, 13.07, 13.35, 13.76, 14.29, and 15.80 μ ; UV (EtOH) λ_{\max} 267.5 nm (ϵ 19 100); MS *m/e* 422.17843 (calcd for C₃₁H₂₂N₂, *m/e* 422.17830).

Anal. Calcd for C₃₁H₂₂N₂: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.27; H, 5.20; N, 6.54.

Exploratory Sensitized Photolysis of 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene. The photolysis was carried out on the “Black Box”⁵ apparatus as described for the direct photolysis of this diene (vide supra) except that a filter solution combination of (a) 1.71 M nickel sulfate in 10% sulfuric acid, (b) 1.0 M cobalt sulfate in 10% sulfuric acid, and (c) 0.0133 M stannous chloride in concentrated hydrochloric acid was used. This combination gave maximum transmission at 324 nm (22%) and was opaque above 353 nm and below 305 nm. A solution of 506 mg (1.20 mmol) of 3,3-dicyano-1,1,5,5-

tetraphenyl-1,4-pentadiene in 30 mL of acetophenone and 720 mL of anhydrous *tert*-butyl alcohol was degassed for 45 min before and during photolysis with purified nitrogen⁴⁷ and then irradiated until 0.966 mEinsteins had been absorbed (ca. 53 min). The solvent was removed in vacuo and the residue chromatographed on a 3 × 56.5 cm silica gel column and 40-mL fractions were collected: Fractions 1–298, 0.5% ether in hexane; fractions 299–347, 5% ether in hexane. Fractions 190–260 gave 279 mg (0.66 mmol) of the starting diene and fractions 261–347 yielded 220 mg (0.520 mmol) of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (mass balance 98.5%).

The spectral and physical properties of the vinylcyclopropane obtained here were identical with those measured for material from the direct photolysis.

Exploratory Direct Photolysis of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. A solution of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (266 mg, 0.629 mmol) in 220 mL of benzene was purged 1 h with purified nitrogen⁴⁷ and irradiated through a Pyrex filter with a 450-W Hanovia medium pressure lamp for 44 min. At 4.0 and 16.0 min of irradiation, 10.0-mL aliquots were withdrawn via syringe.

Concentration of the photolysate in vacuo yielded 262 mg of light purple oil. The ¹H NMR (100 MHz) showed ca. 75% conversion to three photoproducts, 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15), 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane (16), and 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (17) in a ratio of 5:3:1. The aliquots taken at 4 and 16 min were concentrated and analyzed by 270-MHz FT NMR, giving product ratios (15:16:17) of 1:1.4:1.6 (4.0 min) and 1.5:1.5:1.0 (16.0 min). The crude photolysate was chromatographed on a silica gel column (1.8 × 92 cm) slurry packed in hexane and eluted in 100-mL fractions as follows: fractions 1–5, hexane, nil; 6–10, 1% ether in hexane, nil; 11–19, 2% ether in hexane, nil; 20–21, 2% ether in hexane, 53.4 mg of a mixture of dicyanovinylcyclopropane 17 and an unidentified impurity (not present in the crude photolysate); 22, 2% ether, 4.5 mg of overlap; 23–24, 2% ether, 30.3 mg of diene 3, nearly pure by ¹H NMR analysis; 25, 2% ether, 41.3 mg of overlap, ca. 1:1 diene 3:diphenylvinylcyclopropane 15 by NMR; 26–29, 2% ether, 85.4 mg of diphenylvinylcyclopropane 15, essentially pure by NMR analysis; 30–32, 10% ether in hexane, 28.3 mg of dicyanovinylcyclopropane 16. This compound was found to decompose slowly on silica gel, thus accounting for its poor isolated yield.

1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15) was recrystallized from ethanol, and proved identical with material described below for acetophenone sensitized experiments.

1,1,2,3-Tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane (16) was recrystallized from hexane, mp 161–162 °C. The spectral data were: ¹H NMR (CDCl₃) τ 2.4–3.0 (m, 21 H, arom and vinyl), 4.53 (s, 1 H, cyclopropyl); IR (KBr) 3.22, 3.28, 4.48 (C≡N), 6.30, 6.65, 6.90, 13.00, and 14.30 μ ; MS *m/e* 422.180 (calcd for C₃₁H₂₂N₂, *m/e* 422.178).

Anal. Calcd for C₃₁H₂₂N₂: C, 88.15; H, 5.21. Found: C, 88.20; H, 5.32.

Exploratory Sensitized Photolysis of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. A solution of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (500 mg, 1.18 mmol) and acetophenone (20.0 g) in 525 mL of benzene was purged 1 h with purified nitrogen⁴⁷ and irradiated for 10.0 min through a Pyrex filter with a 450-W Hanovia medium pressure lamp. Concentration of the light yellow solution at aspirator pressure and subsequent bulb-to-bulb distillation (0.01 Torr at 25 °C) to remove sensitizer afforded 544 mg of an off-white fine crystalline solid. The NMR showed essentially total conversion to 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (17). Recrystallization from ethanol gave 379 mg (75.8%) of colorless crystals of 17, mp 221–223 °C. Concentration of the mother liquors and chromatography of the residue on silica gel yielded an additional 69.3 mg of 17 (total 448 mg, 89.7%). Several recrystallizations from ethanol gave an analytical sample, mp 224–225 °C.

The spectral data for 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (17) were: ¹H NMR (CDCl₃) τ 2.32–3.02 (m, 21 H, arom and vinyl), 5.87 (d, 1 H, cyclopropyl, *J* = 6.0 Hz); IR (KBr) 3.25, 3.28, 4.40 (C≡N), 6.29, 6.65, 6.69, 8.85, 13.40, 13.65 and 14.30 μ ; UV (EtOH) λ_{\max} 225 (ϵ 23 500), 267 (10 200); MS *m/e* 422.1780 (calcd for C₃₁H₂₂N₂, 422.1780).

Anal. Calcd for C₃₁H₂₂N₂: C, 88.15; H, 5.21. Found: C, 87.95; H, 5.49.

Exploratory Direct Photolysis of 1,1-Dicyano-2,2-diphenyl-3-

(2,2-diphenylvinyl)cyclopropane. In the Hanovia apparatus, equipped with Pyrex filter, a solution of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane 15 (131 mg, 0.309 mmol) in 130 mL of benzene was degassed 1 h with nitrogen, and irradiated for 2.25 h. Concentration in vacuo of the clear light yellow solution yielded 145 mg of oily crystals. Careful analysis by ¹H NMR showed only resonances for starting material.

The crude product was chromatographed over silica gel to yield 123 mg (94.3%) of faintly yellow crystals, mp 178–180 °C, identical with starting material.

Exploratory Direct Photolysis of 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. A solution of 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (103.2 mg, 0.2443 mmol) in 125 mL of benzene was purged 1 h with purified nitrogen⁴⁷ and irradiated for 4.0 min through Pyrex. Concentration in vacuo afforded 108 mg of oily crystals. Analysis by ¹H NMR at 100 MHz showed a mixture of starting material, 1,1-dicyano-3,3,5,5-tetraphenyl-1,3-pentadiene (3) and 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15) in a ratio of ca. 1:1.2:1, along with a small amount of 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane.

The crude photolysate was chromatographed on a 1.8 × 90 cm silica gel column, slurry packed in hexane, and eluted as follows: fractions 1–3, 200 mL each, 2% ether in hexane, nil; fractions 4–5, 200 mL each, 3% ether in hexane, 34.7 mg of nearly pure dicyanovinylcyclopropane 17; fractions 6–9, 75 mL each, 3% ether in hexane, 63.7 mg of mixtures of 1,1-dicyanodiene 3 and diphenylvinylcyclopropane 15 (ratio ca. 1.3:1). The overall mass balance was 95%.

In other experiments, prolonged irradiation (20 min for a 70 mg sample) afforded mixtures containing predominantly diphenylvinylcyclopropane 15 along with a small amount of dicyanovinyl isomer 16.

Exploratory Direct Photolysis of 1,1,2,3-Tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane. A solution of 40 mg (0.095 mmol) of 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane in 120 mL of benzene was purged with purified nitrogen⁴⁷ for 1 h before and then during photolysis. The solution was irradiated through Pyrex by using a 450-W Hanovia medium pressure mercury lamp for 20 min. Solvent was removed in vacuo to yield 37 mg of photolysate whose NMR spectrum proved identical with that of starting material.

Exploratory Sensitized Photolysis of 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. A solution of 40 mg (0.095 mmol) of 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane and 5.0 g (0.040 mol) of acetophenone in 120 mL of benzene was purged with purified nitrogen⁴⁷ for 1 h before and then during photolysis. The solution was then irradiated through Pyrex for 20 min by using a 450-W Hanovia medium pressure mercury lamp. The solvent and sensitizer were then removed in vacuo to give 38 mg of material whose NMR showed only resonances ascribable to starting dicyanovinylcyclopropane.

3,3-Di-*p*-tolylacrolein. *N*-Methylformanilide (11.3 g, 83.4 mmol) was added dropwise to phosphorus oxychloride (25.6 g, 167 mmol), with mechanical stirring under a nitrogen atmosphere. After 90 min, 1,1-di-*p*-tolylethylene⁴⁸ (17.4 g, 83.4 mmol) in 45 mL of trichloroethylene was added dropwise, with the reaction temperature maintained below 20 °C. The deep red mixture was stirred overnight, poured into ice-water, neutralized with NaOH, and then steam distilled, with collection of ca. 0.6 L of distillate. The remaining two phase mixture was extracted three times with 250-mL portions of ether and the combined extracts were dried over magnesium sulfate and concentrated in vacuo. The residual oily solid was passed rapidly through a 2.6 × 28 cm slurry packed silica gel column. Elution with 0.7 L of 1:1 ether in hexane afforded 17.5 g of light yellow crystals, mp 82–84 °C. Recrystallization from hexane gave 14.9 g (75.7%), mp 85–85.5 °C.

The spectral data were: ¹H NMR (CDCl₃) τ 0.45 (d, 1 H, CHO, *J* = 4.0 Hz), 2.76 (m, 8 H, arom), 3.42 (d, 1 H, vinyl, *J* = 4.0 Hz), 7.55 (s, 3 H, CH₃), 7.61 (s, 3 H, CH₃); IR (CCl₄) 3.29, 3.53, 5.95 (s), 6.19, 6.26, 7.44, 8.42, 8.63, 8.86, and 9.78 μ ; UV (EtOH) λ_{\max} 312 nm (ϵ 19 960), 228 (15 700).

Anal. Calcd for C₁₇H₁₆O: C, 86.40; H, 6.83. Found: C, 86.62; H, 6.77.

1,1-Dicyano-4,4-di-*p*-tolyl-1,3-butadiene. To a stirring 0 °C solution under nitrogen of 3,3-di-*p*-tolylacrolein (5.00 g, 21.2 mmol) and malononitrile (1.43 g, 21.6 mmol) in 20 mL of dry dioxane was added dropwise 0.30 mL of piperidine. The mixture was allowed to warm to ambient temperature and stir overnight, with formation of a heavy precipitate. Dilution with ether (50 mL), filtration, and rinsing

Table V. Direct Quantum Yield Photolyses of 3,3-Dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene Yielding 1,1-Dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**) and 1,1,4,4-Tetraphenyl-1,3-butadiene

run	reactant, mmol	light absorbed, mEinstein	% conversion	photoproduct, mmol	Φ
1	0.057	0.0025	0.7	0.000355 ^a 0.000044 ^b	0.142 0.018
2	0.032	0.0031	1.4	0.000398 ^a 0.000052 ^b	0.129 0.019
3	0.031	0.0045	2.4	0.000670 ^a 0.000086 ^b	0.148 0.020
4	0.033	0.0096	4.1	0.00120 ^a 0.00016 ^b	0.125 0.017
5	0.032	0.0130	4.6	0.00125 ^a 0.00018 ^b	0.097 0.014
6	0.031	0.163	6.5	0.00176 ^a 0.00026 ^b	0.108 0.016

^a Photoproduct **14**. ^b 1,1,4,4-Tetraphenyl-1,3-butadiene.

with ether yielded 3.32 g of bright yellow crystals. Concentration of the filtrate and rinsing with ether gave an additional 2.41 g of product (total 5.73 g, 95.1%). One recrystallization from 95% ethanol afforded 5.01 g (83.3%) of bright yellow crystals, mp 157.5–158 °C.

The spectral data were: ¹H NMR (CDCl₃) τ 2.24–2.96 (m, 10 H, arom and vinyl), 7.56 (s, 3 H, CH₃), 7.62 (s, 3 H, CH₃); IR (CHCl₃) 4.48 (s, C≡N), 6.19, 6.35, 7.30, 7.51, 7.88, 8.33, 8.85, 9.80, 10.3, 10.4, 10.6, and 12.1 μ ; UV (EtOH) λ_{\max} 382 nm (ϵ 32 400), 245 (12 100); MS *m/e* 284.1314 (calcd for C₂₀H₁₆N₂, 284.1312).

Anal. Calcd for C₂₀H₁₆N₂: C, 84.47; H, 5.67. Found: C, 84.31; H, 5.83.

Control Experiment: Direct Photolysis of 1,1-Dicyano-4,4-di-*p*-tolyl-1,3-butadiene. A solution of 1,1-dicyano-4,4-di-*p*-tolyl-1,3-butadiene (256 mg, 0.899 mmol) in 245 mL of rigorously purified benzene was purged 1 h with purified nitrogen⁴⁷ and irradiated for 6.8 h in the Hanovia apparatus through a 2-mm Pyrex filter. Concentration of the clear yellow solution in vacuo gave 250 mg (98%) of bright yellow crystals, mp 157–158 °C, identical with starting material.

Control Experiment: Photolysis of a Mixture of 1,1-Dicyano-4,4-di-*p*-tolylbutadiene and 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. A solution of 1,1-dicyano-4,4-di-*p*-tolylbutadiene (102.3 mg, 0.360 mmol) and dicyanovinylcyclopropane **17** (74.6 mg, 0.177 mmol) in 245 mL of benzene was degassed 1 h with purified nitrogen and irradiated through a 2-mm Pyrex filter in the Hanovia apparatus for 90 min. Concentration in vacuo yielded 201 mg of light brown oily solid, which was applied to a 1.7 × 94 cm silica gel column, slurry packed in hexane. Elution was with 5% ether in hexane in 100-mL fractions as follows: fractions 1–3, nil; 4–6, 100 mg (98% recovery) of dicyano-di-*p*-tolylbutadiene **20**, identical with starting material; 7, 14.1 mg of light yellow crystals, nearly pure 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene, **3**; 8–11, 54.4 mg of white crystals, nearly pure 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane **15**, contaminated with ca. 10% diene **3**; 12–13, 50% ether in hexane, 7.8 mg of crystalline solid, identified as 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane (**16**).

The total mass balance was 177 mg (99.9%).

Characterization of 1,1-Dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane. In a sealed capillary tube, 15 mg (0.035 mmol) of 1,1-dimethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane was heated to 240 °C for 30 min. The yellow reaction mixture was dissolved in 2 mL of benzene and subjected to thick-layer chromatography on a 20 × 20 cm silicic acid plate, eluting with 30% benzene in hexane. Extraction with benzene and concentration in vacuo gave 6 mg of a white solid, mp 200–202 °C, whose NMR spectrum was identical with that of an authentic sample of 1,1,4,4-tetraphenyl-1,3-butadiene.

Characterization of 1,1,2,3-Tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane. A 97-mg (0.23 mmol) sample of 1,1,2,3-tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane was chromatographed on a 2 × 35 cm slurry packed alumina (Fisher, 80–200 mesh, activity III) column. Elution with 400 mL of 30% benzene in hexane gave 20 mg of an unidentified product; the next 150 mL gave 68 mg of a mixture of starting dicyanovinylcyclopropane and 1,2,2,3-tetraphenylcyclo-

propane-1-carboxaldehyde, 1:1 by NMR. This mixture was subjected to two elutions with a 9:1 mixture of benzene and hexane on a 20 × 20 cm thick plate of silica gel. The faster moving band (*R_f* 0.4 overall) gave 43 mg of 1,2,2,3-tetraphenylcyclopropane-1-carboxaldehyde, mp 156–157 °C, having NMR and IR spectra identical with those of authentic material.¹² The slower band (*R_f* 0.35 overall) was 28 mg of unreacted starting dicyanovinylcyclopropane.

Characterization of 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. A 135-mg (0.30 mmol) sample of 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane was eluted through a 2 × 45 cm slurry packed alumina (Fisher, 80–200 mesh, activity III) column with 40% benzene in hexane; 125-mL fractions were collected. Fraction 2 gave 53 mg of 2:3 mixture of starting dicyanovinylcyclopropane and 2,2,3,3-tetraphenylcyclopropane-1-carboxaldehyde. Fraction 3 gave 48 mg of a 1:1 mixture of the same compounds and fractions 4–5 contained 32 mg of the pure cyclopropanecarboxaldehyde.

Fractions 2–3 were recrystallized from ethanol and gave 60 mg of pure starting dicyanovinylcyclopropane; a second crop gave 32 mg of the pure 2,2,3,3-tetraphenylcyclopropane-1-carboxaldehyde, mp 206–208 °C, whose spectral data were identical with those of authentic material.¹²

Characterization of 1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane. A modification of the procedure reported by Brandon and Gardner⁴⁹ was used to prepare 1,1-dicyano-4,4-diphenyl-1,3-butadiene.⁵⁰ To a solution of 1.04 g (5.00 mmol) of 3,3-diphenylacrolein⁵¹ in 5 mL of dioxane was added 330 mg (5.00 mmol) of malononitrile and 0.05 mL of piperidine. The mixture was stirred for 20 h, then poured into 250 mL of water, and ether extracted. The extract was washed with 10% hydrochloric acid and saturated aqueous sodium bicarbonate, then dried over magnesium sulfate, and concentrated in vacuo. The solid residue was recrystallized once from dichloromethane and hexane and once from ethanol to yield 941 mg (73.5%) of yellow laminae, mp 115–115.5 °C (lit.⁵⁰ mp 112–113 °C). The spectral data were: NMR (CCl₄) τ 2.34–2.84 (m, arom and vinyl); IR (KBr) 4.48, 4.50, and 6.37 μ ; UV (EtOH) λ_{\max} 366 nm (ϵ 32 230), (hexane) λ_{\max} 356 nm (ϵ 34 500).

The butadiene from above (512 mg, 2.00 mmol) was placed in a 10-mL round-bottomed flask which was equipped for magnetic stirring and for flushing with nitrogen. Heating was applied and maintained at 125 °C. To the melt was added 776 mg (4.00 mmol) of diphenyldiazomethane dissolved in 0.6 mL of benzene over a 2-h period via syringe. After this period, heating was removed and the reaction mixture chromatographed on a 2.5 × 52 cm silica gel column; 200-mL fractions were collected: 1–43, 5% dichloromethane in hexane; 44–55, 1% ether in hexane. Fractions 1–5 gave 62.2 mg of an unidentified material, 36–43 gave 27.9 mg of benzophenone azine containing a small amount of the starting butadiene, 44–45 gave a 1:1 mixture of the azine and 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane, and 46–55 yielded 444 mg (52.7%) of the vinylcyclopropane. The spectral and physical properties of this material were identical with those obtained for the vinylcyclopropane prepared by direct or sensitized photolysis of 3,3-dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene.

Photolysis Equipment for Quantum Yield Determinations. All

Table VI. Direct Quantum Yield Photolyses of 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene Yielding 1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane, Photoproduct 15

run	reactant, mmol	light absorbed, mEinstein	% conversion	photoproduct 15, mmol	Φ
1	0.195	0.0302	1.3	0.00258	0.086
2	0.154	0.0521	2.3	0.00351	0.067
3	0.103	0.0688	3.5	0.00355	0.052
4	0.080	0.0813	4.8	0.00387	0.048

Table VII. Sensitized Quantum Yield Photolyses of 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene Yielding 1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane, Photoproduct 15

run	reactant, mmol	light absorbed, mEinstein	% conversion	photoproduct 15, mmol	Φ
1	0.239	0.00875	1.8	0.00433	0.495
2	0.242	0.0178	3.5	0.00839	0.472
3	0.234	0.0324	5.8	0.01355	0.419

Table VIII. Direct Quantum Yield Photolyses of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene Yielding 1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15), 1,1,2,3-Tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane (16), and 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (17)

run	reactant, mmol	solvent	light absorbed, mEinstein	% conversion	photoproduct, mmol	Φ
1	0.122	benzene	0.00755	1.0	0.00034 ^a	0.045
					0.00045 ^b	0.059
					0.00038 ^c	0.051
2	0.0914	benzene	0.0335	5.2	0.00143 ^a	0.0427
					0.00153 ^b	0.0525
					0.00176 ^c	0.0457
3	0.0561	benzene	0.0211	5.4	0.00086 ^a	0.0407
					0.00110 ^b	0.0522
					0.00104 ^c	0.0492
4	0.1200	benzene	0.104	11.4	0.00419 ^a	0.0404
					<i>d</i>	
					0.00443 ^c	0.0427
5	0.0580	benzene	0.113	18.0	0.00303 ^a	0.0268
					0.00452 ^b	0.0400
					0.00247 ^c	0.0219
6	0.123	<i>t</i> -BuOH	0.0124	1.6	0.00040 ^a	0.032
					0.00016 ^b	0.013
					0.00145 ^c	0.117
7	0.129	<i>t</i> -BuOH	0.0258	4.0	0.00082 ^a	0.032
					0.00029 ^b	0.011
					0.00406 ^c	0.157
8	0.120	<i>t</i> -BuOH	0.0488	5.5	0.00125 ^a	0.026
					0.00052 ^b	0.012
					0.00489 ^c	0.100
9	0.100	<i>t</i> -BuOH	0.0634	8.6	0.00191 ^a	0.030
					0.00078 ^b	0.012
					0.00584 ^c	0.092

^a Photoproduct 15. ^b Photoproduct 16. ^c Photoproduct 17. ^d Not determined.

quantum yields were performed on the microoptical bench,⁵ except where noted. Light output was measured with a digital actinometer^{14a} calibrated by ferrioxalate actinometry.^{14b} The monochromator entrance and exit slits were set at 5.4 and 3.0 mm, respectively, to give a band pass of 22 nm at half-peak height.

Direct Quantum Yields. 3,3-Dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene. All runs were performed in *n*-pentane and irradiated at 300 nm. The solvent, after photolysis, was removed in vacuo and the residue taken up in 10 mL of 0.25 N sulfuric acid to hydrolyze unreacted starting diene to 1,1,5,5-tetraphenyl-1,4-pentadien-3-one. The hydrolysate was washed three times with water and dried over magnesium sulfate and the solvent removed in vacuo. The photolysate was then analyzed by HPLC using a 50 × 0.94 cm column of porous, spherical silica beads (10 μ m),⁵² eluting with 15% ether in hexane at

2.3 mL per min, using benzophenone as internal standard. Results are summarized in Table V.

Sensitized Quantum Yields. 3,3-Dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene. This was performed on the "Black Box"⁵ apparatus. The light was filtered through a triple compartment cell containing (a) 0.23 M nickel sulfate hexahydrate in 10% sulfuric acid, (b) 2.0 M cobalt sulfate heptahydrate in 5% hydrochloric acid, (c) 0.2 M stannous chloride in 15% hydrochloric acid. This combination gave a transmission maximum at 347 nm (30%) and was opaque above 375 nm and below 327 nm. Light output was measured in the usual manner.¹⁴ A solution of 1.14 g of xanthone and 0.25 g (0.58 mmol) of 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene in 250 mL of benzene was irradiated for 3 h and 1.53 mEinstein was absorbed. The solvent was removed in vacuo and the sample was prepared for HPLC

Table IX. Sensitized Quantum Yield Photolyses of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene Yielding 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane, Photoproduct 17

run	reactant, mmol	light absorbed, mEinstein	% conversion	photoproduct 17, mmol	Φ
1	0.090	0.0066	5.4	0.0049	0.74
2	0.093	0.0112	8.4	0.0078	0.70
3	0.044	0.0058	8.5	0.0038	0.64
4	0.045	0.0095	11.1	0.0051	0.53
5	0.090	0.0166	11.4	0.0103	0.62

Table X. Direct Quantum Yield Photolyses of 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane Yielding 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (3) and 1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15)

run	reactant, mmol	light absorbed, mEinstein	% conversion	photoproduct, mmol	Φ
1	0.127	0.0177	6.1	0.00548 ^a	0.310
				0.00230 ^b	0.130
2	0.052	0.0101	8.3	0.00318 ^a	0.315
				0.00114 ^b	0.113
3	0.045	0.0226	20.2	0.00567 ^a	0.251
				0.00347 ^b	0.154
4	0.047	0.0253	20.6	0.00668 ^a	0.264
				0.00295 ^b	0.117

^a Photoproduct 3. ^b Photoproduct 15.

Table XI. 1,3-Cyclohexadiene Quenched Photolyses of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene

run	reactant	quencher	light absorbed, mEinstein	% conversion	photoproduct, mmol	Φ
1 ^d	0.0618 mmol 0.00124 M	1.00 mmol 0.020 M	0.108	23	0.003 ^a	0.03
					0.0042 ^b	0.039
2 ^d	0.0573 mmol 0.00115 M	5.12 mmol 0.102 M	0.0374	5.7	0.00155 ^a	0.041
					0.00171 ^b	0.046
					^c	
3 ^e	0.0999 mmol 0.002 M	50.0 mmol 1.00 M	0.0401	3	0.001 ^a	0.03
					0.001 ^b	0.03
					^c	

^a Photoproduct 15. ^b Photoproduct 17. ^c Photoproduct 16 not determined due to overlap of ¹H NMR resonance with cyclohexadiene dimer. ^d Monochromator set at 313 nm. ^e Monochromator set at 335 nm.

analysis as previously described for the direct quantum yield runs (vide supra). Assuming that 0.05% of the vinylcyclopropane photoproduct could have been detected, $\Phi_{\text{sens}} \leq 0.00018$.

Direct Quantum Yields. 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene. All runs were performed in 42 mL of *tert*-butyl alcohol, purged for 0.5 h with purified nitrogen before and then during photolysis and irradiated at 290 nm. All runs were analyzed by HPLC on a 25 × 0.67 cm column of 5- μ m porous silica gel beads⁵² eluting with 5% anhydrous ether and 0.05% methanol in dry hexane. Benzophenone azine was added as an internal standard. Results are summarized in Table VI.

Sensitized Quantum Yields. 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene. All runs were performed in 39 mL of benzene and 3 mL of acetophenone. Irradiation was at 325 nm and analyses were done by using the same method employed for the direct quantum yield runs. Results are summarized in Table VII.

Direct Quantum Yields. 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. All runs were performed on the microoptical bench,⁵ with the monochromator set at 320 nm. Solutions of 20–50 mg of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene in 50 mL of benzene or *tert*-butyl alcohol were purged with a stream of purified nitrogen⁴⁷ for 1 h before and throughout irradiation. An electronic actinometer^{14a} was employed, calibrated with ferrioxalate actinometry.^{14b} Photoproduct formation was analyzed by 270-MHz FT NMR, with 1,1,5,5-tetraphenyl-1,4-pentadien-3-one, added as internal standard. Results are summarized in Table VIII.

Sensitized Quantum Yields. 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. All runs were performed in 40 mL of benzene containing 3.0 g of acetophenone, purged for 1 h with purified nitrogen⁴⁷ before and then during photolysis, and irradiated at 340 nm. All runs were analyzed by 270-MHz NMR with 1,1,5,5-tetraphenyl-1,4-pentadien-3-one added as an internal standard. The single photoproduct was 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. Results are summarized in Table IX.

Direct Irradiation Quantum Yields. 1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane. All runs were performed with benzene as solvent, as described above for 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. The photoproducts were 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (3) and 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (15). Results are summarized in Table X.

1,3-Cyclohexadiene Quenching of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. Solutions of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene in benzene were irradiated in the presence of 1,3-cyclohexadiene as a quencher. The conditions employed for the photolyses were in all other respects identical with those used for the direct quantum yield photolyses of this diene. Results are summarized in Table XI.

Emission Studies. Purification of Solvents, 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene and 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene. Isopentane and methylcyclohexane were purified by repeated washings with 10% fuming sulfuric acid until the washings

Table XII. Single Photon Counting Data for 3,3-Dicyano-1,1,5,5-tetraphenyl-1,4-pentadiene: Data at 77 K

run	OD	λ_{ex} , nm	λ_{em} , nm	τ , ns	$^1k_{dt} \times 10^{-8}$, s ⁻¹	A value ^a
1	1.0	260	320	2.19	4.57	0.0454
2	1.1	265	325	2.38	4.20	0.0446
3	1.7	270	320	2.23	4.49	0.0457
4	1.0	270	320	2.24	4.45	0.0438
5	0.8	275	315	2.24	4.46	0.0457
6	0.8	285	325	1.55	6.45	0.0485
7	1.2	280	330	1.48	6.74	0.0426
8	0.8	280	325	1.63	6.14	0.0445
9	1.4	285	320	1.47	6.82	0.0480
10	2.0	285	325	2.05	4.87	0.0496
11	1.7	280	320	1.45	6.89	0.0485
12	2.0	275	315	1.67	5.97	0.0459
M = 16			av:	1.82 ± 0.23	5.50 ± 0.69	

^a See reference 15.**Table XIII.** Single Photon Counting Data for 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene: Data at 77 K

run	OD	λ_{ex} , nm	λ_{em} , nm	τ , ns	$^1k_{dt} \times 10^{-9}$, s ⁻¹	A value ^a
1	1.4	255	325	0.183	5.46	0.0485
2	1.4	265	330	0.219	4.57	0.0496
3	0.72	255	325	0.294	3.40	0.0404
4	0.72	260	320	0.251	3.98	0.0407
5	0.72	265	330	0.188	5.32	0.0439
6	1.1	255	325	0.239	4.18	0.0447
7	1.1	260	320	0.221	4.52	0.0458
M = 247			av:	0.228 ± 0.014	4.49 ± 0.30	

^a See reference 15.

were colorless, refluxed over a saturated solution of potassium permanganate in 10% sulfuric acid, washed with water, dried over phosphorus pentoxide, and passed twice through a 2.5 × 80 cm column of 10% silver nitrate on alumina, discarding early and late fractions. Solvents prepared in this manner were transparent in the ultraviolet and emission free. The 1,1- and 3,3-dicyanodienes were recrystallized from the purified methylcyclohexane until free from spurious emission.

Single Photon Counting. The apparatus and procedure have been previously described in detail.⁵³ The method uses a high pressure (80–90 psi) nitrogen flash lamp with a half-width of less than 3.5 ns when run at 18–25 kHz, an 1P28 photomultiplier to trigger the start of a time-to-amplitude converter, excitation and emission monochromators, an RCA 8850 photomultiplier and an Ortec model 463 constant timing discriminator, and a 12-bit Northern Scientific A/D converter interfaced with a PDP8/I-FPPI2 minicomputer. The minicomputer was used as a 512-word multichannel analyzer and to do on line deconvolution by reiterative convolution as previously described.⁵³ Independent studies have established⁵⁴ a 32-ps error limit. Experiments were run to a minimum of 1000 counts in the highest channel when collecting at less than 5% of the lamp frequency. The 5% factor assures that few double photons were collected. Excitation was in the range 260–285 nm; emission was detected in the range 315–330 nm. Optical densities were adjusted to 0.8–2.0 at excitation wavelengths. All runs were performed at 77 K in a 4:1 methylcyclohexane-isopentane glass.

Magic Multipliers. Fluorescence emission spectra were obtained at 77 and 295 K in 4:1 methylcyclohexane-isopentane solution under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W xenon lamp. Optical densities were adjusted to 0.8–1.7 to minimize scatter. Excitation wavelengths in the range 260–275 nm were employed. Magic multipliers were obtained for individual samples by integration of emission intensity bands at the two temperatures.

The results of the single photon counting experiments and magic multiplier measurements are presented in Tables XII and XIII.

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Photochemistry of *cis*-1-Phenylcyclohexene. Proof of Involvement of Trans Isomer in Reaction Processes

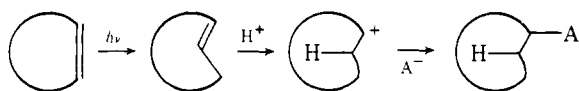
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Abstract: Kinetic studies showed that the formation of a [2 + 2] dimer in the direct irradiation of *cis*-1-phenylcyclohexene in methanol proceeds in the singlet manifold, possibly involving an excimer. The generation of a Markownikoff-type ether results from a common intermediate in the direct and the sensitized irradiation. Low-temperature studies indicate that *trans*-1-phenylcyclohexene is this intermediate. Evidence for the existence of a free *trans*-1-phenylcyclohexene is found in the structure of a [4 + 2] dimer formed in irradiations of *cis*-1-phenylcyclohexene in methanol at -75°C .

Introduction

In the past decade much interest has been shown in the photoinduced addition of protic solvents to cyclic olefins.^{2-4,6} In most such studies, compounds with simple ethylenic double bonds were employed and, thus, an aromatic hydrocarbon sensitizer had to be used for activation of the unsaturated linkage. The protic solvent addition reaction appeared to be acid catalyzed and the product formation was dependent upon the ring size of the cycloalkene.³ Generally, the results have been interpreted in terms of the photoinduced formation of a strained ground state trans double bond which reacts readily with a proton to yield a carbocation, followed by the addition of a nucleophilic species. Indeed, Marshall has shown that the

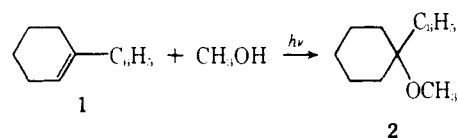


stereochemistry of the protonation is in agreement with the suggestion of a *trans* olefin as an intermediate.⁴ However, in all the cases studied, the reaction of a triplet state (possibly

orthogonal) with protic solvents cannot be ruled out on the basis of the existing data.

In order to obtain a better evaluation of the nature of this photochemical solvent addition, a study using 1-phenylcyclohexene was initiated. With this substituted olefin it would be possible to apply direct as well as sensitized irradiation conditions. Furthermore, the presence of the benzene ring would permit the introduction of substituents on the ring and in this manner the importance of meta vs. para substitution could be evaluated, an approach used so successfully in interpreting the mechanism of aromatic photosubstitution and photosolvolysis.⁵

The photoaddition of methanol to *cis*-1-phenylcyclohexene (1) has been reported by Kropp, using a 0.13 M solution of 1



in methanol; a 13% formation of the Markownikoff ether 2 at