Unusual Rearrangements in Di-π-methane Systems: Mechanistic and Exploratory Organic Photochemistry[1,2]

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The triplet photochemistry of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene was investigated to determine if the high reactivity of di-π-methane systems with central diphenyl substitution derived from electronic or from steric effects. Sensitized photolysis of the dicyanopentadiene afforded 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane as the singlet photoproduct with an efficiency of $\phi = 0.041$. This is intermediate between the inefficiently reacting dienes with central methyl substitution and the highly reactive dienes having central phenyl groups. Direct irradiation of the dicyanopentadiene led to four primary photoproducts. The first was the di-π-methane product observed in the triplet photochemistry. The second was *cis*-1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene, which is related to the reactant by a 1,3-shift of an isopropyl group. The third was *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene, also related to the reactant by 1,3-displacement of an isopropyl group. The last was 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene, a product in which an isopropyl group has been lost. The photochemistry of the two isopropyl-shifted dienes was also investigated. The 1,3-heptadiene underwent further di-π-methane rearrangement, while the 4,6-heptadiene gave rise to three photochemical reactions affording naphthalene derivatives.

Introduction

Nearly two decades ago we suggested that the often observed lack of triplet reactivity of di-π-methane systems derives from a free-rotor effect in which π-bond twisting is more rapid than reaction and provides an approach of excited- and ground-state surfaces.[3] An apparent contradiction to this idea was encountered in the high reactivity of a number of di-π-methane systems having central substitution either by large and delocalizing groups such as phenyl[4] or smaller groups such as cyano[4b] or carbomethoxy.[4c]

The question remained whether or not triplet reactivity in these systems resulted from molecular congestion and inhibition of the free-rotor effect, or instead as a result of a delocalization effect involving substituents on the central, "methane" carbon. One means of answering the question involves the study of molecules in which the central phenyl is replaced by isopropyl substitution. Indeed, we have used this approach in the study of 1,1,5,5-tetraphenyl-1,4-pentadienes.[5] The investigation of systems analogous to the previously studied 5,5-dicyano[4b] and 5,5-dicarbomethoxy[4c] dienes was also of interest.

Therefore, the present research addressed the photochemistry of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene, which has terminal dicyano substitution and isopropyl groups replacing central phenyls.

Results

Synthesis of Photochemical Reactants of Interest. The synthesis of the dicyanodiene **5** is outlined in Scheme I. Under standard Knoevenagel conditions with malononitrile, aldehyde **4** proved unreactive, which is perhaps not surprising in view of the drastic steric hindrance at the aldehyde carbonyl provided by geminal isopropyl substitution. However, a modification of the method of Lehnert[6] afforded the desired **5**, albeit in ca. 15% yields.

It was surmised that if dicyano diene **5** gave rise to di-π-methane reactivity, the two potential di-π-methane photoproducts would be **6** and **7**. These were independently synthesized as shown in Scheme II.

One interesting feature of the first synthesis is the use of the preformed enolate of ethyl chloroacetate for the cyclopropanation of alkylidenemalononitrile **8**. This arose from the need for a highly nucleophilic cyclopropanation reagent capable of addition to the very hindered β-carbon of **8**. Although the reaction of an α-halo enolate with a Michael system under equilibrating conditions has ample precedent,[7] the present system required a preformed enolate since the Michael system **8** merely deprotonated under the standard conditions. Another point of interest is the use of sodium bis(2-methoxyethoxy)aluminum hydride to reduce the carbethoxy group to carboxaldehyde in the presence of the two cyano groups in **9**. A final step worthy of comment is the use of the oxadi-π-methane rearrangement in converting the diphenylenal **4** to the cyclopropyl aldehyde **11**, thus providing an otherwise difficulty accessible compound.

Because the chemistry in Scheme II utilized somewhat cyclic reasoning in employing an oxadi-π-methane rearrangement to establish the structure of a potential di-π-methane photoproduct (i.e. (dicyanovinyl)cyclopropane **7**), the intermediate aldehyde **11** was converted to the tetraphenylvinylcyclopropane **12** whose structure was known,[5] having been established by X-ray.

Exploratory Sensitized Photochemistry of the Dicyano Diene 5. Since the triplet photochemistry of this diene proved to be simpler than the singlet behavior, this is discussed first. Acetophenone-sensitized irradiation of dicyano diene **5** nicely led to a single photoproduct. This proved identical with the (diphenylvinyl)cyclopropane **6**,

(1) This is paper 157 of our photochemical series and paper 217 of the general series.

(2) For paper 156, see: Zimmerman, H. E.; St. Clair, J. D. *J. Org. Chem.* **1989**, *54*, 2125.

(3) (a) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 1409-1411. (b) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267-6271. (c) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718-3725. (d) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; Edited by DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

(4) (a) Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155-2163. (b) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367-6383. (c) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, Supplement 1, 125-141.

(5) Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196-207.

(6) Lehnert, W. *Tetrahedron* **1973**, *29*, 635-638.

(7) (a) McCoy, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 2246-2249. (b) Tsugi, T.; Nishida, S. In *The Chemistry of the Cyclopropyl Group*; Rapoport, Z., Ed.; Wiley: New York, 1987; Part 1, pp 307-374. (c) Preformed α-chloro ester enolates have been used in cyclopropanation of a Michael acceptor previously.[7d] (d) Kyriakakou, G.; Ruox-Schmitt, M. C.; Seyden-Penne, J. *Tetrahedron* **1973**, *31*, 1883-1888.

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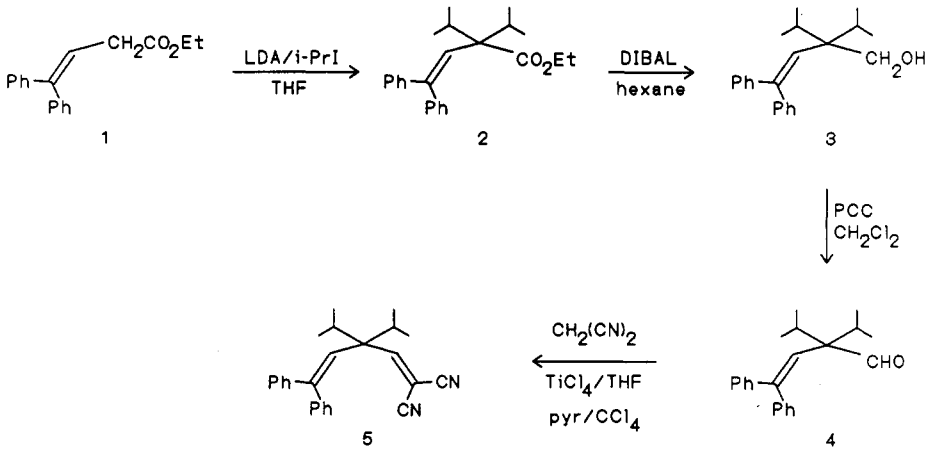
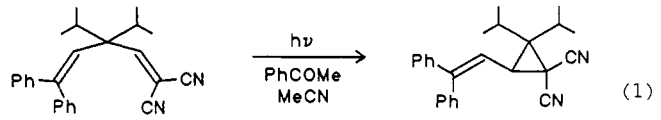
Scheme I. Synthesis of Dicyano Diene 5

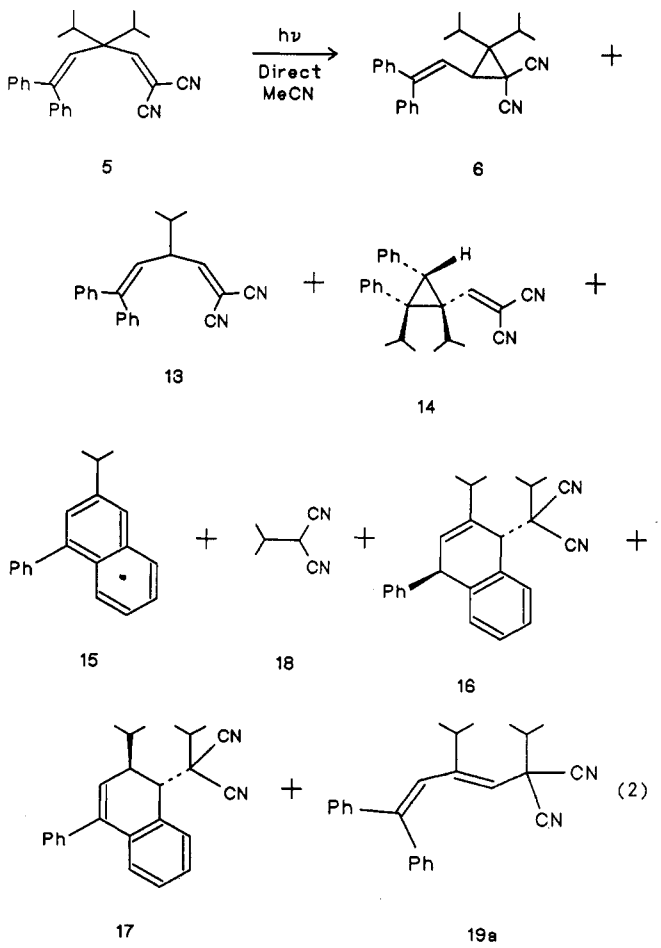


which had been synthesized as a potential photoproduct. The regioisomeric vinylcyclopropane **7** was not observed in the photolysate. Thus the sensitized photochemistry of dicyano diene **5** can be depicted as in eq 1.



5 6

Exploratory Direct Photochemistry of the Dicyano Diene 5. In contrast to the sensitized irradiation of dicyano diene **5**, the direct irradiation afforded eight distinct photoproducts. The reaction course is delineated in eq 2. Interestingly, whether dihydronaphthalene **16** was formed or, instead, isomer **17** depended on the intensity of the lamp utilized. Isomer **16** was produced in irradiations using an immersion well apparatus with a 450-W medium-pressure mercury lamp (ca. 5.4 mEinsteins/h) while isomer **17** was formed when an optical bench employing a 200-W high-pressure mercury lamp with a monochromator (ca. 0.003 mEinsteins/h) was used. This result was independent of the irradiation wavelength employed. Finally, the *trans*-4,6-heptadiene **19a** was observable at very low conversions under the low-intensity conditions.



The first photoproduct **6** had been synthesized as has been discussed above. The structures of monoisopropyl diene **13** and phenylisopropylnaphthalene **15** were established by independent synthesis as detailed in Scheme III. Isopropyltetralone **24**, which was required as a precursor to phenylisopropylnaphthalene **15**, is a known compound. However, both of the reported syntheses[8] involve seven-step procedures. We therefore developed the more efficient two-step approach shown. The structure of 4,6-heptadiene **19a** was also established by independent synthesis as described below (see Scheme IV).

Isopropylmalononitrile (**18**) is a known compound[9] and was compared with an authentic sample. The structures of the two dihydronaphthalene photoproducts **16** and **17** as well as the structure of (dicyanovinyl)cyclopropane **14** were established by X-ray diffractometry (see the Experimental Section and supplementary material for X-ray details).

Synthesis of Potential Reaction Intermediates. The formation of (dicyanovinyl)cyclopropane **14**, phenylisopropylnaphthalene **15**, and dihydronaphthalenes **16** and **17** as photoproducts clearly involved deep-seated rearrangements. Consideration of possible reaction mechanisms led us to synthesize 1,3-heptadiene **26** and 4,6-heptadiene **19a** as potential reaction intermediates. These syntheses are outlined in Scheme IV.

The sequence shown for conversion of aldehyde **28** to unsaturated nitrile **29** was used when the corresponding Horner–Emmons[10] procedure proved subject to too much steric hindrance. The double-bond stereochemistry in

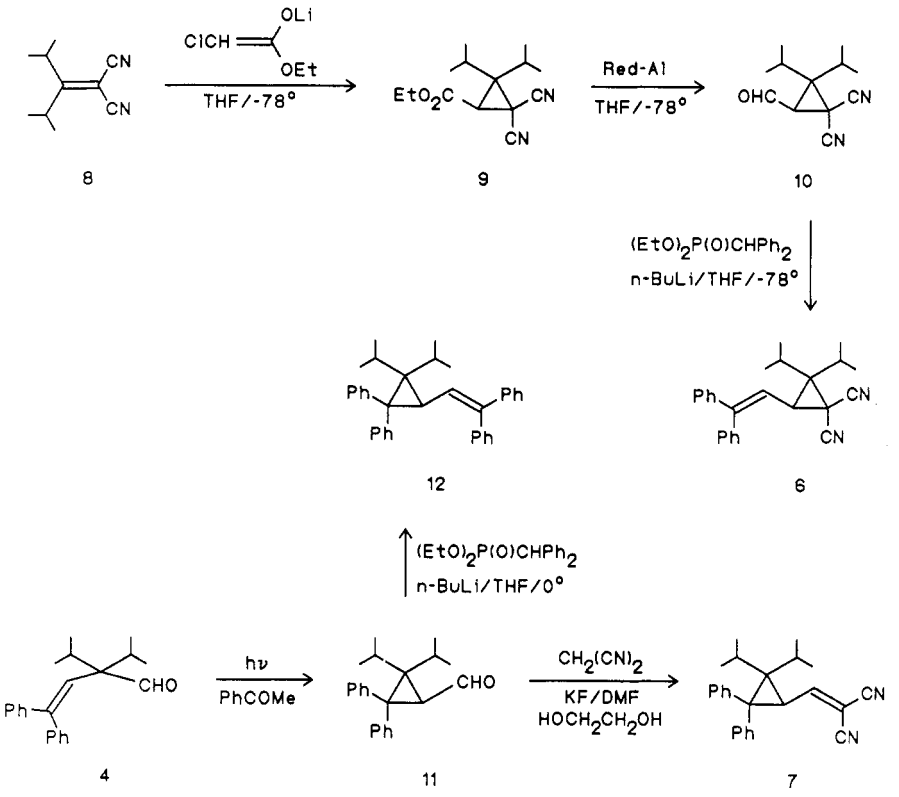
(8) (a) Kasturi, T. R.; Sivaramakrishnan, R. *Ind. J. Chem.* **1975**, *13*, 648–651. (b) Card, A.; Gautheron, B.; Besancon, J. *Bull. Chim. Soc.* **1974**, 1607–1613.

(9) Henry, P. *Chem. Ber. (Referate)* **1891**, *24*, 73–74.

(10) For the preparation and use of diethyl 1-cyano-2-methylpropylphosphonate, see: Freerksen, R. W.; Selikson, S. J.; Wroble, R. R.; Kyler, K. S.; Watt, D. S. *J. Org. Chem.* **1983**, *48*, 4087–4096.

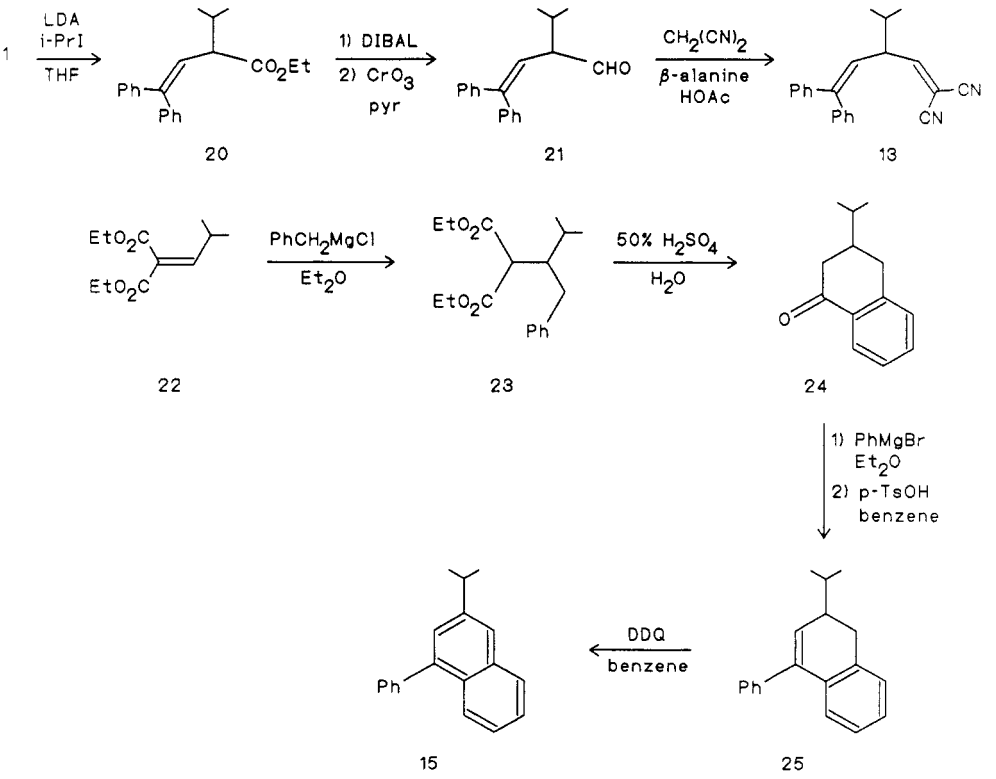
(11) (a) The mechanism of the di-π-methane rearrangement and recognition of the reaction generality was first reported in 1967.[11b] (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933.

Scheme II. Synthesis of Di-π-methane Potential Photoproducts



8 9 10 12 6 4 11 7

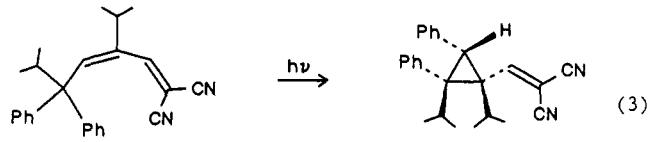
Scheme III. Syntheses of Monoisopropyl Diene 13 and Phenylisopropylnaphthalene 15



20 21 13 22 23 24 15 25

heptadienes **19a** and **26** was established by NOE difference measurements and X-ray diffractometry, respectively (details are given in the Experimental Section and supplementary material).

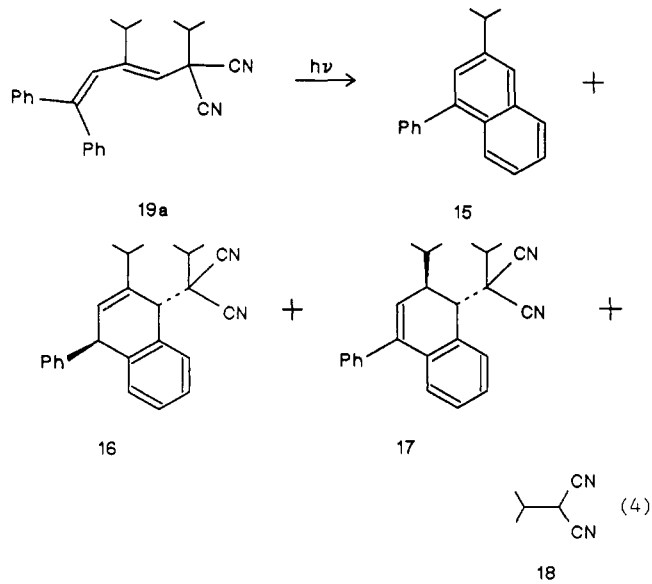
The Photochemistry of 1,3-Heptadiene 26 and 4,6-Heptadiene 19. Since at this point it was suspected that these dienes might be reaction intermediates, their photochemistry was of importance. Direct irradiation of 1,3-heptadiene **26** led to (dicyanovinyl)cyclopropane **14**, which had been encountered earlier in the photochemistry of dicyanodiene **5**. The reaction of **26**, depicted in eq 3, is a typical di-π-methane rearrangement.[3d,10] The stereochemistry is of interest since the reaction proved stereoselective, leading exclusively to one of two possible stereoisomers. The mechanistic source of this stereoselectivity is discussed below.



(3)

26 14

The second potential intermediate, 4,6-heptadiene **19a**, was also investigated. Irradiation of the trans stereoisomer **19a** led to four photoproducts—**15**, **16**, **17**, and **18**—which had been encountered previously in the photochemistry of dicyano diene **5**. This photochemistry is shown in eq 4. Interestingly, the cis stereoisomer **19b** was quite unreactive and led slowly to the trans stereoisomer **19a** along with the same photoproducts observed from **19a**.



(4)

A finding of particular interest regards the formation of dihydronaphthalenes **16** and **17** from 4,6-heptadiene **19a**. As observed earlier in the photolysis of dicyano diene **5**, the conjugated isomer **17** was formed only when light of low intensity was employed. Conversely, the unconjugated isomer **16** was formed only with high-intensity light. This effect is considered below.

Quantum Yield Determinations. Quantum yields of formation were measured for the photoproducts of the dicyano diene **5** and for those of the suspected intermediates 1,3-heptadiene **26** and 4,6-heptadiene **19**. All quantum yields were obtained by extrapolation to 0% conversion. This extrapolation was generally straightforward, either with little dependence on the extent of conversion or in being nicely linear. However, phenylisopropylnaphthalene **15** and (dicyanovinyl)cyclopropane **14** were exceptions with large and nonlinear dependences, and quantum yields for formation of these compounds were not reliably determined.

It proved possible to determine the quantum yield for formation of 4,6-heptadiene **19a**, which seemed likely to be responsible for formation of photoproducts phenylisopropylnaphthalene **15** and dihydronaphthalene **17**. However, the second presumed intermediate, namely 1,3-heptadiene **26** was not detectable, suggesting that it rapidly rearranged to (dicyanovinyl)cyclopropane **14**.

Nevertheless, it was possible to determine the quantum yield of formation of intermediate **26**. This is based on the realization that the secondary photoproducts fall into two groups: B (those formed from intermediate **26**) and C (those formed from intermediate **19a**). For convenience, the reactant dicyano diene **5** is here designated as "A" while

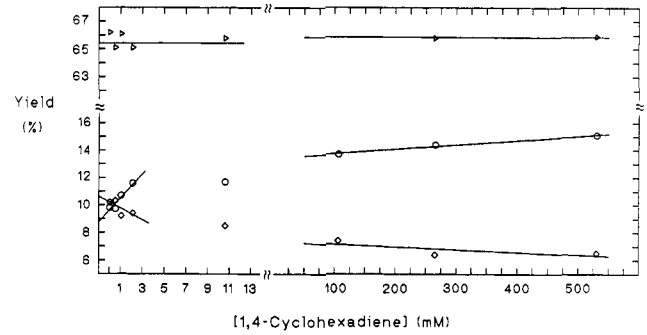
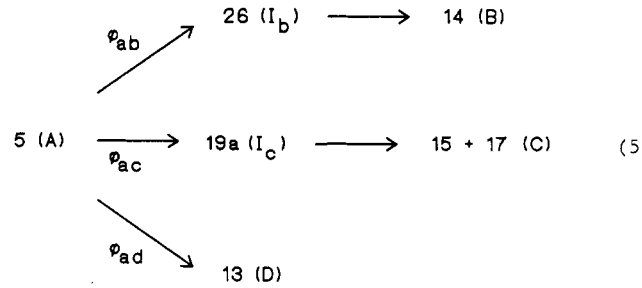


Figure 1. Plot of B (squares), C (triangles), and D (circles) type product yield (in percent of total photoproduct) versus 1,4-cyclohexadiene concentration.

the primary photoproduct monoisopropyl diene **13** is termed a "D type" product. Equation 5 shows the partition of this photochemistry into the three pathways leading to products of types B, C, and D.



(5)

The ratio of the secondary photoproducts B and C is determined by the ratio of the initial quantum yields leading in these two directions. ϕ_{ab} corresponds to the unknown efficiency of formation of intermediate **26** (I_b) while ϕ_{ac} corresponds to the known efficiency of formation of the observable intermediate **19a** (I_c). In high-conversion runs where the intermediates I_b and I_c have been completely converted to products B and C, respectively, the ratio of these two quantum yields is given in eq 6 as the ratio of group B products to group C products. Since in

$$\phi_{ab}/\phi_{ac} = (\text{total of B products})/(\text{total of C products}) \quad (6)$$

this equation all variables are known except for ϕ_{ab}, the desired efficiency of formation of **26**, we can solve for this quantum yield. Finally, Table I lists all the quantum yields obtained. In runs with the dicyano diene **5**, the secondary photoproducts (dicyanovinyl)cyclopropane **14**, phenylisopropylnaphthalene **15**, and dihydronaphthalene **17** were detectable, but extrapolation to 0% conversion minimized their interference.

Trapping of Radical Dissociation Products. One of the most interesting reactions observed was the 1,3-sigmatropic isopropyl rearrangement of the reactant dicyano diene **5**. Two mechanisms seemed likely. One is a concerted 1,3-shift and the other involves dissociation to afford isopropyl radical (**31**) and 1,1-dicyano-5,5-diphenyl-3-isopropylpentadienyl radical (**32**) with subsequent recombination. These possibilities suggested radical trapping experiments. For this purpose 1,4-cyclohexadiene seemed ideal. It is transparent in the ultraviolet at the wavelengths of interest and is an efficient radical trap.[12]

Photolyses were carried out in acetonitrile in the presence of increasing concentrations of 1,4-cyclohexadiene.

(12) (a) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964–4975. (b) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091–4096. (c) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082–4090.

Scheme IV. Syntheses of Potential Photochemical Intermediates

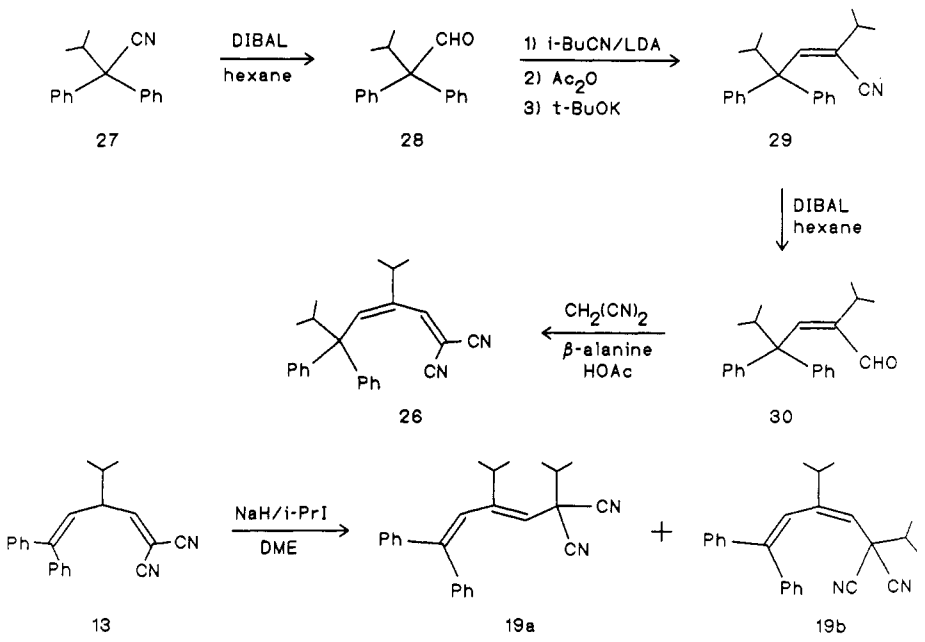


Table I. Quantum Yield Results

reactant	wavelength, nm	quantum yield[a]	product
dicyano diene **5**[b]	302	0.0049	monoisopropyl diene **13**
		0.0041	(diphenylvinyl)cyclopropane **6**
		0.0067	4,6-heptadiene **19a**
		0.0013[c]	1,3-heptadiene **26**
dicyano diene **5**	366[d]	0.041	(diphenylvinyl)cyclopropane **6**
dicyano diene **5**	366[d]	0.037	(diphenylvinyl)cyclopropane **6**
1,3-heptadiene **26**	302	0.018	(dicyanovinyl)cyclopropane **14**
trans-4,6-heptadiene **19a**	302	0.27	dihydronaphthalene **17**
		0.066	phenylnaphthalene **15**
cis-4,6-heptadiene **19b**	302	<0.02	*trans*-4,6-heptadiene **19b**
trans-4,6-heptadiene **19a**	302[e]	0.31	dihydronaphthalene **17**
		0.16	phenylnaphthalene **15**

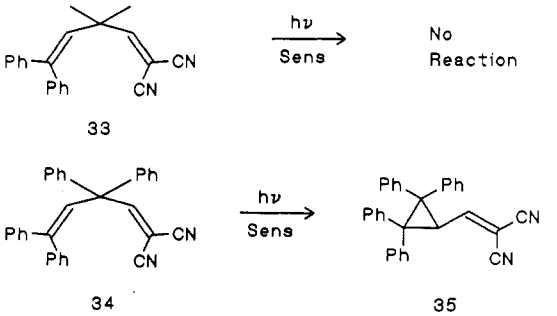
[a] Extrapolated to 0% conversion. Error of ±10%. All photolyses at 23 °C in acetonitrile unless otherwise noted. [b] Primary photoproducts only. [c] Calculated value (vide infra). [d] Thioxanthone added as sensitizer; identical results were obtained with xanthone. [e] Photolysis at 52 °C.

Figure 1 shows a plot of the yield of monoisopropyldiene **13** (a type D product) versus the radical trap concentration. Also included are the yields of the type B product **14** and the combined yield of the two type C products **15** and **16**.

Several points are noteworthy. First, it is seen that with increasing 1,4-cyclohexadiene concentration, the yield of the monoisopropyl diene **13** (D) increases from 9.8% to 15.2%, while that of (dicyanovinyl)cyclopropane **14** (B) shows a corresponding decrease from 10.2% to 6.6%, with the error in these values being ca. ±1 percentage unit. These changes of 5.3% and 3.7% in the absolute yields represent an increase in the production of monoisopropyldiene **13** (D) and a decrease in the formation of (dicyanovinyl)cyclopropane **14** (B). These variations are identical within experimental error, with the percent change in each averaging 45%. Secondly, the yield of both B and D changes rapidly at low concentrations of 1,4-cyclohexadiene but then levels off at higher concentrations. Thus, the initial slopes shown for B and D on the left side of Figure 1 are nearly 300-fold greater than the final slopes shown on the right side of the plot. Third, formation of type C products **15** and **16** is unaffected by cyclohexadiene over the full range of concentrations.

Interpretative Discussion

The Di-π-methane Rearrangement of the Triplet. The triplet photochemistry of dicyano diene **5**, as observed in the acetophenone-sensitized irradiations, is of interest since most often the triplet excited states of acyclic 1,4-dienes are unreactive due to radiationless decay via the free-rotor effect.[3,13] The results can be compared to the sensitized photochemistry of the closely related dimethyl dicyano diene[14] **33** and the tetraphenyl dicyano diene[4b] **34**. The first has been reported[14] to have an unreactive triplet state while the latter proved quite reactive with a quantum efficiency of 0.79 (note eq 7 and 8).



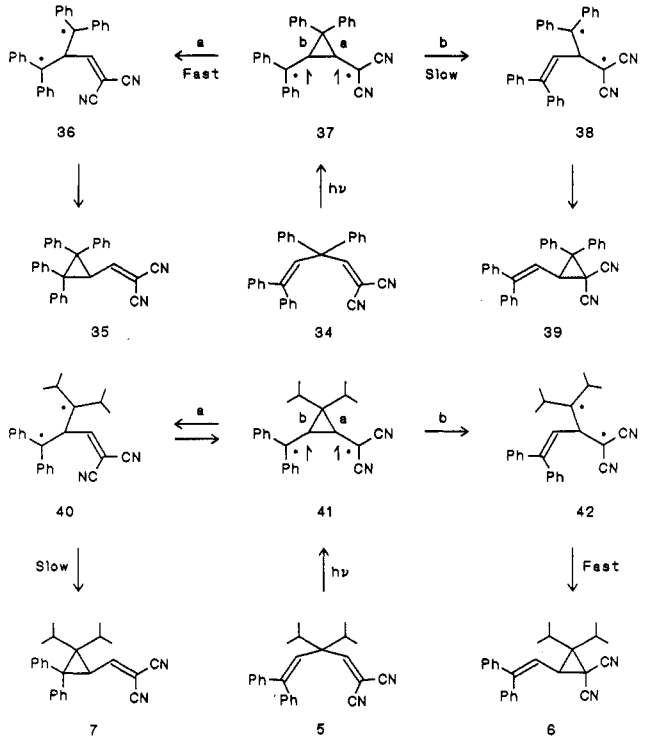
(7)

(8)

(13) The free-rotor effect[3] has sometimes been misunderstood as deriving from the triplet rapidly spinning about the excited π-bond. Instead, what is meant is that free rotation permits approach of the T_1 and S_0 surfaces at 90°, thus providing facile radiationless decay and conversion to a vibrationally excited ground state.

(14) Alexander, D. W.; Pratt, A. C.; Rowley, D. H.; Tipping, A. E. *J. Chem. Soc., Chem. Commun.* **1978**, 101–102.

Scheme V. Mechanism of Triplet Rearrangement of Tetraphenyl Diene 34 and of Dicyano Diene 5



The ability of the tetraphenyl dicyano diene triplet **34** to rearrange was ascribed[4] to both steric inhibition of free rotor energy dissipation and also to more facile ring opening of the cyclopropyldicarbinyl diradical species formed by vinyl–vinyl bridging. The present system, with two isopropyl groups on the central (methane) carbon, provides an example where the steric effect is present but the delocalization effect is lacking. The intermediate quantum yield of 0.041 suggests that there is steric inhibition of free-rotor triplet decay in dicyano diene **5** and that delocalization by the central phenyl substituents in tetraphenyl diene **34** further increases triplet reactivity by enhancing ring opening of the cyclopropyldicarbinyl diradical (i.e. **37**, see Scheme V).

Also of interest is the observation that the triplet excited state of dicyano diene **5** does not undergo the 1,3-sigmatropic rearrangements observed for the S_1 counterpart. This point is considered below in connection with the singlet photochemistry.

Still another item of interest is the regioselectivity seen in the di-π-methane rearrangement of dicyano diene **5**. We see a striking reversal of regioselectivity in the present di-π-methane rearrangement of dicyano diene **5** relative to the corresponding tetraphenyl dicyano diene **34**. As depicted in Scheme V, in the case of tetraphenyl dicyano diene **34** it is bond a of the cyclopropyldicarbinyl diradical (**37**) which is broken while the rearrangement of dicyano diene **5** occurs with loss of bond b in the corresponding diradical **41**. Yet the only structural difference between these systems is the diisopropyl substitution on the methane carbon in **5** contrasted with diphenyl substitution in **34**.

Actually, to form the more stable of two diradicals (i.e. **36** rather than **38** and **40** rather than **42**), one would anticipate opening of bond a, since cyano substituents are considerably less effective in odd-electron delocalization than are phenyl groups.[15] Thus, the present regioselectivity is unusual. One possible rationale is that three-ring opening is reversible in the case of diradical **41** while it is not in the case of diradical **37**. This would result from ring opening of cyclopropyldicarbinyl diradical **37** having phenyl groups on the central carbon and thus being better able to stabilize the ring-opened diradicals, a situation contrasting with the opening of cyclopropyldicarbinyl diradical **41** where only isopropyl groups are present on the central carbon.

In such a rationale, the preferred kinetic opening of diradical **41** would afford the dicyanovinyl-substituted diradical **40**. However, reversibility would permit diradical **42** to form. A diradical such as **42**, having cyano groups on one odd-electron center, should have an enhanced rate of intersystem crossing from T_1 to S_0. Salem has noted[16] that intersystem crossing to a zwitterionic, or ionic, singlet state is kinetically preferred. Thus **42** would afford its S_0 counterpart in a rate-limiting process followed by rapid three-ring closure to form the observed photoproduct **6**.

The Direct Photochemistry. In addition to di-π-methane rearrangement the primary direct photochemistry of dicyano diene **5** involves isopropyl expulsion, leading to monoisopropyl diene **13** and two different 1,3-sigmatropic rearrangements. These latter two reactions involve initial 1,3-migration of an isopropyl group either to the dicyano-substituted carbon, affording the 4,6-heptadiene **19a**, or to the diphenyl-bearing carbon to give the 1,3-heptadiene **26**. The reaction pathways following each of these isopropyl shifts and the nature of the 1,3-migrations themselves are discussed below. We first note, however, that evidence is not available to establish whether or not the di-π-methane rearrangement observed upon direct irradiation actually results from initial intersystem crossing to the triplet state.

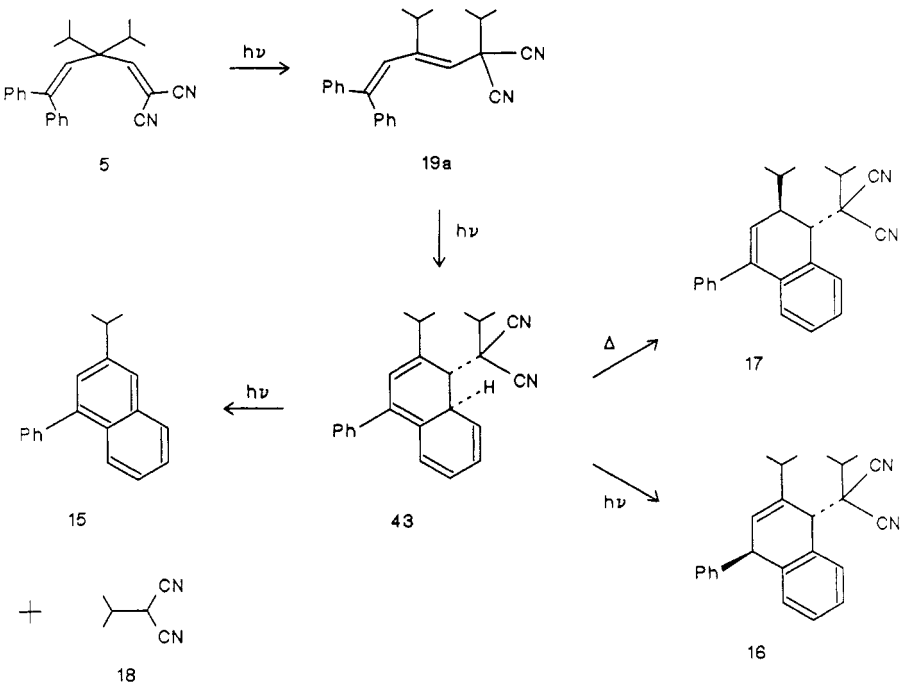
Overall Mechanisms Following Isopropyl Migration to the Dicyano Bearing Carbon. Turning first to the 1,3-isopropyl shift from the methane carbon to the dicyano-substituted carbon (Scheme VI), we note that in this pathway the isopropyl-shifted intermediate **19a** was observed upon photolysis of dicyano diene **5** and also independently synthesized and studied. Four photoproducts—the two dihydronaphthalenes **16** and **17**, phenylisopropylnaphthalene **15**, and isopropylmalononitrile (**18**)—were formed in the independent irradiation of 4,6-heptadiene **19a**, and the appearance of these same products in the photochemistry of dicyano diene **5** is therefore understood in terms of the mechanism in Scheme VI.

The initial step is an electrocyclic closure leading to intermediate dihydronaphthalene **43**. In view of its extended conjugation, **43** is expected to absorb very strongly at the irradiation wavelengths, and therefore it is not surprising that this intermediate was unobservable. Nevertheless, the stereochemistry of **43** may be defined. First, this is the configuration anticipated from conrotatory closure of the trans reactant **19a**. This is consistent with a mechanism utilizing an excited state allowed Möbius six-electron cyclic orbital array.[17] That 4,6-heptadiene **19a** might be cis–trans stereoisomerizing to **19b**, which would give an opposite stereochemical result in the electro-

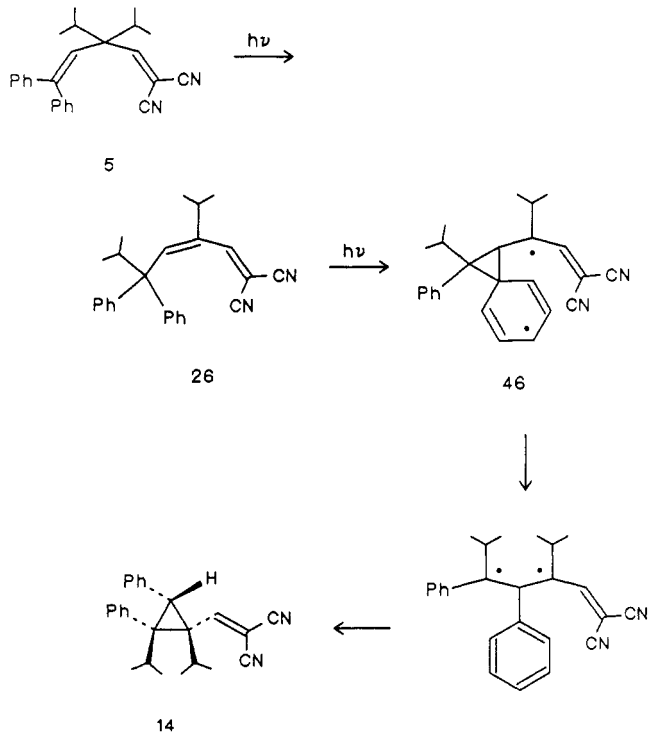
(15) (a) Resonance stabilization of an odd electron by phenyl and cyano groups has been reported as 12.5 and 5 kcal/mol, respectively.[5b-e] (b) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516–1536. (c) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1537–1552. (d) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1978**, *10*, 453–459. (e) King, K. D.; Goddard, R. D. *J. Phys. Chem.* **1976**, *80*, 546–552.

(16) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.

Scheme VI. Rearrangement Pathways Originating from 1,3-Isopropyl Migration to the Dicyano Carbon



Scheme VII. Rearrangement Mechanism Originating from 1,3-Isopropyl Migration to the Diphenyl Carbon



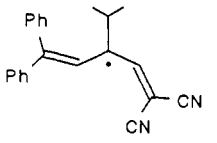
cyclization, was precluded by the observation (vide supra) that the cis stereoisomer **19b** reacts photochemically only slowly. Second, the structures, including configurations, of the dihydronaphthalene photoproducts **16** and **17** have been established by X-ray, and these are also consistent with stereochemistry shown for **43**.

Dihydronaphthalene **17** can be seen to be the product of a suprafacial 1,5-sigmatropic hydrogen shift, while dihydronaphthalene **16** derives from a suprafacial 1,3-hydrogen shift. Hence one can reason backwards to confirm the configuration of intermediate **43**. These reactions follow the Möbius–Hückel predictions.[17]

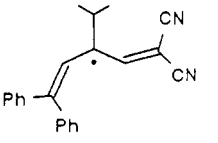
It has been noted above that dihydronaphthalene isomer **17** is formed only at low light intensities while isomer **16** is formed with high intensities. This suggests that the 1,5-sigmatropic hydrogen shift in precursor **43** has an opportunity to occur thermally at low light intensities while the photochemical 1,3-sigmatropic shift takes precedence when **43** reacts via its excited rather than its ground state.

The phenylisopropylnaphthalene **15** arises from the same intermediate **43** by an interesting elimination of isopropylmalononitrile to afford the product **15**.

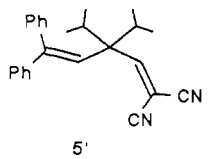
Having discussed the stereochemistry of the reaction of 4,6-heptadiene **19a**, we now turn to the stereochemistry of its formation. While the matter of the precise nature of the 1,3-sigmatropic isopropyl shift to afford **19a** is discussed separately below, it is clear that all mechanisms involve the π-system of the substituted pentadienyl radical **32**, whether this is free or, instead, is bonded to the migrating isopropyl group. For pentadienyl radical **32** there are two "half-U" conformations, shown as **32′** and **32″**.



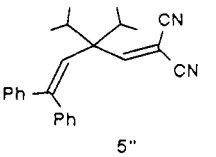
32′



32″



5′



5″

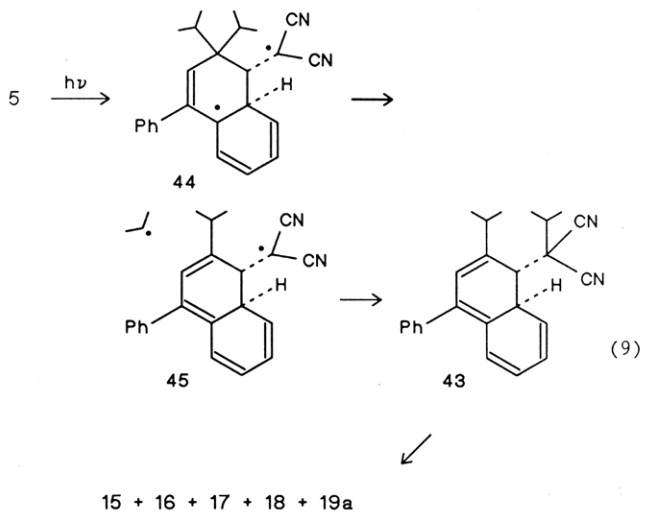
Molecular mechanics[18] showed a 1.8 kcal/mole difference favoring radical **32″** over **32′** with the imposition of coplanarity of the entire π-system including the phenyl

(17) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564–1565. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272–280.

(18) (a) MMP-1987 was used.[18b] (b) Gajewski, J. J.; Gilbert, K. E., available from Serena Software, Indiana University, Bloomington, IN. We thank the authors for a copy of this program.

groups and only a smaller difference in energies of the optimized reactant half-U conformers 5′ and 5″ (favoring 5″ by 0.17 kcal/mol). The "W" and "full-U" of dicyano diene **5** were still higher in energy by 1.52 and 2.87 kcal/mol, respectively. These four conformers of **5** did correspond to energy minima. The preference for the radical species **32″** accounts for the formation of product **19a** since **32″** has the proper conformation. Additionally, **32″** as an intermediate accounts for formation of 1,3-heptadiene **26** whose formation is discussed below.

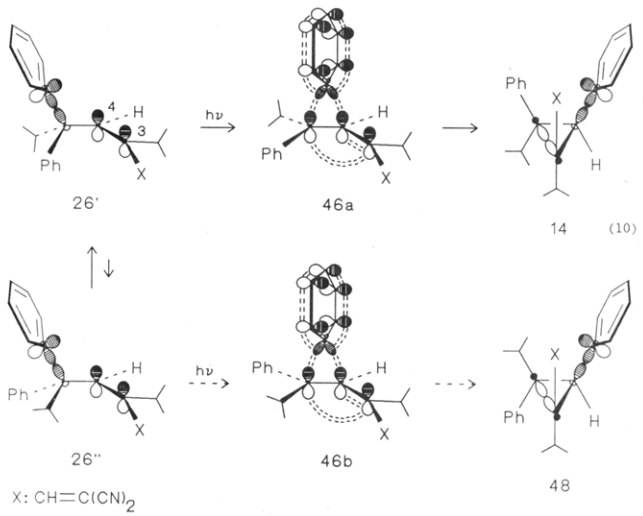
One alternative mechanism needed to be considered. This is shown in eq 9. However, the intermediacy of radical pair **45** in production of the type C products phenylisopropylnaphthalene **15** and dihydronaphthalenes **16** and **17** was ruled out by the observation that the yield of these products was unaffected by 1,4-cyclohexadiene. A direct 1,3-isopropyl migration leading from the bridged diradical **44** to dihydronaphthalene **43**, without involving the radical pair **45**, can be envisaged but is without precedent. Thus, the alternative mechanism seems unlikely.



Overall Mechanisms Following Isopropyl Migration to the Diphenyl Bearing Carbon (Scheme VII). We are now concerned with the reaction of 1,3-heptadiene **26**, which is an aryl–vinyl type of di-π-methane rearrangement.[3d] Two aspects of the reaction stereochemistry are of particular interest.

The first concerns the stereochemical disposition of the migrating group relative to the groups on the double bond which is dissipated upon formation of the cyclopropane product. The reactant **26** has a cis configuration about double bond 3,4 (i.e. dicyanovinyl cis to the phenyl-bearing carbon, note eq 10) which gives rise to the product having the migrated phenyl group and the dicyanovinyl groups cis on the three-membered ring. This stereochemical result follows the pattern observed for other di-π-methane systems,[19] wherein the substituent cis to the methane carbon of the reactant becomes cis to the migrated group in the cyclopropane product, while the trans substituent on this double bond becomes trans to the migrated group. This anti-disrotatory reaction stereochemistry is shown in eq 10.

The second stereochemical aspect is the disposition of the nonmigrating phenyl and the isopropyl group, which are bonded to the original methane carbon. As shown in



eq 10, the cisoid relationship of the dicyanovinyl group to the nonmigrating phenyl in diradical **46a** leads to the observed product **14** in which these two groups are cis and the two isopropyl groups are cis. The preference for this reaction stereochemistry is supported by molecular mechanics treatment of reactant **26**. Conformer **26′**, having the vinyl hydrogen s-cis to isopropyl, was preferred by 1.5 kcal/mol over conformer **26″**, which has the vinyl hydrogen s-cis to a phenyl group. This energy difference results when the ipso p orbital of the migrating phenyl group is constrained to be coplanar with the p orbital at C-4. If in addition, we require the entire dicyanobutadienyl system to be coplanar, the energy difference is 5.1 kcal/mol. Furthermore, a molecular mechanics comparison of diradicals **46a** and **46b** in which the dicyanoallyl group is taken as planar leads to a preference of 6.8 kcal/mol favoring **46a**, a difference which seems larger than anticipated. In any case, the prediction is in agreement with the observed preference for product **14**.

The Mechanism of the 1,3-Sigmatropic Isopropyl Shifts. Given the two 1,3-sigmatropic isopropyl shifts (reaction types B and C above), one needs to consider whether mechanistically these are intramolecular or intermolecular. The literature provides examples of the intramolecular[20] variety and examples[21] where at least some portion of the reaction involves radical dissociation–recombination. In the present instance, the observation of ca. 10% of the monoisopropyl diene **13** demonstrates that minimally one-tenth of those singlet excited-state molecules of dicyano diene **5** which react expel an isopropyl group homolytically.

The use of increasing amounts of 1,4-cyclohexadiene as a radical trap (vide supra and Figure 1) provided further evidence on this point. Thus, progressively increasing concentrations of this radical trap caused the yield of monoisopropyl diene **13** (a type D photoproduct) to increase with a concomitant decrease in the yield of the type B product, (dicyanovinyl)cyclopropane **14**. These changes represent a ca. 45% enhancement in production of monoisopropyl diene **13** (D) and a corresponding suppression

(19) (a) Zimmerman, H. E.; Baeckstrom, P.; Johnson, T.; Kurtz, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5504–5505. (b) Note also the elegant stereochemical studies by Mariano.[19c-e] (c) Mariano, P. S.; Ko, J. *J. Am. Chem. Soc.* **1973**, *95*, 8670–8678. (d) Mariano, P. S.; Watson, D. G.; Bay, E. *Tetrahedron* **1977**, *33*, 11–17.

(20) (a) Brown, R. F. C.; Cookson, R. C.; Hudec, J. *Tetrahedron* **1968**, *24*, 3955–3964. (b) Cookson, R. C.; Gogte, V. N.; Hudec, J.; Mirza, N. A. *Tetrahedron Lett.* **1965**, 3955–3959. (c) Sharma, M. *J. Am. Chem. Soc.* **1975**, *97*, 1153–1160. (d) Padwa, A.; Akiba, M.; Cohen, L. A.; MacDonald, J. G. *Tetrahedron Lett.* **1981**, 2435–2438.

(21) (a) Cookson, R. C.; Kemp, J. E. *J. Chem. Soc., Chem. Commun.* **1971**, 385–386. (b) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276–6289. (c) Shaffer, G. W.; Pesaro, M. *J. Org. Chem.* **1974**, *39*, 2489–2492. (d) Cargill, R. L.; Gimarc, B. M.; Pond, D. M.; King, T. Y.; Sears, B. S.; Willcott, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3809–3810.

of the formation of (dicyanovinyl)cyclopropane **14** (B). The fact that 45% of the reaction leading to this latter product can be diverted to give the monoisopropyl diene **13** in the presence of 1,4-cyclohexadiene indicates that ca. half of the (dicyanovinyl)cyclopropane **14** which is generated in the photolysis of dicyano diene **5** arises by recombination of radicals which have escaped from the solvent cage.

There still remains the question of what proportion of (dicyanovinyl)cyclopropane **14** is formed by this fragmentation–recombination process within the solvent cage. For very stable radical pairs, the evidence[22] indicates that cage escape corresponds to 65–80%. In the limit of nonstabilized radical pairs, the radical dissociation–recombination of methyl radicals from azomethane proceeds with 40% cage escape.[23] In the present instance radical **32** is especially stabilized while the isopropyl radical is not, and we can assume an intermediate situation with somewhere between the extremes of 40 and 80% cage escape.

This suggests that a major portion (50–100%) of the type B sigmatropic rearrangement proceeds by a dissociative pathway. We note, however, that this is a relatively minor pathway in the overall direct photochemistry of dicyano diene **5**.

Interestingly, in the major reaction pathway leading to the type C photoproducts **15** and **16** the yields were unaffected by 1,4-cyclohexadiene despite the fact that a 1,3-sigmatropic isopropyl migration is the primary step. This suggests that, in contrast to the type B photochemistry, radical dissociation is not involved.

Rationale for Different Behavior of the Singlet and Triplet Excited States. Occasionally in organic photochemistry one observes different behavior of the triplet and singlet excited states. In the present instance the singlet led primarily to products deriving from 1,3-sigmatropic rearrangements while the triplet led exclusively to a di-π-methane rearrangement. In addition, the singlet excited state was responsible for isopropyl radical expulsion.

In earlier studies it has been noted that singlet vs triplet differences may often be ascribed to an effect of the exchange integral, K, of intermediate diradicals.[4b,c,24] In this approach, it has been suggested that there are "small K type reactions" and "large K type reactions" and that singlet excited states prefer the small K type reactions while triplets prefer large K reactions. Small K reactions are exemplified by pericyclic processes. Among the most characteristic large K reactions are those proceeding via diradical species, especially those lacking strongly electron donating and/or withdrawing groups on the diradical centers. Di-π-methane rearrangements of both singlets and triplets are known, and for this reaction there are both small K and large K variations of the mechanism. In the present instance, the singlet reacts by a pericyclic reaction (i.e. a small K type) while the triplet undergoes a di-π-methane rearrangement.

The concept is based on the energetics depicted in Figure 2. It is seen that the lower energy pathway available to a triplet is the large K route while the lower energy mechanism possible for a singlet is the small K route. However, this picture is idealized in assuming the same energetic "center of gravity" for the large K and small K reactions. Extraneous factors such as serious steric hindrance appearing in just one of the two reactions will tend to selectively raise the energy of the corresponding singlet and triplet.

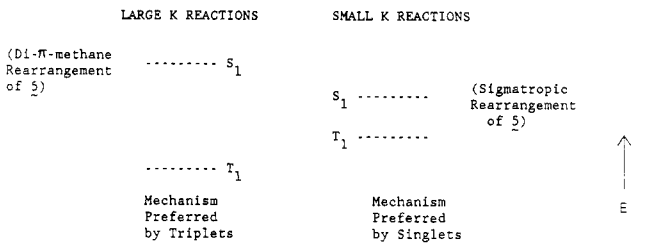


Figure 2. Schematic representation of energetics for small K and large K reactions showing preference for one type of mechanism by each multiplicity species along a reaction coordinate.

Conclusion

The original aim of the present study, namely to assess the source of triplet reactivity of centrally substituted di-π-methane systems, has established that both electronic delocalization and steric congestion give rise to enhanced reactivity. Additionally, the present study has revealed a number of unusual photochemical processes in what would otherwise appear to be a typical di-π-methane system. Thus, even this highly developed area of organic photochemistry needs further investigation before reactivity predictions can be made with certainty.

Experimental Section[25]

Ethyl 4,4-Diphenyl-2-isopropyl-3-butenoate (20). To a solution of 24 mL (0.17 mol) of diisopropylamine in 300 mL of dry tetrahydrofuran at −78 °C was added dropwise 77 mL (0.12 mol) of 1.5 M *n*-butyllithium solution in hexane. After 30 min a solution of 30.9 g (0.116 mol) of ethyl 4,4-diphenyl-3-butenoate (**I**)[28] in 200 mL of tetrahydrofuran was added dropwise over 1

(22) (a) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, pp 157–189. (b) Lorand, J. P. *Prog. Inorg. Chem.* **1972**, *17*, 207–325. (c) Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900–911. (d) Nelsen, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 143–149. (e) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867–874.

(23) (a) This value derives from photolysis of azomethane at 25 °C in isooctane solution.[23b] (b) Herk, L.; Feld, M.; Swarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 2998–3005.

(24) Zimmerman, H. E.; Penn, J. H.; Johnson, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021–2025.

(25) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921. All reactions were performed under an atmosphere of dry nitrogen. Anhydrous magnesium sulfate was used as the drying agent. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. Deactivation of thick-layer plates was accomplished by pre-elution with either 1% triethylamine in pentane or with neat methanol, and drying for ca. 30 min under a stream of nitrogen before use. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector an LDC 6000-psi minipump, using a 0.95 × 50 cm polished stainless steel column packed with 8–12 μm porous silica beads.[26] Neutral workup refers to quenching the reaction with water, ether extraction, washing the organic layer with water and brine, drying, filtering, and concentration in vacuo. Acidic workup included a 2 M aqueous hydrochloric acid wash after ether extraction. Basic workup included a saturated aqueous sodium bicarbonate wash after ether extraction. Basic–acidic workup involved sequential base and acid washings after ether extraction. Except where otherwise noted, exploratory photolyses were conducted with a Hanovia 450-W medium-pressure mercury lamp equipped with a Pyrex filter. All photolysis solutions were thoroughly purged with purified nitrogen[27] both prior to and during photolysis. Acetonitrile and benzene were distilled from calcium hydride. Dichloromethane was purified by distillation from phosphorous pentoxide. Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by storage over potassium hydroxide, followed by successive distillation, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Hexane used for HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine, dried over calcium chloride, passed through alumina, and distilled from calcium hydride.

(26) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K., unpublished results.

(27) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

h. The resulting solution was stirred for an additional 10 min at −78 °C, and then 24 mL (0.24 mol) of isopropyl iodide was added dropwise. After addition was complete, the solution was allowed to slowly warm to room temperature and stirred for 18 h before being quenched with 10% hydrochloric acid. Acidic–basic workup[25] gave 36.6 g of brown oil, which was fractionally distilled to give 35.0 g (97%) of ethyl 4,4-diphenyl-2-isopropyl-3-butenoate as an oil, bp 155–157 °C (0.25 mm).

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.39–7.16 (m, 10 H, arom), 6.11 (d, J = 10.7 Hz, 1 H, Ph_2C=CH), 4.15 (m, 2 H, CH_2), 2.90 (dd, J = 10.7 Hz, J = 8.6 Hz, 1 H, CH), 2.08 (m, 1 H, Me_2CH), 1.26 (t, J = 7.1 Hz, 3 H, CH_3), 0.89 (d, J = 6.7 Hz, 3 H, CH_3), 0.86 (d, J = 6.7 Hz, 3 H, CH_3); IR (neat) 3040, 3010, 2950, 2920, 2860, 1725, 1600, 1490, 1465, 1445, 1390, 1370, 1240, 1225, 1180, 1155, 1030 cm^{-1}; MS m/e 308.1770 (calcd for $C_{21}H_{24}O_2$ m/e 308.1776).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.57; H, 7.62.

Ethyl 4,4-Diphenyl-2,2-diisopropyl-3-butenoate (2). To a solution of 6.8 mL (49 mmol) of diisopropylamine in 40 mL of dry 1,2-dimethoxyethane at −78 °C was added dropwise 20 mL (32 mmol) of 1.6 M n-butyllithium solution in hexane. After the mixture was stirred for 20 min, a solution of 10.0 g (32.4 mmol) of ethyl 4,4-diphenyl-2-isopropyl-3-butenoate (**20**) in 40 mL of 1,2-dimethoxyethane was added dropwise over 30 min, and the resulting solution was allowed to warm to 0 °C. After 30 min at 0 °C, 16 mL (160 mmol) of isopropyl iodide was added. The resulting solution was stirred at 0 °C for an additional 90 min and then at room temperature for 115 h before being quenched with 10% hydrochloric acid. Acidic–basic workup[25] gave 11.02 g of a yellow, oil which was chromatographed on a 5.5 cm × 50 cm silica column: fraction 1, 2 L of 0.5% ether in hexane, nil; 2, 2 L of 1% ether in hexane, nil; 3, 5 L of 2% ether in hexane, 10.41 g (92%), of ethyl 4,4-diphenyl-2,2-diisopropyl-3-butenoate as an oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.18–7.32 (m, 10 H, arom), 6.09 (s, 1 H, Ph_2C=CH), 3.77 (q, J = 7.1 Hz, 2 H, CH_2), 2.23 (sept, J = 6.8 Hz, 2 H, Me_2CH), 1.16 (t, J = 7.1 Hz, 3 H, CH_3), 0.94 (d, J = 6.8 Hz, 6 H, CH_3), 0.92 (d, J = 6.8 Hz, 6 H, CH_3); IR (neat) 3080, 3050, 3020, 2970, 2870, 1720, 1600, 1555, 1490, 1465, 1445, 1385, 1370, 1310, 1220, 1125, 1030 cm^{-1}; MS m/e 350.2238 (calcd for $C_{24}H_{30}O_2$, m/e 350.2246).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.31; H, 8.59.

4,4-Diphenyl-2,2-diisopropyl-3-buten-1-ol (3). To a solution of 9.37 g (26.7 mmol) of ethyl 4,4-diphenyl-2,2-diisopropyl-3-butenoate (**2**) in 185 mL of dry hexane at 0 °C was added dropwise 56 mL (56 mmol) of 1.0 M diisobutylaluminum hydride in hexane. After addition was complete the solution was stirred at room temperature for 2 h, cooled to 0 °C, and quenched by cautious dropwise addition of 2 M hydrochloric acid.. Acidic workup[25] gave 8.35 g of white solid, which was recrystallized from hexane to give 6.64 g (81%) of 4,4-diphenyl-2,2-diisopropyl-3-buten-1-ol as a white crystalline solid, mp 58–59 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.12–7.39 (m, 10 H, arom), 5.81 (s, 1 H, Ph_2C=CH), 3.29 (s, 2 H, CH_2), 2.09 (sept, J = 6.9 Hz, 2 H, Me_2CH), 1.07 (d, J = 6.9 Hz, 6 H, CH_3), 1.00 (d, J = 6.9 Hz, 6 H, CH_3); IR ($CHCl_3$) 3400 (br), 3070, 3050, 3010, 2960, 1600, 1490, 1470, 1450, 1380, 1030 cm^{-1}; MS m/e 308.2140 (calcd for $C_{22}H_{28}O$ m/e 308.2140).

Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.88; H, 9.07.

4,4-Diphenyl-2,2-diisopropyl-3-butenal (4). To a vigorously stirred slurry of 6.98 g (32.4 mmol) of pyridinium chlorochromate in 35 mL of dry dichloromethane was added a solution of 6.64 g (21.5 mmol) of 4,4-diphenyl-2,2-diisopropyl-3-buten-1-ol (**3**) in 35 mL of dry dichloromethane. The resulting mixture was stirred for 8.5 h and then diluted with anhydrous ether and filtered through Florisil to give 6.65 g of crude product as a white solid. Recrystallization from hexane gave 6.26 g (95%) of 4,4-diphenyl-2,2-diisopropyl-3-butenal as a white crystalline solid, mp 94.2–94.7 °C.

(28) Kansal, V. K.; Bhaduri, A. P. *Z. Naturforsch.* **1979**, *34b*, 1567–1569.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.15 (s, 1 H, CHO), 7.10–7.40 (m, 10 H, arom), 5.96 (s, 1 H, Ph_2C=CH), 2.25 (sept, J = 7.0 Hz, 2 H, Me_2CH), 1.08 (d, J = 7.0 Hz, 6 H, CH_3), 0.89 (d, J = 7.0 Hz, 6 H, CH_3); IR ($CHCl_3$) 3070, 3050, 3010, 2960, 2930, 2870, 1710, 1600, 1490, 1470, 1450, 1390, 900 cm^{-1}; MS m/e 306.1983 (calcd for $C_{22}H_{26}O$ m/e 306.1984).

Anal. Calcd for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 85.95; H, 8.68.

1,1-Dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (5). To 32 mL of dry tetrahydrofuran at 0 °C was added dropwise a solution of 15.0 mL (140 mmol) of titanium tetrachloride in 11 mL of dry carbon tetrachloride. To the resulting yellow slurry was added a solution of 5.37 g (17.5 mmol) of 4,4-diphenyl-2,2-diisopropyl-3-butenal (**4**) and 21.6 g (327 mmol) of malononitrile in 38 mL of dry tetrahydrofuran. The mixture was stirred at 0 °C for 25 min, and then a solution of 21 mL (0.26 mol) of dry pyridine in 11 mL of carbon tetrachloride was added. The mixture was stirred at room temperature for 5.5 h and at then at 43 °C for 60 h. After cooling to room temperature, the mixture was diluted with 700 mL of 2 M hydrochloric acid, and subsequent acidic–basic workup[25] gave 15.2 g of a brown oil, which was chromatographed on a 3.8 cm × 60 cm Florisil column: fraction 1, 10 L of 0.5% ether in hexane, nil; 2, 4 L of 0.5% ether in hexane, 2.87 g (53%) of the starting material; 3, 3 L of 20% ether in hexane, 869 mg (16%) of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene as a pale yellow solid. Recrystallization from hexane gave 742 mg (14%) of pure white crystalline material, mp 111–112 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.49 (m, 10 H, arom), 6.92 (s, 1 H, $(NC)_2C$=CH), 5.90 (s, 1 H, Ph_2C=CH), 2.56 (sept, J = 6.8 Hz, 2 H, Me_2CH), 1.04 (d, J = 6.8 Hz, 6 H, CH_3), 1.00 (d, J = 6.8 Hz, 6 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.94 (m, 10 H, arom), 6.74 (s, 1 H, $(CN)_2C$=CH), 5.61 (s, 1 H, Ph_2C=CH), 2.23 (sept, J = 6.8 Hz, 2 H, Me_2CH), 0.73 (d, J = 6.8 Hz, 6 H, CH_3), 0.59 (d, J = 6.8 Hz, 6 H, CH_3); IR ($CHCl_3$) 3020, 2960, 2230, 1590, 1490, 1470, 1450, 1390 cm^{-1}; UV (95% EtOH) λ_{max} 251 (ε 21 500); MS m/e 354.2100 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.46; H, 7.23.

Exploratory Sensitized Photolysis of 1,1-Dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (5). A solution of 51.0 mg (0.144 mmol) of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene and 10 mL (86 mmol) of acetophenone in 170 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 10 min. Concentration in vacuo and removal of acetophenone by bulb-to-bulb distillation (40 °C, 0.10 mm) gave 56.2 mg of a pale yellow oil, which was subjected to HPLC. Elution with 1% ether in hexane gave fraction 1, 31.6 mg (62%) of the starting material **5** as a colorless oil; fraction 2, 17.8 mg (35%) of 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane (**6**) as a colorless oil. The material from fraction 1 was recrystallized from hexane to give 27.4 mg (54%) of the pure starting material, mp 111–112 °C. The material from fraction 2 was recrystallized from pentane to give 9.3 mg (18%) of vinylcyclopropane **6**, mp 76–77 °C.

The spectral data for 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.50 (m, 10 H, arom), 5.90 (d, J = 9.6 Hz, 1 H, Ph_2C=CH), 2.56 (d, J = 9.6 Hz, 1 H, CH), 2.05 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.80 (sept, J = 7.2 Hz, 1 H, Me_2CH), 1.30 (d, J = 7.2 Hz, 3 H, CH_3), 1.21 (d, J = 7.0 Hz, 3 H, CH_3), 1.18 (d, J = 7.0 Hz, 3 H, CH_3), 1.04 (d, J = 7.2 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz), δ 7.04–7.23 (m, 10 H, arom), 5.97 (d, J = 9.6 Hz, 1 H, Ph_2C=CH), 2.51 (d, J = 9.6 Hz, 1 H, CH), 1.85 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.41 (sept, J = 7.2 Hz, 1 H, Me_2CH), 0.96 (d, J = 7.2 Hz, 3 H, CH_3), 0.77 (d, J = 7.0 Hz, 3 H, CH_3), 0.73 (d, J = 7.0 Hz, 3 H, CH_3), 0.72 (d, J = 7.2 Hz, 3 H, CH_3); IR (neat) 3080, 3050, 2960, 2920, 2240, 1655, 1600, 1580, 1450, 1320, 1280 cm^{-1}; UV (95% EtOH) λ_{max} 268 (ε 15 500); MS m/e 354.2094 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.76; H, 7.60.

Exploratory Direct Photolysis of 1,1-Dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (5). A solution of 63.0 mg (0.178 mmol) of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-

1,4-pentadiene in 170 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 1.5 h. After concentration in vacuo at room temperature, 2.1 mg (11%) of isopropylmalononitrile was removed from the photolysate by bulb-to-bulb distillation (35 °C, 0.50 mm) into a cooled (−78 °C) receiver. The spectral data for this material were identical with those of an authentic sample.[9] The nonvolatile remainder of the photolysate was found by ^{1}H NMR analysis to be a mixture of the starting dicyano diene (**5**), 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (**14**), 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (**13**), 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane (**6**), 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**), and 1-phenyl-3-isopropylnaphthalene (**15**) in a ratio of 2.8:1.0:1.2:1.7:0.56:6.5.

This mixture was chromatographed on a methanol-deactivated[25] 20 cm × 20 cm silica thick-layer plate. One elution with 10% ether in pentane gave: band 1 (R_f =0.9), 18.1 mg (41.3%) of 1-phenyl-3-isopropylnaphthalene (**15**) as a faintly yellow oil; band 2 (R_f = 0.4), 31.0 mg of a slightly yellow oil, which was found by ^{1}H NMR analysis to be a mixture of the starting dicyano diene **5**, (dicyanovinyl)cyclopropane **14**, monoisopropyl diene **13**, (diphenylvinyl)cyclopropane **6**, and 1,4-dihydronaphthalene **16** in a ratio of 2.8:1.0:0.95:1.7:0.54.

The material from band 1 was recrystallized from ethanol to give 11.4 mg (26%) of 1-phenyl-3-isopropylnaphthalene as a white crystalline solid, mp 51–52 °C. The band 2 mixture was chromatographed on a methanol-deactivated[25] 20 cm × 20 cm silica thick-layer plate. Two elutions with 5% ether in pentane gave: band 1 (R_f = 0.40), 21.1 mg of a slightly yellow oil, which was found by ^{1}H NMR analysis to be a 2.8:1.7:0.51 mixture of the starting dicyano diene **5**, (diphenylvinyl)cyclopropane **6**, 1,4-dihydronaphthalene **16**; band 2 (R_f = 0.35), 7.8 mg of a slightly yellow oil, which was found by ^{1}H NMR analysis to be a 1.0:0.82 mixture of (dicyanovinyl)cyclopropane **14** and monoisopropyl diene **13**.

The mixture of starting dicyano diene **5**, (diphenylvinyl)-cyclopropane **6**, and dihydronaphthalene **16** was separated by HPLC. Elution with 1% ether in hexane gave: fraction 1, 1.8 mg (2.9%) of pure dihydronaphthalene **16** as a white solid, mp 144–145 °C; fraction 2, 10.6 mg (16.8%) of dicyano diene **5** as a white solid, which was recrystallized from hexane to give 4.9 mg (7.8%) of pure material, mp 111–112 °C; fraction 3, 6.6 mg (10.4%) of (diphenylvinyl)cyclopropane **6** as a colorless oil, which was recrystallized from hexane to give 1.0 mg (1.6%) of white solid, mp 75–76 °C.

The mixture of monoisopropyl diene **13** and (dicyanovinyl)-cyclopropane **14** was chromatographed on a 20 cm × 20 cm silica thick-layer plate, which had been deactivated by elution with 30% methanol in pentane. Three elutions with 2% ether in pentane gave two closely spaced bands: band 1 (R_f = 0.40), 4.5 mg (7%) of an 18:1.0 mixture of (dicyanovinyl)cyclopropane **14** and monoisopropyl diene **13**, which was recrystallized from hexane to give 1.2 mg (1.9%) of pure (dicyanovinyl)cyclopropane **14**, mp 157–158 °C; band 2 (R_f = 0.37), 3.0 mg of pure 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (**13**) as a colorless oil. The spectral data for (diphenylvinyl)cyclopropane **6** were identical with those observed for the material produced in the sensitized photolysis of dicyano diene **5**.

The spectral data for 1-phenyl-3-isopropylnaphthalene (**15**) were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.85 (m, 2 H, arom), 7.66 (br s, 1 H, arom), 7.33–7.53 (m, 8 H, arom), 3.10 (sept, J = 6.9 Hz, 1 H, Me_2CH), 1.37 (d, J = 6.9 Hz, 6 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.98 (m, 2 H, arom), 7.74 (m, 2 H, arom), 7.57 (br s, 1 H, arom), 7.18–7.45 (m, 6 H, arom), 2.89 (sept, J = 6.9 Hz, 1 H, Me_2CH), 1.24 (d, J = 6.9 Hz, 6 H, CH_3); IR ($CHCl_3$) 3040, 3020, 2950, 2920, 2860, 1600, 1495, 1400, 900, 790, 755, 710 cm^{-1}; UV (95% EtOH) λ_{max} 291 (ε 10425), sh 325 (ε 1026); MS m/e 246.1414 (calcd for $C_{19}H_{18}$ m/e 246.1408).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.36. Found: C, 92.82; H, 7.62.

The spectral data for 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**) were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.14–7.41 (m, 8 H, arom), 6.83 (br d, J = 7.2 Hz, 1 H, arom), 6.13 (br s, 1 H, CH), 5.08 (d, J = 1.9 Hz, 1 H, CH), 3.89 (d, J = 1.9 Hz, 1 H, CH), 2.73 (m, 1 H, CH), 2.37 (sept, J = 6.6 Hz, 1 H, Me_2CH), 1.42 (d, J = 6.6 Hz, 3 H, CH_3), 1.30 (d, J = 6.9 Hz, 3 H, CH_3), 1.27 (d, J = 6.9 Hz, 3 H, CH_3), 1.07 (d, J = 6.6 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.91-7.12 (m, 9 H, arom), 6.14 (br s, 1 H, CH), 5.38 (d, J = 1.9 Hz, 1 H, CH), 3.74 (d, J = 1.9 Hz, 1 H, CH), 2.75 (m, 1 H, CH), 2.04 (sept, J = 6.6 Hz, 1 H, Me_2CH), 1.13 (d, J = 6.6 Hz, 3 H, CH_3), 0.93 (d, J = 6.9 Hz, 3 H, CH_3), 0.92 (d, J = 6.9 Hz, 3 H, CH_3), 0.89 (d, J = 6.6 Hz, 3 H, CH_3); IR ($CHCl_3$) 3065, 3030, 2965, 2940, 2895, 2255, 1600, 1495, 1470, 1400, 1380, 1370 cm^{-1}; UV (95% EtOH) λ_{max} 261 (ε 1264), 267 (ε 1396), 272 (ε 1257), 274 (ε 1261); MS m/e 354.2094 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.96; H, 7.48.

The spectral data for 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (**14**) were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.12–7.45 (m, 7 H, arom and $(CN)_2C$=CH), 6.90 (m, 2 H, arom), 6.58 (m, 2 H, arom), 2.53 (s, 1 H, CH), 2.45 (sept, J = 7.0 Hz, 1 H, Me_2CH), 2.06 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.28 (d, J = 7.1 Hz, 3 H, CH_3), 1.25 (d, J = 7.1 Hz, 3 H, CH_3), 0.91 (d, J = 6.7 Hz 3 H, CH_3), 0.82 (d, J = 6.7 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.80–7.50 (m, 7 H, arom and CH), 6.56 (m, 2 H, arom), 6.49 (m, 2 H, arom), 2.12 (s, 1 H, CH), 1.84 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.48 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.05 (d, J = 7.1 Hz, 3 H, CH_3), 0.82 (d, J = 7.1 Hz, 3 H, CH_3), 0.67 (d, J = 6.7 Hz, 3 H, CH_3), 0.56 (d, J = 6.7 Hz, 3 H, CH_3); IR ($CHCl_3$) 3015, 2985, 2870, 2840, 1600, 1590, 1500, 1460, 1445, 1385, 1370 cm^{-1}; UV (95% EtOH) 310 (sh, ε 1795); MS m/e 354.2099 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.50; H, 7.46.

The spectral data for 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (**13**) were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.16–7.49 (m, 11 H, arom and $(CN)_2C$=CH), 5.88 (d, J = 9.2 Hz, 1 H, Ph_2C=CH), 3.32 (ddd, J = 11.2, 9.2 Hz, 8.2 Hz, 1 H, CH), 1.86 (m, 1 H, Me_2CH), 1.01 (d, J = 6.7 Hz, 3 H, CH_3), 0.91 (d, J = 6.7 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.92–7.26 (m, 10 H, arom), 6.06 (d, J = 11.2 Hz, 1 H, $(CN)_2C$=CH), 5.33 (d, J = 9.2 Hz, 1 H, Ph_2C=CH), 3.12 (ddd, J = 11.2 Hz, 9.2 Hz, 8.2 Hz, 1 H, CH), 1.14 (m, 1 H, Me_2CH), 0.57 (d, J = 6.7 Hz, 3 H, CH_3), 0.39 (d, J = 6.7 Hz, 3 H, CH_3); IR (neat) 3080, 3060, 3020, 2960, 2930, 2870, 2235, 1600, 1495, 1465, 1445, 1390, 1370, 1075, 1030 cm^{-1}; UV (95% EtOH) λ_{max} 247 (ε 20900); MS m/e 312.1624 (calcd for $C_{22}H_{20}N_2$ m/e 312.1626).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45. Found: C, 84.27; H, 6.27.

Ethyl 2,2-Dicyano-3,3-diisopropylcyclopropanecarboxylate (9). To a solution of 19 mL (14 mmol) of diisopropylamine in 90 mL of dry tetrahydrofuran at −78 °C was added dropwise 6.1 mL (9.2 mmol) of 1.5 M *n*-butyllithium solution in hexane. The resulting solution was stirred for 15 min, and then 0.98 mL (9.2 mmol) of freshly distilled ethyl chloroacetate was added dropwise. After the mixture was stirred for 5 min at −78 °C, a solution of 1.50 g (9.2 mmol) of 1,1-dicyano-2-isopropyl-3-methyl-1-butene (**8**)[29] in 6.0 mL of tetrahydrofuran was added dropwise, and the resulting solution was stirred for 30 min and then quenched at −78 °C by addition of brine. After warming to room temperature, acidic workup[25] gave 1.97 g of a brown oil, which was chromatographed on a 3.8 cm × 30 cm silica column: fraction 1, 250 mL of hexane, nil; 2, 2.5 L of 1% ether in hexane, 658 mg (44%) of the starting dinitrile; 3, 2 L of 10% ether in hexane, 829 mg (36%) of ethyl 2,2-dicyano-3,3-diisopropylcyclopropanecarboxylate as a colorless oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.23 (q, J = 7.1 Hz, 2 H, CH_2), 2.50 (s, 1 H, CH), 2.19 (sept, J = 7.1 Hz, 1 H, Me_2CH), 1.92 (sept, J = 7.2 Hz, 1 H, Me_2CH), 1.27 (t, J = 7.1 Hz, 3 H, CH_3), 1.27 (d, J = 7.2 Hz, 3 H, CH_3), 1.23 (d, J = 7.1 Hz, 3 H, CH_3), 1.16 (d, J = 7.2 Hz, 3 H, CH_3), 1.00 (d, J = 7.1 Hz, 3 H, CH_3); IR ($CHCl_3$) 2970, 2930, 2870, 2240, 1745, 1470, 1380, 1360, 1215, 1180, 1040 cm^{-1}; MS m/e 248.1525 (calcd for $C_{14}H_{20}N_2O_2$ m/e 248.1525).

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.72; H, 8.12. Found: C, 67.65; H, 8.31.

1,1-Dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane (6). To a solution of 60 mg (0.24 mmol) of ethyl 2,2-dicyano-3,3-diisopropylcyclopropanecarboxylate (**9**) in 5.0 mL of

(29) Hart, H.; Kim, Y. C. *J. Org. Chem.* **1966**, *31*, 2784–2789.

dry tetrahydrofuran at −78 °C was added dropwise 0.14 mL (0.24 mmol) of 1.7 M sodium bis(2-methoxyethoxy)aluminum hydride solution in toluene. The resulting solution was stirred at −78 °C for 40 min and then quenched at this temperature by addition of 2 M hydrochloric acid. After the solution was warmed to room temperature, neutral workup[25] gave 43 mg (87%) of 2,2-dicyano-3,3-diisopropylcyclopropanecarboxaldehyde (**10**) as a colorless oil, which was nearly pure by ^{1}H NMR analysis. This material was insufficiently stable for chromatography and, without further purification, was dissolved in 2.0 mL of dry tetrahydrofuran and cooled to −78 °C. A solution of 96 mg (0.32 mmol) of diethyl (diphenylmethyl)phosphonate in 2.0 mL of dry tetrahydrofuran was cooled to −78 °C and treated with 0.15 mL (1.5 mmol) of a 1.5 M solution of *n*-butyllithium in hexane. After this mixture was stirred for 20 min at −78 °C, the cold solution of the phosphonate reagent was added dropwise (by cannula) to the cyclopropyl aldehyde solution at −78 °C, and the resulting solution was stirred at −78 °C for 30 min and then poured into 2 M hydrochloric acid. Neutral workup[25] gave 111 mg of yellow oil, which was chromatographed on a 20 cm × 20 cm silica thick-layer plate. Four elutions with 1% ether in pentane gave band 1 (R_f = 0.4), 6.4 mg of uncharacterized material; band 2 (R_f = 0.3), 17.1 mg (20% based on ester) of pure 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane as a colorless oil. Recrystallization from hexane gave 11.3 mg (13% based on ester) of white crystalline solid, mp 76–77 °C.

The spectral data for 2,2-dicyano-3,3-diisopropylcyclopropanecarboxaldehyde were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.65 (d, J = 4.0 Hz, 1 H, CHO), 2.59 (d, J = 4.0 Hz, 1 H, CH), 2.18 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.98 (sept, J = 7.1 Hz, 1 H, Me_2CH), 1.34 (d, J = 7.0 Hz, 6 H, CH_3), 1.23 (d, J = 7.1 Hz, 3 H, CH_3), 1.10 (d, J = 7.1 Hz, 3 H, CH_3); IR ($CHCl_3$) 2970, 2930, 2880, 2740 (w), 2250, 1725, 1420, 1400, 1380, 1210, 1100 cm^{-1}; MS m/e 204.1263 (calcd for $C_{12}H_{16}N_2O$ m/e 204.1250).

The spectral data for 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.50 (m, 10 H, arom), 5.90 (d, J = 9.6 Hz, 1 H, Ph_2C=CH), 2.56 (d, J = 9.6 Hz, 1 H, CH), 2.05 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.80 (sept, J = 7.1 Hz, 1 H, Me_2CH), 1.30 (d, J = 7.1 Hz, 3 H, CH_3), 1.21 (d, J = 7.0 Hz, 3 H, CH_3), 1.18 (d, J = 7.0 Hz, 3 H, CH_3), 1.04 (d, J = 7.1 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.04–7.23 (m, 10 H, arom), 5.97 (d, J = 9.6 Hz, 1 H, Ph_2C=CH), 2.51 (d, J = 9.6 Hz, 1 H, CH), 1.85 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.41 (sept, J = 7.1 Hz, 1 H, Me_2CH), 0.96 (d, J = 7.1 Hz, 3 H, CH_3), 0.77 (d, J = 7.0 Hz, 3 H, CH_3), 0.73 (d, J = 7.0 Hz, 3 H, CH_3), 0.72 (d, J = 7.1 Hz, 3 H, CH_3); IR (neat) 3080, 3050, 2960, 2920, 2240, 1655, 1600, 1580, 1450, 1320, 1280 cm^{-1}; UV (95% EtOH) λ_{max} 268 (ε 15 500); MS m/e 354.2094 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.76; H, 7.60.

2-(2,2-Dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (7). A solution of 200 mg (0.653 mmol) of 4,4-diphenyl-2,2-diisopropyl-3-butenal (**4**) and 7.6 mL (65 mmol) of acetophenone in 190 mL of benzene was irradiated (450-W Hanovia)[25] through a Pyrex filter for 30 min and concentrated in vacuo. The acetophenone was then removed by bulb-to-bulb distillation at 40 °C and 0.010 mm to give 223 mg of 2,2-diphenyl-3,3-diisopropylcyclopropanecarboxaldehyde (**11**) as a sensitive yellow oil, which was pure by ^{1}H NMR spectroscopy. This material was insufficiently stable for chromatography and, without further purification, was dissolved in 1.6 mL of dry *N,N*-dimethylformamide. To this solution was added 444 mg (6.72 mmol) of malononitrile and a solution of 20 mg (0.34 mmol) of anhydrous potassium fluoride in 2.0 mL of dry ethylene glycol. After being stirred for 6 h at room temperature the solution was diluted with water and acidic–basic workup[25] gave 285 mg of a brown oil. This material was chromatographed on a 2.2 cm × 35 cm silica column: fraction 1, 600 mL of 0.5% ether in hexane, nil; 2, 600 mL of 2% ether in hexane, 117 mg of faintly yellow solid, which was recrystallized from ether to give 105 mg (45%) of 2-(2,2-dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane as a white crystalline solid, mp 189–190 °C.

The spectral data for 2,2-diphenyl-3,3-diisopropylcyclopropanecarboxaldehyde were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.07 (d, J = 7.5 Hz, 1 H, CHO), 7.00–7.38 (m, 10 H, arom), 2.35 (d, J = 7.5 Hz, 1 H, CH), 2.20 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.44 (d, J = 6.9 Hz, 3 H, CH_3), 1.02 (m, 10 H, Me_2CH and 3 CH_3's); IR (neat) 3025, 2965, 2875, 1690, 1600, 1495, 1370, 1360, 1155, 1145, 1130 cm^{-1}; MS m/e 277.1951 (calcd for $C_{21}H_{25}$ (parent − CHO) m/e 277.1956).

The spectral data for 2-(2,2-dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.11–7.39 (m, 10 H, arom), 7.07 (d, J = 12.1 Hz, 1 H, $(CN)_2C$=CH), 2.91 (d, J = 12.1 Hz, 1 H, CH), 1.94 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.50 (d, J = 7.0 Hz, 3 H, CH_3), 1.36 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.14 (d, J = 7.0 Hz, 3 H, CH_3), 1.13 (d, J = 7.0 Hz, 3 H, CH_3), 1.06 (d, J = 7.0 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.24 (m, 2 H, arom), 6.81–7.03 (m, 8 H, arom), 6.61 (d, J = 12.1 Hz, 1 H, $(CN)_2C$=CH), 2.84 (d, J = 12.1 Hz, 1 H, CH), 1.29 (sept, J = 7.0 Hz, 1 H, Me_2CH), 1.16 (sept, J = 7.0 Hz, 3 H, Me_2CH), 1.10 (d, J = 7.0 Hz, 1 H, CH_3), 0.86 (d, J = 7.0 Hz, 3 H, CH_3), 0.76 (d, J = 7.0 Hz, 3 H, CH_3), 0.41 (d, J = 7.0 Hz, 3 H, CH_3); IR ($CHCl_3$) 3015, 2995, 2985, 2220, 1585, 1580, 1495, 1450, 1395, 1375, 1180 cm^{-1}; MS m/e 354.2097 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.73; H, 7.44.

2-(2,2-Diphenylvinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (12).[5] A solution of 220 mg (0.718 mmol) of 4,4-diphenyl-2,2-diisopropyl-3-butenal and 8.4 mL (72 mmol) of acetophenone in 200 mL of benzene was irradiated (450-W Hanovia)[25] through a Pyrex filter for 40 min and then concentrated in vacuo. The acetophenone was then removed by bulb-to-bulb distillation at 40 °C and 0.010 mm to give 225 mg of 2,2-diphenyl-3,3-diisopropylcyclopropanecarboxaldehyde (**10**) as a yellow oil, which was pure by ^{1}H NMR analysis. Without further purification, this material was dissolved in 4.0 mL of dry 1,2-dimethoxyethane and added dropwise to a solution of the lithium salt of diethyl (diphenylmethyl)phosphonate[30] (prepared by addition of 0.88 mL (1.4 mmol) of 1.5 M *n*-butyllithium solution in hexane to 441 mg (1.45 mmol) of the phosphonate in 3.0 mL of dry 1,2-dimethoxyethane at 0 °C). The resulting solution was stirred for 30 min at 0 °C and then poured into 2 M hydrochloric acid. Neutral workup[25] gave 700 mg of a yellow oil, which was chromatographed on a 2.8 cm × 60 cm silica column: fraction 1, 2 L of hexane, nil; 2, 4 L of hexane, 204 mg (62%) of 2-(2,2-diphenylvinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane as a white solid. Recrystallization from ether gave 198 mg (60%) of white crystalline solid, mp 123–124 °C (lit.[5] mp 123–124 °C), which was identical with an authentic sample.

Direct Photolysis of 2-(2,2-Dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (7). A solution of 14.1 mg (0.0398 mmol) of 2-(2,2-dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (**7**) in 150 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 15 min. Concentration in vacuo gave 14.0 mg of a pale yellow oil. ^{1}H NMR analysis of the photolysate showed ca. 20% conversion to photoproducts, which did not include those observed in direct or sensitized photolyses of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (**5**) (see supplementary material for more detail).

Sensitized Photolysis of 2-(2,2-Dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (7). A solution of 15.2 mg (0.0428 mmol) of 2-(2,2-dicyanovinyl)-1,1-diphenyl-3,3-diisopropylcyclopropane (**7**) and 10 mL (8.1 mmol) of acetophenone in 150 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 15 min. Concentration in vacuo and bulb-to-bulb removal of acetophenone (40 °C, 0.10 mm) gave 15.3 mg of pale yellow oil. ^{1}H NMR analysis of the photolysate showed ca. 90% conversion to photoproducts, which did not include those observed in direct or sensitized photolyses of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (**5**) (see supplementary material for more detail).

Ethyl 3-Benzyl-2-carbethoxy-4-methylpentanoate (23). To a solution of 20.0 g (93.3 mmol) of diethyl isobutylidenemalonate (**22**)[31] in 20 mL of dry benzene was added dropwise 69 mL (100 mmol) of 1.5 M benzylmagnesium chloride solution in ether at a rate such that gentle reflux was maintained. After an additional

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(31) Cope, A. C.; Hofmann, C. M.; Wyckoff, C.; Hardenbergh, E. *J. Am. Chem. Soc.* **1941**, *63*, 3452–3456.

1 h at reflux, the solution was cautiously poured into 2 M hydrochloric acid, and neutral workup[25] then gave 21.7 g of a pale yellow oil, which was fractionally distilled to give 20.9 g (73%) of ethyl 3-benzyl-2-carbethoxy-4-methylpentanoate as a colorless liquid, bp (0.45 mm) 134–136 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.13–7.31 (m, 5 H, arom), 4.14 (q, J = 7.1 Hz, 2 H, OCH_2), 3.99 (m, 2 H, CH_2), 3.47 (d, J = 6.8 Hz, 1 H, $(EtO_2C)_2CH$), 2.72 (m, 2 H, $PhCH_2$), 2.53 (m, 1 H, CH), 1.84 (m, 1 H, Me_2CH), 1.25 (t, J = 7.1 Hz, 3 H, CH_3), 1.19 (t, J = 7.1 Hz, 3 H, CH_3), 0.94 (d, J = 6.9 Hz, 3 H, CH_3), 0.88 (t, J = 6.9 Hz, 3 H, CH_3); IR ($CHCl_3$) 3020, 2950, 1730, 1605, 1495, 1460, 1395, 1370, 1155, 1035 cm^{-1}; MS m/e 307.1909 (calcd for $C_{18}H_{27}O_4$ (M + 1) m/e 307.1909).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.44; H, 8.61.

3-Isopropyl-α-tetralone (24). To a mixture of 9.00 g (29.4 mmol) of diethyl (1-benzylisobutyl)malonate (**23**) and 300 mL of water in a flask fitted with an efficient reflux condenser was added 300 mL of concentrated sulfuric acid, and the resulting mixture was heated at reflux for 5 h. Hexane extraction and neutral workup gave 5.16 g of a yellow oil, which was chromatographed on a 5.5 cm × 50 cm silica column: fraction 1, 7 L of 1% ether in hexane, nil; 2, 4 L of 3% ether in hexane, 4.98 g (90%) of 3-isopropyl-α-tetralone[8] as an oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.01 (dd, J = 1.1 Hz, 7.8 Hz, 1 H, arom), 7.47 (dt, J = 1.4 Hz, 7.4 Hz, 1 H, arom), 7.25–7.33 (m, 2 H, arom), 2.96 (ddd, J = 1.9 Hz, 3.8 Hz, 16.4 Hz, 1 H, CH_2), δ 2.72–2.82 (m, 2 H, CH_2), 2.36 (dd, J = 12.9 Hz, 16.4 Hz, 1 H, CH_2), 1.93–2.07 (m, 1 H, Me_2CH), 1.68 (m, 1 H, CH), 0.995 (d, J = 6.8 Hz, 3 H, CH_3), 0.988 (d, J = 6.8 Hz, 3 H, CH_3); IR ($CHCl_3$) 3065, 3025, 2960, 2870, 1685, 1600, 1455, 1435, 1415, 1370, 1385, 1310, 1300, 1285, 1220, 1150, 1110 cm^{-1}; MS m/e 188.1201 (calcd for $C_{13}H_{16}O$ m/e 188.1201).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.20; H, 8.45.

1-Phenyl-3-isopropyl-3,4-dihydronaphthalene (25). To a solution of phenylmagnesium bromide, prepared from 1.9 mL (18 mmol) of bromobenzene and 445 mg (18.3 mmol) of magnesium in 10 mL of ether, was added dropwise a solution of 2.87 g (15.2 mmol) of 3-isopropyl-α-tetralone in 3 mL of ether. The resulting solution was stirred at room temperautre for 1 h, and then poured into 2 M hydrochloric acid and extracted with ether. The ether layer was concentrated in vacuo, and the residue was dissolved in 250 mL of benzene. After addition of 94 mg of *p*-toluenesulfonic acid the solution was heated at reflux for 30 min, with water being azeotropically removed by a Dean–Stark trap. Subsequent basic workup[25] gave 3.34 g of a yellow oil, which was chromatographed on a 3.8 cm × 70 cm silica column: fraction 1, 2 L of hexane, nil; 2, 3 L of hexane, 3.06 g (81%) of 1-phenyl-3-isopropyl-3,4-dihydronaphthalene as a colorless oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.96–7.64 (m, 9 H, arom), 6.00 (d, J = 3.6 Hz, 1 H, =CH), 2.81 (br s, 1 H, CH_2), 2.78 (d, J = 3.0 Hz, 1 H, CH_2), 2.45 (m, 1 H, Me_2CH), 1.78 (m, 1 H, CH), 1.00 (d, J = 6.7 Hz, 3 H, CH_3), 0.98 (d, J = 6.7 Hz, 3 H, CH_3); IR (neat) 3040, 3010, 2940, 2860, 2820, 1600, 1490, 1450, 1385, 1370 cm^{-1}; MS m/e 248.1565 (calcd for $C_{19}H_{20}$ m/e 248.1565).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.92; H, 8.07.

1-Phenyl-3-isopropylnaphthalene (15). To a solution of 1.27 g of 1-phenyl-3-isopropyl-3,4-dihydronaphthalene (**25**) in 20 mL of dry benzene was added 1.16 g (5.13 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and the resulting dark solution was stirred at room temperature for 12 h. Dilution with hexane and repeated washing with 2% aqueous sodium hydroxide until the aqueous layer remained colorless, followed by neutral workup[25] gave 1.23 g of a brown oil, which was chromatographed on a 3.8 cm × 65 cm silica column: fraction 1, 2 L of hexane, nil; 2, 3 L of hexane, 847 mg (67%) of 1-phenyl-3-isopropylnaphthalene as a colorless oil, which crystallized from ethanol. Recrystallization (ethanol) gave 770 mg of thin plates, mp 51–52 °C. The spectral data were identical with those found for the material produced in the direct photolysis of dicyano diene **5**.

4,4-Diphenyl-2-isopropyl-3-buten-1-ol. To a solution of 4.43 g (14.4 mmol) of ethyl 4,4-diphenyl-2-isopropyl-3-butenoate (**20**) in 60 mL of dry hexane at 0 °C was added dropwise 33 mL (33 mmol) of 1.0 M diisobutylaluminum hydride solution in hexane. The resulting solution was stirred at room temperature for 2.5 h, cooled to 0 °C, and quenched by cautious dropwise addition of 10% hydrochloric acid. Acidic workup[25] gave 4.24 g of pale yellow oil, which was chromatographed on a 5.5 cm × 50 cm Florisil column: fraction 1, 2 L of 6% ether in hexane, nil; 2, 2 L of 10% ether in hexane, nil; 3, 5 L of 20% ether in hexane, nil; 4, 5 L of 30% ether in hexane, 3.52 g (92%) of 4,4-diphenyl-2-isopropyl-3-buten-1-ol as a colorless oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20–7.40 (m, 10 H, arom), 5.96 (d, J = 10.8 Hz, 1 H, Ph_2C=CH), 3.71 (dd, J = 10.7 Hz, 5.4 Hz, 1 H, CH_2), 3.58 (dd, J = 10.7 Hz, 8.1 Hz, 1 H, CH_2), 2.31 (m, 1 H, CH), 1.73 (m, 1 H, Me_2CH), 0.93 (d, J = 6.8 Hz, 3 H, CH_3), 0.87 (d, J = 6.8 Hz, 3 H, CH_3); IR (neat) 3340 (br), 3060, 3040, 3010, 2940, 2910, 2850, 1600, 1490, 1465, 1445, 1385, 1365, 1070, 1060, 1040 cm^{-1}; MS m/e 266.1671 (calcd for $C_{19}H_{22}O$ m/e 266.1671).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.61; H, 8.31.

4,4-Diphenyl-2-isopropyl-3-butenal (21). To a solution of 17 mL of dry pyridine in 210 mL of dry dichloromethane was added 9.04 g (90.4 mmol) of chromium trioxide. The resulting solution was stirred for 15 min, and then a solution of 3.52 g (13.2 mmol) of 4,4-diphenyl-2-isopropyl-3-buten-1-ol in 50 mL of dichloromethane was added dropwise. After stirring for 1.5 h, the mixture was diluted with ether and washed with 5% aqueous sodium hydroxide, after which acidic–basic workup[25] gave 3.16 g (90%) of 4,4-diphenyl-2-isopropyl-3-butenal as an oil. This material was insufficiently stable for analysis. The (2,4-dinitrophenyl)hydrazone melted at 157–158 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.63 (d, J = 2.7 Hz, 1 H, CHO), 7.14–7.42 (m, 10 H, arom), 6.01 (d, J = 10.4 Hz, 1 H, Ph_2C=CH), 2.97 (ddd, J = 10.4 Hz, 7.5 Hz, 2.7 Hz, 1 H, CH), 1.99 (m, 1 H, Me_2CH), 0.98 (d, J = 6.9 Hz, 3 H, CH_3), 0.91 (d, J = 6.9 Hz, 3 H, CH_3); IR (neat) 3040, 3010, 2940, 2910, 2860, 2800, 2700, 1720, 1595, 1490, 1465, 1445, 1385, 1370, 1075, 1040 cm^{-1}; MS m/e 264.1507 (calcd for $C_{19}H_{20}O$ m/e 264.1514).

The spectral data for the (2,4-dinitrophenyl)hydrazone were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 11.01 (s, 1 H, NH), 9.11 (d, J = 2.6 Hz, 1 H, arom), 8.30 (m, 1 H, arom), 7.86 (d, J = 9.6 Hz, 1 H, arom), 7.19–7.49 (m, 11 H, arom and N=CH), 6.08 (d, J = 10.2 Hz, 1 H, Ph_2C=CH), 3.10 (m, 1 H, CH), 2.01 (m, 1 H, Me_2CH), 1.02 (d, J = 6.7 Hz, 3 H, CH_3), 0.95 (d, J = 6.7 Hz, 3 H, CH_3); IR ($CHCl_3$) 3310, 3100, 3080, 3060, 3030, 2960, 2875, 1620, 1595, 1520, 1430, 1335, 1310, 1280, 1140 cm^{-1}; MS m/e 444.1785 (calcd for $C_{25}H_{24}N_2O_4$ m/e 444.1797).

Anal. Calcd for $C_{25}H_{24}N_2O_4$: C, 67.55; H, 5.44. Found: C, 67.21; H, 5.58.

1,1-Dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (13). In a flask fitted with a Dean–Stark trap, a mixture of 3.15 g (11.9 mmol) of 4,4-diphenyl-3-isopropyl-3-butenal (**21**), 791 mg (12.0 mmol) of malononitrile, 12 mg of β-alanine, 0.16 mL of acetic acid, and 3.0 mL of dry benzene was heated at reflux for 45 min. Acidic–basic workup[25] gave 3.65 g (98%) of 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene as a yellow oil, which was pure by ^{1}H NMR analysis. This material decomposed rapidly upon attempted chromatographic purification on standard adsorbents. A 77.0-mg analytical sample was further purified by chromatography on a methanol-deactivated[25] 20 cm × 20 cm silica preparative thick-layer plate. One elution with 10% ether in pentane gave a single major band (R_f = 0.5), which contained 64.7 mg (84%) of the pentadiene as a colorless oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.16–7.49 (m, 11 H, arom and $(CN)_2C$=CH), 5.88 (d, J = 9.2 Hz, 1 H, Ph_2C=CH), 3.32 (ddd, J = 11.1 Hz, 9.2 Hz, 8.1 Hz, 1 H, CH), 1.86 (m, 1 H, Me_2CH), 1.01 (d, J = 6.7 Hz, 3 H, CH_3), 0.91 (d, J = 6.7 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.92–7.26 (m, 10 H, arom), 6.06 (d, J = 11.2 Hz, 1 H, $(CN)_2C$=CH), 5.33 (d, J = 9.5 Hz, 1 H, Ph_2C=CH), 3.12 (ddd, J = 11.1 Hz, 9.5 Hz, 8.2 Hz, 1 H, CH), 1.14 (m, 1 H, Me_2CH), 0.57 (d, J = 6.7 Hz, 3 H, CH_3), 0.39 (d, J = 6.7 Hz, 3 H, CH_3); IR (neat) 3080, 3060, 3020, 2960, 2930, 2870, 2235, 1600, 1495, 1465, 1445, 1390, 1370, 1075, 1030 cm^{-1}; MS m/e 312.1624 (calcd for $C_{22}H_{20}N_2$ m/e 312.1626).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.70; H, 7.39. Found: C, 84.46; H, 7.23.

***cis*- and *trans*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19).** A solution of 2.64 g (8.45 mmol) of 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (**13**) in 14 mL of dry 1,2-dimethoxyethane was added dropwise to a vigorously stirred slurry of sodium hydride (406 mg (10.1 mmol) of a 60% oil dispersion of NaH, washed several times with 1,2-dimethoxyethane) in 14 mL of 1,2-dimethoxyethane. The resulting mixture was stirred for 10 min, and then 8.4 mL (84 mmol) of isopropyl iodide was added. After the mixture was stirred for 32 h, basic workup[25] gave 3.11 g of a dark brown oil, which was found by ^{1}H NMR analysis to contain a 1:1 mixture of *cis*- and *trans*-dienes. After 3 mL of ether was added, 952 mg of a yellow solid crystallized from the crude material. Recrystallization from ethyl acetate gave 897 mg (30%) of pure *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19a**), mp 131–132 °C.

An analytical sample of the cis isomer was obtained by chromatographing 140 mg of the remaining brown oil on a triethylamine-deactivated[25] 20 cm × 20 cm silica preparative thick-layer plate. One elution with a 1:20:80 mixture of triethylamine, ether, and pentane gave: band 1 (R_f = 0.44), 26 mg of *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene as a pale yellow solid; band 2 (R_f = 0.45), 59 mg of pure *cis*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19b**) as a colorless oil.

The spectral data for *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.17–7.39 (m, 10 H, arom), 6.46 (d, J = 1.2 Hz, 1 H, Ph_2C=CH), 4.76 (d, J = 1.2 Hz, 1 H, =CH), 3.27 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.85 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.29 (d, J = 6.7 Hz, 6 H, CH_3), 0.82 (d, J = 6.7 Hz, 6 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.08–7.25 (m, 10 H, arom), 6.43 (d, J = 1.2 Hz, 1 H, $(CN)_2C$=CH), 4.70 (d, J = 1.2 Hz, 1 H, Ph_2C=CH), 3.45 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.34 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.15 (d, J = 6.7 Hz, 6 H, CH_3), 0.51 (d, J = 6.7 Hz, 6 H, CH_3). An NOE difference experiment[32] with irradiation of the methyl protons of the C-5 isopropyl group showed a ca. 10% enhancement of the C-6 (diphenylvinyl) proton signal but no enhancement of the C-4 vinylic proton signal, indicating a trans relationship between the C-5 isopropyl group and C-4 hydrogen: IR ($CHCl_3$) 3020, 2970, 2940, 2880, 2245, 1600, 1490, 1465, 1445, 1400, 1380, 1365, 1075 cm^{-1}; UV (95% EtOH) λ_{max} 292 (ε 13 200); MS m/e 354.2104 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.73; H, 7.34.

The spectral data for *cis*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.23–7.35 (m, 10 H, arom), 6.80 (d, J = 1.8 Hz, 1 H, Ph_2C=CH), 5.10 (dd, J = 1.8 Hz, 1.3 Hz, 1 H, =CH), 2.26 (sept, J = 6.7 Hz, 1 H, Me_2CH), 2.11 (d sept, J = 6.8 Hz, 1.3 Hz, 1 H, Me_2CH), 1.25 (d, J = 6.7 Hz, 6 H, CH_3), 0.94 (d, J = 6.8 Hz, 6 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.01–7.45 (m, 11 H, arom and Ph_2C=CH), 4.91 (dd, J = 1.8 Hz, 1.3 Hz, 1 H, =CH), 2.11 (d sept, J = 6.8 Hz, 1.3 Hz, 1 H, Me_2CH), 1.59 (sept, J = 6.7 Hz, 1 H, Me_2CH), 0.85 (d, J = 6.7 Hz, 6 H, CH_3), 0.79 (d, J = 6.8 Hz, 6 H, CH_3). An NOE difference experiment[32] with irradiation of the methyl protons of the C-5 isopropyl group showed enhancements of both the C-6 (diphenylvinyl) proton signal (ca. 4%) and the C-4 vinyl proton (ca. 6%), indicating a cis relationship between the C-5 isopropyl and the C-4 hydrogen: IR ($CHCl_3$) 3060, 3020, 2970, 2940, 2870, 2240, 1635, 1495, 1465, 1445, 1395, 1380, 1360, 1160, 1075, 1030 cm^{-1}; UV (95% EtOH) λ_{max} 286 (ε 11 660); MS m/e 354.2119 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.32; H, 7.37.

Exploratory Photolysis of *trans*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19a). A solution of 47.1 mg (0.133 mmol) of *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene in 170 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 15 min. Concentration in vacuo gave 46.4 mg of a slightly yellow oil, which was determined by ^{1}H NMR analysis to be a 3.2:1.6:1.0 mixture of 1-phenyl-3-isopropylnaphthalene (**15**), isopropylmalononitrile (**18**) and 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**). This material was chromatographed on a triethylamine-deactivated[25] 20 cm × 20 cm silica thick-layer plate. One elution with a 1:10:90 mixture of triethylamine, ether, and pentane gave: band 1 (R_f = 0.8), 21.7 mg (68%) of 1-phenyl-3-isopropylnaphthalene (**15**) as a colorless oil which was recrystallized from 95% ethanol to give 15.2 mg (47%) of white crystalline material, mp 51–52 °C; band 2 (R_f = 0.3), 11.9 mg (26%) of 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**) as a white solid, which was recrystallized from hexane to give 7.0 mg (15%) of white crystalline material, mp 145–146 °C. The spectral data for both photoproducts were identical with those found for the material produced in the direct photolysis of dicyano diene **5**.

Exploratory Photolysis of *cis*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19b). A solution of 19.3 mg (0.0544 mmol) of *cis*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene in 170 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 15 min. Concentration in vacuo gave 19.8 mg of a slightly yellow oil. ^{1}H NMR analysis of the crude photolysate showed very little conversion, with the starting *cis*-diene **19b**, 1-phenyl-3-isopropylnaphthalene (**15**), 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**), and *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19a**) in the ratio 93:17:3.3:1.0. This material was chromatographed on a triethylamine-deactivated[25] 20 cm × 20 cm silica thick-layer plate. One elution with a 1:10:90 mixture of triethylamine, ether, and pentane gave: band 1 (R_f = 0.8), 2.6 mg (20%) of 1-phenyl-3-isopropylnaphthalene (**15**) as a colorless oil, which was pure by ^{1}H NMR; band 2 (R_f = 0.4), 13.9 mg (73%) of the starting *cis*-diene **19b** as a colorless oil; band 3 (R_f = 0.3), 0.4 mg (2%) of 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**) as a colorless oil. The spectral data for the photoproducts were identical with those found for the material produced in the direct photolysis of dicyano diene **5**.

Exploratory Low-Intensity Photolysis of *trans*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19a). A solution of 12.4 mg (0.0350 mmol) of *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19a**) in 50 mL of acetonitrile was irradiated for 21 h at 302 nm on the microoptical bench.[33] Concentration in vacuo at room temperature gave 12.6 mg of yellow oil, which was found by ^{1}H NMR analysis to be a 5.8:6.0:1.7:1.0 mixture of the starting *trans*-diene **19a**, 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-3,4-dihydronaphthalene (**17**), 1-phenyl-3-isopropylnaphthalene (**15**), and isopropylmalononitrile (**18**).[9] The mixture was chromatographed on a triethylamine-deactivated[25] 20 cm × 20 cm silica thick-layer plate. One elution with a 1:10:90 mixture of triethylamine, ether, and pentane gave: band 1 (R_f = 0.8), 1.0 mg (12%) of 1-phenyl-3-isopropylnaphthalene (**15**) as a colorless oil, which was pure by ^{1}H NMR; band 2 (R_f = 0.4), 5.1 mg (41%) of the starting *trans*-diene **19a** as a colorless oil; band 3 (R_f = 0.3), 5.3 mg (43%) of 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-3,4-dihydronaphthalene (**17**) as a colorless oil. The spectral data for 1-phenyl-3-isopropylnaphthalene were identical with those found for the material produced in the direct photolysis of dicyano diene **5**.

The spectral data for dihydronaphthalene **17** were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.14–7.43 (m, 9 H, arom), 6.03 (dd, J = 6.6 Hz, 0.9 Hz, 1 H, =CH), 3.36 (s, 1 H, CH), 2.56 (m, 1 H, CH), 2.38 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.63 (m, 1 H, Me_2CH), 1.40 (d, J = 6.6 Hz, 3 H, CH_3), 1.29 (d, J = 6.6 Hz, 3 H, CH_3), 0.98 (d, J = 6.7 Hz, 3 H, CH_3), 0.95 (d, J = 6.7 Hz, 3 H, CH_3); ^{1}H NMR (C_6D_6, 270 MHz) δ 7.57 (m, 2 H, arom), 6.90–7.28 (m, 7 H, arom), 5.76 (dd, J = 6.6 Hz, 0.9 Hz, 1 H, =CH), 3.13 (s, 1 H, CH), 2.34 (m, 1 H, CH), 1.88 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.37 (m, 1 H, Me_2CH), 1.01 (d, J = 6.6 Hz, 3 H, CH_3), 0.89 (d, J = 6.6 Hz, 3 H, CH_3), 0.68 (d, J = 6.7 Hz, 3 H, CH_3), 0.95 (d,

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J = 6.7 Hz, 3 H, CH_3); IR ($CHCl_3$) 3060, 3025, 2960, 2940, 2870, 2245, 1600, 1495, 1470, 1450, 1400, 1395, 1380, 1370 cm^{-1}; UV (95% EtOH) λ_{max} 270 (ϵ 7050); MS m/e 354.2087 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.61; H, 7.44.

2,2-Diphenyl-3-methylbutanal (28). To a solution of 7.47 g (31.8 mmol) of 2,2-diphenyl-3-methylbutanenitrile (**27**)[34] in 75 mL of dry toluene at 0 °C was added dropwise 38 mL (38 mmol) of 1.0 M diisobutylaluminum hydride solution in hexane. The resulting solution was allowed to warm to room temperature and was stirred for 18 h and then poured into 600 mL of saturated aqueous ammonium chloride. After further acidification with 100 mL of 2 M hydrochloric acid, the layers were separated, and the aqueous layer was extracted with ether, allowed to stand for 30 min, ether extracted again, further acidified with 50 mL of concentrated hydrochloric acid, and ether extracted once more. The combined organic layers were then subjected to normal basic workup[25] to give 6.05 g of a colorless oil. Crystallization from hexane gave 5.77 g (76%) of 2,2-diphenyl-3-methylbutanal as a white crystalline solid, mp 67–68 °C.

The spectral data were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 9.64 (s, 1 H, CHO), 7.18–7.42 (m, 10 H, arom), 3.23 (sept, J = 6.7 Hz, 1 H, Me_2CH), 0.86 (d, J = 6.7 Hz, 6 H, CH_3); IR (neat) 3040, 3010, 2950, 2920, 2860, 2800, 2690, 1725, 1595, 1575, 1490, 1465, 1400, 1390, 1370 cm^{-1}; MS m/e 238.1357 (calcd for $C_{17}H_{18}O$ m/e 238.1358).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.83; H, 7.70.

3-Cyano-5,5-diphenyl-2,6-dimethyl-3-heptene (29). To a solution of 5.1 mL (36 mmol) of diisopropylamine in 60 mL of dry tetrahydrofuran at −78 °C was added dropwise 16.1 mL (24.2 mmol) of 1.5 M *n*-butyllithium solution in hexane. The resulting solution was stirred for 15 min, and then 2.7 mL (25 mmol) of isovaleronitrile was added dropwise. This solution was stirred at −78 °C for 45 min and then at 0 °C for 30 min. After the solution was cooled back down to −78 °C, a solution of 5.77 g (24.2 mmol) of 2,2-diphenyl-3-methylbutanal (**28**) in 120 mL of tetrahydrofuran was added dropwise, and the resulting solution was stirred at −78 °C for 15 min and then at 20 °C for 90 min. To this solution was added 11.4 g (102 mmol) of solid potassium *tert*-butoxide, and the resulting mixture was stirred for 1 h and then poured into 2 M hydrochloric acid. Acidic–basic workup[25] gave 7.59 g of a dark yellow oil, which was chromatographed on a 5.5 cm × 50 cm silica column: fraction 1, 2 L of 2% ether in hexane, nil; 2, 4 L of 4% ether in hexane, 6.43 g of a pale yellow oil, which was recrystallized from hexane to give 6.09 g (83%) of 3-cyano-5,5-diphenyl-2,6-dimethyl-3-heptene as a white crystalline solid, mp 64–65 °C. Although it was possible to isolate the β-hydroxy- and β-acetoxynitrile intermediates in this sequence, the one-pot procedure described was considerably more efficient.

The spectral data were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 7.19–7.33 (m, 10 H, arom), 6.75 (d, J = 0.8 Hz, 1 H, =CH), 3.35 (sept, J = 6.6 Hz, 1 H, Me_2CH), 2.58 (d sept, J = 6.8 Hz, 0.8 Hz, 1 H, Me_2CH), 1.13 (d, J = 6.8 Hz, 6 H, CH_3), 0.88 (d, J = 6.6 Hz, 6 H, CH_3); IR (neat) 3080, 3060, 3030, 2960, 2930, 2840, 2210, 1600, 1495, 1465, 1450, 1390, 1370 cm^{-1}; MS m/e 303.1978 (calcd for $C_{22}H_{25}N$ m/e 303.1987).

Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30. Found: C, 87.47; H, 8.36.

4,4-Diphenyl-2-isopropyl-5-methyl-2-hexenal (30). To a solution of 1.84 g (6.06 mmol) of 3-cyano-5,5-diphenyl-2,6-dimethyl-3-heptene (**29**) in 150 mL of dry hexane at 0 °C was added dropwise 7.3 mL (7.3 mmol) of a 1 M solution of diisobutylaluminum hydride in hexane, and the resulting solution was allowed to warm to room temperature. After being stirred for 2 h the solution was poured into 600 mL of saturated aqueous ammonium chloride and further acidified with 100 mL of 2 M hydrochloric acid. Acidic–basic workup[25] then gave 1.72 g of colorless oil, which was recrystallized from hexane to give 1.57 g (84%) of 4,4-diphenyl-2-isopropyl-5-methyl-2-hexenal as a white crystalline solid, mp 77–78 °C.

The spectral data were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 9.31 (s, 1 H, CHO), 7.12–7.36 (m, 10 H, arom), 7.01 (d, J = 0.6 Hz, 1 H, =CH), 3.11 (sept, J = 6.7 Hz, 1 H, Me_2CH), 3.02 (d sept, J = 6.9 Hz, 0.6 Hz, 1 H, Me_2CH), 1.13 (d, J = 6.9 Hz, 6 H, CH_3), 0.91 (d, J = 6.7 Hz, 6 H, CH_3); IR ($CHCl_3$) 3090, 3060, 3030, 2960, 2930, 2880, 1670, 1600, 1495, 1465, 1445, 1390, 1380, 1370 cm^{-1}; MS m/e 306.1986 (calcd for $C_{22}H_{26}O$ m/e 306.1984).

Anal. Calcd for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 86.38; H, 8.51.

1,1-Dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (26). A mixture of 3.34 g (10.9 mmol) of 4,4-diphenyl-2-isopropyl-5-methyl-2-hexenal (**30**), 0.760 g (11.5 mmol) of malononitrile, 11 mg of β-alanine, 0.14 mL of glacial acetic acid, and 2.8 mL of benzene was heated at reflux for 1.5 h in a flask equipped with a Dean–Stark trap. Acidic–basic workup[25] then gave 4.07 g of a pale yellow oil, which was chromatographed on a 3.8 cm × 65 cm silica column: fraction 1, 2 L of 1% ether in hexane, nil; 2, 4 L of 1% ether in hexane, 3.93 g of a colorless oil, which was recrystallized from hexane to give 3.70 g (96%) of 1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene as a white crystalline solid, mp 59–60 °C.

The spectral data were the following: ^1H NMR ($CDCl_3$, 270 MHz) δ 7.22–7.37 (m, 10 H, arom), 6.95 (d, J = 1.1 Hz, 1 H, $(CN)_2C$=CH), 6.71 (m, 1 H, =CH), 3.00 (br sept, J = 6.7 Hz, 1 H, Me_2CH), 2.90 (sept, J = 6.7 Hz, 1 H, Me_2CH), 1.20 (d, J = 6.7 Hz, 6 H, CH_3), 0.87 (d, J = 6.7 Hz, 6 H, CH_3); ^1H NMR (C_6D_6, 270 MHz) δ 6.90–7.18 (m, 10 H, arom), 6.65 (d, J = 1.1 Hz, 1 H, $(CN)_2C$=CH), 6.43 (m, 1 H, =CH), 2.65 (br sept, J = 6.7 Hz, 1 H, Me_2CH), 2.51 (sept, J = 6.7 Hz, 1 H, Me_2CH), 0.87 (d, J = 6.7 Hz, 6 H, CH_3), 0.69 (d, J = 6.7 Hz, 6 H, CH_3); IR (neat) 3080, 3060, 3030, 2960, 2920, 2880, 2840, 2230, 1595, 1580, 1560, 1490, 1460, 1445, 1385, 1370 cm^{-1}; UV (95% EtOH) λ_{max} 305 (ϵ 10630); MS m/z 354.2106 (calcd for $C_{25}H_{26}N_2$ m/e 354.2096).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.70; H, 7.39. Found: C, 84.67; H, 7.39.

Exploratory Photolysis of 1,1-Dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (26). A solution of 49.5 mg (0.140 mmol) of 1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (**26**) in 160 mL of acetonitrile was irradiated (450-W Hanovia)[25] for 15 min and then concentrated in vacuo to give 49.9 mg of a yellow oil, which was chromatographed on a 20 cm × 20 cm silica thick-layer plate. Elution with 5% ether in pentane gave a dark band 1 (R_f = 0.6) which contained 40.9 mg (83%) of 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2i-diisopropylcyclopropane (**14**) as a white solid, which was recrystallized from hexane to give 32.2 mg (65%) of white crystalline material, mp 157–158 °C. The spectral data for (dicyanovinyl)cyclopropane **14** were identical with those found for the material produced in the direct photolysis of dicyano diene **5**.

Photolysis Equipment for Quantum Yield Determinations. All direct and sensitized quantum yields were determined using a microoptical bench[33] equipped with an Osram 200-W high-pressure mercury lamp and a Bausch & Lomb Model 33-86-79 monochromator. The monochromator entrance and exit slits were set to 5.4 and 3.0 mm, respectively, to give a 22-nm band pass (width at half-height). Light output was measured with a digital actinometer[35] calibrated by ferrioxalate actinometry.[36] All runs were analyzed by 270-MHz ^1H NMR spectroscopy using diphenylacetonitrile as an internal standard. In the direct and sensitized runs with dicyano diene **5** it was necessary to use C_6D_6 as the NMR solvent to avoid overlap of photoproduct signals, and this solvent was also used for the runs with 4,6-heptadiene **19**. In runs with 1,3-heptadiene **26** the analysis was simplified by using $CDCl_3$ as the NMR solvent.

Summary of Direct Quantum Yield Results for 1,1-Dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (5). All runs were done in acetonitrile at 302 nm. Under the low-intensity irradiation conditions used, none of the 1,4-dihydronaphthalene **16** was formed. No attempt was made to prevent loss of the volatile isopropylmalononitrile in vacuo, and its quantum yield of formation was not determined. It was not possible reliably to

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Table II. Summary of Radical Trapping Results

	photoproduct distribution[b]				
1,4-CHD,[a] mM	13, %	14, %	15, %	16, %	6, %
0.00	9.8	10.2	59.7	6.5	13.6
0.53	9.7	10.3	58.5	6.6	14.9
1.06	10.7	9.2	59.6	6.5	14.0
2.12	11.6	9.4	58.7	6.5	13.7
10.6	11.7	8.5	59.9	5.9	14.0
106	13.7	7.4	58.0	6.1	14.8
265	14.4	6.4	60.8	5.4	13.0
530	15.2	6.6	60.5	6.0	11.6

[a] 1,4-Cyclohexadiene. [b] Given as percent of total photoproduct.

extrapolate the quantum yields for formation of the secondary photoproducts 1-phenyl-3-isopropylnaphthalene (**15**) and 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (**14**) to 0% conversion, since negative deviations from linearity occurred at low conversion. Quantum yields for formation of primary photoproducts 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane (**6**), 1,1-dicyano-5,5-diphenyl-3-isopropyl-1,4-pentadiene (**13**), and *trans*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19a**) did show linear dependence on extent of conversion and were extrapolated to 0% conversion. Extrapolated values were 0.0041, 0.0049, and 0.0067, respectively.

Summary of Sensitized Quantum Yield Results for 1,1-Dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (5). All runs were done in acetonitrile or benzene at 366 nm. Thioxanthone was used as the sensitizer, and identical results were obtained when xanthone was used. Extrapolation of the quantum yield for formation of 1,1-dicyano-2-(2,2-diphenylvinyl)-3,3-diisopropylcyclopropane (**6**) to 0% conversion gave values of 0.041 and 0.037 for the acetonitrile and benzene runs, respectively.

Summary of Direct Quantum Yield Results for *trans*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19a). All runs were done in acetonitrile at 302 nm. Under the low-intensity irradiation conditions used, none of the 1,4-dihydronaphthalene **16** was formed. No attempt was made to prevent loss of the volatile isopropylmalononitrile in vacuo, and its quantum yield of formation was not determined. Extrapolation of the quantum yields for formation of 1-phenyl-3-isopropylnaphthalene (**15**) and 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-3,4-dihydronaphthalene (**17**) to 0% conversion gave values of 0.066 and 0.27, respectively.

Summary of Direct Quantum Yield Results for *cis*-3,3-Dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (19b). A solution of 12.2 mg (0.0344 mmol) of *cis*-3,3-dicyano-7,7-diphenyl-5-isopropyl-2-methyl-4,6-heptadiene (**19b**) in 50 mL of acetonitrile was irradiated on a microoptical bench[33] until 0.0028 mEinstein had been absorbed. ^{1}H NMR analysis of the photolysate showed no detectable conversion of the diene, indicating a quantum yield of less than 0.02.

Summary of Direct Quantum Yield Results for 1,1-Dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (26). All runs were done in acetonitrile at 302 nm. Extrapolation of the quantum yield for formation of 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (**14**) to 0% conversion gave a value of 0.018.

General Procedure for Radical Trapping Experiments. Solutions of 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (**5**) in acetonitrile containing varying amounts of 1,4-cyclohexadiene were prepared in 7 cm × 0.8 cm Pyrex tubes. These solutions were 3.7×10^{-3} M in dicyano diene **5** and up to 0.53 M in 1,4-cyclohexadiene. After purging the samples with nitrogen, the tubes were sealed and strapped to the lamp housing of a Hanovia immersion well apparatus, which contained a 450-W medium-pressure mercury lamp with a Pyrex filter. The temperature of the samples during photolysis was maintained by immersion in a water-cooled bath. After 1 h of irradiation the samples were concentrated in vacuo and analyzed by ^{1}H NMR using diphenylacetonitrile as an internal standard. Conversions were ca. 30%. Under these high-intensity photolysis conditions neither 4,6-heptadiene **19a** nor 3,4-dihydronaphthalene **17** were observed, and no attempt was made to prevent loss of the volatile isopropylmalononitrile in vacuo. Overlap of photoproduct signals was avoided by use of C_6D_6 as the NMR solvent. The results are summarized in Table II.

General Procedure for Single-Crystal X-ray Structure Determination. X-ray crystals of 2-(2,2-dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (**14**), 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (**16**), and 1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (**26**) were prepared by slow crystallization from hexane while those of 4-(1,1-dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-3,4-dihydronaphthalene (**17**) were crystallized by vapor diffusion of hexane into toluene. Data were collected on a Nicolet (Syntex) P3/F diffractometer for single crystals of each compound. Unit cell parameters were determined by least-squares refinement of 25 reflections from rotation photographs. Data were collected at 22 °C with three reflections monitored after every 96, and data having $F > 3\sigma(F)$ were rejected. Lorentz and polarization corrections were applied, and each structure was solved under appropriate space-group symmetry by direct methods using either

Table III. Summary of Crystal Data Collection Parameters for 2-(2,2-Dicyanovinyl)-*cis*-1,3-diphenyl-*cis*-1,2-diisopropylcyclopropane (14), 4-(1,1-Dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-1,4-dihydronaphthalene (16), 4-(1,1-Dicyano-2-methylpropyl)-1-phenyl-3-isopropyl-3,4-dihydronaphthalene (17), and 1,1-Dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene (26)

parameter	cyclopropane 14	1,4-dihydronaphthalene 16	3,4-dihydronaphthalene 17	1,3-heptadiene 26
a axis, Å	8.553 (2)	6.518 (2)	8.417 (2)	9.280 (3)
b axis, Å	24.224 (7)	18.099 (5)	10.041 (3)	9.970 (3)
c axis, Å	10.704 (3)	17.177 (4)	13.469 (2)	12.769 (3)
α angle, deg	90.00 (0)	90.00 (0)	68.66 (2)	68.79 (2)
β angle, deg	100.88 (2)	90.79 (2)	73.01 (2)	73.36 (2)
γ angle, deg	90.00 (0)	90.00 (0)	89.53 (2)	76.62 (2)
molecules/cell (*Z*)	4	4	2	2
space group	$P2_1/C$	$P2_1/C$	$P\bar{1}$	$P\bar{1}$
μ, mm^{-1}	0.6	0.6	0.6	0.6
radiation type	Mo Kα	Mo Kα	Mo Kα	Cu Kα
scan mode	ω	ω	ω	ω
2θ limits, deg	4.0–45.8	4.0–45.8	4.5–115.0	4.0–45.8
minimum (*h*,*k*,*l*)	(0,–27,–12)	(0,0,–19)	(0,–11,–15)	(0,–11,–14)
maximum (*h*,*k*,*l*)	(10,0,12)	(8,20,19)	(10,11,15)	(11,11,14)
scan range, deg	0.7/0.7	0.5/0.5	0.8/0.8	0.7/0.7
measured reflections	3161	3169	2892	3053
unique reflections	2841	2766	2671	2844
observed reflections	1910	1843	2315	2318
least-squares param	348	322	322	322
goodness of fit	1.79	1.73	1.86	2.14
$R_1(F)$	0.045	0.075	0.045	0.053
$R_W(F)$	0.056	0.074	0.081	0.064

Table IV. MMP Results for Dicyano Diene 5 and Pentadienyl Radical 32 Conformers

conformer	steric energy, kcal/mol	dihedral C1,C2,C3,C4, deg	dihedral C2,C3,C4,C5, deg
	Dicyano Diene **5**		
"half-U" **5′**	48.43	32.3	151.6
"half-U" **5″**	48.39	148.6	32.9
"W"	49.77	157.1	138.0
"U"	51.12	44.6	47.4
	Pentadienyl Radical **32**		
"half-U" **32′**	108.48	0.0	180.0
"half-U" **32″**	106.64	180.0	0.0

Table V. MMP Steric Energies of 1,3-Heptadiene 26 Conformers

conformer	steric energy, kcal/mol	dihedral C3,C4,C5,Ci,[a] deg	dihedral C1,C2,C3,C4, deg
26′[b]	38.20	−58.9	117.5
26′[c]	40.71	−90.0	102.7
26′[c,d]	51.13	−90.0	180.0
26″[b]	38.99	57.6	103.1
26″[c]	42.20	33.5	119.3
26″[c,d]	56.23	36.2	180.0

[a] Ci = ipso carbon of migrating phenyl. [b] Fully optimized. [c] p orbitals at C4 and ipso carbon of migrating phenyl fixed coplanar. [d] Butadienyl group (C1–C4) fixed planar.

SHELXS86[37] or, in the case of dicyanovinylcyclopropane **14**, MULTAN80.[38] Hydrogen atoms were located by difference Fourier synthesis, and full-matrix least-squares refinement was carried out using anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The results of the structure determinations are summarized in Table III, and final parameters are available as supplementary material.

Molecular Mechanics Calculations. All molecular mechanics calculations employed Gajewski's MMP program.[18b] For the reactant 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (**5**), minima were found which correspond to the "W", "U", and the two "half-U" conformations of the pentadiene skeleton. The MMP steric energy for each of these is given in Table IV with the C1,C2,C3,C4 and C5,C4,C3,C2 dihedral angles for each to indicate the orientations of the two vinyl groups. Also listed in Table IV are the steric energies and corresponding dihedral angles for the conformers **32′** and **32″** of the 1,1-dicyano-5,5-diphenyl-3-isopropylpentadienyl radical. In these latter two calculations, all atoms of the π-system were constrained to be coplanar. In calculations on radicals and diradicals where torsional or bending constants were not available, constants approximating them were used.

The MMP calculations on *cis*-1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene **26** showed minima at C3,C4,C5,C6 dihedral angles of 58 and 177°, with the latter preferred by 0.8 kcal/mol. When the p orbitals involved in phenyl–vinyl bridging (ipso on the migrating phenyl and at C4) were made coplanar, this energy difference increased to 1.5 kcal/mol. A still larger energy difference (5.1 kcal/mol) resulted when the butadienyl moiety (C1–C4) was constrained to be in a planar s-trans conformation. In each case, the conformer corresponding to **26′** was favored over that corresponding to **26″**. These results are summarized in Table V.

Calculations on the cyclopropyldicarbinyl diradicals corresponding to structures **46a** and **46b** treated these species as cyclopropanes with the odd-electron centers (the para carbon of the bridging phenyl and the dicyanovinyl-substituted carbinyl carbon) represented by sp^2 carbons. The migrating phenyl was constrained to be planar, and the rotational orientation used for the bond between the three-ring and this carbinyl carbon was that which allows maximum overlap of the carbinyl p orbital with the two adjacent "cyclopropane" bonds (note eq 10). The MMP steric energies calculated for diradicals **46a** and **46b** were 63.43 and 70.24 kcal/mol, respectively.

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Supplementary Material Available: Tables of direct quantum yield results for **5**, **19a**, and **26** in acetonitrile and sensitized quantum yield results of **5** in acetonitrile and benzene; experimental data for the photomixtures obtained from direct and sensitized photolyses of **7**; ORTEP drawings of **14**, **16**, **17**, and **26**; tables of positional parameters, interatomic distances, bond angles, anisotropic temperature factors, and isotropic temperature factors for **14**, **16**, **17**, and **26** (22 pages). Ordering information is given on any current masthead page.

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Microbial Products. 9. Roxaticin, a New Oxo Pentaene Antibiotic

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Roxaticin, produced by an unidentified streptomycete, has been identified as [(13*S*,14*R*,16*R*,18*R*,20*R*,22*S*,24*R*,26*R*,29*S*,30*S*)-(*all-E*)]-14,16,18,20,22,24,26-heptahydroxy-13,29-dimethyl-30-(1-methylethyl)oxacyclotriaconta-3,5,7,9,11,27-hexaen-2-one (**1**). It is the first example of an oxo polyene whose structure was solved by Roentgen diffraction analysis of a crystalline derivative. Roxaticin and the mycotins are now the only oxo polyenes with known configurations. Based on the available results, the topography of most stereogenic centers of roflamycoin and the dermostatins can be proposed.

Known representatives of the oxo polyene macrolide antibiotics[1] include oxo pentaenes and oxo hexaenes. Mycoticins A (**2a**) and B (**2b**)[2] (flavofungins)[3] and roflamycoin (flavomycoin, **3**)[4,5] are those oxo pentaenes that

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