Substituent Effects and the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry.[1,2]

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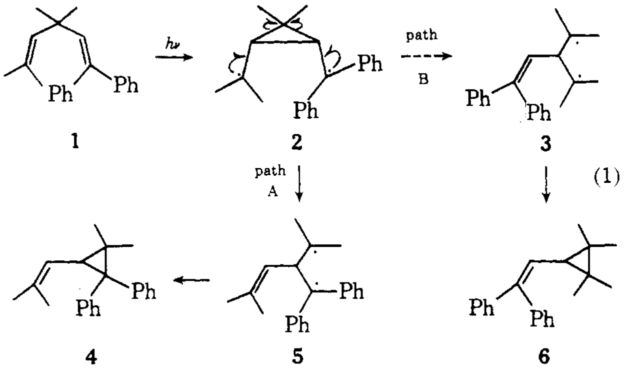
Abstract: 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene were synthesized for comparison of their photochemistry with the parent diene, 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, studied previously. Reaction regiospecificity, reaction efficiency, and excited state rates were investigated. The dicyanodiene gave only one of two *a priori* products, namely 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. The alternate product, 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane, was independently synthesized but was absent in the diene photolysis. Thus the reaction was highly regiospecific. In the case of the tetracyanodiene, irradiation afforded 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. This structure, as well as that of the dicyanodiene product, was proven by degradation to synthesized compounds. The direct irradiation quantum yield for the dicyanodiene reaction was $\phi = 0.094$ and that for the tetracyanodiene was $\phi = 0.165$. In contrast, benzophenone sensitization gave no reaction. Excited state rate constants were obtained relative to the tetraphenyldiene by the fluorescence method described by us earlier; absolute rates were obtained by single photon counting calibration. It was observed that dicyanodiene excited singlet rearranged *ca.* 50% faster than the tetraphenyldiene while the tetracyanodiene excited state rearranged 2.4 times as rapidly as the tetraphenyldiene. The rates were 2.2×10^{11} and 3.3×10^{11} sec^{-1} for the di- and tetracyanodienes. The excited state decay rates surprisingly were quite similar for all three dienes: 2.3×10^{12} and 2.0×10^{12} sec^{-1} for the di- and tetracyanodienes compared with 1.8×10^{12} sec^{-1} for the parent tetraphenyldiene. Thus the effect of cyano substitution on regiospecificity is much greater than on the excited state rate of rearrangement. This and related results are considered.

Our aim has been to investigate the di-π-methane rearrangement in sufficient depth that its mechanistic subtleties are understood and that it becomes a reaction of general synthetic utility. One aspect of the di-π-methane rearrangement of special import is the regiospecificity often observed.[3] For example, in the case of the irradiation of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**1**) only one of the two *a priori* products is formed,[4] namely cyclopropane **4** but not **6**. The preference for path A was attributed to a molecular demand for maximum electron delocalization during the ring opening process of species **2**.



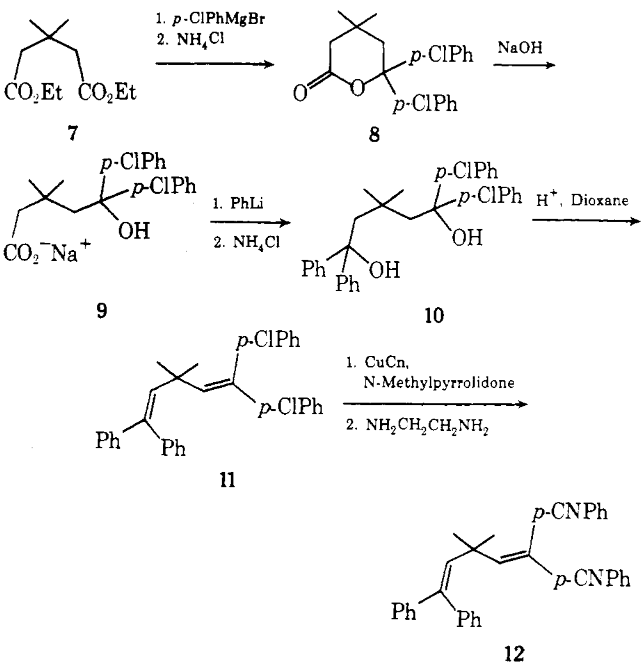
The present study had as one of its objectives the determination of the effect of para substituents on the regiospecificity of a tetraphenyldiene. Parallel to this, determination of the rate constants of the excited state reaction promised to cast further light on the mechanism.

Results and Discussion

Synthesis of Photochemical Reactants. The desired 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene was synthesized *via* the route depicted in Chart I and described in detail in the Experimental Section.

The second diene required, namely 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene, was prepared as depicted in Chart II, and again, detailed in the Experimental Section.

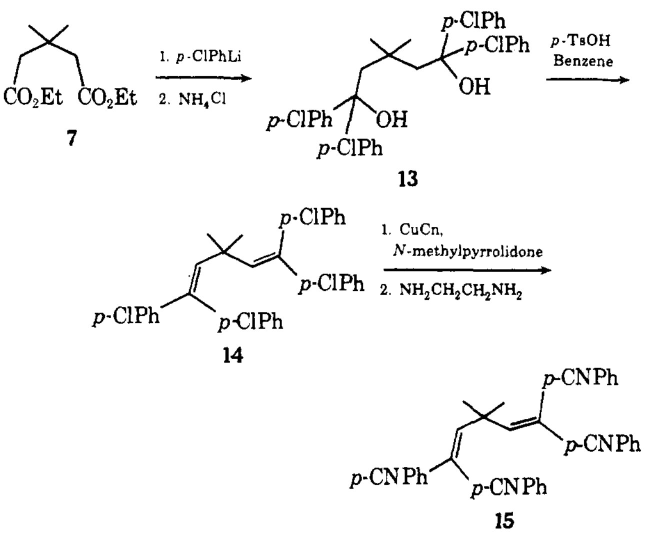
Chart I. Synthesis of 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene



Exploratory Photolysis of 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene and 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. Irradiation of 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene in *tert*-butyl alcohol in the "black box" apparatus[5] for 3 hr using a 250–310-nm solution filter led to 31% conversion to a single product. Higher conversions were found to lead to secondary photochemistry. Silica gel chromatography afforded a single, crystalline photoproduct **16**, mp 250–252°.

Similar irradiation of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in *tert*-butyl alcohol, however, using a 450-W Hanovia immersion well apparatus, gave 66% conversion to primary photoproduct after 45 min. Crystallization allowed isolation of a single photoprod-

Chart II. Synthesis of 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene



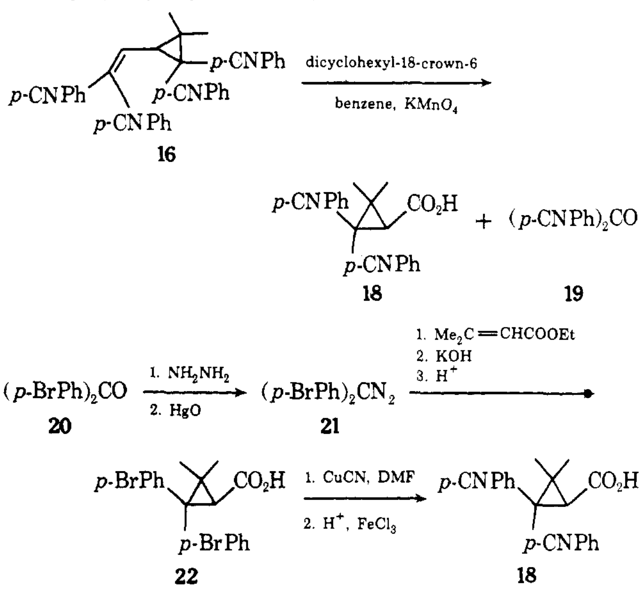
uct **17**, mp 183–184.5°. A careful search for additional primary photoproducts revealed none.

Structure Elucidation of the Photoproducts. In the case of the mp 250–252° photoproduct **16**, elemental analysis revealed it to be an isomer of 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene (**15**). The nmr spectrum revealed a vinyl doublet at τ 4.23, coupled (10.5 Hz) with a methine doublet at τ 8.61. Besides the expected 16 aromatic hydrogen absorption, two nonequivalent and unsplit methyl peaks were discerned at τ 8.61 and 8.97. This and the ubiquity[3] of the di-π-methane rearrangement provided suggestive evidence for 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane as the structure of photoproduct **16**.

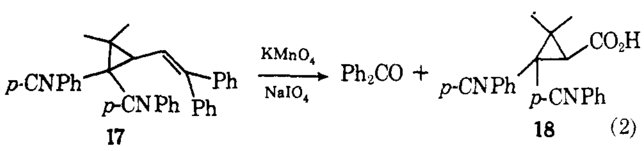
Unambiguous evidence was provided by the degradation and synthesis outlined in Chart III. Thus, treatment of photoproduct **16** with the Sam-Simmons permanganate-crown ether reagent[6] led to an acid, mp 234–236°. The nmr revealed two nonequivalent methyl absorptions at τ 8.51 and 8.88 and a methine singlet at τ 7.64. The spectrum was reminiscent of that of 2,2-diphenyl-3,3-dimethylcyclopropanecarboxylic acid (**23**), obtained in our earlier work.[7] The 234–236° mp acidic degradation product was synthesized as delineated in Chart III. The hydrazone of *p,p'*-dibromobenzophenone (**20**) was oxidized with mercuric oxide to yield di-*p*-bromophenyldiazomethane (**21**) which on reaction with ethyl 3-methyl-2-butenoate, followed by saponification, yielded 2,2-di-*p*-bromophenyl-3,3-dimethylcyclopropanecarboxylic acid (**22**). The cyclopropyl acid **22** on treatment with cuprous cyanide in refluxing *N,N*-dimethylformamide gave 2,2-di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic acid (**18**) which proved to be identical with that from degradation of the vinylcyclopropane **16**. This then proved the structure of the unknown photoproduct **16**, mp 250–252°, to be 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane.

Turning attention to the photoproduct **17**, mp 183–184.5°, derived from photolysis of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**), we noted from elemental analysis that this again was isomeric with the diene reactant. The nmr spectrum, with a vinyl proton at τ 4.46, coupled (10.5 Hz) with a methine proton at τ 7.82 and two methyl singlets at τ 8.72 and 9.06 suggested that again a di-π-methane rearrangement had occurred. Which vinylcyclopropane of the two *a priori* possibilities was being formed was, however, not known.

Chart III. Degradation of 1,1-Di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane and Synthesis of 2,2-Di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic Acid



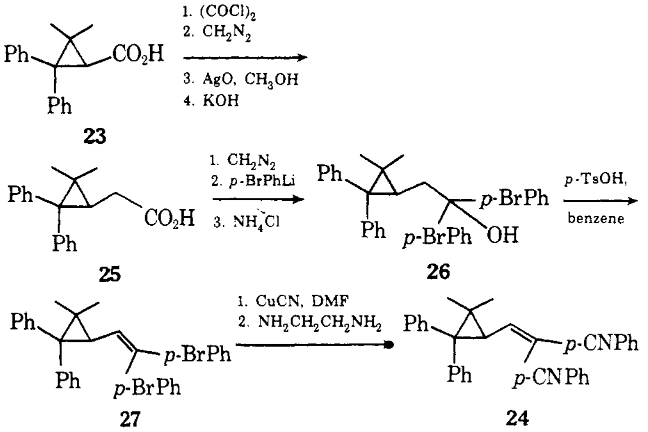
Unambiguous evidence was derived from oxidative degradation; note eq 2. Thus Lemieux-von Rudloff[8] degradation gave the previously synthesized (*vide supra*) 2,2-di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic acid (**18**) and benzophenone, proving the identity of photoproduct **17** to be 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane.



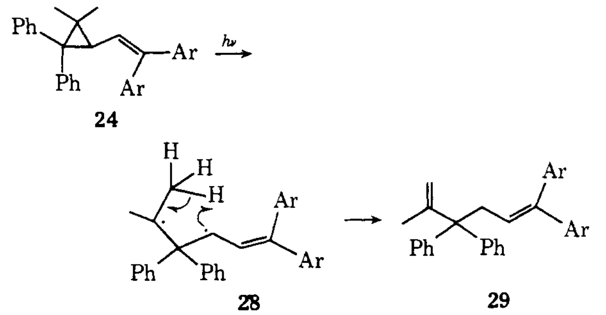
It was also deemed important to have authentic 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**) available, since only then would reference material be available to allow one to look effectively for this product in the photolysis and place an upper limit on the amount which might be formed. The synthesis is outlined in Chart IV. Arndt-Eistert homologation of the known[7] 2,2-diphenyl-3,3-dimethylcyclopropanecarboxylic acid (**23**) gave 2,2-diphenyl-3,3-dimethylcyclopropaneacetic acid (**25**) which on treatment with *p*-bromophenyllithium yielded 1,1-di-*p*-bromophenyl-2-(2,2-diphenyl-3,3-dimethylcyclopropane)ethanol (**26**). The alcohol **26** was dehydrated with *p*-toluenesulfonic acid to give 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-bromophenylvinyl)cyclopropane (**27**). This, on treatment with cuprous cyanide in refluxing *N,N*-dimethylformamide, gave the desired 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**).

One control experiment was necessary to ascertain that 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**) was not being formed and subsequently converted to the observed 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**17**) or being consumed. Thus, the photochemistry of vinylcyclopropane **24** was investigated and observed to afford 1,1-di-*p*-cyanophenyl-4,4-diphenyl-5-methyl-1,5-hexadiene (**29**) as shown in eq 3 but no 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**17**). Diene **29** was not observed in any of the photolyses of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**) and it therefore can be concluded that 1,1-diphenyl-2,2-dimethyl-3-

Chart IV. Synthesis of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane



(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**) was not formed transiently.



(3)

Ar = *p*-CNPh

High Speed Liquid Chromatography Analysis of Photolysis Mixtures, Quantum Yield Determinations, and Determination of Reaction Multiplicity. A rapid but precise method of assay for preparative and quantum yield photolyses was required, and attention was turned toward high speed liquid chromatography (hslc). Using a 10 ft × ⅛ in. column packed with silicic acid surfaced microbeads, eluted with 35% ether in hexane, and using 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**) as an internal standard, it was found that 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene (**15**) and 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**16**) could be separated analytically for quantum yield determinations.

Similarly, preparative hslc using a 1.5 in. × 6 ft steel column packed with Mallinckrodt 200–320 mesh Silicar (silicic acid) and eluted with 20% ether in hexane proved to be a fast, precise method for gravimetric quantum yield determinations of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**), giving baseline separation between the diene **12** and 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**17**). The gravimetric runs allowed identification of the materials in the eluted peaks and proved a check on the runs using peak areas.

High speed liquid chromatography was also used to put a limit on the regiospecificity of the reaction of the dicyanodiene **12**. It was observed that the retention volume characteristic of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**) coincided with that of the starting diene **12**. An irradiation was run to *ca.* 96% conversion; this used the black box apparatus[9] with the 250–310-nm solution filter. The material by hslc analysis at the retention volume of vinylcyclopropane isomer **24** and starting material was only $\frac{1}{24}$th of the major photoproduct. Nmr analysis revealed reactant diene plus secondary photoproducts but no vinylcyclopropane **24**. Thus, it could be concluded that the overall regiospecificity favored the formation of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**17**) over 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**) by greater than 24:1.

For determination of reaction quantum yields, the usual black box[9] and organic chemists' optical bench[9] were used. The former used the 250–310-nm solution filter for direct irradiations. For sensitized irradiations a solution filter opaque below 315 nm and above 385 nm with a maximum transmission at 344 nm was used. The optical bench apparatus used a Bausch and Lomb high intensity monochromator. Low conversion photolyses were used to minimize absorption of light by photoproduct. The results of quantum yield determinations are listed in Table I.

It is seen that 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene (**15**) has a quantum yield of 0.165 and 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**) has a quantum yield of 0.094 on direct irradiation.

Included in Table I are the runs designed to test reaction multiplicity. In the case of the tetracyanodiene **15**, the sensitized quantum yield was shown to be less than 0.005 while that of the dicyanodiene **12** was less than 0.003. That triplet energy transfer actually was occurring was demonstrated by the benzophenone–benzhydrol reaction[10] which is quenched by both dienes.

Determination of Singlet Excited State Reaction Rates. Initially attempts were made to study the rates of rearrangement and excited state decay using the single photon counting technique described by us recently.[11] However, this method utilizes fluorescence emission at both room and low (*e.g.*, 77°K) temperatures. At 77°K, new emissions (350 nm for the tetracyanodiene **15** and 354 nm for the dicyanodiene **12**) were observed. These are attributed to temperature-dependent exciplex formation between the two diarylvinyl moieties. This result meant that the method of "magic multipliers" would be difficult if not impossible, since that method uses the variation in emission intensity for one species as a function of temperature. Diminution of intensity due to exciplex formation complicates the situation.

However, the method described by us earlier[12] and independently by Dalton and Turro[13] in which one uses the natural rate of fluorescence coupled with the fluorescence and reaction quantum yields as given in eq 4a, b, and c proved

$$\phi_f = k_f/k_{dt} \tag{4a}$$

$$\phi_r = k_r/k_{dt} \tag{4b}$$

$$k_r = k_f\phi_r/\phi_f \tag{4c}$$

useful. Since our previous studies have shown the method is reliable only in giving relative rate values, it was presently employed to give fluorescence quantum yields and rates relative to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**30**) whose rate of decay at room temperature has already been measured[11] as 1.8×10^{12} sec^{-1}. These results are compiled in Table II. The errors indicated are derived from the 33% standard deviation in the relative rates obtained in the fluorescence method[12] relative to the single photon counting results.[11]

Interpretative Discussion. The first observation is that the gross reaction course again follows the basic di-π-methane rearrangement route. Another point is that our earlier generalization regarding the preference for singlet reactivity by acyclic di-π-methane systems again is followed, with the triplet being unreactive.

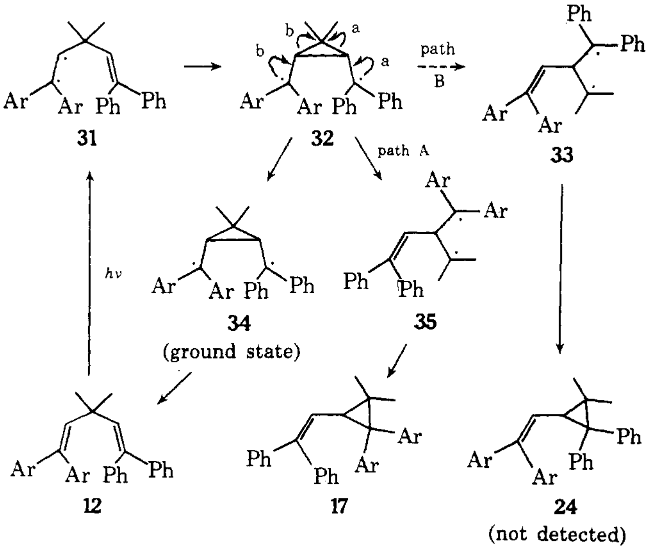
Table I. Quantum Yield Determinations

Run	Reactant (*M*)	Added reagents (*M*)	λ_{irrad}, nm	ϕ_r (di-π)[a]	ϕ_r (pinacol)[b]	% conversion
1	Diene 15[c,d] (9.50×10^{-4})		295	0.16		10.6
2	Diene 15[c,d] (9.45×10^{-4})		295	0.17		10.7
3	Diene 15[c,d] (6.47×10^{-4})	Ph_2CO (3.82×10^{-2})	344	<0.005		0
4	Diene 12[e,d] (1.33×10^{-3})		282	0.072		29.1
5	Diene 12[e,d] (1.30×10^{-3})		282	0.092		9.5
6	Diene 12[e,d] (1.44×10^{-3})		282	0.095		5.1
7	Diene 12[e,f] (6.62×10^{-4})		282	0.086		11.2
8	Diene 12[e,g] (6.72×10^{-4})		282	0.097		10.4
9	Diene 12[e,d] (1.47×10^{-3})	Ph_2CO (7.06×10^{-2})	344	<0.003		0
10	Ph_2CO (2.93×10^{-2}) Ph_2CHOH (1.45×10^{-2})		344		0.124	51
11	Ph_2CO (2.93×10^{-2}) Ph_2CHOH (1.45×10^{-2})	Diene 15[c] (9.92×10^{-4})	344		0.022	12
12	Ph_2CO (2.93×10^{-2}) Ph_2CHOH (1.45×10^{-2})	Diene 12[e] (1.17×10^{-3})	344		0.035	18

[a] Quantum yield for vinylcyclopropane formation. [b] Quantum yield for benzpinacol formation. [c] Refers to 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. [d] Photolysis in *tert*-butyl alcohol. [e] Refers to 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. [f] Photolysis in ethanol. [g] Photolysis in cyclohexane.

A most striking result presently is the extreme regiospecificity in the rearrangement of the dicyanodiene **12** which afforded only 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**17**) and no 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane (**24**). This is depicted in the usual resonance terms in Chart V.

Chart V. Regiospecificity of the Di-π-Methane Rearrangement of 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene



Ar = *p*-CNPh

To the extent that the di-π-methane rearrangement is considered to involve an effective 1,2-vinyl migration, one might advance the viewpoint that the lower energy vinyl chromophore is the one utilized in three ring formation and that the higher energy vinyl chromophore is the one which migrates and survives the reactions. While this superficially fits most examples,[3,12] it does not accord with all.[12] In the present instance we know that the diphenylvinyl moiety absorbs at 256 nm and the di-*p*-cyanophenylvinyl chromophore absorbs at 267 nm, with the latter thus being lower in energy by 7 kcal/mol, and it is the higher energy diphenylvinyl group which survives the reaction.

A more reasonable explanation is the one[4] based on maintenance of maximum electron delocalization along the reaction coordinate. Thus, specificity is determined at the stage of the mechanism where the excited cyclopropyldicarbinyl diradical (*e.g.*, **32** in Chart V) opens. Presently, the observed path A retains dicyanobenzhydryl delocalization while path B retains only benzhydryl stabilization. With the former being more extensive, this pathway then is preferred electronically.

Next discussed is the effect of cyano substitution on the overall reaction efficiency and on the rate of singlet excited state rearrangement. Looking first at reaction efficiencies, we see that the dicyanodiene **12** is only very slightly more efficient than the Mariano diene **30.** The tetracyanodiene **15,** however, has a quantum yield which is nearly twice that of the dicyanodiene **12.** Nevertheless, we recognize that quantum yields, merely being probabilities of excited states giving product, really should not be taken too seriously in correlating photochemical reactivity with structure. However, excited state reaction rates do give a direct measure of reactivity. Table II reveals that the puzzling similarity in efficiency for the Mariano compound **30** and dicyanodiene **12** is illusory rather than real in terms of reactivity. Thus, k_r (tetraphenyldiene **30**) is 1.4×10^{11} sec^{-1} compared with k_r (dicyanodiene **12**) which is 2.2×10^{11} sec^{-1}. Furthermore, the tetracyanodiene **15** has a still greater rate of $k_r = 3.3 \times 10^{11}$. We see a steady progression toward greater reactivity with increasing para-cyano substitution. The similarity in quantum yields for the Mariano diene **30** and the dicyanodiene **12** is due to a rate of decay, k_{dt}, which in-

Table II. Excited State Rate Processes of Dienes

Diene	ϕ_f^{rel}	ϕ_r	k_f (sec^{-1})[c]	k_{dt} (sec^{-1})	k_r (sec^{-1})
Tetraphenyl[a,b]	1.00	0.080	7.3×10^8	1.8×10^{12}	1.4×10^{11}
Dicyano[d,f]	0.94	0.094	8.7×10^8	2.3×10^{12}	2.2×10^{11}
Tetracyano[e,f]	1.35	0.165	1.1×10^9	2.0×10^{12}	3.3×10^{11}

[a] Refers to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. [b] References 7 and 11. [c] Apparent fluorescence rate calculated from the absorbtion spectra. [d] Refers to 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. [e] Refers to 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. [f] The error margin for k_{dt} and k_r is 33%.

creases on introduction of the two *p*-cyano groups to almost the same extent as k_r increases, thus keeping the ratio $\phi_r = k_r/k_{dt}$ relatively insensitive to structure.

The nearly linear increase in excited state reactivity with increasing numbers of cyano groups (note k_r in Table II) accords nicely with the view[11] that the rate limiting portion of the excited state mechanism occurs early along the reaction coordinate where bridging is occurring. If cyclopropyl cleavage of the cyclopropyldicarbinyl diradical (*e.g.*, **32**) controlled the rate, the tetraphenyl diene **30** and the dicyanodiene **12** should have similar rates since in both cases a benzhydryl radical center is converted to a diphenylvinyl moiety; the tetracyanodiene **15** should react more slowly since extra dicyanobenzhydryl radical delocalization is lost.

One other point deals with the total rate of decay, k_{dt}. Previously, we have noted a parallelism between k_r and k_{dt} and have commented[11] that this is reasonable if both processes involve bridging. Presently this is not the case, and k_{dt} does not seem to change systematically. The evidence is insufficient for discussion; however, it does suggest that in the present systems the insensitivity of k_{dt} to the structural factors affecting k_r is due to a heavy contribution from radiationless decay which is unrelated to the rearrangement mechanism.

The final point is the fascinating apparent paradox wherein the regiospecificity is over 24:1 as a result of di-*p*-cyanophenyl substitution and yet the excited state reaction rates are enhanced only by a factor of 1.6. This paradox is more apparent than real and suggests that regiospecificity is determined in a stage of the reaction much later and different from that which determines the rate. Thus bridging is the major process affecting rate (note Chart V) while regiospecificity is determined *via* partitioning in a process occurring subsequent to bridging.[14]

Experimental Section[15]

Diethyl 3,3-Dimethylglutarate. This material was prepared from 3,3-dimethylglutaric acid (Aldrich) by a slight modification of the method of Reid and Gompf.[16]

1,1,5,5-Tetra-*p*-chlorophenyl-3,3-dimethylpentane-1,5-diol. To a solution of 0.210 mol of *p*-chlorophenyllithium,[17] generated from 0.210 mol of 2 *M* *n*-butyllithium in hexane and 45.0 g (0.235 mol) of *p*-chlorobromobenzene in 300 ml of anhydrous ether, a solution of 6.50 g (0.030 mol) of diethyl 3,3-dimethylglutarate in 20 ml of anhydrous ether was added dropwise. After 18 hr at room temperature the mixture was poured into saturated aqueous ammonium chloride at 0°. Ether extraction and concentration *in vacuo* gave 24.6 g of product which was chromatographed on a 5 × 30 cm alumina column slurry packed with 10% ether in hexane. Elution with 2 l. of 10% ether in hexane gave aromatic impurities; 2 l. of 1:1:8 hexane-methanol-ether gave 7.42 g of crude product. Recrystallization from ether-hexane gave 4.37 g (25.3%) of the diol, mp 159.5-161°.

The spectral data were the following: ir (CCl_4) 2.78, 2.90, 6.29, 6.72, 7.13, 7.31, 7.31, 9.14, 9.87, and 12.03 μ; nmr (CCl_4) τ 2.81 (s, 16 H, arom), 5.54 (s, 2 H, OH), 7.52 (s, 4 H, CH_2), and 9.63 (s, 6 H, CH_3).

1,1,5,5-Tetra-*p*-chlorophenyl-3,3-dimethyl-1,4-pentadiene. A solution of 0.972 g (1.69 mmol) of 1,1,5,5-tetra-*p*-chlorophenyl-3,3-dimethylpentane-1,5-diol and 74.7 mg of *p*-toluenesulfonic acid in 100 ml of benzene was refluxed 3 hr and concentrated *in vacuo*. The crude product was chromatographed on a 2.5 × 90 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60-200 mesh) slurry packed and eluted with hexane; 100-ml fractions were collected. Fractions 8-13 gave 0.737 g of crude diene which was recrystallized from ether-ethanol to give 0.572 g (62.9%) of the desired diene, mp 162-164°.

The spectral data were the following: ir (CCl_4) 6.40, 6.72, 7.13, 9.17, 9.88, and 12.17 μ; nmr ($CDCl_3$) τ 2.55-3.15 (m, 16 H, arom), 4.10 (s, 2 H, =CH), and 8.98 (s, 6 H, CH_3).

1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. A solution of 5.28 g (9.82 mmol) of 1,1,5,5-tetra-*p*-chlorophenyl-3,3-dimethyl-1,4-pentadiene and 15.2 g (0.180 mol) of cuprous cyanide in 60.0 ml of N-methyl-2-pyrrolidone[18] was refluxed 70 hr with Trubore stirring under nitrogen. The reaction mixture was cooled, poured into 100 ml of ethylenediamine, set aside 1 hr, poured onto ice, and shaken with 1.0 l. of ether to give a thick suspension which was filtered through sand. The aqueous phase was dichloromethane extracted and the combined organic phase was concentrated *in vacuo*, taken up in ether, washed, dried, and concentrated *in vacuo* to give 4.88 g of crude product. This was passed through a 5 × 15 cm column of silica gel slurry packed and eluted with 30% ether in dichloromethane. Recrystallization from ethyl acetate-ethanol gave 2.14 g (43.8%) of the desired diene, mp 216-218°.

The spectral data were the following: ir ($CHCl_3$) 4.47, 6.35, 6.68, 8.81, 9.02, 11.03, and 11.97 μ; nmr ($CDCl_3$) τ 2.25-3.15 (m, 16 H, arom), 3.98 (s, 2 H, =CH), and 8.92 (s, 6 H, CH_3); uv λ_{max}^{EtOH} 268 (ϵ 39,300).

Exploratory Photolysis of 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. A solution of 309 mg (0.618 mmol) of 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene in 750 ml of *tert*-butyl alcohol was purged with purified nitrogen[19] 1.0 hr before and during photolysis. Irradiation was on the "black box" apparatus[5] for 3 hr using a solution filter combination (*vide infra*) with maximum transmission at 282 nm (30%) and opaque below 250 nm and above 310 nm. The photolysate was concentrated *in vacuo* and chromatographed on a 3.5 × 105 cm silica gel column, (Matheson Coleman and Bell, Grade 62, 60-200 mesh), slurry packed in 10% cyclohexane in methylene chloride. Eluent absorbance was scanned at 292 nm and 40-ml fractions were collected. Elution with 4.0 l. of 10%, 3.0 l. of 7% cyclohexane in dichloromethane, and 4.5 l. of dichloromethane gave nil, 4.5 l. of dichloromethane gave 94.9 mg of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane which was recrystallized from dichloromethane-methanol to give 83.6 mg, mp 250-252°, and 2 l. of 10% ether in dichloromethane gave 202 mg of diene. The mass balance was 95.8%.

The spectral data for the vinylcyclopropane were the following: ir ($CHCl_3$) 4.46, 6.23, 6.65, 6.89, 7.10, 8.98, 9.82, 11.02, 11.47, and 11.97 μ; nmr ($CDCl_3$) τ 2.0-3.0 (m, 16 H, arom), 4.23 (d, J = 10.5 Hz, 1 H, =CH), 7.91 (d, J = 10.5 Hz, 1 H, cyclopropyl), 8.66 (s, 3 H, CH_3), and 8.97 (s, 3 H, CH_3); uv λ_{max}^{EtOH} 287 (ϵ 28,800).

Characterization of 1,1-Di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. Permanganate Crown Ether Cleavage. To a mixture of 400 mg (1.08 mmol) of dicyclohexyl-18-crown-6 and 170 mg (1.08 mmol) of potassium permanganate in 150 ml of benzene (the Sam-Simmons reagent[6]), stirred 0.5 hr at room temperature, a solution of 153 mg (0.307 mmol) of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane in 5.0 ml of benzene was added. Manganese dioxide precipitated within 5 min. After 1 hr the solution was poured into 0.06 *N* hydrochloric acid and dichloromethane extracted. The extract was dried, concentrated *in vacuo*, and chromatographed on a 95 × 2 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60-200 mesh) slurry packed with 50% dichloromethane in cyclohexane. Elution with 1 l. of 50% dichloromethane in cyclohexane gave nil, 1 l. of 70% dichloromethane in cyclohexane gave 57.0 mg of *p,p'*-dicyanobenzophenone, mp 159-161°, 1.5 l. of 6:7:3 ether-dichloromethane-cyclohexane and 0.5 l. of ether gave nil, and 1.5 l. of 10% methanol in ether gave 93.5 mg of 2,2-di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic acid, mp 234-236°. Infrared and nmr spectra of both degradation products were identical with those of authentic material (*vide infra*). The mass balance was 90.4%.

***p,p′*-Dibromobenzophenone.** This material was prepared by a slight modification of the method of Norris and Green[20] in a 23.4% yield.

***p,p′*-Dibromobenzophenone Hydrazone.** A mixture of 45.3 g (0.133 mol) of *p,p′*-dibromobenzophenone and 30.0 g (0.600 mol) of hydrazine hydrate in 125 ml of ethanol was refluxing 18 hr. On cooling, 41.6 g (88.8%) of the desired hydrazone crystallized, mp 95–97°.

***p,p′*-Dibromophenyldiazomethane.** This material was prepared from *p,p′*-dibromobenzophenone hydrazone in a manner exactly analogous to the preparation of diphenyldiazomethane.[21] The yield of *p,p′*-dibromophenyldiazomethane was 93.3%, mp 97–100°.

The spectral data were the following: ir ($CHCl_3$) 4.89, 6.31, 6.71, 7.61, 7.78, 9.31, 9.93, 10.80, and 12.18 μ; nmr ($CDCl_3$) τ 2.31–2.97 (m, 8 H, arom).

Derivatization. A solution of 0.830 g (2.36 mmol) of the diazo compound and 2.00 g of benzoic acid in 50 ml of ether had lost the red color after 24 hr. The ether solution was washed with 5% sodium hydroxide and concentrated *in vacuo* leaving 1.06 g of di-*p*-bromobenzhydryl benzoate which was recrystallized from hexane to give 0.562 g (53.4%) of the ester, mp 96–98°.

2,2-Di-*p*-bromophenyl-3,3-dimethylcyclopropanecarboxylic Acid. A solution of 36.5 g (0.104 mol) of *p,p′*-dibromophenyldiazomethane in 250.0 g (1.95 mol) of ethyl 3-methyl-2-butenoate, in a 1-l. acid-washed[22] flask, had lost the red color after 4 days at 65–70°. Unreacted ester was distilled, the remaining material was taken up in ether, and crystalline dimeric material (16.7 mg) was filtered. The filtrate was concentrated *in vacuo* and taken up in 200 ml of ethanol, 17.5 g (0.313 mol) of potassium hydroxide in 25 ml of water was added, and the mixture was refluxed 1 hr, concentrated *in vacuo,* taken up in water, and ether and then benzene extracted. The aqueous phase at 0° was acidified (Methyl Orange) with hydrochloric acid. Ether extraction, concentration *in vacuo,* and recrystallization from ether gave 3.26 g (7.4%) of 2,2-di-*p*-bromophenyl-3,3-dimethylcyclopropanecarboxylic acid, mp 223–224.5°.

The spectral data were the following: ir ($CHCl_3$) 3.0–3.9 (br), 5.88, 6.72, 7.02, 8.36, 9.00, 9.31, and 9.91 μ; nmr ($CDCl_3$) τ 0.85–1.55 (br, 1 H, CO_2H), 2.40–3.05 (m, 8 H, arom), 7.75 (s, 1 H, cyclopropyl), 8.56 (s, 3 H, CH_3), and 8.93 (s, 3 H, CH_3).

2,2-Di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic Acid. A solution of 1.63 g (3.84 mmol) of 1,1-di-*p*-bromophenyl-2,2-dimethyl-3-cyclopropanecarboxylic acid and 2.50 g (27.3 mmol) of cuprous cyanide in 20.0 ml of *N,N*-dimethylformamide was refluxed 16 hr under nitrogen with Trubore stirring. The cooled solution was poured into a solution of 20.0 g of ferric chloride in 200 ml of 6 *M* hydrochloric acid, stirred 0.5 hr, and ether extracted. The extract was washed, dried and concentrated *in vacuo* to give 0.973 g of product. Recrystallization from benzene gave 0.653 g (53.2%) of 2,2-di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic acid, mp 236–238°.

The spectral data were the following: ir ($CHCl_3$) 3.00–4.10 (br), 4.47, 5.84, 6.21, 6.62, 6.93, 7.09, 7.22, 8.53, 8.97, 11.02, 11.92, and 12.20 μ; nmr ($CDCl_3$) τ 0.94 (s, 1 H, CO_2H), 2.31–2.78 (m, 8 H, arom), 7.64 (s, 1 H, cyclopropyl), 8.51 (s, 3 H, CH_3), and 8.88 (s, 3 H, CH_3).

***p,p′*-Dicyanobenzophenone.** This material, mp 163–165°, was prepared in a 37% yield by a slight modification of the method of Tadros, Akhnookh, and Aziz.[23]

The spectral data were the following: ir ($CHCl_3$) 4.44, 5.99, 6.22, 7.10, 7.61, 7.73, 7.85, 9.81, 10.78, 11.62, and 11.88 μ; nmr ($CDCl_3$) τ 2.16 (s, 8 H, arom).

3,3-Dimethyl-5,5-di-*p*-chlorophenyl-5-hydroxypentanoic Acid Lactone. To a stirred solution of 30.0 g (0.139 mol) of diethyl 3,3-dimethylglutarate was added dropwise a solution of 0.320 mol of *p*-chlorophenylmagnesium bromide, prepared from 61.2 g (0.320 mol) of 1-bromo-4-chlorobenzene, and 7.78 g (0.320 mol) of magnesium turnings in 250 ml of anhydrous ether. The reaction mixture was refluxed 1.0 hr and then poured onto ice–HCl. The ether layer was washed with water, dried, and concentrated *in vacuo* yielding 42.3 g of yellow oil. Unreacted diester was distilled at 87–91° (1.5 mm). The remaining oil was chromatographed on a 5 × 30 cm column slurry packed with silicic acid (Mallinckrodt Silicar CC-7, 100–200 mesh) in hexane. Elution was with 1.5 l. of hexane and 1.5 l. of benzene; the benzene fraction gave 22.6 g (46.7%) of the desired lactone as an oil. A portion was crystallized to mp 45–47° by use of cold cyclohexane.

The spectral data were the following: ir ($CHCl_3$) 3.30, 3.36, 3.47, 5.76, 6.22, 6.71, 7.13, 8.05, 9.13, 9.73, 9.90, and 12.22 μ; nmr ($CDCl_3$) τ 2.42–3.03 (m, 8 H, arom), 7.47 (s, 2 H, CH_2), 7.85 (s, 2 H, CH_2), and 9.02 (s, 6 H, CH_3).

1,1-Di-*p*-chlorophenyl-3,3-dimethyl-5,5-diphenylpentane-1,5-diol. To a solution of 25.9 g (0.0732 mol) of 3,3-dimethyl-5,5-di-*p*-chlorophenyl-5-hydroxypentanoic acid lactone in 300 ml of ethanol was added a solution of 25.0 g (0.625 mol) of sodium hydroxide in 50 ml of water. The solution was refluxed 0.75 hr and concentrated *in vacuo.* The material was taken up in ether, washed, dried over magnesium sulfate, and concentrated *in vacuo* to give 28.4 g of a tacky solid, sodium 3,3-dimethyl-5,5-di-*p*-chlorophenyl-5-hydroxypentanoate. This material was used without additional purification.

The spectral data were the following: ir ($CHCl_3$) 2.73, 3.05 (br), 3.37, 6.25, 6.72, 7.13, 7.98, 9.15, 9.88, and 12.00 μ; nmr (acetone-d_6) τ 2.33–2.88 (m, 8 H, arom), 4.50–5.23 (br, 1 H, -OH), 7.50 (s, 2 H, CH_2), 7.65 (s, 2 H, CH_2), and 9.32 (s, 6 H, CH_3).

To a solution of 0.633 mol of phenyllithium, prepared from 9.00 g (1.30 mol) of freshly cut lithium and 100.0 g (0.633 mol) of bromobenzene in 500 ml of anhydrous ether, a solution of 28.4 g (0.0731 mol) of sodium 3,3-dimethyl-5,5-di-*p*-chlorophenyl-5-hydroxypentanoate in 250 ml of anhydrous ether was added dropwise. The solution was refluxed 2 hr, stirred 18 hr at room temperature, and then poured onto an ice-aqueous ammonium chloride solution. The ether phase was washed, dried, and concentrated *in vacuo* to give 76.8 g of brown oil, which was chromatographed on a 5 × 36 cm column of alumina slurry packed in hexane. Elution with 1250 ml of hexane, 500 ml of 2%, and 2500 ml of 5% ether in hexane gave aromatic impurities, 500 ml of 10%, 1000 ml of 15%, and 1000 ml of 20% ether gave triaryl compounds, and 1000 ml of 20% and 2750 ml of 40% ether in hexane gave 10.27 g of crude diol which was recrystallized from hexane to give 7.23 g (19.6%) of 1,1-di-*p*-chlorophenyl-3,3-dimethyl-5,5-diphenylpentane-1,5-diol, mp 145–146°.

The spectral data were the following: ir ($CHCl_3$) 2.78, 2.94, 3.38, 6.29, 6.73, 6.92, 7.15, 7.88, 8.51, 9.17, 9.53, 9.88, 10.09, 11.04, 12.01, and 14.37 μ; nmr ($CDCl_3$) τ 2.39–2.88 (m, 18 H, arom), 5.10–6.65 (br, 2 H, OH), 7.34 (s, 2 H, CH_2), 7.42 (s, 2 H, CH_2), and 9.60 (s, 6 H, CH_3).

1,1-Di-*p*-chlorophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 3.13 g (6.20 mmol) of 1,1-di-*p*-chlorophenyl-3,3-dimethyl-5,5-diphenylpentane-1,5-diol and 0.50 ml of 3 *N* hydrochloric acid in 75 ml of dioxane was refluxed 1 hr and concentrated *in vacuo.* The resulting oil was chromatographed on a 5 × 15 cm alumina column (Fisher, neutral activity, 80–200 mesh) slurry packed in hexane. Elution with 1.0 l. of hexane gave 2.19 g (75.5%) of the desired diene, mp 89–90.5°. Recrystallization did not raise the melting point.

The spectral data were the following: ir (CCl_4) 3.37, 6.28, 6.72, 6.93, 7.12, 7.36, 9.17, 9.87, 12.12, and 14.35 μ; nmr (CCl_4) τ 2.67–3.32 (m, 18 H, arom), 4.13 (s, 2 H, =CH), and 8.97 (s, 6 H, CH_3).

1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 4.29 g (9.17 mmol) of 1,1-di-*p*-chlorophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 6.00 g (32.9 mmol) of cuprous cyanide in 35.0 ml of *N*-methyl-2-pyrrolidone[18] was refluxed 40 hr under nitrogen with Trubore stirring. After cooling, the reaction mixture was poured into 75 ml of ethylenediamine, set aside 2.0 hr, and poured into 0.5 l. of ice water. The aqueous mixture was ether extracted and the combined ether extract was washed with brine, dried, filtered, and concentrated *in vacuo* to give 3.63 g of yellow oil which was chromatographed on a 5 × 31 cm column of silicic acid (Mallinckrodt Silicar CC-7, 100–200 mesh), slurry packed in hexane. Elution with 500 ml of 1% and 500 ml of 4% ether in hexane gave nil, 500 ml of 6% and 1400 ml of 12% ether gave 0.712 g of monocyano compounds, and 1600 ml of 12%, 500 ml of 30% ether in hexane, and 1000 ml of ether gave 2.03 g of crude dicyanodiene. Decolorization on a silica gel-Norit column and recrystallization from chloroform–ether gave 0.756 g (18.4%) of pure 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, mp 156.5–158°.

The spectral data were the following: ir ($CHCl_3$) 3.31, 3.37, 4.47, 6.27, 6.71, 6.93, 8.17, 8.32, 9.33, 9.83, 11.97, and 14.33 μ; nmr (CCl_4) τ 2.33–3.27 (m, 18 H, arom), 4.00 (s, 1 H, =CH), 4.22 (s, 1 H, =CH), and 8.96 (s, 6 H, CH_3); uv λ_{max}^{EtOH} 265 (ϵ 24,500).

Photolysis of 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.602 g (1.34 mmol) of the diene in 450 ml of *tert*-butyl alcohol was purged with purified[19] nitrogen 1.0 hr before and then during the photolysis. The irradiation was carried out using a 450-W Hanovia medium-pressure lamp with a 2.0-mm Vycor glass filter, all in a water-cooled immersion well for 0.75 hr. Solvent removal *in vacuo* gave 0.717 g of yellow oil. Crystallization from ether gave 402 mg (66%) of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane, mp 179–182°.

This was purified by recrystallization from methanol giving 0.347 g, mp 183–184.5°. 1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane was not detected by nmr in the mother liquors.

The spectral data for the vinylcyclopropane were the following: ir (CCl_4) 4.47, 6.22, 6.65, 6.91, 7.10, 8.97, 9.81, 11.00, 12.13, and 14.26 μ; nmr (CCl_4) τ 2.25–2.95 (m, 18 H, arom), 4.46 (d, 1 H, J = 10.5 Hz, =CH), 7.82 (d, 1 H, J = 10.5 Hz, cyclopropyl), 8.71 (s, 3 H, CH_3), and 9.06 (s, 3 H, CH_3), uv λ_{max}^{EtOH} 272 sh (ϵ 21,000).

High Conversion Photolysis of 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. Analysis for 1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. A solution of 0.197 g (0.437 mmol) of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 750 ml of *tert*-butyl alcohol was purged with purified nitrogen[19] for 1.0 hr and photolyzed 5.0 hr (19.8 mEinsteins) on the "black box" apparatus[5] using a solution filter combination (*vide infra*) giving 60-nm band width and a 282 nm maximum (30% transmission). Concentration *in vacuo* gave 0.201 g of material. Nmr showed only traces of the diene.

A 0.146-g portion (72.3%) of the photolysate was subjected to high-pressure liquid chromatography using a 1.5 in. × 6 ft steel column packed with silicic acid (Mallinckrodt Silicar CC-7, 200–320 mesh), 20% ether in hexane at 1.1 l./hr scanning at 280 nm and collection of 40-ml fractions. Fractions 3–97 contained 23.7 mg, a third of which was diene reactant, based on nmr and 98–180 contained 116.6 mg of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. The mass balance for the portion chromatographed was 98.6%. No 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane was detectable by nmr.

The remaining 0.0556-g portion of the photolysate was used for analytical hplc. Silicic acid surfaced glass bead packing[24] was eluted with 50% ether in hexane using an 8 ft × ⅛ in. column with 254-nm uv scanning. Calibration runs with authentic compounds gave base line separation of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane from starting diene, but recycling did not separate the diene and 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. A small peak due to the latter vinylcyclopropane and the diene was detected in the photolysate which sets a lower limit of 23.8:1 as the ratio of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane to 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. Since the preparative runs showed some diene but no 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane, the ratio of the two vinylcyclopropanes is greater.

Characterization of 1,1-Di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. The Lemieux–von Rudloff reagent[8] was used for oxidation. Thus, to a solution of 0.228 g (0.507 mmol) of 1,1-di-*p*-cyanophenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane in 200 ml of dioxane, a solution of 2.15 g (10.0 mmol) of sodium metaperiodate, 100.0 mg (0.724 mmol) of potassium carbonate, and 0.101 g (0.640 mmol) of potassium permanganate in 200 ml of water was added; the resulting solution was stirred 1.0 hr at 55°, giving a manganese dioxide precipitate. The reaction solution was diluted with water and ether extracted. The aqueous phase was then acidified with hydrochloric acid and ether extracted; the ether extracts were combined, washed, dried, and concentrated *in vacuo* to give 0.323 g of material which was chromatographed on a 2 × 86 cm column, slurry packed with 30% Celite (Eagle-Pitcher FW 80) and 70% silicic acid (Mallinckrodt Silicar CC-7, 200–320 mesh) in 5% ether in hexane. Elution with 250 ml of hexane, 250 ml of 2%, 250 ml of 4%, and 250 ml of 6% ether in hexane gave nil, 250 ml of 8% ether gave 24.3 mg of benzophenone, mp 48–50.5°, 250 ml of 10%, 750 ml of 12%, and 750 ml of 15% ether gave nil, 1750 ml of 20% ether gave 36.3 mg of vinylcyclopropane, 750 ml of 25%, 250 ml of 35%, and 250 ml of 40% ether gave 51.6 mg of partially oxidized vinylcyclopropane, 1250 ml of 50% ether, and 1500 ml of 10% methanol in ether gave 86.0 mg, recrystallized from chloroform to give 37.1 mg of 2,2-di-*p*-cyanophenyl-3,3-dimethylcyclopropanecarboxylic acid, mp 235–237.5°. The mass balance was 78% and spectral data of the cyclopropyl acid were identical with those of synthesized material (*vide infra*).

2,2-Diphenyl-3,3-dimethylcyclopropanecarboxylic Acid. A solution of 97.3 g (0.502 mol) of diphenyldiazomethane[21] in 400.0 g (3.12 mol) of ethyl 3-methyl-2-butenoate heated in a 1-l. acid-washed[22] flask at 60° had lost the red color after 3 days. Unreacted ester was distilled; the residue was taken up in ether and crystalline dimeric material (28.2 g) was filtered. The filtrate was concentrated *in vacuo*, taken up in 300 ml of absolute ethanol, and 35 g of potassium hydroxide (0.635 mol) in 50 ml of water was added and the mixture was refluxed 2 hr, concentrated *in vacuo*, taken up in water, and ether and then benzene extracted. The aqueous phase was acidified (Methyl Orange) at 0° with hydrochloric acid and ether extracted. The extract was dried, concentrated *in vacuo*, and triturated with cold ether to give 20.36 g (15.3% based on diphenyldiazomethane) of the desired cyclopropyl acid, mp 230–233° (reported[7] mp 231–233.5°). Spectral data were identical with those reported by Zimmerman and Mariano[7] for the compound.

2,2-Diphenyl-3,3-dimethylcyclopropaneacetic Acid. A suspension of 11.2 g (0.0423 mol) of 2,2-diphenyl-3,3-dimethylcyclopropanecarboxylic acid, 15.0 g (0.118 mol) of oxalyl chloride, and 0.050 ml of *N,N*-dimethylformamide in 250 ml of benzene was stirred 3.0 hr under nitrogen and concentrated *in vacuo* to give 12.4 g of crystalline acid chloride. This in 100 ml of anhydrous ether was added dropwise to an excess of diazomethane in ether at room temperature under a stream of nitrogen. The resulting diazo ketone[25] in 150 ml of purified[26] dioxane was added dropwise to a stirred suspension of 2.00 g of silver oxide in 350 ml of methanol at 60°. An additional 18.0 g of silver oxide was added in 2.0 g portions at 20-min intervals. The reaction mixture was stirred 6 hr at 65°, filtered, and concentrated *in vacuo*. Product was taken up in 300 ml of absolute ethanol, 30 g (0.0527 mol) of potassium hydroxide in 50 ml of water was added, refluxed 1.5 hr, concentrated *in vacuo*, taken up in water, and ether extracted. The aqueous phase at 0° was acidified (Methyl Orange) with hydrochloric acid and ether extracted; the ether extract was dried, filtered, and concentrated *in vacuo*. Recrystallization from chloroform–ether gave 3.52 g of the desired product, mp 198.5–200°.

The spectral data were the following: ir ($CHCl_3$) 2.80–4.30 (br), 5.86, 6.59, 7.07, 7.72, 8.30, 8.85, 9.25, 9.73, and 14.15 μ; nmr ($CDCl_3$) τ 1.35 (s, 1 H, CO_2H), 2.40–3.00 (m, 10 H, arom), 7.40–7.70 (m, 2 H, CH_2), 8.27 (t, 1 H, J = 7.5 Hz, cyclopropyl), 8.85 (s, 3 H, CH_3), and 9.03 (s, 3 H, CH_3).

1,1-Di-*p*-bromophenyl-2-(2,2-diphenyl-3,3-dimethylcyclopropane)ethanol. To a solution of 12.0 mmol of *p*-bromophenyllithium,[17] prepared by addition of 12.0 mmol of *n*-butyllithium (2 *M* in hexane) to 5.67 g (24.0 mmol) of *p*-dibromobenzene in 50 ml of anhydrous ether under nitrogen at room temperature and cooled to 0° after 15 min, a solution of 0.847 g (2.88 mmol) of methyl 2,2-diphenyl-3,3-dimethylcyclopropaneacetate, prepared by diazomethane esterification of 2,2-diphenyl-3,3-dimethylcyclopropaneacetic acid, in 20.0 ml of anhydrous ether was added dropwise. After 0.5 hr the action was quenched with water, and the ether phase was washed, dried, and concentrated *in vacuo* to give 4.08 g of oil which was chromatographed on a 2.5 × 80 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed with 0.5% ether–hexane. Elution with 900 ml of hexane gave aromatic impurities, 400 ml of 1%, 1100 ml of 2%, 500 ml of 4%, and 400 ml of 6% ether in hexane gave nil, and 800 ml of 8% ether in hexane gave 1.33 g of the desired alcohol, mp 152–156°, which was recrystallized from ether–hexane to give 1.163 g (69.6%), mp 156–158°.

The spectral data were the following: ir ($CHCl_3$) 2.77, 6.25, 6.72, 6.90, 7.17, 9.30, 9.92, 11.06, 12.25, and 14.17 μ; nmr ($CDCl_3$) τ 2.40–3.10 (m, 18 H, arom), 7.23 (C portion of ABC pattern, 1 H, J_{AC} = 2.0 Hz, J_{BC} = −13.0 Hz, J_{AB} = 8.0 Hz, CH_2), 7.82 (s, 1 H, OH), 8.23 (B portion of ABC pattern, 1 H, CH_2), 8.60 (A portion of ABC pattern, 1 H, cyclopropyl), 9.06 (s, 3 H, CH_3), and 9.21 (s, 3 H, CH_3). The coupling constants were derived from inspection and agreed with PDP8/I computer simulation.[27]

1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-bromophenylvinyl)cyclopropane. A solution of 1.76 g (3.05 mmol) of 1,1-di-*p*-bromophenyl-2-(2,2-diphenyl-3,3-dimethylcyclopropane)ethanol, 1.63 g of phthalic anhydride, and 45.8 mg of *p*-toluenesulfonic acid in 330 ml of benzene was refluxed 1.0 hr, concentrated *in vacuo*, and chromatographed on a 2.5 × 70 cm silica gel column (Grace, Grade 62, 60–200 mesh) slurry packed and eluted with hexane; 250 ml fractions were collected. Fractions 5–8 contained 1.28 g of the desired product. Recrystallization from ether–methanol gave 0.967 g (56.8%) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-bromophenylvinyl)cyclopropane, mp 116–168°.

The spectral data were the following: ir (CCl_4) 6.25, 6.72, 6.92, 7.19, 8.97, 9.33, 9.91, 10.72, 12.13, and 14.20 μ; nmr ($CDCl_3$) τ 2.35–3.12 (m, 18 H, arom), 4.38 (d, 1 H, J = 10.5 Hz, =CH), 7.93 (d, 1 H, J = 10.5 Hz, cyclopropyl), 8.72 (s, 3 H, CH_3), and 9.01 (s, 3 H, CH_3).

1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. A solution of 2.85 g (5.18 mmol) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-bromophenylvinyl)cyclopropane and 4.03 g (0.0478 mol) of cuprous cyanide in 40 ml of *N,N*-dimethylformamide[18] was refluxed 17 hr with Trubore stirring under nitrogen, cooled, poured into 75.0 ml of ethylenediamine, set aside 1 hr, and then poured onto ice. The aqueous phase was ether extracted; the extract was dried, filtered, and concentrated *in vacuo* to give 2.33 g of vinylcyclopropane, mp 175–180°, which was decolorized with Norit and recrystallized from ethanol to give 1.22 g (52.1%) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane, mp 188–190°.

The spectral data were the following: ir ($CHCl_3$) 4.48, 6.25, 6.70, 6.92, 8.97, 9.80, 11.93, and 14.33 μ; nmr ($CDCl_3$) τ 2.10–3.10 (m, 18 H, arom), 4.11 (d, 1 H, J = 10.5 Hz, =CH), 8.01 (d, 1 H, J = 10.5 Hz, cyclopropyl), 8.69 (s, 3 H, CH_3), and 9.01 (s, 3 H, CH_3); uv λ_{max}^{EtOH} 297 (ϵ 23,100).

Photolysis of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane. A solution of 497 mg (0.939 mmol) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane in 1.0 l. of *tert*-butyl alcohol was purged with purified nitrogen[19] 1.0 hr before and then during photolysis. Irradiation was carried out using a 450-W Hanovia medium-pressure lamp with a 2.0-mm Vycor glass filter in a water-cooled immersion well for 0.5 hr. Solvent removal *in vacuo* gave 480 mg of photolysate which was chromatographed on a 2.5 × 80 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60–200 mesh) slurry packed in 3% ether in hexane. Elution with 500 ml of 3% and 500 ml of 6% ether in hexane gave 62.2 mg of an unidentified photoproduct, 500 ml of 10% gave nil, and 500 ml of 15% gave a mixture of 407 mg of the starting vinylcyclopropane and an isomeric photoproduct. Crystallization from carbon tetrachloride gave 217 mg of the vinylcyclopropane. The mother liquors were concentrated *in vacuo* and rechromatographed on a 2.5 × 80 cm column, slurry packed with silica gel in 5% ether in hexane. Elution was with 10% ether in hexane; 100-ml fractions were collected. Fractions 11–13 contained 92.8 mg of a photoproduct, identified spectrally as 1,1-di-*p*-cyanophenyl-4,4-starting vinylcyclopropane. The total recovery of 1,1-diphenyl-2,2-dimethyl-3-(2,2-di-*p*-cyanophenylvinyl)cyclopropane was 255 mg (54.3%) and the mass balance was 89.6%. No isomeric vinylcyclopropane could be detected.

The spectral data for 1,1-di-*p*-cyanophenyl-4,4-diphenyl-5-methyl-1,5-hexadiene were the following: ir ($CHCl_3$) 4.47, 6.25, 6.70, 11.93, and 14.30 μ; nmr ($CDCl_3$) τ 2.1–3.1 (m, 18 H, arom), 3.71 (t, 1 H, J = Hz, Ar_2C=CH), 4.86 (br s, 1 H, =CH*H*), 5.02 (s, 1 H, =CH*H*), 6.92 (d, 2 H, J = 7 Hz, CH_2), and 8.46 (br s, 3 H, CH_3).

Photolysis Equipment and Quantum Yield Determinations. Quantum yield irradiations were performed on the "black box" apparatus[5] or on the microoptical bench. Light output was monitored by ferrioxalate actinometry[28] and the light absorbed in the reaction cell was determined by the splitting ratio technique.[5]

For the microoptical bench runs, the monochromator inlet slit was set at 5.4 mm and the exit slit at 3 mm, giving a bank pass of 22 nm at half-peak height. For direct "black box" irradiation, the solution filters used were: filter A (a) 2 M nickel sulfate hexahydrate in 5% sulfuric acid; (b) 1 M cobalt sulfate heptahydrate in 5% sulfuric acid; (c) 2 × 10^{-4} M bismuth(III) chloride in 10% hydrochloric acid. This combination (2.4-cm thickness for each of three cells) gave a transmission maximum at 282 nm (30% transmission) and was opaque above 310 nm and below 250 nm. In the sensitized runs, the filter solutions employed were: filter B (a) 26.3 g of nickel sulfate hexahydrate in 1 l. of 10% sulfuric acid; (b) 112.5 g of cobalt sulfate hepahydrate in 1 hydrochloric acid. This combination gave a transmission maximum at 344 nm (54% transmission) and was opaque above 385 nm and below 315 nm.

Direct Quantum Yields, 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. Quantum yield photolyses were run on an optical bench apparatus as described by Zimmerman.[5] Approximately 10^{-3} M solutions in 40.0 ml of purified *tert*-butyl alcohol under deoxygenated nitrogen at 31° were photolyzed with the monochromator set at 295 nm. Analysis was with high pressure liquid chromatography using a 10 ft × ⅛ in. column packed with Waters Associates' Corasil II and eluting with 35% ether in hexane. 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene was used as an internal standard. Data for the individual quantum yields are as follows.

Run 1. Starting diene used, 3.80 × 10^{-2} mmol; 2.52 × 10^{-2} mEinsteins absorbed; vinylcyclopropane product formed, 4.04 × 10^{-3} mmol; Φ = 0.16, 10.6% conversion.

Run 2. Starting diene, 3.78 × 10^{-2} mmol; 2.66 × 10^{-2} mEinsteins; vinylcyclopropane, 4.06 × 10^{-3} mmol; Φ = 0.17; 10.7% conversion.

Sensitized Quantum Yield, 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. A solution of 24.2 mg (0.0484 mmol) of 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene and 522 mg (2.86 mmol) of benzophenone in 75.0 ml of *tert*-butyl alcohol was purged with purified[19] nitrogen for 1.0 hr before and during irradiation with 0.381 mEinsteins on the "black box" apparatus[5] using filter combination B (*vide supra*). The photolysate was concentrated *in vacuo* and passed through a 1.0 × 10.0 column packed and eluted with 0.5 l. of hexane to remove benzophenone (0.518 g). Elution with 10% ether in dichloromethane gave 26.7 mg of tetracyanophenyl compounds. Analysis was with high-pressure liquid chromatography using a 12 ft × ⅜ in. column packed with silicic acid (Mallinckrodt Silicar CC-7, 200–325 mesh), eluting with 50% ether–cyclohexane, and scanning at 254 nm. An authentic sample containing 10.6 mg of diene and 0.96 mg of vinylcyclopropane was used for calibration. No vinylcyclopropane was detected in the photolysate, and, assuming 1.0 mg (2.0 × 10^{-3} mmol) could have been detected as with standard, Φ_{sens} <5.3 × 10^{-3}.

Direct Quantum Yields, 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. Direct quantum yields were run on the "black box" apparatus[5] in 750 ml of solvent purged with purified nitrogen[19] 1.0 hr before and then during photolysis. Filter combination A (*vide supra*) was used. After photolysis the solvent was removed *in vacuo*.

Quantum yield runs 1–3 were analyzed by chromatography on a 4 × 130 cm silica gel column (Grace, Grade 62, 60–200 mesh), packed and eluted with 10% ether in hexane; 40-ml fractions were collected. Fractions 55–145 contained the starting diene and fractions 150–260 contained the vinylcyclopropane.

Runs 4–5 were analyzed by isolation using preparative high-pressure liquid chromatography employing a 1 in. × 6 ft steel column packed with silicic acid (Mallinckrodt CC-7, 200–325 mesh), 20% ether in hexane, 1.2 l./hr, scanning at 280 nm, and collection of 40-ml fractions. Fractions 32–81 contained the starting diene. Fractions 82–140 contained the vinylcyclopropane photoproduct.

The data are reported as follows.

Run 1. *tert*-Butyl alcohol solvent; starting diene used, 1.01 mmol; 4.12 mEinsteins absorbed; vinylcyclopropane product formed, 0.295 mmol; Φ = 0.072; 29.1% conversion.

Run 2. *tert*-Butyl alcohol solvent; starting diene, 0.978 mmol; 1.02 mEinsteins; vinylcyclopropane, 0.0927 mmol; Φ = 0.092; 9.5% conversion.

Run 3. *tert*-Butyl alcohol solvent; starting diene, 1.08 mmol; 0.581 mEinsteins; vinylcyclopropane, 0.0549 mmol; Φ = 0.095; 5.1% conversion.

Run 4. Ethanol solvent; starting diene, 0.497 mmol; 0.652 mEinsteins; vinylcyclopropane, 0.0556 mmol; Φ = 0.086; 11.2% conversion.

Run 5. Cyclohexane solvent; starting diene, 0.503 mmol; 0.534 mEinsteins, vinylcyclopropane, 0.0524 mmol; Φ = 0.097, 10.4%

conversion.

Sensitized Quantum Yield, 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A sample of 0.495 g (1.10 mmol) of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 9.63 g (52.9 mmol) of benzophenone in 750 ml of *tert*-butyl alcohol was irradiated on the black box apparatus[5] with 7.06 mEinsteins using filter B (*vide supra*).

The photolysate was chromatographed on a 4 × 135 cm silica gel column (Grace, Grade 62, 60–200 mesh), slurry packed and eluted with 10% ether in hexane; 40-ml fractions were collected. Fractions 40–78 contained 9.53 g of benzophenone; fractions 106–312 contained 0.490 g of the diene. Total diene recovery was 99.1%. No vinylcyclopropane was detected, and assuming 10.0 mg of the vinylcyclopropane could be detected, $\Phi_{\mathrm{sens}} < 3.0 \times 10^{-3}$.

Energy Transfer Tests. Quenching of Benzophenone Triplets by 1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and by 1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. Irradiation was carried out on the "black box" apparatus[5] using filter B (*vide supra*). Potassium ferrioxalate actinometry[28] was employed.

A solution of 0.400 g (2.20 mmol) of benzophenone and 0.200 g (1.09 mmol) of benzhydrol in 75.0 ml of *tert*-butyl alcohol was purged with deoxygenated[19] nitrogen for 1.5 hr before and during the 1.5 hr irradiation. Similarly, a solution of 0.400 g of benzophenone, 0.200 g of benzhydrol, and 39.4 mg (0.0876 mmol) of 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 75.0 ml of *tert*-butyl alcohol and a solution of 0.400 g of benzophenone, 0.200 g of benzhydrol, and 37.1 mg (0.0743 mmol) of 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene in 75.0 ml of *tert*-butyl alcohol were purged and irradiated. Analysis was with high-pressure liquid chromatography using an 8 ft × ⅛ in. column packed with Waters Associates' Corasil *II*, eluting with 1.5% ether in hexane and with *p*-benzoquinone as an internal standard. Results are as follows.

Run 1. No quencher; 4.48 mEinsteins absorbed; benzophenone recovered, 297 mg; benzpinacol, 204 mg; $\Phi = 0.124$; 0% quenching.

Run 2. Quencher, 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene; 2.80 mEinsteins; benzophenone, 341 mg; benzpinacol, 35.9 mg; $\Phi = 0.035$; 71.7% quenching.

Run 3. Quencher, 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene; 2.99 mEinsteins; benzophenone, 384 mg; benzopinacol, 24.1 mg; $\Phi = 0.022$; 82.3% quenching.

These results show that both dienes effectively quench benzpinacol formation and thus the benzophenone triplet transfers energy to the dienes.

Emission Studies. Purification of Solvent. Isopentane and methylcyclohexane were purified by repeated washing with 10% fuming sulfuric acid until the washings were colorless, then with water, then with 5% aqueous potassium hudroxide, drying over calcium chloride, and distilling. The solvent was then passed through a 2.5 × 80 cm alumina column containing 10% of silver nitrate.[29] The early and late fractions were discarded, and the solvent was redistilled. *tert*-Butyl alcohol was fractionally recrystallized and distilled from calcium hydride. Solvents prepared in these ways were transparent in the ultraviolet and fluorescence free.

4-Biphenylyl Phenyl Ether. This material was prepared by the method of Suzumua.[30]

Determination of Relative Fluorescence Quantum Yields. An Aminco-Keirs spectrofluorimeter, equipped with an Hanovia 901C-1 xenon lamp, was used to obtain the relative fluorescence quantum yields for the dienes. The emission maxima for the compounds were: 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, 310 nm; 1,1-di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 328 nm; 1,1,5,5-tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene, 321 nm. Photomultiplier response was shown to vary by less than 10% in the 300–370-nm range by comparison of experimental emission spectra of 1,1-diphenylethylene and 4-biphenyl phenyl ether with the corrected spectra published by Berlman.[31]

Solutions of the dienes in methylcyclohexane–isopentane (MCIP, 1:4) or *tert*-butyl alcohol were of equivalent (0.85) optical densities at the excitation wavelength. No significant solvent effect was observed on the fluorescence quantum yields. Results are as follows.

Run 1. MCIP solvent; 242 nm excitation; Φ_f^{rel} (tetraphenyldiene) = 1.00; Φ_f^{rel} (dicyanodiene) = 0.85; Φ_f^{rel} (tetracyanodiene) = 1.24.

Run 2. MCIP solvent; 247 nm excitation; Φ_f^{rel} (tetraphenyldiene) = 1.00; Φ_f^{rel} (dicyanodiene) = 1.00; Φ_f^{rel} (tetracyanodiene) = 1.46.

Run 3. *tert*-Butyl alcohol solvent; 243 nm excitation; Φ_f^{rel} (tetraphenyldiene) = 1.00; Φ_f^{rel} (dicyanodiene) = 0.96; Φ_f^{rel} (tetracyanodiene) = 1.34

Excited State Rate Processes of Dienes. Excited state rate processes are calculated by the method of Zimmerman and Baum.[12] For 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, k_{dt} was obtained by single photon counting,[11] and values of k_{dt} for the other dienes are computed relative to that value. The results are as follows.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. $\Phi_f^{\mathrm{rel}} = 1.00$; $\Phi_r = 0.080$; k_r (apparent) = 7.3×10^8 sec^{-1}; $k_{\mathrm{dt}} = 1.8 \times 10^{12}$ sec^{-1}; $k_r = 1.4 \times 10^{11}$ sec^{-1}.

1,1-Di-*p*-cyanophenyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. $\Phi_f^{\mathrm{rel}} = 0.94$; $\Phi_r = 0.094$; k_f (apparent) = 8.7×10^8 sec^{-1}; $k_{\mathrm{dt}} = 2.3 \times 10^{12}$ sec^{-1}; $k_r = 2.2 \times 10^{11}$ sec^{-1}.

1,1,5,5-Tetra-*p*-cyanophenyl-3,3-dimethyl-1,4-pentadiene. $\Phi_f^{\mathrm{rel}} = 1.35$; $\Phi_r = 0.165$; k_f (apparent) = 1.1×10^9 sec^{-1}; $k_{\mathrm{dt}} = 2.0 \times 10^{12}$ sec^{-1}; $k_r = 3.3 \times 10^{11}$ sec^{-1}.

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References and Notes

(1) This is Paper 90 of our photochemical series.

(2) For the previous paper of this series, see H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 4630 (1974).

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(14) The use of the valence bond picture in Chart V is not inconsistent with the view of the reaction as a ${}_{\sigma}2_a + {}_{\pi}2_a + {}_{\pi}2_a$ symmetry allowed process.[2,4,7] The biradical formulation **32** can be considered a gradation which occurs early along the reaction coordinate in which overlap between C-1 and C-3 still is relatively weak.

(15) (a) Melting points were taken on a hot stage apparatus calibrated with compounds of known melting points. (b) Satisfactory carbon-hydrogen analyses were obtained for all new compounds and were made available to the referees and Editor.

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(25) All glassware coming into contact with the diazo ketone was cleaned with a saturated solution of potassium hydroxide in ethanol.

(26) Dioxane was freshly distilled from lithium aluminum hydride.

(27) (a) Ph.D. Thesis of D. F. Juers, University of Wisconsin, 1970. (b) Program available from Digital Equipment Users Society No. 8-194.

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