Molecular Control of Excited Cross-Conjugated Triene Rearrangements. Exploratory and Mechanistic Organic Photochemistry[1,2]

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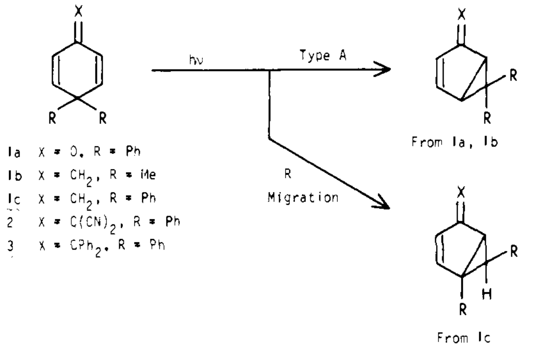
Abstract: The photochemistry of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene and 1-diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene was investigated for comparison with 4,4-diphenylcyclohexadienone, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene, and 1-methylene-4,4-dimethyl-2,5-cyclohexadiene. All of the trienes rearranged via their singlet excited states but had unreactive triplets. The diphenyldicyanotriene rearranged with phenyl migration to give α,α-dicyano-3,4-diphenyltoluene. In contrast, the tetraphenyltriene rearranged with vinyl-vinyl bridging in a Type A rearrangement to give 2-diphenylmethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene. *cis*- and *trans*-2-dicyanomethylene-5,6-diphenylbicyclo[3.1.0]hex-3-ene and 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene were synthesized as potential intermediates in the rearrangement of the diphenyldicyanotriene. Only the first two bicyclic dienes gave solely the same product while the 6,6-diphenylbicyclic diene led to both α,α-dicyano-2,3-diphenyltoluene and α,α-dicyano-3,4-diphenyltoluene with the former predominating 2:1. The 5,6-diphenylbicyclic dienes were excluded as intermediates in the rearrangement of the diphenyldicyanotriene using a tracer experiment. This employed the photolysis of a mixture of tritiated diphenyldicyanotriene and nonradioactive 5,6-diphenylbicyclic diene; after partial conversion, recovered 5,6-diphenylbicyclic diene was nonradioactive. Sensitization of the bicyclic dienes gave no reaction in the case of the 6,6-diphenylbicyclic diene and only cis-trans isomerization from the 5,6-diphenyl stereoisomers. The rates of excited singlet rearrangement of the diphenyldicyanotriene (${}^1k_r = 2.76 \times 10^9\ s^{-1}$) and the tetraphenyltriene (${}^1k_r = 3.50 \times 10^{10}\ s^{-1}$) were determined by single photon counting. A theoretical treatment of the systems studied is offered with SCF-CI calculations along the various reaction coördinates. The effect of phenyl substitution on the exomethylene group of the triene is to alter vinyl-vinyl bridging from an excited state forbidden to an allowed process and the effect is interpreted. The SCF-CI calculations of potential energy surfaces correctly predict the observed photochemical preferences. The intervention of ground-state zwitterions analogous to those of ketone photochemistry is discussed.

Introduction

Previously we have studied the photochemistry of a number of molecules having the general structure **1**.[3,4] In the case of the 2,5-cyclohexadienones (e.g., **1a**) a Type A rearrangement[3] is the ubiquitous pathway followed, and the n-π^* triplet excited state is utilized. The hydrocarbon analogue, 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**1b**), also gives a Type A rearrangement, but from the singlet excited state and with very low efficiency.[4] In contrast, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**1c**) rearranges only with phenyl migration, and here the singlet is involved.[4]

The pattern of behavior was too limited to determine the controlling factors determining the differing reactivity. Thus, one of the original ideas in our study of the 1-methylene dienes **1b** and **1c** was to determine the photochemical course where the exocyclic atom had no unshared electrons and thus no n-π^* state. However, the methylene analogues were imperfect models since they lacked polarization of the exocyclic bond.[5] Hence we initiated a study of two additional methylene dienes. One of these, 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene (**2**), incorporated the desired polarized bond and the other, 1-diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene (**3**), was designed to incorporate extended conjugation without polarization. Beyond this initial reasoning, it has been our observation that photochemical study of a closely related series of molecules is necessary to an understanding of the individual reactions and commonly leads to new phenomena.



(1a)

(1b)

Synthesis of Reactants and Potential Photochemical Products. The two photochemical reactants, **2** and **3**, were synthesized as shown in Scheme I. Also included in this scheme are syntheses of four 2-methylenebicyclo[3.1.0]hex-3-enes which were considered potential photochemical products (i.e., **7**, **10**, **13**, and **15**).

One interesting feature of the bicyclic syntheses is the selenoxide elimination (i.e., reaction with PhSeBr and base followed by peroxide).[6] Commonly, selenoxides formed from allyl anions tend to undergo a [2,3] rearrangement with formation of allylic alcohols.[7,8] Also, the reaction of diphenyldiazomethane with cyclopentenone provided a more convenient, one-step synthesis of 6,6-diphenylbicyclo[3.1.0]hexan-2-one (**11**) than our previous route involving the reaction with cyclopentadiene.[10] Finally, diphenyldiazomethane reacted with diphenylfulvene at the electron-rich five-ring π system rather than the electron-deficient exocyclic bond and provided a useful approach to tetraphenylbicyclohexene **15**.

During the course of our studies, some additional compounds were encountered and independent syntheses were required. Similarly, tritiated diphenyldicyanotriene **2** was needed. Thus Scheme II depicts the synthesis of tritiated **2** and also the preparation of α,α-dicyano-2,3-diphenyltoluene (**23**) and α,α-dicyano-3,4-diphenyltoluene (**18**).

Exploratory Photochemistry of Trienes. Results. Preparative irradiations of the diphenyldicyanotriene **2** were carried out using a 450-W immersion lamp and Pyrex filter. A single photoproduct, mp 109-111 °C, was obtained in 78% yield. The spectral evidence—NMR, infrared, and UV—suggested a substituted *o*-terphenyl. Independent synthesis as in Scheme II confirmed the α,α-dicyano-3,4-diphenyltoluene (**18**)

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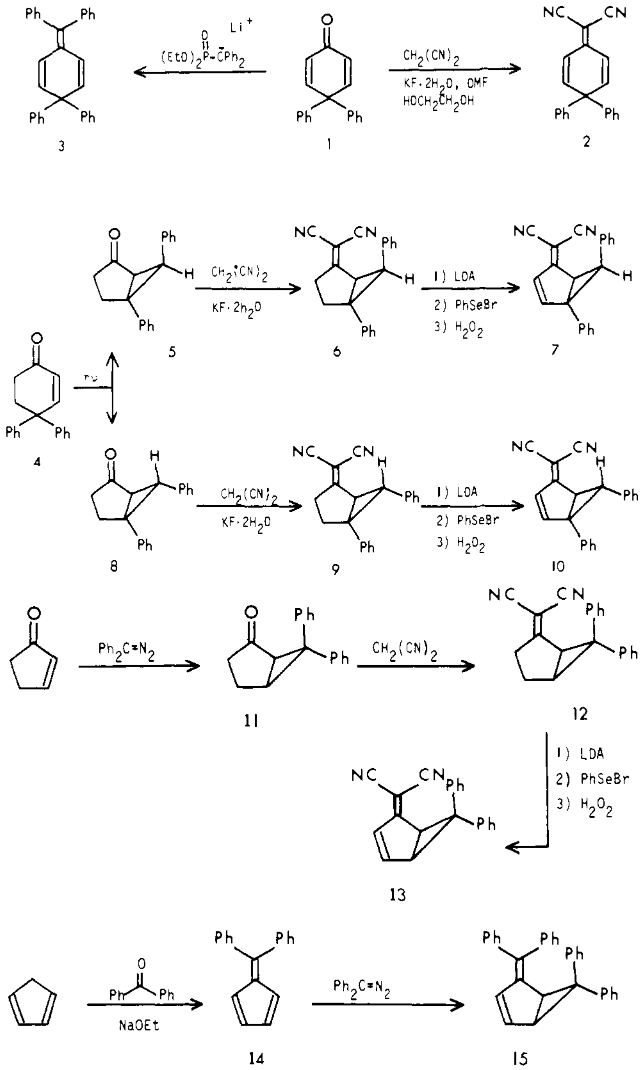
Scheme I. Synthesis of Photochemical Reactants and Potential Photoproducts



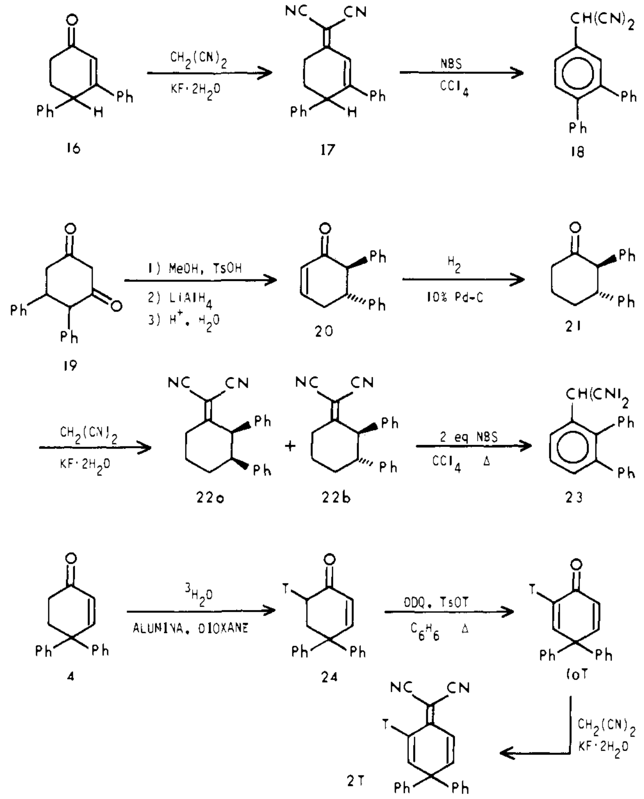
structure of the photoproduct. The photochemical rearrangement is depicted in eq 2 of Scheme III.

Similar photolysis of tetraphenyltriene **3** proceeded to give one, exclusive photoproduct, mp 141–142 °C, again in a synthetically useful reaction. This transformation proved to be considerably more rapid than that of the dicyano example above. In the present instance the spectral data revealed that the photoproduct was not a terphenyl. This data pointed to a 5,6-diphenyl or 6,6-diphenyl substituted bicyclo[3.1.0]hexene derivative. The independent syntheses in Scheme I provided authentic 2-diphenylmethylene-6,6-diphenylbicyclo[3.1.0]-hexene (**15**) and this proved identical with the 141–142 °C photoproduct. This rearrangement is shown in eq 3 of Scheme III. In contrast to the photochemistry of the diphenyldicyanotriene **2**, this rearrangement can be seen to involve a Type A skeletal change.

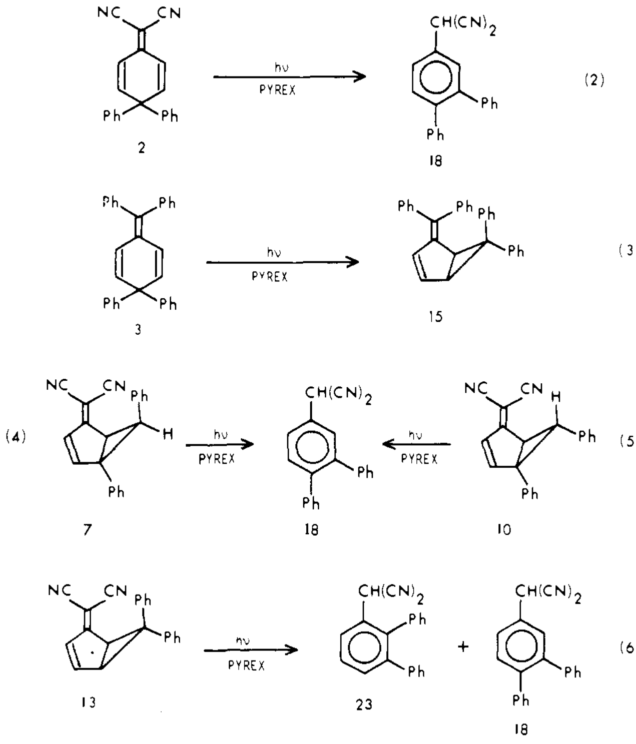
Sensitized irradiations of the trienes used both *p*-dimethylaminobenzophenone and Michler's ketone. Both of these possess sufficient energy to excite the diphenyldicyanotriene **2** and the tetraphenyltriene **3**; yet no reaction was observed. To make certain in these experiments that light was captured only by sensitizer and not by triene, the Black Box apparatus[11] giving relatively narrow band light was used.

Exploratory Photochemistry of Bicyclics. Results. In the case of the diphenyldicyanotriene **2**, a phenyl migration is involved. However, a priori, one can envisage either a direct conversion of diphenyldicyanotriene **2** to afford the α,α-dicyano-3,4-diphenyltoluene product (**18**) or, alternatively, a two-step (i.e., two-photon) rearrangement proceeding by way of bicyclic intermediates. Thus, the cis and trans isomers (i.e., **10** and **7**, respectively) of the dicyanomethylene 5,6-diphenylbicyclic diene as well as the 6,6-diphenyl (i.e., **13**) counterpart seemed to be potential intermediates, and we needed to study their photochemistry.

Scheme II. Synthesis of the Dicyanodiphenyltoluenes and Tritiated Diphenyldicyanotriene



Scheme III. Direct Photolyses of Trienes **2** and **3** and Bicyclic Dienes **7**, **10**, and **13**



Irradiation of each of the two 5,6-diphenyl isomers (**7** and **10**) afforded in a very rapid conversion a quantitative yield of

Table I. Emission Spectra of Trienes **2** and **3**

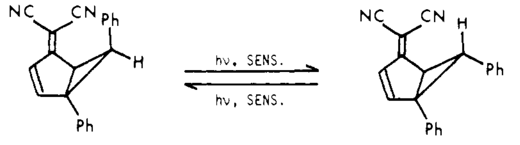
compd	solvent	λ, nm excitation	*T*, K	λ, nm emission
diphenyldicyanotriene **2**	methylcyclohexane-isopentane (4:1)	320	293	405[a]
			77	405[a]
			77	585[b]
diphenyldicyanotriene **2**	ethanol-ether (2:1)	320	293	467[a]
			77	405[a]
tetraphenyltriene **3**	methylcyclohexane-isopentane (4:1)	310	293	410[a]
			77	410[a]
tetraphenyltriene **3**	ethanol-ether (2:1)	310	293	410[a]
			77	410[a]

[a] Fluorescence maximum. [b] Phosphorescence maximum.

α,α-dicyano-3,4-diphenyltoluene (**18**) (note eq 4 and 5 of Scheme III).

Parallel photolysis of dicyanomethylene 6,6-diphenylbicyclic diene **13** afforded both α,α-dicyano-3,4-diphenyltoluene (**18**) and α,α-dicyano-2,3-diphenyltoluene (**23**). The 2,3 isomer predominated in a 2:1 ratio, an interesting point which is discussed below. Also, this rearrangement was comparably facile and quantitative relative to the irradiation of the 5,6-diphenyl isomers **7** and **10**. This reaction is depicted in eq 6 of Scheme III.

On sensitized irradiation the 6,6-diphenylbicyclic diene **13** proved unreactive. However, the cis and trans 5,6-diphenylbicyclic diene isomers **7** and **10** were found to interconvert as noted in eq 7.



7 10 (7)

Quantum Yield Determinations. Results. The quantum yields were determined using the Black Box as well as the organic chemist's Microbench described earlier.[11] Electronic actinometry[12] was utilized; however, each run was separately calibrated with ferrioxalate.[13] All quantum yields were determined by extrapolation of several runs made below 20% conversion. Without such extrapolation, product light absorption led to artificially low values. Even at 20% conversion a ca. 20% error was encountered. The quantum yield results are summarized in Tables II and III and detailed in the Experimental Section.

Sensitized quantum yields, again, utilized both *p*-dimethylaminobenzophenone (E_T = 65 kcal/mol[14]) and Michler's ketone (E_T = 62 kcal/mol[15]). The triplet energy of diphenyldicyanotriene **2** was determined by its phosphorescence emission (maximum 585 nm, estimated 0-0 565 nm) and corresponded to a triplet energy of 50.6 kcal/mol.[16] This is close to the 47.5 kcal/mol[17] triplet energy of the isoconjugate hexatriene. The more extended conjugation of the tetraphenyltriene **3** ensured a still lower triplet energy. Thus energy transfer at the concentrations used should be efficient. In absence of any observed reaction, the sensitized runs on trienes **2** and **3** afforded upper limit values. Note Table II. In the case of the 6,6-diphenylbicyclic diene **13** an upper limit for the triplet efficiency was set. For the cis and trans 5,6-diphenylbicyclic dienes **7** and **10** runs were extrapolated to zero conversion (Table II).

Table II. Summary of Quantum Yield Results in *tert*-Butyl Alcohol Solvent[a]

reactant	additive	λ, nm irradiation	Φ[b]
diphenyldicyanotriene **2**	none	328	0.0076
	p-dimethylaminobenzophenone	420	<0.0006[c]
	Michler's ketone	420	<0.0009[c]
tetraphenyltriene **3**	none	316	0.0511
	p-dimethylaminobenzophenone	420	<0.0013[c]
	Michler's ketone	420	<0.0005[c]
dicyanobicyclo[3.1.0]hexene **7**	none	312	0.156
	p-dimethylaminobenzophenone	420	0.0032
dicyanobicyclo[3.1.0]hexene **10**	none	312	0.090
	p-dimethylaminobenzophenone	420	0.0003
dicyanobicyclo[3.1.0]hexene **13**	none	312	0.136[d] 0.067[e]
	p-dimethylaminobenzophenone	420	<0.0004[c]
	Michler's ketone	420	<0.0002[c]

[a] For individual runs see Experimental Section. [b] Quantum yields extrapolated to 0% conversion. [c] Quantum yield of disappearance of starting material. [d] α,α-Dicyano-2,3-diphenyltoluene. [e] α,α-Dicyano-3,4-diphenyltoluene.

Table III. Solvent Dependence of Quantum Yield for Diphenyldicyanotriene **2**

solvent	Φ[a-c]	solvent	Φ[a-c]
cyclohexane	0.010	aqueous dioxane, pH 5.5	0.0046
tert-butyl alcohol	0.0076		
unbuffered dioxane	0.0065	aqueous dioxane, pH 1.5	0.0046

[a] See Experimental Section for Details. [b] Quantum yields were run to less than 15% conversion and extrapolated to 0% conversion based on at least three runs. [c] λ irradiation 328 nm.

In the case of the diphenyldicyanotriene **2** the emission spectra proved to be a function of solvent polarity in contrast to the tetraphenyltriene **3** (note Table I). Thus for this compound (i.e., **2**) the quantum yields were obtained in several solvents of different polarity. See Table III.

Excited Singlet Rate Determinations by Single Photon Counting. Results. Since excited-state reactivity is best given by the first-order rate constants, we employed the single photon counting based method described by us earlier.[18] The primary information derived from the method is the rate of excited singlet decay (i.e., ${}^1K_{dt}$). Since the presently studied triene systems decayed too rapidly for measurement at room temperature, the decay rates were obtained at 77 K and then converted into room temperature rates by the method of magic multipliers.[18a] The rates derived for the two trienes **2** and **3** are listed in Table IV.

Reaction Intermediate Trapping Experiments. Results. In considering the rearrangement of the diphenyldicyanotriene **2** to α,α-dicyano-3,4-diphenyltoluene (**18**), 6,6-diphenylbicyclic diene **13** could be ruled out as a reaction intermediate since bicyclic diene **13** was known to give not only the photoproduct **18** but also the 2,3-diphenyl isomer **23**. However, it seemed possible that either the cis or the trans isomer (or both) of the 5,6-diphenylbicyclic diene (i.e., **7** and **10**), was initially formed and then consumed to form the final dicyanotoluene product **18**. This corresponds to path II in Scheme IV. Since the extinction coefficients for the 5,6-diphenylbicyclic dienes **7** and **10** were comparable to that for reactant diphenyldicyanotriene **2** and their quantum yields (note Table II) were ca. 20-fold that of consumption of reactant **2**, it seemed possible that a reaction pathway proceeding via the bicyclic dienes **7**

Table IV. Single Photon Counting Rates for Trienes **2** and **3**[a,b]

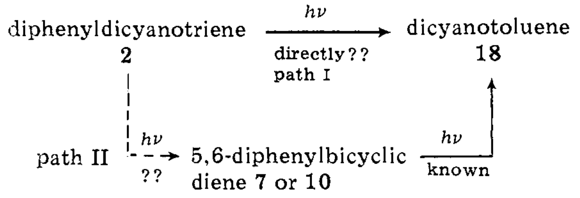
compd	λ collection, nm	MM[a,c]	temp, K	τ, ps	^1k_r, sec^{-1} [d]
diphenyldicyanotriene **2**	405-415	365	77	1000	
			293	2.75	2.76×10^9
tetraphenyltriene **3**	405-415	580	77	841	
			293	1.45	3.50×10^{10}

MM = magic multiplier = $(^{77}\Phi_f)/(^{RT}\Phi_f)$

$\tau^{RT} = \tau^{77}/\text{MM}$ $\quad {}^1k^{RT}_{reac} = \Phi_{reac}{}^1k^{RT}_{dt}$

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

Scheme IV. Two Possible Routes for Formation of Dicyanotoluene **18**



and **10** could occur without these being found experimentally. Alternatively, dicyanotoluene **18** could be formed directly as in path I in Scheme IV.

A solution to this dilemma was found in an experiment utilizing photolysis of a 5:2 mixture of tritiated diphenyldicyanotriene **2** and nonradioactive 5,6-diphenylbicyclic diene **7** (or **10**); in this experiment irradiation was continued until 50% of the bicyclic diene was consumed. To the extent that path I, involving direct conversion of the triene **2** to dicyanotoluene **18**, obtains, the recovered 5,6-diphenylbicyclic diene (i.e., **7** or **10**) will have no radioactivity. On the other hand, if path II is used, radioactive 5,6-diphenylbicyclic diene is produced, and the recovered bicyclic diene (**7** and **10**) will be radioactive, with the level of activity being a function of extent conversion and the relative rates of consumption and formation of 5,6-diphenylbicyclic diene. For a mixture of the two mechanisms, intermediate radioactivity will be encountered.

Owing to the complexity of the kinetics in Scheme IV, computer simulation was used to indicate the variation of bicyclic diene (**7** or **10**) as a function of time of photolysis and with different assumed amounts of utilization of pathway II.

For simplicity compounds **2, 7** (or **10**), and **18** are termed A, B, and C, respectively. We can then describe the variation of each of compounds A, B, and C in the generalized scheme A → B → C as in the equations

$$\Delta[\text{A}] = -(k_{ab} + k_{ac})[\text{A}]\Delta t \tag{8a}$$

$$\Delta[\text{B}] = (k_{ab}[\text{A}] - k_{bc}[\text{B}])\Delta t \tag{8b}$$

$$\Delta[\text{C}] = (k_{ac}[\text{A}] + k_{bc}[\text{B}])\Delta t \tag{8c}$$

Here Δ[A], Δ[B], and Δ[C] are increments to the concentrations for a given time interval. However, the rate constants here are really not true constants but are functions of time as given in the equations

$$k_{ab} = f(t) = (\phi_{ab}\epsilon_a I_0)/(\epsilon_a[\text{A}] + \epsilon_b[\text{B}] + \epsilon_c[\text{C}]) \tag{9a}$$

$$k_{bc} = g(t) = (\phi_{bc}\epsilon_b I_0)/(\epsilon_a[\text{A}] + \epsilon_b[\text{B}] + \epsilon_c[\text{C}]) \tag{9b}$$

$$k_{ac} = h(t) = (\phi_{ac}\epsilon_a I_0)/(\epsilon_a[\text{A}] + \epsilon_b[\text{B}] + \epsilon_c[\text{C}]) \tag{9c}$$

The time functionality derives from the various concentrations changing with time. The computer program determines each new concentration by adding each increment (i.e., ΔA, ΔB, or ΔC) to the previous value of concentration.

Quantum yields ϕ_{bc} and ϕ_{obsd} are known, with the latter being the empirically observed conversion of dicyanotriene (i.e., A) to final dicyanotoluene product (i.e., C). Hence only values of ϕ_{ac} and ϕ_{ab} fitting the equation

$$\phi_{obsd} = \phi_{ac} + \phi_{bc}\phi_{ab} \tag{10}$$

are of interest, where ϕ_{obsd}, ϕ_{bc} are experimentally determined.

Figure 1 gives the variation with time (or extent conversion) of the concentration of A, B, and C with different choices of the two unknowns in eq 10, namely, ϕ_{ac} and ϕ_{ab}.

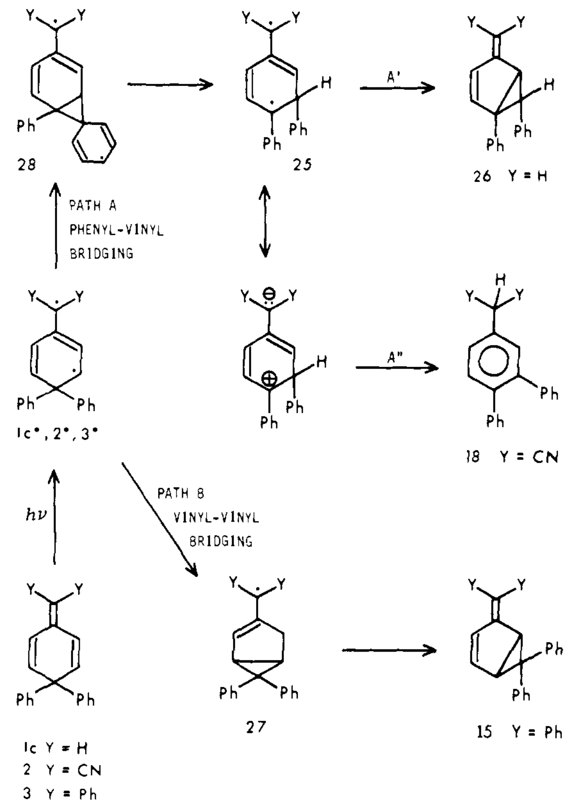
The photolyses were carried to partial conversion and the unreacted cis and trans diphenylbicyclic dienes **7** and **10** (i.e., B) were recovered using HPLC and then recrystallization to constant radioactivity. Comparison of the amount of radioactive 5,6-bicyclic diene predicted by the computer simulations with the experimentally encountered amount revealed that less than 0.003% of the reaction proceeds via the two-step (i.e., A → B → C) mechanism and thus at least 99.997% by the direct route (i.e., A → C).

Interpretative Discussion. Gross Reaction Mechanisms in the Photochemistry of the Trienes. The first point which derives from the above studies is the finding that the 1-(disubstituted methylene)-2,5-cyclohexadienes (i.e., **1b, 1c, 2,** and **3**) exhibit both the Type A rearrangement[3] and phenyl migration reactions depending on substitution on the exomethylene moiety. This is seen from inspection of eq 1a, 1b, 2, and 3.

In order to understand these patterns of behavior we first need to consider the gross reaction mechanisms. Thus Scheme V outlines the different reaction courses encountered. The first mechanistic decision is made by the excited state derived from the 1-methylene reactant, **1c, 2,** or **3**. Path A involves phenyl–vinyl bridging and is selected by the simple 1-methylene and the dicyanomethylene excited states (i.e., **1c*** and **2***). Path B proceeds by vinyl–vinyl bridging and is invoked by the diphenylmethylene excited state **3***. The factors controlling this partition are considered below. A second mechanistic decision is made by molecules following pathway A wherein diradical species **25** either follows pathway A′ which requires 2,4 bridging to give a methylenebicyclo[3.1.0]hex-3-ene system (**7, 10,** or **26**) or instead follows pathway A″ with eventual aromatization. In Scheme V species **25** is meant to be unexcited in analogy to our previous mechanisms.

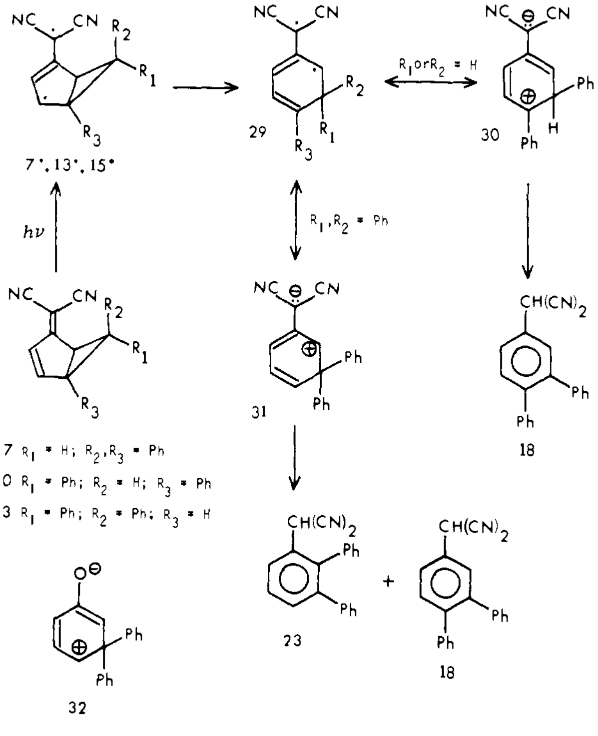
Relative to the first partition (i.e., between pathways A and B) an a priori prediction for each of the set of reactants is difficult without resorting to molecular orbital considerations, and these are discussed below. However, an empirical trend is seen wherein the molecule (i.e., the tetraphenyltriene) having the most delocalization of exomethylene electronic excitation is the one preferring vinyl–vinyl bridging. Here phenyl is more effective in lowering of polyene excited state energy than cyano. Another point is that phenyl–vinyl bridging, as in path A, corresponds to the beginning of a di-π-methane rearrangement.[19] While vinyl–vinyl bridging appears to be a di-π-methane process, the cyclically conjugated system makes it only formally such a process.[20]

Scheme V. Vinyl–Vinyl Bridging and Phenyl Migration Mechanisms in the Triene Photochemistry



In the case of the second partition in which the phenyl-migrated diradical **25** either aromatizes (route A″) or closes to give a bicyclo[3.1.0] system (route A′), it is of interest to note that the ground-state species **25** might be expected to be zwitterionic where Y is cyano. Yet, to the extent that negative charge is indeed heavily localized on the exocyclic dicyanomethyl group, bicyclo[3.1.0] closure to form the unobserved **10** is electronically forbidden. This is because top–top (i.e., Hückel) bonding of terminal p orbitals, as needed for this closure, then proceeds with only four electrons in the cyclic array. Thus, Hückel four-electron closure is forbidden[22] while top–bottom (i.e., Möbius)[22] terminal overlap is stereochemically impossible. The situation is analogous to the situation in

Scheme VI. Mechanism of Singlet Rearrangements of Dicyanobicyclic Dienes 7, 10, and 13



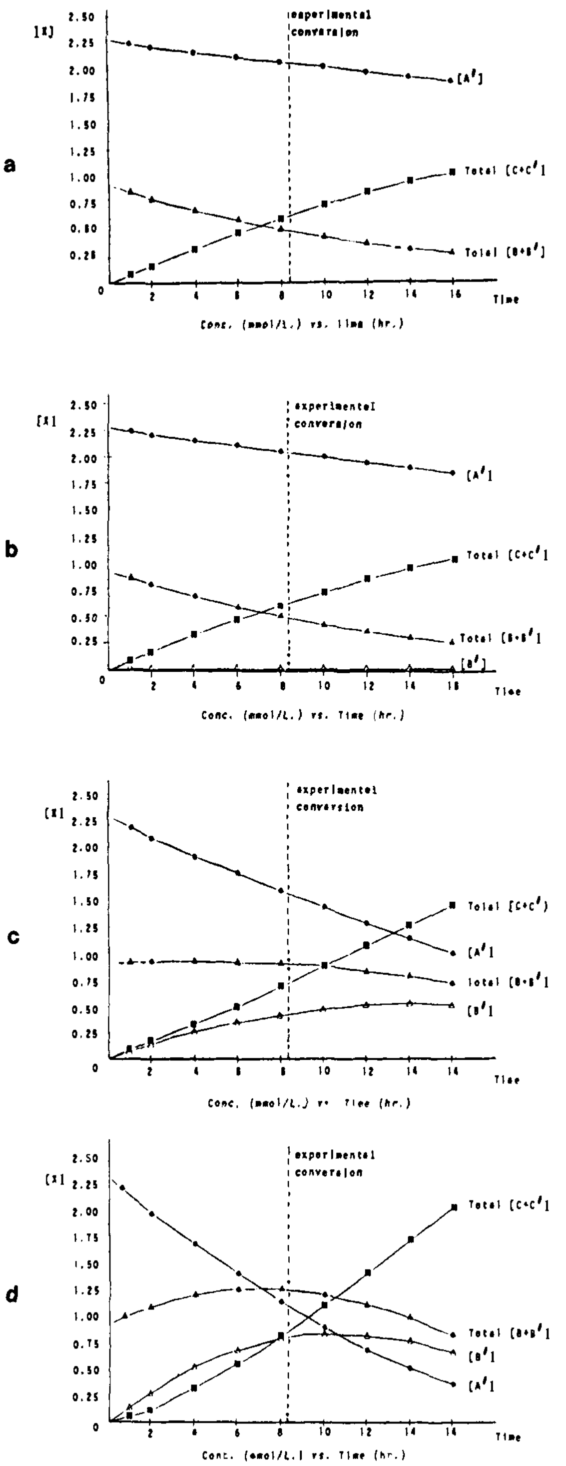


Figure 1. (a) Concentration vs. time for mechanism: 100% direct (A → C), 0% indirect (A → B → C), quantum yields: Φ_{ac} = 0.0076, Φ_{ab} = 0.000, Φ_{bc} = 0.156. Note: # refers to tritium-labeled material. (b) Concentration vs. time for mechanism: 99% direct (A → C), 1% indirect (A → B → C). Quantum yields: Φ_{ac} = 0.0075, Φ_{ab} = 0.0005, Φ_{bc} = 0.156. Note: # refers to tritium-labeled material. (c) Concentration vs. time for mechanism: 50% direct (A → C), 50% indirect (A → B → C). Quantum yields: Φ_{ac} = 0.0038, Φ_{ab} = 0.024, Φ_{bc} = 0.156. Note: # refers to tritium-labeled material. (d) Concentration vs. time for mechanism: 0% direct (A → C), 100% indirect (A → B → C). Quantum yields: Φ_{ac} = 0.0000, Φ_{ab} = 0.049, Φ_{bc} = 0.156. Note: # refers to tritium-labeled material.

dienone photochemistry where $-\overset{=}{C}(CN)_2$ is replaced by $-O^-$ (note species **32** in Scheme VI) and closure is not observed.[21b,23] However, proton loss with aromatization is molecularly acceptable and leads to the observed product **18.** In the case of the simple exomethylene reactant (i.e., Y = H) such negative charge localization on the exocyclic atom is not likely. By polarization in the reverse direction, the reaction becomes electronically allowed.

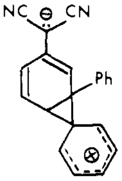
Finally the lack of triplet reactivity of the trienes has precedent in the photochemistry of the simple methylene analogue **1c**[4] and also in many systems having such potential free rotors.[18b,24]

Interpretative Discussion. Gross Reaction Mechanisms in the Photochemistry of the Bicyclics. Scheme VI outlines reaction mechanisms in resonance terms for the rearrangement of the 5,6-diphenyl- and 6,6-diphenyldicyanobicyclics **7, 10,** and **13.**

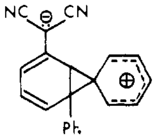
Interestingly, the characteristic reaction of the diphenyldicyanomethylenebicyclic dienes **7, 10,** and **13** is opening of the internal (i.e., 1-5) bond; this is depicted as giving ground-state diradical **29.** This six-ring species is analogous to zwitterionic species **25** encountered in path A of Scheme V. The photochemistry encountered is reminiscent of the behavior of zwitterion **32** (note Scheme VI again) which proved to be an intermediate in the photochemistry of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[3,21,23] Thus zwitterions **30** and **31** may well be involved in the present photochemistry.

Supporting this suggestion is the observation that the irradiation of 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene (**13**) gives both the 2,3-diphenyldicyanotoluene **23** and the 3,4-diphenyl isomer **18** in analogy to the dienone-related photochemistry. More impressive, the predominance of the 2,3-isomer **23** over the 3,4-isomer **18** was shown[3,21,23,25] to be characteristic of the Type B zwitterions first proposed by Zimmerman.[3,26]

The rationale proposed for the preferential migration to C-2[3,21,23,25] applies nicely to the present example. Thus of two partially phenyl migrated species, **33** and **34,** it is seen that the species leading to 2,3-diphenyl substitution (i.e., zwitterion **34**) has greater electron delocalization than the zwitterion **33** leading to the 3,4-diphenyltoluene product. The zwitterion **33** has only two anionic resonance structures compared to three for the linearly conjugated zwitterion **34.**

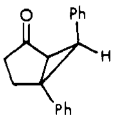


33

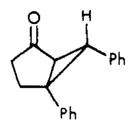


34

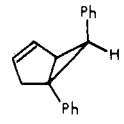
Finally, the multiplicity dependence of the reaction course observed for the 5,6-diphenyldicyanobicyclic dienes **7** and **10** is of interest. Clearly, the singlet photochemistry derives from a six-ring species (e.g., the zwitterions **30** or **31**) in which the internal three-ring bond has opened. The stereoisomerization encountered in the triplet photochemistry could arise, in principle, from such a species reclosing or from one of the two out of plane three-ring bonds opening. Our research has encountered such a situation twice previously.[27a,b] Thus, in the triplet photochemistry of 5,6-diphenylbicyclo[3.1.0]hexan-2-one (**35a,b**) studies of optically active material and correlation of configurations of the cis and trans isomers showed[27b] that it was primarily the out of plane bonds whose fission resulted in the stereoisomerization. Again, in the case of the triplet photochemistry of 5,6-diphenylbicyclo[3.1.0]hex-2-ene[27a] (**36a,b**) stereoisomerization was shown by the same technique to derive preferentially from scission of the out of plane three-ring bond.



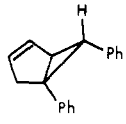
35a



35b



36a



36b

Interpretative Discussion. Molecular Orbital and Theoretical Considerations. In order to understand the effects of structure on reaction course we need to consider the relative facility of vinyl-vinyl bridging of the excited singlets of trienes **1b, 1c, 2,** and **3.** We also need to consider the relative ability of these compounds to bond phenyl-vinyl. Then we need to compare vinyl-vinyl with phenyl-vinyl bondings. Beyond this, we then need to consider the reaction mechanism subsequent to occurrence of these initial processes.

Considering first the effect of structure on facility of vinyl-vinyl bridging, we find of most utility the simple one-electron correlation diagrams for bridging between the two vinyl groups. Use of simple Hückel or SCF calculations proved qualitatively equivalent and SCF-CI calculations were used to check the nature of the excitations and the species along the reaction coordinate. Two models were used. The simplest considered only the initial stages of the bridging process, wherein the vinyl group p orbitals approach one another engendering a fulvene-like array; the correlation diagram for this process is given in Figure 2. Nonconjugated phenyls are omitted. The second model included all of the orbitals needed to form the Walsh cyclopropane of the bridged species **27**; in this model, a phenyl group at carbon 4 was also included. This second model was also subjected to SCF and SCF-CI calculations.

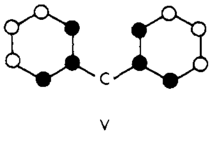
In inspecting Figure 2 we focus attention on MOs I, II, III, and IV. We note that two of the three correlation diagrams are patterned similarly, these being for the dimethyltriene **1b** (the same as the diphenyltriene **1c**) and for the dicyanodiphenyltriene **2.** Characteristically the highest two bonding MOs (i.e., I and II) cross while the first antibonding MO (i.e., III) of reactant correlates with the first antibonding MO of product. Note Figures 2a and 2b.

Owing to the crossing of bonding MOs I and II the reaction is photochemically forbidden; an adiabatic transformation leads to a doubly excited configuration.

In contrast, the tetraphenyltriene **3** has a correlation diagram (note Figure 2c) lacking crossing of the two highest energy bonding MOs (formerly I and II). This correlation diagram corresponds to an allowed photochemical reaction.

Thus the simple one-electron correlation diagram treatment does agree with the observation of vinyl-vinyl bridging and a subsequent Type A rearrangement only in the molecule bearing phenyl groups on the exomethylene group.

In order to understand the effect of the introduction of the extra phenyl groups on the reaction electronics, it is convenient to consider the diagram in Figure 3a with two crossing MOs of opposite symmetry, a situation encountered often and presently in the crossing of MOs I and II. If we add to the system a strongly interacting moiety which has an MO such as V which can mix with the upper MO II of reactant and the lower MO I of product, the crossing can be eliminated as shown in Figure 3b. This is precisely the situation obtaining in the correlation diagram for bridging of the tetraphenyltriene; note Figure 2c. In the case of the tetraphenyltriene **3** the moiety introduced is the combination of two phenyl groups on the exomethylene and the strongly interacting MO V is the sym-



V

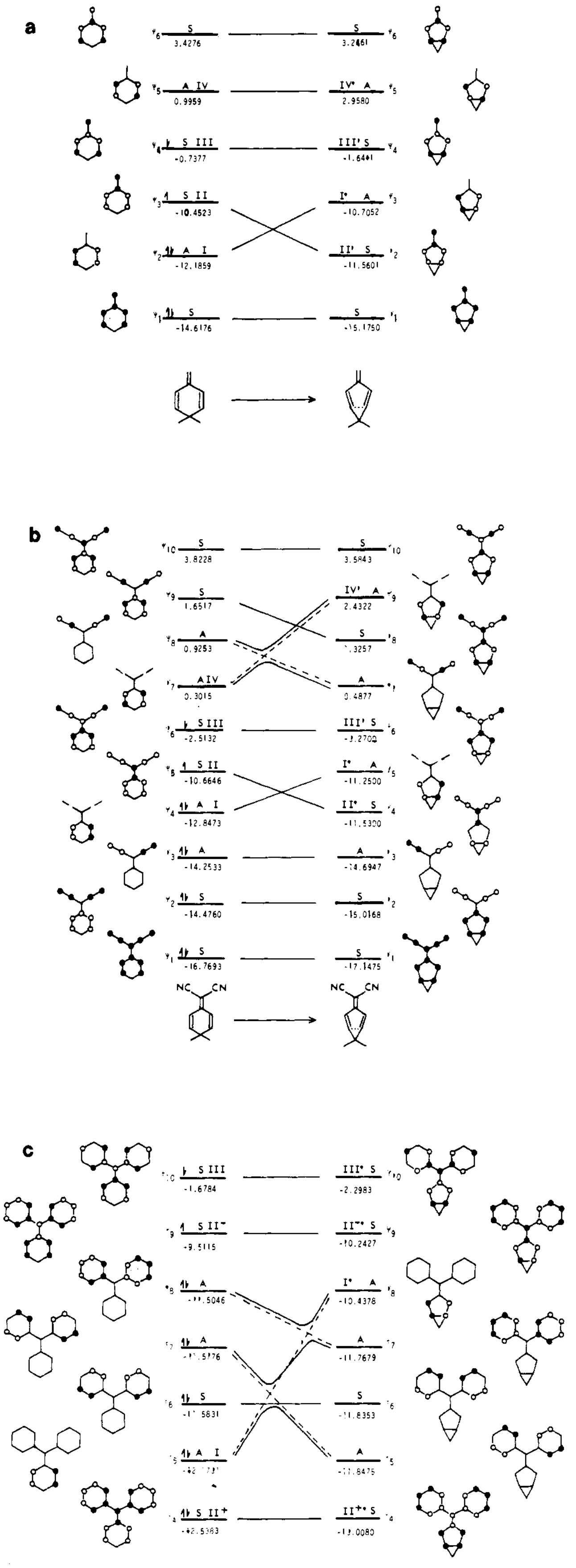


Figure 2. (a) Correlation diagram for vinyl–vinyl bridging of the 1-methylene-2,5-cyclohexadiene. SCF energies in eV; I, II, III, and IV are the two bonding and two antibonding MOs characteristic of the reaction. (b) Correlation diagram for vinyl–vinyl bridging of 1-dicyanomethylene-2,5-cyclohexadiene. SCF energies in eV. (c) Correlation diagram for vinyl-vinyl bridging of 1-diphenylmethylene-2,5-cyclohexadiene. Energies in eV. Selected MOs shown.

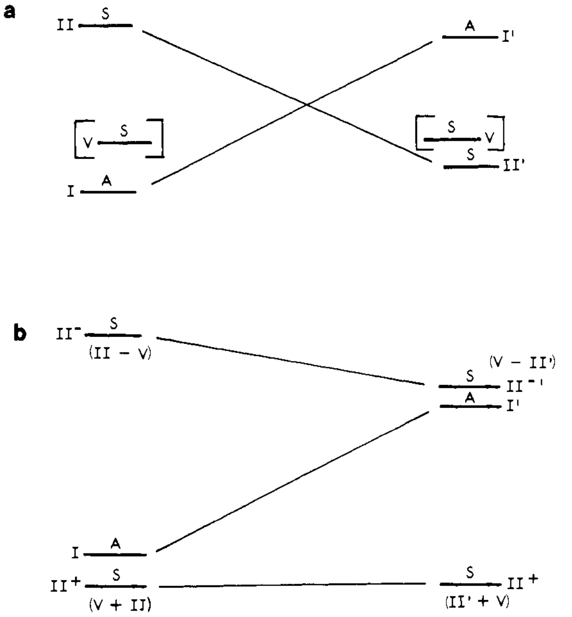
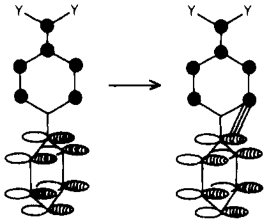


Figure 3. (a) Correlation of MOs leading to forbidden reaction. Two top bonding MOs I and II and isolated MO V. (b) Correlation of MOs leading to allowed reaction. Splitting of MOs I and II due to interaction with MO V.

Scheme VII

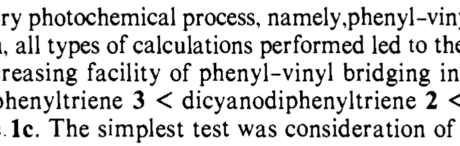


% OVERLAP	S_1 STABILIZATION (eV)		
	Y = H	CN	Ph
25%	-0.043	-0.038	-0.037
50%	-0.167	-0.149	-0.145
75%	-0.363	-0.329	-0.315

metric combination of benzene MOs. Owing to injection of the new MO, the crossing is eliminated and the reaction allowed.

We now turn our attention to the relative ease of the other primary photochemical process, namely,phenyl-vinyl bridging. Again, all types of calculations performed led to the prediction of increasing facility of phenyl-vinyl bridging in the series: tetraphenyltriene **3** < dicyanodiphenyltriene **2** < diphenyltriene **1c**. The simplest test was consideration of the energy change in the Hückel approximation on introducing an increasing resonance integral between the p orbitals of C-3 of the triene moiety and C-1′ of the phenyl group. This is shown and tabulated in Scheme VII for the Hückel situation.

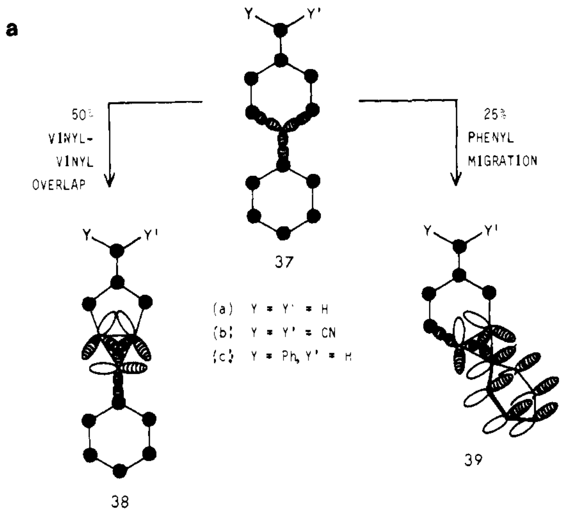
SCF-CI calculations on the energy of bridging using a more extensive basis set, where all orbitals involved in formation of a phenonium-type bridged species were included, led to the same ordering. Thus for the transformation in eq 11 the relative



(11)

	Y = H	Y = CN	Y = Ph
S_1 STABILIZATION :	-0.5836 eV	-0.3362 eV	-0.3035 eV

facility of bridging in S_1 obtained from SCF-CI calculations was ordered the same as for the simple Hückel results with diphenylvinyl substitution being least favorable for the phenyl



S_1 (eV)	38	39	Δ (39-38)
(a)	-294.7290	-295.1297	-0.4077
(b)	-358.5078	-359.1112	-0.6034
(c)	-377.8437	-377.4526	+0.3871

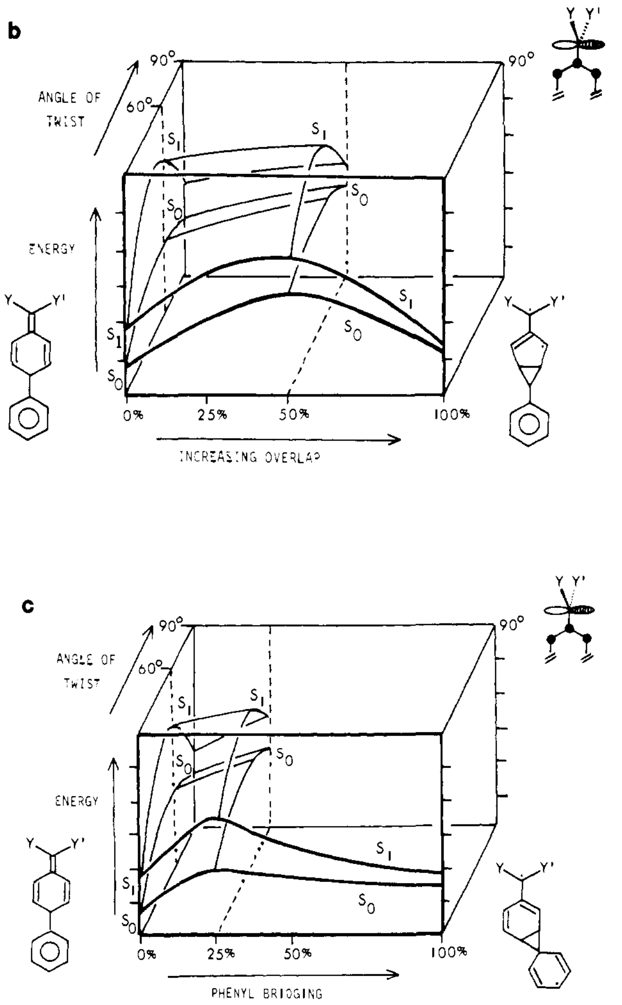


Figure 4. (a) SCF-CI singlet excited state energies of bridged transition states. (b) Vinyl-vinyl bridging hypersurfaces. (c) Phenyl-vinyl bridging hypersurfaces.

migration and the simple exomethylenetriene **1c** being most favorable.

The above discussions of vinyl-vinyl bridging and phenyl-vinyl bridging have assumed that the simple HOMO-LUMO excitation corresponds to S_1 (i.e., the p band). However, often in alternate hydrocarbons the lowest excited state derives from first-order interaction between the configurations $\Psi_{HOMO} \rightarrow \Psi_{LUMO+1}$ and $\Psi_{HOMO-1} \rightarrow \Psi_{LUMO}$.[28] The excited state corresponding to the negative linear combination thus corresponds to the Sklar α band (excitation)[28b] of alternant hydrocarbons.

However, our configuration interaction calculations confirmed that it was the simple HOMO-LUMO (i.e., p band) configuration which was lowest in energy and heavily dominant for the various triene cases. The one exception was the diphenyltriene **1c** where excitation initially was found in the phenyl groups but diffused to the triene moiety as the reaction coordinate was traversed. Eventually the simple HOMO-LUMO configuration did become dominant. Thus our mechanistic discussion based on this excitation is proper.

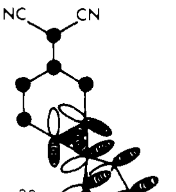
Another result derived from inspection of the SCF-CI energies for species interpolated along the reaction pathways leading to the vinyl-vinyl bridged and phenyl-vinyl bridged species. Interestingly, energy maxima for the S_1 surfaces were obtained at ca. 50% bridging for vinyl-vinyl bonding and 25% bridging for phenyl-vinyl bonding. Furthermore, if one compares energies at the energy maxima,[29] the complete pattern of reactivity is correctly predicted. Thus, one cannot only compare relative facility of reaction of a given type for the variously substituted reactants but also one can compare the two types of reaction, Type A and phenyl migration. Note Figures 4a-c. An interesting point is the near degeneracy (approach of S_1 and S_0) as the bridging processes are completed, thus giving a route from S_1 to S_0. This follows our 1966 suggestion.[22b,d]

One other point was considered. This was whether twisting of the exomethylene groups of the reactants might be responsible for the observed reactivity. However, in all cases the energy rose sharply on twisting, independent of the position of the species along the reaction coordinate. After an energy barrier the energy diminished and reached a minimum at 90° twist. Interestingly, as noted above in the Results section, irradiation in *tert*-butyl alcohol diminished the reaction efficiency in the case of dicyanotriene **2** and also anomalous fluorescence from a new species was found. This suggests that 90° rotation leads to a nonreacting zwitterion which is unreactive but which provides a route for return to ground state. The corresponding tetraphenyltriene **3** did not show parallel fluorescence dependence on solvent polarity.

Finally, it is of interest to consider the preferential formation of the 2,3-diphenyldicyanotoluene **23** rather than the 3,4-isomer **18**. This was rationalized in qualitative resonance terms above.

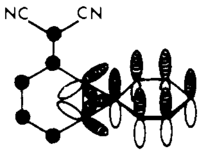
We used the basis set shown for zwitterions **33** and **34**; this comprised the π systems of the dicyanomethyl moiety, the six-ring, the bridging phenyl, plus the Walsh cyclopropane orbitals. The relative energies of the two systems were obtained from a zeroth-order SCF calculation (i.e., effectively a Hückel calculation using SCF parameters). The energies are listed below the two structures (i.e., **33** and **34**), and it is seen that the phenonium structure for migration to carbon 2 is lower in energy than for migration to carbon 4. We note that the reaction is a ground-state process, although the zwitterion derives from an excited-state species; in the case of the analogous zwitterion of ketone photochemistry (i.e., species **32**) it was shown[21b,23] that the rearranging species was unexcited.

Finally left for discussion is the partition of species **25** between pathways A′ (bicyclohexane formation) and A″ (aromatization). A qualitative rationale was given above based on



33

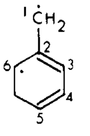
$S_0 = -391.2938$ eV



34

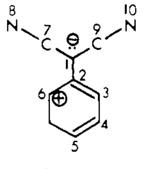
$S_0 = -391.4198$ eV

the reluctance of an electrocyclic closure involving four electrons as required to give bicyclic product in path A′. A consideration of 5,6-bond orders as a function of the presence or absence of the cyano groups led to the results shown in the structures below. These bond orders derive from simple Hückel calculations. In the case of diradical **40,** the problem of dealing with a degenerate nonbonding MO pair and two electrons for population of these was resolved by using the MO which had maximum 5,6-bond order and leaving unpopulated that MO with a zero bond order since it is the former MO which becomes populated along the reaction coordinate for bicyclohexane formation.



40

S_0 $P_{5,6} = 0.4772$



41

S_0 $P_{5,6} = -0.3896$

Interestingly, while the 5,6-bond order is positive for the simple methylene diradical **40,** it is negative for the dicyano diradical **41**.

Conclusion

Thus, a large and varied assortment of photochemical behavior is readily accommodated by simple theory based on the assumption that electronically excited species react by pathways minimizing energy as the reaction coordinate is traversed. This is the hypothesis advanced by us 17 years earlier.[3a]

Experimental Section[31]

1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene. The fluoride catalysis procedure described by ApSimon was used.[32] To a mixture of 1.00 g (4.08 mmol) of 4,4-diphenyl-2,5-cyclohexadienone, 1.00 g (10.6 mmol) of potassium fluoride dihydrate, and 8.0 mL of dimethylformamide was added 2.04 g (1.70 mL, 30.9 mmol) of malononitrile in 12.0 mL of ethylene glycol. The solution was stirred under nitrogen at room temperature for 12 h, diluted with water, ether–hexane (1:1) extracted, and then ether extracted. The water washed extract was dried and concentrated in vacuo leaving 0.929 g of a yellow oil. Crystallization from 95% ethanol gave 747 mg (2.54 mmol, 62.3%) of light yellow crystals, mp 163–165 °C. Recrystallization from 95% ethanol gave 711 mg (2.42 mmol, 59.3%) of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene as colorless crystals, mp 166–167 °C. The spectral data follow: NMR (benzene-d_6) τ 2.80–3.05 (m, 6 H, aromatic), 3.10–3.30 (m, 4 H, aromatic), 3.52 (d, 2 H, J = 10 Hz, vinyl), 3.72 (d, 2 H, J = 10 Hz, vinyl); IR ($CHCl_3$) 4.47, 6.06 μ; MS (70 eV) *m/e* (rel abundance) 295 (24), 294 (100), 266 (13), 217 (12), 115 (4), 77 (16); UV (EtOH) λ_{max} 326 nm (ϵ 31 300), 252 (2800), 220 (20 000). High-resolution MS: calcd for $C_{21}H_{14}N_2$, *m/e* 294.115 70; found, *m/e* 294.115 53.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.55; H, 4.67.

1-Diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene. To a solution of 2.51 g (8.22 mmol) of diethyl diphenylmethylphosphonate[33] in 35.0 mL of anhydrous dimethoxyethane was added 5.70 mL of 1.45 M (8.27 mmol) *n*-butyllithium in hexane at 0 °C under nitrogen. After 0.5 h, 1.25 g (5.08 mmol) of 4,4-diphenyl-2,5-cyclohexadienone in 10.0 mL of anhydrous dimethoxyethane was added. The reaction mixture was stirred at 0 °C for 3 h, poured into water, ether extracted, dried, filtered, and concentrated, leaving 2.55 g of a yellow oil. Chromatography on a 2.5 × 95 cm silica gel column slurry packed in 2% ether in hexane with elution in 500-mL fractions gave fractions 1–2, 2% ether in hexane, 1.59 g (4.01 mmol, 78.6%) of colorless 1-diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene, mp 146–151 °C; 3–9, 4–8% ether in hexane, 96 mg, oil; 10–12, 16% ether in hexane, 121 mg (0.491 mmol, 9.66%) of recovered 4,4-diphenyl-2,5-cyclohexadienone. Crystallization from dichloromethane–hexane gave 1.22 g (3.23 mmol, 63.3%) of white, crystalline 1-diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene, mp 149–151 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.76–3.04 (m, 20 H, aromatic), 3.46 (d, 2 H, J = 9.8 Hz, vinyl), 3.98 (d, 2 H, J = 9.8 Hz, vinyl); MS (70 eV) *m/e* (rel abundance) 397 (34), 396 (100), 319 (53), 241 (48), 165 (44), 91 (12), 77 (10); UV (EtOH) λ_{max} 312 nm (ϵ 27 400), 260 (8600), 246 (12 200), 233 (11 200). High-resolution MS: calcd for $C_{31}H_{24}$, *m/e* 396.187 80; found, *m/e* 396.188 07.

Anal. Calcd for $C_{31}H_{24}$: C. 93.89; H, 6.10. Found: C, 93.80; H, 6.03.

***cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one.** Using the procedure of Zimmerman, Albrecht, and Haire,[34] the irradiation of 10.6 g of 4,4-diphenyl-2-cyclohexenone gave 7.45 g of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 70.7% yield and 2.18 g of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 20.4% yield.

2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. Using the fluoride catalysis procedure described above,[31b] a mixture of 500 mg (2.01 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, 500 mg (5.49 mmol) of potassium fluoride dihydrate, 5.0 mL of dimethylformamide, and 1.35 g (1.12 mL, 20.4 mmol) of malononitrile in 6.0 mL of ethylene glycol was reacted for 22 h to yield 573 mg of yellow oil. After chromatography on a 2.5 × 45 cm silica gel column slurry packed in 2% ether in hexane 514 mg (1.73 mmol, 86.8%) of 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane was obtained as a colorless oil. Crystallization from ether–hexane gave 456 mg (1.54 mmol, 77.0%) of 2-dicyanomethylene-*trans*- 5,6-diphenylbicyclo[3.1.0]hexane as colorless crystals, mp 114–115 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.28–2.64 (m, 10 H, aromatic), 6.48 (d, 1 H, J = 10 Hz, cyclopropyl), 6.68 (d, 1 H, J = 10 Hz, cyclopropyl), 6.92–7.32 (m, 1 H, methylene), 7.34–7.60 (m, 2 H, methylene), 8.60 (d of t, 1 H, J = 8, 19 Hz, methylene); IR (KBr) 4.50, 6.29 μ; MS (70 eV) *m/e* (rel abundance) 296 (12), 234 (13), 217 (9.9), 194 (14), 160 (35), 146 (41), 115 (30), 91 (51), 41 (100); UV (EtOH) λ_{max} 289 nm (ϵ 12 850), λ_{sh} 219 (18 150). High-resolution MS: calcd for $C_{21}H_{16}N_2$, *m/e* 296.131 35; found, *m/e* 296.132 29.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.09; H, 5.44. Found: C, 85.16; H, 5.42.

2-Dicyanomethylene-3-phenylseleno-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. To a stirred solution of 3.00 mmol of lithium diisopropylamide in 10.0 mL of tetrahydrofuran prepared from 0.450 mL (0.300 g, 3.00 mmol) of diisopropylamine and 2.0 mL of 1.50 M *n*-butyllithium in hexane at −78 °C under nitrogen was added dropwise a solution of 752 mg (2.54 mmol) of 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 2.0 mL of tetrahydrofuran. After 15 min a solution of 2.88 mmol of phenylselenium bromide[6] prepared from 0.450 g (1.44 mmol) of diphenyl diselenide and 0.080 mL (0.240 g, 1.50 mmol) of bromine in 2.0 mL of tetrahydrofuran was added rapidly. After stirring for 5 min at −78 °C the reaction mixture was poured into 25.0 mL of 0.5 N hydrochloric acid and 20.0 mL of 50% ether in hexane. The organic layer was washed with water, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo leaving 1.19 g of a black oil which solidified. Trituration of a chloroform solution with hexane gave 913 mg (2.02 mmol, 79.9%) of the selenide product as brown crystals, mp 173–178 °C, NMR pure. Recrystallization from dichloromethane-hexane gave 753 mg (1.67 mmol, 65.9%) of 2-dicyanomethylene-3-phenylseleno-*trans*-5,6-diphenylbicyclo[3.1.0]hexane as light yellow crystals, mp 177–178.5 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.36–3.04 (m, 15 H, aromatic), 6.58 (t, 1 H, J = 6 Hz, methine), 6.78–7.48 (m, 4 H, methylene and cyclopropyl); IR (KBr) 4.50, 6.35 μ; MS (70 eV) *m/e* (rel abundance) 452 (0.3), 450 (1.0), 314 (10), 312 (9), 294 (11), 157 (16), 154 (11), 91 (15), 83 (100). High-resolution MS: calcd for $C_{27}H_{20}N_2Se$, *m/e* 452.079 16; found, *m/e* 452.078 03.

Anal. Calcd for $C_{27}H_{20}N_2Se$: C, 71.68; H, 4.42; N, 6.19. Found: C, 71.50; H, 4.45; N, 6.23.

2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. To a solution of 667 mg (1.48 mmol) of 2-dicyanomethylene-3-phenylseleno-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 14.0 mL of dichloromethane containing 0.28 mL (0.280 g, 3.54 mmol) of pyridine was added 12.3 mmol of hydrogen peroxide (1.4 mL of 30% hydrogen peroxide in 1.4 mL of water). After vigorous stirring under nitrogen at room temperature for 30 min, the reaction mixture was poured into dichloromethane and saturated sodium bicarbonate extracted. The aqueous layer was dichloromethane extracted, and the combined organic layers were washed with 5% hydrochloric acid, water, and brine, dried, and concentrated leaving 448 mg of an orange oil. After chromatography on a 2.5 × 45 cm silica gel column slurry packed in 5% ether in hexane, 394 mg (1.34 mmol, 90.5%) of 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene was obtained as a light yellow oil. Crystallization from ether–hexane gave 248 mg (0.845 mmol, 57.1%) of 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene as nearly white crystals, mp 114–115 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.50–2.98 (m, 10 H, aromatic), 3.04 (d, 1 H, J = 5.5 Hz, vinyl), 3.84 (d of d, 1 H, J = 1, 5.5 Hz, vinyl), 4.18 (d, 1 H, J = 9 Hz, cyclopropyl), 4.56 (d of d, 1 H, J = 1, 9 Hz, cyclopropyl); IR (KBr) 4.50, 6.33 μ; MS (70 eV) *m/e* (rel abundance) 295 (23), 294 (100), 228 (9), 190 (8), 149 (6), 57 (23), 56 (25); UV (EtOH) λ_{max} 312 nm (ϵ 11 750), λ_{sh} 220 (16 600). High-resolution MS: calcd for $C_{21}H_{14}N_2$; *m/e* 294.115 70; found, *m/e* 294.115 96.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.49; H, 4.89.

2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. Using the fluoride catalysis procedure described above,[31b] a mixture of 2.00 g (8.06 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, 2.00 g (21.3 mmol) of potassium fluoride dihydrate, 20.0 mL of dimethylformamide, and 5.40 g (4.50 mL, 81.8 mmol) of malononitrile in 24.0 mL of ethylene glycol was reacted for 16 h to yield 1.84 g of an orange oil. After chromatography on a 2.5 × 85 cm silica gel column slurry packed in 2% ether in hexane, 1.37 g (4.63 mmol, 57.5%) of colorless 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane, mp 119–122 °C, was obtained. Recrystallization from ether–hexane gave 1.13 g (3.81 mmol, 47.6%) of 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane as colorless crystals, mp 121–123 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.62–3.20 (m, 10 H, aromatic), 6.74 (d, 1 H, J = 4 Hz, cyclopropyl), 7.10 (d, 1 H, J = 4 Hz, cyclopropyl), 6.40–7.80 (m, 4 H, methylenes); IR (KBr) 4.50, 6.31 μ; MS (70 eV) *m/e* (rel abundance) 297 (25), 296 (100), 281 (13), 268 (19), 219 (42), 205 (36), 191 (29), 165 (21), 115 (20), 91 (59); UV (EtOH) λ_{max} 279 nm (ϵ 12 600), λ_{sh} 220 (12 500). High-resolution MS: Calcd for $C_{21}H_{16}N_2$; *m/e* 296.131 35; found, *m/e* 296.132 12.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.09; H, 5.44. Found: C, 85.23; H, 5.50.

2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. Using the general procedure for the selenation–selenoxide elimination reactions described above,[31b] to a stirred solution of 4.50 mmol of lithium diisopropylamide and 1.14 g (3.86 mmol) of 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 20.0 mL of tetrahydrofuran was added 4.02 mmol of phenylselenium bromide in 3.0 mL of tetrahydrofuran. Workup as usual gave 1.79 g of a brown solid, which was rapidly chromatographed on a 3.5 × 45 cm silica gel column slurry packed in 4% ether in hexane to give 83 mg (0.26 mmol, 13.3%) of recovered diphenyl diselenide and 1.18 g (2.62 mmol, 67.8%) of 2-dicyanomethylene-3-phenylseleno-*cis*-5,6-diphenylbicyclo[3.1.0]hexane as a dark yellow powder, NMR pure, mp 165–172 °C. A 200-mg sample was washed with cold ether to provide bright yellow selenide product, mp 171–174 °C. The remainder of the material was used without further purification (vide infra). The spectral data for the selenide follow: NMR ($CDCl_3$) τ 2.19–3.28 (m, 15 H, aromatic), 5.24 (t, 1 H, J = 5 Hz, methine), 6.28 (d, 1 H, J = 4 Hz, cyclopropyl), 6.68 (d, 1 H, J = 4 Hz, cyclopropyl), 7.06 (d, 2 H, J = 5 Hz, methylene); IR (KBr) 4.50, 6.29 μ; MS (70 eV) *m/e* (rel abundance) 452 (3), 450 (2), 314 (11), 312 (10), 294 (100), 218 (33), 158 (36), 91 (98). High-resolution MS: calcd for $C_{27}H_{20}N_2Se$, *m/e* 452.079 16; found, *m/e* 452.079 69.

A solution of 1.08 g (0.240 mmol) of 2-dicyanomethylene-3-phenylseleno-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 15.0 mL of dichloromethane containing 0.15 mL (0.15 mg, 1.90 mmol) of pyridine and 22.0 mmol of hydrogen peroxide was reacted to yield 698 mg of a brown oil. Rapid chromatography on a 2.5 × 85 cm silica gel column slurry packed in 4% ether in hexane gave 63 mg (0.202 mmol) of recovered diphenyl diselenide and 581 mg (1.98 mmol, 82.3%) of 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene as a light yellow oil, NMR pure. Crystallization from dichloromethane–hexane gave 240 mg (0.816 mmol, 34.0%) of pure diene product as nearly white crystals, mp 107–108 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.58–3.20 (m, 11 H, aromatic and vinyl), 3.47 (d, 1 H, J = 5 Hz, vinyl), 6.22 (d of d, 1 H, J = 1, 4 Hz, cyclopropyl), 6.92 (d, 1 H, J = 4 Hz, cyclopropyl); IR (KBr) 4.50, 6.38 μ; MS (70 eV) *m/e* (rel abundance) 294 (13), 183 (25), 103 (26), 84 (11), 77 (46); UV (EtOH) λ_{max} 348 nm (ϵ 11 650), λ 280 (10 200), λ_{sh} 225 (14 000). High-resolution MS: calcd for $C_{21}H_{14}N_2$, *m/e* 294.115 70; found, *m/e* 294.117 70.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.42; H, 4.90.

1-Dicyanomethylene-3,4-diphenyl-2-cyclohexene. Using the general fluoride catalysis procedure described above,[31b] a mixture of 2.00 g (8.06 mmol) of 3,4-diphenyl-2-cyclohexenone,[35] 2.00 g (21.2 mmol) of potassium fluoride dihydrate, 20.0 mL of dimethylformamide, and 4.70 g (3.92 mL, 71.2 mmol) of malononitrile in 24.0 mL of ethylene glycol was reacted for 16 h in the dark. The precipitated product was filtered, washed with cold ethanol, and dried in vacuo leaving 2.09 g (7.29 mmol, 90.4%) of 1-dicyanomethylene-3,4-diphenyl-2-cyclohexene as bright yellow crystals, mp 155–156 °C. The spectral data follow: NMR ($CDCl_3$) τ2.42–2.95 (m, 11 H, aromatic and vinyl), 5.65 (t, 1 H, J = 4 Hz, benzyl), 6.98–7.92 (m, 4 H, methylenes); IR (KBr) 4.50, 6.29 μ; MS (70 eV) *m/e* (rel abundance) 297 (21), 296 (100), 218 (33), 205 (27), 191 (20), 91 (54); UV (EtOH) λ_{max} 350 nm (ϵ 27 800), λ 243 (6300). High-resolution MS: calcd for $C_{21}H_{16}N_2$, *m/e* 296.131 35; found, *m/e* 296.131 06.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.09; H, 5.44. Found: C, 85.29; H, 5.57.

α,α-Dicyano-3,4-diphenyltoluene. A solution of 500 mg (1.69 mmol) of 1-dicyanomethylene-3,4-diphenyl-2-cyclohexene, 267 mg (1.50 mmol) of *N*-bromosuccinimide, and 10 mg (0.041 mmol) of benzoyl peroxide in 25.0 mL of carbon tetrachloride was refluxed under nitrogen with tungsten lamp irradiation for 30 min. The reaction mixture was cooled to 0 °C, filtered, and concentrated, leaving 502 mg of a brown powder, which was chromatographed in four portions on four 20 × 20 × 0.2 cm preparative silica gel plates eluted twice with 20% ether in hexane to give, from the combined bands of R_f 0.65, 236 mg (0.797 mmol, 47.1%) of recovered 1-dicyanomethylene-3,4-diphenylcyclohex-2-ene as yellow crystals, and R_f 0.25, 76 mg (0.258 mmol, 15.3% isolated yield, 29.1% based on recovered starting material) of α,α-dicyano-3,4-diphenyltoluene as a yellow oil. Crystallization from hexane gave 37 mg (0.125 mmol, 7.39%) of α,α-dicyano-3,4-diphenyltoluene as white crystals, mp 109.5–111 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.45 (pseudo s, 3 H, arom), 2.58–2.92 (m, 10 H, aromatic), 4.86 (s, 1 H, methine); IR (KBr) 4.45 (v weak) μ; MS (70 eV) *m/e* (rel abundance) 294 (100), 229 (76), 129 (23); UV (EtOH) λ 325 nm (ϵ 5800), λ_{sh} 257 (16 300), λ_{max} 237 (30 000). High-resolution MS: calcd for $C_{21}H_{14}N_2$, *m/e* 294.115 70; found, *m/e* 294.114 74.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.84; H, 5.00.

6,6-Diphenylbicyclo[3.1.0]hexan-2-one.[10] The following provides a convenient approach to this bicyclic ketone. To 15.4 g (0.188 mol) of 2-cyclopentenone stirred in an acid-washed flask under nitrogen at 120 °C was added dropwise 6.60 g (34.0 mmol) of diphenyldiazomethane dissolved in 1.00 g (11.9 mmol) of 2-cyclopentenone over 3 h. The reaction mixture was stirred at 120 °C for 4 h and at room temperature for 14 h, and then distilled at 49–50 °C (10 mmHg) to give 11.5 g (0.140 mol, 70.0%) of recovered 2-cyclopentenone. The pot residue, crude product, was chromatographed on a 2.5 × 86 cm silica gel column slurry packed in 1% ether in hexane to give 2.84 g (11.4 mmol, 34.7%) of 6,6-diphenylbicyclo[3.1.0]hexan-2-one as an oil and 3.55 g (14.3 mmol, 43.3%) of 3-diphenylmethyl-2-cyclopentenone as an oil. Crystallization from ether–hexane gave 2.03 g (8.16 mmol, 24.8%) of 6,6-diphenylbicyclo[3.1.0]hexan-2-one as white crystals, mp 105–106 °C (lit.[10] 104.5–105 °C). Crystallization from chloroform–hexane gave 2.51 g (10.1 mmol, 30.7%) of 3-diphenylmethyl-2-cyclopentenone as white crystals, mp 71–73 °C. The spectral data for the bicyclo ketone follow: NMR ($CDCl_3$) τ 2.58–2.96 (m, 10 H, aromatic), 7.26 (pseudo t, 1 H, J = 6 Hz, cyclopropyl), 7.52 (d, 1 H, J = 6 Hz, cyclopropyl), 7.60–8.32 (m, 3 H, methylene), 9.06 (d of t, 1 H, J = 8, 18 Hz, methylene); IR (KBr) 5.80 μ; MS (70 eV) *m/e* (rel abundance) 249 (3), 248 (15), 206 (83), 191 (18), 165 (20), 91 (23). High-resolution MS: calcd for $C_{18}H_{16}O$, *m/e* 248.120 11; found, *m/e* 248.119 87.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.05; H, 6.49. Found: C, 87.21; H, 6.51.

The spectral data for 3-diphenylmethyl-2-cyclopentenone follow: NMR ($CDCl_3$) τ 2.68–2.98 (m, 10 H, aromatic), 4.26 (d, 1 H, J = 1 Hz, vinyl), 5.04 (s, 1 H, benzhydryl), 7.44–7.78 (m, 4 H, methylene); IR (KBr) 5.89 μ; MS (70 eV) *m/e* (rel abundance) 249 (14), 248 (67), 206 (100), 165 (34), 129 (28), 128 (22), 91 (26); UV (EtOH) λ 305 nm (ϵ 50), 250 (4700), 230 (17 200). High-resolution MS: calcd for $C_{18}H_{16}O$, *m/e* 248.120 11; found, *m/e* 248.120 52.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.05; H, 6.49. Found: C, 87.21; H, 6.52.

2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hexane. Using the general fluoride catalysis procedure described above,[31b] a mixture of 1.00 g (4.03 mmol) of 6,6-diphenylbicyclo[3.1.0]hexan-2-one, 1.00 g (10.6 mmol) of potassium fluoride dihydrate, 10.0 mL of dimethylformamide, and 2.70 g (2.25 mL, 40.9 mmol) of malononitrile in 12.0 mL of ethylene glycol was reacted for 50 h to yield, after filtration, 1.02 g (3.46 mmol, 85.8%) of colorless 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hexane, mp 188–189 °C. Recrystallization from dichloromethane–hexane gave 940 mg (3.18 mmol, 78.8%) of colorless product, mp 189–190 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.56–2.90 (m, 10 H, aromatic), 6.81 (d, 1 H, J = 5 Hz, cyclopropyl), 7.04 (pseudo t, 1 H, J = 5 Hz, cyclopropyl), 7.12–8.00 (m, 3 H, methylenes), 8.72 (d of t, 1 H, J = 8, 18 Hz, methylene); IR (KBr) 4.50, 6.33 μ; MS (70 eV) *m/e* (rel abundance) 297 (22), 296 (100), 218 (34), 206 (47), 165 (50), 91 (47); UV (EtOH) λ_{sh} 230 nm (ϵ 10 700). High-resolution MS: calcd for $C_{21}H_{16}N_2$, *m/e* 296.131 35; found, *m/e* 296.132 35.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.09; H, 5.44. Found: C, 85.08; H, 5.45.

2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene. Using the general procedure for the selenation–selenoxide elimination reactions described above,[31b] to a solution of 3.0 mmol of lithium diisopropylamide and 752 mg (2.54 mmol) of 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hexane in 17.5 mL of tetrahydrofuran was added 5.76 mmol of phenylselenium bromide in 4.0 mL of tetrahydrofuran. Workup as usual gave 1.60 g of a yellow oil which was rapidly chromatographed on a 2.5 × 48 cm silica gel column slurry packed in 5% ether in hexane to give 406 mg (1.29 mmol, 44.8%) of recovered diphenyl diselenide and 938 mg (2.07 mmol, 82.8%) of 2-dicyanomethylene-3-phenylseleno-6,6-diphenylbicyclo[3.1.0]hexane, NMR pure, as a light yellow oil. Rigorous solvent removal in vacuo gave the selenide product as a yellow solid, mp 48–55 °C, which was used without further purification (vide infra). The spectral data for the selenide follow: NMR ($CDCl_3$) τ 2.38–2.94 (m, 15 H, aromatic), 6.12 (t, 1 H, J = 6 Hz, methylene), 6.40–7.50 (m, 4 H, methylene and cyclopropyl); IR (KBr) 4.49, 6.25 μ; MS (70 eV) *m/e* (rel abundance) 452 (2), 450 (1.5), 314 (42), 312 (39), 294 (100), 268 (27), 115 (20), 91 (63). High-resolution MS: calcd for $C_{27}H_{20}N_2Se$, *m/e* 452.079 15; found, *m/e* 452.079 73.

A solution of 927 mg (2.05 mmol) of 2-dicyanomethylene-3-phenylseleno-6,6-diphenylbicyclo[3.1.0]hexane in 15.0 mL of dichloromethane containing 0.15 mL (0.150 g, 1.90 mmol) of pyridine and 15.8 mmol of hydrogen peroxide was reacted to yield 604 mg (2.05 mmol, 100%) of diene product, NMR >95% pure. Crystallization from dichloromethane–hexane gave 240 mg (0.816 mmol, 39.9%) of 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene as light yellow crystals, mp 167–168 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.60–2.96 (m, 10 H, aromatic), 3.04 (d of d, 1 H, J = 1, 5 Hz, vinyl), 3.88 (d, 1 H, J = 5 Hz, vinyl), 6.40 (d, 1 H, J = 4 Hz, cyclopropyl), 6.54 (d of d, 1 H, J = 1, 4 Hz, cyclopropyl); IR (KBr) 4.50, 6.49 μ; MS (70 eV) *m/e* (rel abundance) 295 (25), 294 (100), 267 (13), 215 (9), 165 (18), 91 (4); UV (EtOH) λ_{max} 342 nm (ϵ 9450), λ 295 (7650), λ_{sh} 225 (15 500). High-resolution MS: calcd for $C_{21}H_{14}N_2$, *m/e* 294.115 70; found, *m/e* 294.115 59.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.42; H, 4.79.

***trans*-5,6-Diphenyl-2-cyclohexenone.** Using an improvement of the procedure of Zimmerman and Schuster,[3c] 4,5-diphenylcyclohexane-1,3-dione was treated with *p*-toluenesulfonic acid in refluxing methanol to give after workup a quantitative conversion to a 50:50 mixture of methyl enol ethers, which, without purification, was reduced with lithium aluminum hydride and worked up in 10% sulfuric acid to give after silica gel column chromatography 4,5-diphenyl-2-cyclohexenone, mp 96–97 °C (lit.[36] 97–97.5 °C), in 50.4% yield and *trans*-5,6-diphenyl-2-cyclohexenone, mp 93–94 °C (lit.[3c] 93–94.5 °C), in 34.5% yield.

***trans*-2,3-Diphenylcyclohexanone.**[37] This compound has been reported previously without details. To a slurry of 750 mg of palladium on carbon in 20.0 mL of 95% ethanol under hydrogen at atmospheric pressure was added a solution of 5.05 g (20.3 mmol) of *trans*-5,6-diphenyl-2-cyclohexenone in 30.0 mL of 50% ether–ethanol. The reaction was initiated upon stirring and progress followed by uptake of hydrogen gas. After consumption of 1.2 equiv (554 mL, 24.7 mmol) of hydrogen the reaction was stopped and the mixture was filtered and concentrated in vacuo leaving 5.03 g (20.1 mmol, 99.1%) of a colorless oil which spontaneously crystallized, mp 91–92 °C. Recrystallization from hexane gave 4.79 g (19.2 mmol, 94.3%) of *trans*-2,3-diphenylcyclohexanone, mp 95.5–96.5 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.80–3.16 (m, 10 H, aromatic), 6.30 (d, 1 H, J = 12 Hz, benzyl), 6.72–7.04 (m, 1 H, benzyl), 7.40–7.65 (m, 2 H, methylene), 7.81–8.36 (m, 4 H, methylene); IR (KBr) 5.87 μ; MS (70 eV) *m/e* (rel abundance) 251 (15), 250 (76), 159 (13), 133 (53), 117 (100), 91 (25). High-resolution MS: calcd for $C_{18}H_{18}O$, *m/e* 250.135 76; found, *m/e* 250.135 67.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.42; H, 7.30.

1-Dicyanomethylene-*cis*- and -*trans*-2,3-diphenylcyclohexane. Using the general fluoride catalysis procedure described above,[31b] a mixture of 1.25 g (5.00 mmol) of *trans*-2,3-diphenylcyclohexanone, 1.25 g (13.3 mmol) of potassium fluoride dihydrate, 12.0 mL of dimethylformamide, and 2.83 g (2.35 mL, 42.8 mmol) of malononitrile in 12.0 mL of ethylene glycol was reacted for 15 h to yield 1.52 g of a yellow oil. Chromatography on a 2.5 × 40 cm silica gel column slurry packed in 2% ether in hexane gave 1.05 g (3.52 mmol, 70.3%) of 1-dicyanomethylene-2,3-diphenylcyclohexane as a colorless oil (1:2.8 ratio cis:trans by NMR assay). Separation of the cis and trans isomeric products was effected by preparative high-pressure liquid chromatography using one 2 ft × 3/8 in. column packed with 15–25 μ porous Carbowax 400 coated silica gel beads,[38] and eluting with 30% anhydrous ether in anhydrous hexane. Taking appropriate cuts with five recycles, a typical 100-mg injection gave 25 mg of pure 1-dicyanomethylene-*cis*-2,3-diphenylcyclohexane as a colorless oil from the faster eluting band and 70 mg of pure 1-dicyanomethylene-*trans*-2,3-diphenylcyclohexane as a colorless oil from the slower eluting band. Attempted crystallization of the isomers was unsuccessful. The spectral data for 1-dicyanomethylene-*cis*-2,3-diphenylcyclohexane follow: NMR ($CDCl_3$) τ 2.82–3.24 (m, 10 H, aromatic), 5.52 (d, 1 H, J = 5 Hz, benzyl), 6.68–8.58 (m, 7 H, benzyl and methylenes); IR (neat) 4.50, 6.27 μ; MS (70 eV) *m/e* (rel abundance) 299 (4), 298 (15), 149 (20), 117 (100), 91 (43). High-resolution MS: calcd for $C_{21}H_{18}N_2$, *m/e* 298.14 700; found, *m/e* 298.146 06.

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.52; H, 6.08. Found: C, 84.30; H, 6.17.

The spectral data for 1-dicyanomethylene-*trans*-2,3-diphenylcyclohexane follow: NMR ($CDCl_3$) τ 2.68–3.04 (m, 10 H, aromatic), 5.74 (d, 1 H, J = 7 Hz, benzyl), 6.48–6.72 (m, 1 H, benzyl), 6.80–7.32 (m, 2 H, methylene), 7.70–8.40 (m, 4 H, methylene); IR (neat), 4.50, 6.27 μ; MS (70 eV) *m/e* (rel abundance) 299 (4), 298 (16), 117 (100), 91 (35). High-resolution MS: calcd for $C_{21}H_{18}N_2$, *m/e* 298.147 00; found, *m/e* 298.146 85.

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.52; H, 6.08. Found: C, 84.38; H, 6.12.

α,α-Dicyano-2,3-diphenyltoluene. A solution of 299 mg (1.00 mmol) of 1-dicyanomethylene-*trans*- and -*cis*-2,3-diphenylcyclohexane (2.8:1 trans:cis ratio), 195 mg (1.09 mmol) of *N*-bromosuccinimide, and 2.0 mg (0.010 mmol) of benzoyl peroxide in 5.0 mL of carbon tetrachloride was refluxed for 16 h under nitrogen. The reaction mixture was cooled to 0 °C, filtered, and concentrated leaving 325 mg of a yellow oil, which was chromatographed in three portions on three 20 × 20 × 0.2 cm preparative silica gel plates eluted once with 20% ether in hexane to give, from the combined bands of R_f 0.76, 30 mg (0.102 mmol, 10.2% isolated yield, 18.1% based on recovered starting material) of α,α-dicyano-2,3-diphenyltoluene as a colorless oil and R_f 0.56, 135 mg (0.453 mmol, 45.3%) of recovered 1-dicyanomethylene-2,3-diphenylcyclohexane. Crystallization from ether–hexane gave 14 mg (0.047 mmol, 4.7%) of α,α-dicyano-2,3-diphenyltoluene as colorless needles, mp 154–155 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.16–2.28 (four-line m, 1 H, aromatic), 2.38–2.50 (three-line m, 1 H, aromatic), 2.64–3.10 (m, 11 H, aromatic), 5.12 (s, 1 H, methine); IR (KBr) 4.44 (v weak) μ; MS (70 eV) *m/e* (rel abundance) 295 (22), 294 (100), 266 (11), 239 (15), 119 (18); UV (EtOH) λ 310 nm (ϵ 2000), λ_{max} 236 (15 100). High-resolution MS: calcd for $C_{21}H_{14}N_2$, *m/e* 294.115 70; found, *m/e* 294.114 80.

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.68; H, 4.79. Found: C, 85.47; H, 4.91.

6,6-Diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene. A 1.00-g (4.35 mmol) portion of 6,6-diphenylfulvene[39] and 0.500 g (2.57 mmol) of diphenyldiazomethane were mixed and heated at 100 °C under nitrogen for 12 h. After cooling, chromatography of the red, solid product mixture on a 3.5 × 45 cm alumina column slurry packed in hexane gave 262 mg (1.14 mmol, 26.5%) of recovered 6,6-diphenylfulvene, 366 mg (0.924 mmol, 36.9%) of 6,6-diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene as a colorless oil, and 100 mg of 75% NMR pure 6,6-diphenyl-2-diphenylmethylenebicyclo[3.1.0]-hex-3-ene. Crystallization from dichloromethane–95% ethanol gave 342 mg (0.863 mmol, 34.5%) of 6,6-diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene as colorless crystals, mp 141–142 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.40–3.12 (m, 20 H, aromatic), 3.86 (d of d, 1 H, J = 2.2, 6 Hz, vinyl), 4.24 (d, 1 H, J = 6 Hz, vinyl), 6.72 (d, 1 H, J = 4.8 Hz, cyclopropyl), 6.96 (d of d, 1 H, J = 2.2, 4.8 Hz, cyclopropyl); MS (70 eV) m/e (rel abundance) 396 (2), 230 (7), 182 (32), 105 (100), 77 (60); UV (EtOH) λ_{max} 321 (ϵ 20 750), λ 241 (19 400). High-resolution MS: calcd for $C_{31}H_{24}$, m/e 396.187 80; found, m/e 396.187 44.

Anal. Calcd for $C_{31}H_{24}$: C, 93.89; H, 6.10. Found: C, 93.71; H, 6.10.

Specific Activity of ^{3}H Compounds. Specific activities were determined by counting 1–10-mg samples in 15.0 mL of scintillation solution consisting of 4.00 g of PPO (2,5-diphenyloxazole, Nuclear-Chicago) and 50 mg of POPOP (1,4-bis[2-(5-phenyloxazoyl)]benzene, Nuclear-Chicago) in 1.0 L of toluene (Matheson Coleman and Bell, scintillation grade) in a Nuclear-Chicago Mark I liquid scintillation counter. Quench-corrected scintillation counting efficiencies were calculated on a PDP-11/T55 computer employing a Fortran IV least-squares curve-fitting program[40] by the channels ratio method using a ^{133}Ba external standard.

***p*-Toluenesulfonic acid-^3H_x.** To a solution of 0.950 g (5.00 mmol) of p-toluenesulfonyl chloride in 5.0 mL of anhydrous benzene was added 0.22 mL (0.220 g, 12.2 mmol, 5.5 mCi, New England Nuclear) of tritium oxide. The reaction mixture was stirred at reflux for 48 h and cooled, and the supernatant benzene–water azeotrope was removed from the precipitated p-toluenesulfonic acid-^3H_x, which was dried in vacuo to give 457 mg (2.40 mmol, 48.1%) of nearly white crystals, mp 103–105 °C, specific activity 0.184 mCi/mmol.

4,4-Diphenyl-2-cyclohexenone-*6*-^3H_x. Using a modified procedure of Zimmerman and Samuelson,[41] 4,4-diphenyl-2-cyclohexenone was refluxed in dioxane with basic alumina and tritium oxide (2.5 mCi) to give 4,4-diphenyl-2-cyclohexenone-*6*-^3H_x, mp 95–96 °C (lit.[41] 94–95 °C), specific activity 75.7 μCi/mmol.

4,4-Diphenyl-2,5-cyclohexadienone-*2*-^3H_x. A solution of 750 mg (3.02 mmol, 75.7 μCi/mmol) of 4,4-diphenyl-2-cyclohexenone-*6*-^3H_x, 892 mg (3.95 mmol) of dicyanodichloroquinone, 4.0 mg (0.023 mmol, 184 μCi/mmol) of p-toluenesulfonic acid-^3H_x, and 5.0 μL (500 μCi) of tritium oxide in 15.0 mL of purified benzene was refluxed under nitrogen for 12 h. The reaction mixture was cooled, filtered, diluted with ether, and extracted with saturated sodium bicarbonate and water. The aqueous layer was ether extracted, and the combined organic layers were dried and concentrated, leaving 659 mg of a yellow oil whose NMR indicated 60% conversion to the desired dienone product. Chromatography on a 2.5 × 95 cm silica gel column slurry packed in 2% ether in hexane gave 56 mg (0.23 mmol, 7.5%) of recovered 4,4-diphenyl-2-cyclohexenone-^3H_x; 74 mg, overlap; and 302 mg (1.23 mmol, 40.6%) of 4,4-diphenyl-2,5-cyclohexadienone-*2*-^3H_x as an oil. Crystallization from 95% ethanol gave pure dienone product, mp 121–122 °C (lit.[21a] 122–123 °C), specific activity 55.1 μCi/mmol.

1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-*2*-^3H_x. Using the procedure reported above for nonradioactive material, 4,4-diphenyl-2,5-cyclohexadienone-2-^3H_x (specific activity 55.1 μCi/mmol) was treated with malononitrile and potassium fluoride dihydrate in a dimethylformamide–ethylene glycol solution to give, after workup and crystallization, 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-*2*-^3H_x (specific activity 41.3 μCi/mmol) in 25.2% isolated yield, mp 166–167 °C.

Photolysis Solvents. Cyclohexane (technical grade, North Central Chemicals) was shaken repetitively with concentrated sulfuric acid, concentrated nitric acid, and water until the washings were colorless, then dried over calcium chloride and distilled from potassium hydroxide through a 6 ft × 1 in. metal helices packed column taking only the central boiling fraction for use. Dioxane (technical grade, North Central Chemicals) was purified by the method of Fieser and Fieser[42] and distilled from sodium metal immediately prior to use. *tert*-Butyl alcohol (commercial grade, Eastman Kodak Chemicals) was refluxed over and distilled from calcium hydride immediately prior to use. For photolyses run in acidic media the following solvents were used: (a) 200 mL of dioxane, 160 mL of acid buffer solution 0.04 M in both phosphoric and acetic acids, and 40 mL of 0.2 M sodium hydroxide[43] (observed pH 5.5); (b) 100 mL of 10% aqueous dioxane and 0.6 mL of 1 N hydrochloric acid (observed pH 1.5).

General Procedure for Exploratory Photolyses. All runs used irradiation through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure mercury lamp and *tert*-butyl alcohol solvent at a reactant concentration of 1 mg/mL of solution. All runs were purged with purified nitrogen[44] for 1 h before and during the photolysis.

Exploratory Photolysis of 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene. A solution of 198 mg (0.673 mmol) of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene was irradiated for 1 h and then concentrated leaving 204 mg of a yellow oil. Chromatography on a 1.2 × 45 cm silica gel column slurry packed in 4% ether in hexane with elution in 100-mL fractions gave fraction 1–2, 4% ether in hexane, 16 mg, unidentifiable, secondary photoproducts; 3, 4% ether in hexane, 18 mg (0.061 mmol, 9.06%) of recovered 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene; 4–7, 154 mg (0.524 mmol, 77.9%) of α,α-dicyano-3,4-diphenyltoluene; 8–9, 16% ether in hexane, nil; 10–11, 64% ether in hexane, 4 mg, unidentified yellow oil (mass balance, 96.9%). Crystallization from ether–hexane gave 103 mg (0.350 mmol, 51.6%) of α,α-dicyano-3,4-diphenyltoluene, mp 109–111 °C. The spectral data were identical with those of independently synthesized material (vide supra).

Exploratory Photolysis of 1-Diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene.[45] A solution of 252 mg (0.636 mmol) of 1-diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene was irradiated for 1 h and then concentrated, leaving 261 mg of a light yellow oil whose NMR showed quantitative conversion to 6,6-diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene. The product was dissolved in ether, filtered through silica gel, and concentrated to give 237 mg (0.598 mmol, 93.5%) of a colorless oil. Crystallization from 95% ethanol gave 202 mg (0.510 mmol, 79.7%) of 6,6-diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene, mp 141–142 °C. The spectral data were identical with those of independently synthesized material (vide supra).

Exploratory Photolysis of 2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 143 mg (0.486 mmol) of 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene was irradiated for 30 min and then concentrated, leaving 160 mg of a yellow oil whose NMR showed quantitative conversion to α,α-dicyano-3,4-diphenyltoluene. Crystallization from ether–hexane gave 105 mg (0.357 mmol, 73.5%) of white crystals, mp 109–110 °C. The spectral data were identical with those of the independently synthesized material (vide supra).

Exploratory Photolysis of 2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 64 mg (0.22 mmol) of 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene was irradiated for 30 min and then concentrated, leaving 60 mg of a yellow oil whose NMR showed quantitative conversion to α,α-dicyano-3,4-diphenyltoluene. Crystallization from ether–hexane gave 32 mg (0.11 mmol, 50.2%) of white crystals, mp 109–110 °C. The spectral data were identical with those of independently synthesized material (vide supra).

Exploratory Photolysis of 2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 100 mg (0.340 mmol) of 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene was irradiated for 15 min and then concentrated, leaving 100 mg of a light yellow oil whose NMR showed quantitative conversion of starting material to a 2:1 mixture of toluene photoproducts. Chromatography on a 20 × 20 × 0.2 cm preparative silica gel plate eluted twice with 30% ether in hexane gave band 1, R_f 0.95, 3 mg, unidentified material; band 2, R_f 0.80, 2 mg, unidentified oil; band 3, R_f 0.72, 51 mg (0.173 mmol, 51.0%) of α,α-dicyano-2,3-diphenyltoluene identified by its spectral properties; band 4, R_f 0.50, 16 mg (0.054 mmol) of overlap of toluenes shown by NMR to consist mainly of the 3,4-diphenyl isomer; band 5, R_f 0.28, 18 mg (0.061 mmol, 18.0%) of α,α-dicyano-3,4-diphenyltoluene identified by its spectral properties; band 6, R_f 0.00, 4 mg, unidentified yellow oil (mass balance, 94.0%). Crystallization of band 3 gave 46 mg (0.156 mmol, 46.0%) of α,α-dicyano-2,3-diphenyltoluene, mp 155–156 °C. The spectral data for α,α-dicyano-2,3-diphenyltoluene and α,α-dicyano-3,4-diphenyltoluene were identical with those of independently synthesized material (vide supra).

Table V. Photolysis of 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene to Afford α,α-Dicyano-3,4-diphenyltoluene Photoproduct

run	reactant, mmol	conditions[a]	added sens, mmol	light absorbed, mEinstein	% convn	photoproduct, mmol	Φ
1	0.340	A	[b]	1.27	2.84	0.0096	0.0076
2	0.342	A	[b]	2.05	4.15	0.0142	0.0074
3	0.340	A	[b]	2.42	5.22	0.0177	0.0074
4	0.341	A	[b]	3.55	7.98	0.0272	0.0077
5	0.340	A	[b]	4.55	10.4	0.0355	0.0078
6	0.350	B	[b]	3.27	9.31	0.0326	0.0100
7	0.347	B	[b]	4.21	12.2	0.0423	0.0100
8	0.350	B	[b]	5.19	14.9	0.0523	0.0100
9	0.352	C	[b]	2.95	5.71	0.0201	0.0069
10	0.341	C	[b]	3.92	6.57	0.0224	0.0058
11	0.346	C	[b]	5.39	8.67	0.0300	0.0056
12	0.344	D	[b]	2.64	2.81	0.0097	0.0037
13	0.350	D	[b]	3.51	4.46	0.0156	0.0044
14	0.350	D	[b]	3.60	4.81	0.0168	0.0047
15	0.364	E	[b]	3.42	4.24	0.0154	0.0045
16	0.349	E	[b]	4.42	5.65	0.0197	0.0045
17	0.355	E	[b]	5.27	6.16	0.0219	0.0041
18	0.364	F	1.90[c]	4.63	1.21	[e]	<0.000 95[f]
19	0.348	F	3.34[d]	5.36	1.00	[e]	<0.000 60[f]

[a] A: Black Box, 750 mL of *tert*-butyl alcohol, filter A. B: Black Box, 250 mL of cyclohexane, filter A. C: Black Box, 250 mL of unbuffered dioxane, filter A. D: Black Box, 250 mL of aqueous dioxane pH 5.5, filter A. E: Black Box, 250 mL of aqueous dioxane pH 1.5, filter A. F: Black Box, 250 mL of *tert*-butyl alcohol, filter C. [b] None added. [c] 4,4′-Bis(dimethylamino)benzophenone. [d] *p*-Dimethylaminobenzophenone. [e] None detected. [f] Quantum yield of disappearance of starting material.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were run on either the "Wisconsin Black Box"[11] or microoptical bench.[11] Light output was measured for each run by a digital electronic actinometer[12] calibrated by ferrioxalate actinometry.[13] Microoptical bench photolyses employed an Osram HBO 200-W high-pressure mercury lamp and Bausch and Lomb Model 33-86-79 monochromator with a 5.4-mm entrance slit and 3.0-mm exit slit giving a band-pass of 22 nm at half-peak height. For "Black Box" photolyses the band pass was controlled by one of a series of filter solution combinations held in a 750-mL total volume three-compartment quartz faced filter solution cell. The filter solutions employed follow: Filter A—cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 2.20 × 10^{-2} M stannous chloride dihydrate in 15% hydrochloric acid; transmission 0% below 310 nm, 25% at 328 nm, 0% above 355 nm. Filter B—cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.1 M cupric sulfate pentahydrate in 5% sulfuric acid; transmission 0% below 285 nm, 36% at 316 nm, 0% above 355 nm. Filter C—cell 1, 0.4 M cobalt sulfate heptahydrate and 1.0 M cupric sulfate pentahydrate in 10% sulfuric acid; cell 2, 1.0 M cupric sulfate pentahydrate in 10% sulfuric acid; cell 3, 1.00 × 10^{-3} M ferric chloride hexahydrate in 40% hydrochloric acid; transmission 0% below 375 nm, 9.8% at 420 nm, 0% above 450 nm.

All quantum yield photolysis mixtures were purged with purified nitrogen for 1 h before and during each run.

Summary of Quantum Yield Results for 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene. All direct runs were analyzed by high-pressure liquid chromatography using two 1 ft × $^1/_8$ in. columns packed with 10-μ porous 3-cyanopropyl coated silica gel beads[38] eluted with 15% anhydrous ether in anhydrous hexane. The internal standard used was 4,4′-dimethoxybenzophenone. The sensitized runs were analyzed by chromatography on a 2.54 × 45 cm silica gel column slurry packed in ether in hexane with elution in 200-mL fractions. For run 18, elution with 10% ether in hexane gave from fractions 2–3 0.360 mmol (99.0%) of recovered starting material, mp 166–167 °C. For run 19, elution with 2% ether in hexane gave from fractions 3–7 0.344 mmol (99.0%) of recovered starting material, mp 166–167 °C. All runs are summarized in Table V.

Summary of Quantum Yield Results for 1-Diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene. All direct runs were analyzed by vapor phase chromatography[46] using a 0.64 × 150 cm column packed with 0.25% Carbowax 20M on Varaport-30 at 200 °C using 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene as internal standard. The sensitized runs were analyzed by chromatography on a 2.54 × 45 cm silica gel column slurry packed in ether in hexane with elution of 200-mL fractions of 2% ether in hexane. For run 6, fraction 2 gave 0.254 mmol (98.4%) of recovered starting material, mp 141–142 °C. For run 7, fraction 2 gave 0.267 mmol (96.5%) of recovered starting material, mp 141–142 °C. All runs are summarized in Table VI.

Summary of Quantum Yield Results for 2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. All direct runs were analyzed by high-pressure liquid chromatography using two 1 ft × $^1/_8$ in. columns packed with 10-μ porous 3-cyanopropyl coated silica gel beads[38] eluted with 15% anhydrous ether in anhydrous hexane. The internal standard used was 4,4′-dimethoxybenzophenone. All sensitized runs were analyzed by high-pressure liquid chromatography using one 2 ft × $^3/_8$ in. column packed with 15–25-μ porous Carbowax 400 coated silica gel beads[38] eluted with 30% anhydrous ether in anhydrous hexane. The internal standard was *p*-dimethylaminobenzophenone. All runs are summarized in Table VII.

Summary of Quantum Yield Results for 2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. All direct runs were analyzed by high-pressure liquid chromatography using one 1 ft × $^1/_8$ in. column packed with 15-μ porous Carbowax 400 coated silica gel beads[38] eluted with 20% anhydrous ether in hexane and 0.05% methanol. The internal standard used was *meso*-dihydrobenzoin. All sensitized runs were analyzed by high-pressure liquid chromatography using one 2 ft × $^3/_8$ in. column packed with 15–25-μ porous Carbowax 400 coated silica gel beads[38] eluted with 30% anhydrous ether in anhydrous hexane. The internal standard was *p*-dimethylaminobenzophenone. All runs are summarized in Table VII.

Summary of Quantum Yield Results for 2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene. All direct runs were analyzed by high-pressure liquid chromatography using one 1 ft × $^1/_8$ in. column packed with 15-μ porous Carbowax 400 coated silica gel beads eluted with 30% anhydrous ether in anhydrous hexane. The internal standard was bibenzyl. The quantum yield of formation of α,α-dicyano-3,4-diphenyltoluene for runs 2–6 was calculated from the 2,3:3,4 ratio determined in run 1, and checked for run 2 by 270-MHz NMR analysis. The sensitized runs were analyzed by high-pressure liquid chromatography using one 2 ft × $^3/_8$ in. column packed with 15–25-μ porous Carbowax 400 coated silica gel beads eluted with 30% anhydrous ether in anhydrous hexane. All runs are summarized in Table VIII.

Photolytic ^{3}H-Labeled Crossover Experiments. The same procedure was used in each run. A solution of [^{3}H]-1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene and either [^{1}H]-2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene or [^{1}H]-2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene in anhydrous *tert*-butyl alcohol was irradiated on the Black Box apparatus through filter A, then concentrated in vacuo, and starting materials were separated

Table VI. Photolysis of 1-Diphenylmethylene-4,4-diphenylcyclohexa-2,5-diene to Afford 6,6-Diphenyl-2-diphenylmethylenebicyclo[3.1.0]hex-3-ene Photoproduct

run	reactant, mmol	conditions[a]	added sens, mmol	light absorbed, mEinstein	% convn	photoproduct, mmol	Φ
1	0.254	A	[b]	0.210	4.16	0.001 06	0.050
2	0.260	A	[b]	0.625	11.8	0.003 07	0.049
3	0.260	A	[b]	1.09	21.2	0.005 51	0.047
4	0.253	A	[b]	2.00	36.2	0.009 15	0.046
5	0.259	A	[b]	4.09	62.8	0.0163	0.040
6	0.258	B	1.87[c]	8.47	1.57	[e]	<0.000 48[f]
7	0.277	B	3.35[d]	7.56	3.68	[e]	<0.0013[f]

[a] A: Black Box, 750 mL of *tert*-butyl alcohol, filter B. B: Black Box, 250 mL of *tert*-butyl alcohol, filter C. [b] None added. [c] 4,4′-Bis(dimethylamino)benzophenone. [d] *p*-Dimethylaminobenzophenone. [e] None detected. [f] Quantum yield of disappearance of starting material.

Table VII. Photolysis of 2-Dicyanomethylene-*trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene to Afford α,α-Dicyano-3,4-diphenyltoluene, and 2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene or 2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene Photoproducts

run	reactants, mmol	conditions[a]	added sens, mmol	light absorbed, mEinstein	% convn	photoproduct, mmol	Φ
t-1	0.0395	A	[b]	0.0117	4.27	0.001 67[d]	0.14
t-2	0.0371	A	[b]	0.0236	8.94	0.003 31[d]	0.14
t-3	0.0344	A	[b]	0.0303	11.7	0.004 03[d]	0.13
t-4	0.0340	A	[b]	0.0365	12.7	0.004 32[d]	0.12
t-5	0.0361	B	0.905[c]	1.20	9.96	0.003 60[e]	0.0030
t-6	0.0378	B	0.912[c]	2.10	14.6	0.005 51[e]	0.0026
t-7	0.0367	B	0.896[c]	2.28	14.9	0.005 46[e]	0.0024
t-8	0.0320	B	0.896[c]	1.80	15.7	0.005 02[e]	0.0028
c-1	0.0418	A	[b]	0.0293	6.06	0.002 53[d]	0.086
c-2	0.0381	A	[b]	0.0381	8.35	0.003 16[d]	0.084
c-3	0.0480	A	[b]	0.0480	11.7	0.003 95[d]	0.082
c-4	0.0306	B	2.24[c]	5.03	4.01	0.001 27[f]	0.000 24
c-5	0.0320	B	2.21[c]	10.0	6.44	0.002 06[f]	0.000 21

[a] A: microoptical bench, 40 mL of *tert*-butyl alcohol, 312 nm. B: Black Box, 80 mL of *tert*-butyl alcohol, filter C. [b] None added. [c] *p*-Dimethylaminobenzophenone. [d] α,α-Dicyano-3,4-diphenyltoluene. [e] 2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene. [f] 2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene.

from photoproduct by preparative high-pressure liquid chromatography using a combination of two columns: (a) 2 ft × 3/8 in. column packed with 15-25-μ porous Carbowax 400 coated silica gel beads, and/or (b) 2 ft × 3/8 in. column pakced with 5-10-μ porous Carbowax 400 coated silica gel beads[38] eluted with 30% anhydrous ether in anhydrous hexane. Isolated, crystallized compounds were assayed for ratioactivity by liquid scintillation counting. Recovered *tert*-butyl alcohol showed no radioactivity in any run.

The data for individual runs are reported as follows: tritium-labeled dicyanotriene (weight, mmol, specific activity), added bicyclic compound (weight, mmol), volume of solvent, amount of light absorbed; recovered labeled dicyanotriene (weight, mmol), number of recrystallizations (95% ethanol), final weight, melting point, asymptotic specific activity (μCi/mmol); isolated radioactive dicyanotoluene (weight, mmol), number of recrystallizations (ether-hexane), final weight, melting point, asymptotic specific activity (μCi/mmol); % labeled dicyanotoluene; recovered bicyclic compound (weight, mmol), number of recrystallizations (ether-hexane), final weight, melting point, asymptotic specific activity (nCi/mmol), μmol labeled compound in recovered bicyclic.

Run 1. 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (151 mg, 0.513 mmol, 1.24 ± 0.01 μCi/mmol), 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (15.9 mg, 5.41 × 10^{-2} mmol), 250 mL, 9.48 mEinsteins.

Recovered 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (130 mg, 0.442 mmol), 3, 56.1 mg, 168-168.5 °C, 1.25 ± 0.01 μCi/mmol.

Isolated α,α-dicyano-3,4-diphenyltoluene (31.0 mg, 0.105 mmol), 2, 10.2 mg, 109-110 °C, 0.88 ± 0.01 μCi/mmol, 66.8% labeled dicyanotoluene.

Recovered 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (5.6 mg, 1.90 × 10^{-2} mmol), 1, 3.3 mg, 3.34 ± 0.06 n Ci/mmol, 4.76 × 10^{-2} μmol labeled material present.

Run 2. 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (503 mg, 1.71 mmol, 22.70 ± 0.11 μCi/mmol), 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (205 mg, 0.699 mmol), 750 mL, 20.1 mEinsteins.

Recovered 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (455 mg, 1.55 mmol), 3, 210 mg, 168-169 °C, 22.80 ± 0.11 μCi/mmol.

Isolated α,α-dicyano-3,4-diphenyltoluene (149 mg, 0.508 mmol), 2, 73.8 mg, 109-110 °C, 7.38 ± 0.07 μCi/mmol, 31.9% labeled dicyanotoluene.

Recovered 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (104 mg, 0.353 mmol), 5, 16.5 mg, 114-115 °C, 0.90 ± 0.05· nCi/mmol, 1.39 × 10^{-2} μmol labeled material present.

Run 3. 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (501 mg, 1.70 mmol, 42.8 ± 0.2 μCi/mmol), 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (201 mg, 0.683 mmol), 750 mL, 20.6 mEinsteins.

Recovered 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene-2-^3H_x (463 mg, 1.58 mmol), 3, 252 mg, 168-169 °C, 42.9 ± 0.2 μCi/mmol.

Isolated α,α-dicyano-3,4-diphenyltoluene (83.6 mg, 0.284 mmol), 2, 36.6 mg, 109-110 °C, 18.8 ± 0.1 μCi/mmol, 45.4% labeled dicyanotoluene.

Recovered 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene (155 mg, 0.527 mmol), 4, 27.0 mg, 107-108 °C, 4.0 ± 0.2 nCi/mmol, 5.06 × 10^{-2} μmol labeled material present.

Emission Studies. Magic Multipliers. The fluorescence spectrum of each compound was measured in a 4:1 methylcyclohexane-isopentane solution at 77 and 295 K using an Aminco-Keirs spectrofluorometer equipped with a Hanovia 901C-1 150-W xenon arc lamp. Concentrations of solutions were adjusted to give optical densities of 0.8-0.9. All solutions were thoroughly degassed immediately before the spectra were obtained. Emission wavelength maxima were found

Table VIII. Photolysis of 2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene to Afford α,α-Dicyano-2,3-diphenyltoluene and α,α-Dicyano-3,4-diphenyltoluene Photoproducts

run	reactant, mmol	conditions[a]	added sens, mmol	light absorbed, mEinstein	% convn	photoproduct, mmol	Φ
1	0.0884	A	[b]	1.65	94.3	0.0559[f]	0.034[f]
						0.0274[g]	0.017[g]
2	0.0367	B	[b]	0.0597	18.2	0.004 43[f]	0.075[f]
						0.002 20[g]	0.037[g]
3	0.0374	B	[b]	0.0516	15.8	0.003 92[f]	0.076[f]
						0.001 94[g]	0.038[g]
4	0.0364	B	[b]	0.385	13.7	0.003 33[f]	0.086[f]
						0.001 65[g]	0.043[g]
5	0.0343	B	[b]	0.358	13.6	0.003 12[f]	0.087[f]
						0.001 55[g]	0.043[g]
6	0.0343	B	[b]	0.202	9.25	0.002 11[f]	0.10[f]
						0.001 05[g]	0.052[g]
7	0.0319	C	2.26[c]	1.55	<2[e]	[h]	<0.000 41
8	0.0377	C	0.926[d]	2.73	<2[e]	[h]	<0.000 27

[a] A: Black Box, 80 mL of *tert*-butyl alcohol, filter A. B: microoptical bench, 40 mL of *tert*-butyl alcohol, 312 nm. C: Black Box, 80 mL of *tert*-butyl alcohol, filter C. [b] None added. [c] *p*-Dimethylaminobenzophenone. [d] 4,4′-Bis(dimethylamino)benzophenone. [e] 2% conversion could have easily been detected. [f] α,α-Dicyano-2,3-diphenyltoluene. [g] α,α-Dicyano-3,4-diphenyltoluene. [h] None detected.

to be independent of excitation wavelength over a 50-nm range. Magic multipliers were calculated by dividing the integrated intensity of fluorescence at 77 K by the integrated intensity of fluorescence at 295 K. The average values obtained for each compound follow: 1-dicyanomethylene-4,4-diphenylcyclohexa-2,5-diene, M = 385 (six runs); 1-diphenylmethylene-4,4-diphenylcyclohexa-2,5-diene, M = 580 (five runs); 2-dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene, M = 3.2 (three runs); 2-dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene, M = 7.1 (three runs); 2-dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene, M = 20 (three runs).

The fluorescence spectrum of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene in 2:1 ethanol-ether was also obtained under conditions described above with results: 295 K, $\lambda_{\text{emission}}$ 467 nm, rel intensity 1; 77 K, $\lambda_{\text{emission}}$ 405 nm, rel intensity 3.

Single Photon Counting. The apparatus and procedure have been described previously.[18a,b] Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range of 0.8–0.9, thoroughly degassed immediately before counting, and counted at 77 K until a minimum of 2000 counts in the maximum channel was obtained. Data was collected at less than 5% lamp flash frequency to ensure exclusion of double photon counting. Excitation wavelength was varied over the range 300–335 nm and emission was monitored over the range 405–415 nm with an RCA 8850 photomultiplier. The decay rate was found to be independent of excitation wavelength, emission wavelength, and optical density to within 5% using the "A value" as a measure of the comparative fit of computer-calculated decay rate to experimentally observed decay rate. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, standard deviation, A value.

(1) 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene, 1.00 ns, 1.00×10^9 s^{-1}, 18, ±0.067, 0.045.

(2) 1-Diphenylmethylene-4,4-diphenyl-2,5-cyclohexadiene, 841 ps, 1.18×10^9 s^{-1}, 12, ±0.054, 0.045.

(3) 2-Dicyanomethylene-*trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene, fluorescence too weak for accurate counting, 27 counts/h in maximum channel.

(4) 2-Dicyanomethylene-*cis*-5,6-diphenylbicyclo[3.1.0]hex-3-ene, fluorescence too weak for accurate counting, 31 counts/h in maximum channel.

(5) 2-Dicyanomethylene-6,6-diphenylbicyclo[3.1.0]hex-3-ene, fluorescence too weak for accurate counting, 4 counts/h in maximum channel.

Control Experiment. Photolysis of α,α-Dicyano-3,4-diphenyltoluene. A solution of 92.5 mg (0.314 mmol) of α,α-dicyano-3,4-diphenyltoluene in 100 mL of anhydrous *tert*-butyl alcohol was irradiated for 1.0 h under typical exploratory photolysis conditions (vide supra). UV analysis of the crude photolysate showed no internal filter formation. Concentration of the photolysate gave a yellow oil whose NMR (100 MHz) showed substantial formation of purely aromatic absorption and a new singlet at τ 5.38, but no singlet at τ 5.12, indicating no formation of α,α-dicyano-2,3-diphenyltoluene. Chromatography on a 20 × 20 × 0.2 cm preparative silica gel plate eluting twice with 20% ether in hexane gave six bands: bands 1–3, R_f 0.79, 0.72, and 0.63, respectively, gave 2.0, 1.9, and 2.5 mg of unidentifiable yellow oils; band 4, R_f 0.46, 24.7 mg (8.40×10^{-2} mmol, 27.1%) of α,α-dicyano-3,4-diphenyltoluene; band 5, R_f 0.33, 28.3 mg, unidentified photoproduct whose NMR showed aromatic absorption and singlet at τ 5.38; band 6, R_f 0.0, 14.3 mg, unidentifiable brown oil whose NMR showed only complex aromatic absorption (mass balance: 78.5%).

Control Experiment. Photolysis of α,α-Dicyano-2,3-diphenyltoluene. A solution of 26.6 mg (9.04×10^{-2} mmol) of α,α-dicyano-2,3-diphenyltoluene in 100 mL of anhydrous *tert*-butyl alcohol was irradiated for 45 min under typical exploratory photolysis conditions (vide supra). UV analysis of the crude photolysate showed no formation of an internal filter. Concentration of the photolysate and analysis by silica gel thin layer chromatography, NMR (100 MHz), and high-pressure liquid chromatography (one 1 ft × ⅛ in. column of 15-μ porous Carbowax 400 coated silica gel beads[38] eluting with 30% anhydrous ether in anhydrous hexane) showed no photoreaction. Chromatography on a 1 × 27 cm silica gel column slurry packed in 10% ether in hexane with elution in 50.0-mL fractions using 10% ether in hexane gave from fraction 2 23.9 mg (8.13×10^{-2} mmol, 90.0%) of α,α-dicyano-2,3-diphenyltoluene, mp 152–154.5 °C.

Control Experiment. Acid Stability of 1-Dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene. A. A solution of 50 mg (0.170 mmol) of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene and 200 mg (1.16 mmol) of *p*-toluenesulfonic acid in 10.0 mL of benzene was refluxed for 6 h, cooled, washed with saturated sodium bicarbonate, water, and brine, dried, and concentrated, leaving 48 mg (0.163 mmol, 96.0%) of recovered starting material, pure by NMR (100 MHz) assay.

B. A solution of 200 mg (0.680 mmol) of 1-dicyanomethylene-4,4-diphenyl-2,5-cyclohexadiene in 10.0 mL of dioxane and 4.0 mL of concentrated hydrochloric acid (pH ~0.0) was stirred at room temperature for 3 h. Silica gel thin layer chromatography analysis showed no spot for starting material and no formation of α,α-dicyano-3,4-diphenyltoluene. The reaction mixture was poured into ether, water washed, dried, and concentrated, leaving 175 mg (0.595 mmol, 87.5%) of recovered starting material, pure by NMR (100 MHz) analysis.

Control Experiment. Resistance of α,α-Dicyano-3,4-diphenyltoluene to Base Extraction. A solution of 257 mg (0.874 mmol) of α,α-dicyano-3,4-diphenyltoluene in ether was extracted ten times with saturated sodium bicarbonate, washed with water, dried, and concentrated, leaving 219 mg (0.745 mmol, 85.2%) of α,α-dicyano-3,4-diphenyltoluene, pure by NMR analysis. The base extracts were acidified to pH <3 and ether extracted. The ether extract was dried and concentrated in vacuo, leaving 38 mg (0.129 mmol, 14.8%) of α,α-dicyano-3,4-diphenyltoluene, pure by NMR analysis.

Control Experiment. Acid Stability of α,α-Dicyano-3,4-diphenyltoluene. A. A solution of 47 mg (0.16 mmol) of α,α-dicyano-3,4-diphenyltoluene in 10.0 mL of aqueous acidic dioxane, pH 1.5, was stirred at room temperature under nitrogen for 3 h, partially concentrated, diluted with ether, water washed, dried, and concentrated, leaving 45.3 mg (0.154 mmol, 96.4%) of recovered starting material, pure by silica gel thin layer chromatography and NMR (100 MHz) analysis.

B. A solution of 38 mg (0.130 mmol) of α,α-dicyano-3,4-diphenyltoluene in 10.0 mL of aqueous dioxane and 4.0 mL of concentrated hydrochloric acid, pH ~0.0, was stirred under nitrogen for 3 h, diluted with ether, water washed, dried, and concentrated, leaving 40.2 mg of an unidentifiable white powder, mp 192–197 °C dec. Silica gel thin layer chromatography and NMR (100 MHz) analysis showed complete consumption of starting material. Analysis of the white powder by IR (KBr) showed typical amide bands of 2.96 (asymmetric N–H) 3.16 (symmetric N–H), 5.92 μ (carbonyl).

Calculations. The Pople semiempirical SCF method[47,48] (complete neglect of differential overlap) was used for closed-shell SCF ground-state calculations. Excited-state energies and wave functions were obtained by a configuration interaction treatment applied to the SCF molecular orbitals including single and double excitations. All MOs were included in single and double excitation calculations, except for systems of greater than 20 basis orbitals where double excitations from the four lowest occupied to the four highest unoccupied MOs were excluded. Important configurations were selected from this set, as determined by the extent of the perturbations on the first two excited states by a representative set of dominant singly excited configurations.

Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of the spin operator S^2 as described by Murrell and McEwen.[49] Matrix elements between configurations were calculated from general formulas obtained by the standard methods for reduction of many-electron integrals.[50]

Valence-state ionization potentials were obtained from Hinze and Jaffe,[51] except for nitrogen, where values compiled by Nishimoto[52] were used. Two-electron repulsion integrals were calculated by the Pariser–Parr method.[47] Resonance integrals were calculated by the following expression:

$$\beta_{ij} = (S_{ij}/1 + S_{ij})(I_i + I_j)K$$

where S_{ij} is the overlap integral[53] and I_i and I_j are the valence state ionization potentials for orbitals i and j, respectively. Nearest-neighbor and selected 1,3 resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene using a configuration interaction calculation that included single and double excitations. The resonance integral for the carbon–nitrogen triple bond was obtained empirically by spectral fitting to benzonitrile.[50d]

Standard geometries for the methylene-2,5-cyclohexadiene and bicyclo[3.1.0]hexene systems were assumed, based on reported model compounds.[54] Geometries for intermediate species were assumed.

Calculations were performed with Fortran IV programs on a PDP-11/T55 computer having 32K words of memory. Direct access to and from two disks of 1.2 × 10^6 words per disk allowed storage and use of the large matrices encountered in configuration interaction calculations.[50d]

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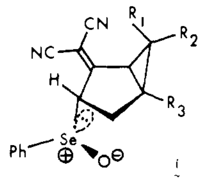
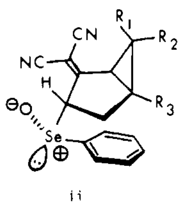
References and Notes

(1) This is part 116 of our photochemical series.
(2) For part 115 see H. E. Zimmerman and T. P. Cutler, *J. Org. Chem.*, **43**, 3283 (1978).
(3) (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., 1961, Abstracts, p 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962).
(4) (a) H. E. Zimmerman, P. Hackett, D. Juers, and B. Schröder, *J. Am. Chem. Soc.*, **89**, 5973 (1967); (b) H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3653 (1971).
(5) Another deficiency was that the dienone rearrangement utilized the triplet excited state while the methylene analogues rearranged by way of the singlet.
(6) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).
(7) (a) H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975); (b) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972).
(8) (a) In the present instance the allylic alcohol product expected would be a cyanohydrin which might lead to an acyl cyanide or acid. However, such products were not encountered. (b) In one example[9] a 1:1 mixture of elimination and [2.3] rearrangement products were obtained from one of two steroid stereoisomers. The chirality of selenium was considered as a factor. In the present instance, it is possible that the selenoxide diastereomer i is preferentially formed; then conformation ii of this isomer needed for the [2.3] rearrangement would be relatively inaccessible owing to phenyl–five-ring interaction. This is especially true in the case of the 5,6-diphenyl isomers where R_3 is phenyl. Note also ref 9b.





(9) (a) W. G. Salmond, M. A. Barta, A. M. Cain, and M. C. Sobata, *Tetrahedron Lett.*, 1683 (1977); (b) D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970); here different rates of elimination were observed for different diastereomers of saturated selenoxides.
(10) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P S. Huyffer, *J. Am. Chem. Soc.*, **91**, 434 (1969).
(11) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).
(12) H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weight, *Mol. Photochem.*, **8**, 379 (1977).
(13) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(14) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).
(15) W. G. Herstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).
(16) This value is uncertain (±1 kcal/mol) owing to lack of vibrational structure. The 0–0 band was taken as one-third of the way from the phosphorescence onset to the maximum.
(17) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).
(18) (a) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974); (b) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *ibid.*, **97**, 3718 (1975); (c) H. E. Zimmerman and T. P. Cutler, ref 2; (d) H. E. Zimmerman, M. G. Steinmetz, and C. L. Kreil, *J. Am. Chem. Soc.*, **100**, 4146 (1978); (e) H. E. Zimmerman and T. R. Welter, *ibid.*, **100**, 4131 (1978).
(19) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) *ibid.*, **91**, 3316 (1969); (d) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(20) Thus, the Type A rearrangement of 4,4-disubstituted 2,5-cyclohexadienones appears superficially to be a di-π-methane reaction. Yet in that case an n-π^* excited triplet is the rearranging species[3] rather than a π-π^* singlet or triplet as in simple hydrocarbon di-π-methane rearrangements. Also, in the Type A rearrangement of dienones, a zwitterionic intermediate has been demonstrated,[3,21] an intermediate not common to simple di-π-methane processes.
(21) (a) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966); (b) H. E. Zimmerman and J. O. Grunewald, *ibid.*, **89**, 5163 (1967); (c) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *ibid.*, **88**, 5352 (1966); (d) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); (e) see also ref 10.
(22) (a) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564 (1966). (b) *ibid.*, **88**, 1565 (1966). (c) *Acc. Chem. Res.*, **4**, 272 (1971). (d) More recently this has been discussed by Michl and such crossing points have been termed "funnels".[22e] (e) J. Michl, *Mol. Photochem.*, **4**, 243, 257 (1972).
(23) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 7806 (1972).
(24) (a) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); (c) see also ref 18b and 27.
(25) (a) H. E. Zimmerman, *Science*, **153**, 837 (1966); (b) *Adv. Photochem.*, **1**, 183 (1963).
(26) (a) More recently the importance of zwitterionic ground states and their nonzwitterionic excited states has been emphasized by Salem et al.;[26b-e] the Salem D, Z_1, and Z_2 states correspond to the diradical S_0, S_1, and S_2 states discussed in our own studies[27] and the S_0 and n-π^* species in ketone photochemistry.[3] (b) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972). (c) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975). (d) L. Salem and W. D. Stohrer, *Chem. Commun.*, 140 (1971); (e) L. Salem, *Science*, **191**, 822 (1976).
(27) (a) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972); (b) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).
(28) (a) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc., London, Sect. A*, **67**, 795 (1954); (b) M. G. Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).
(29) For the species along the reaction coordinate between the vertical excited state and the bridged species the energies are probably exaggerated owing to the approximation wherein all integrals and geometries were simply interpolated thus leading to inappropriate geometry which has not been optimized or selected from known bond lengths.
(30) We also acknowledge the assistance of Miss Susan Boettger in preliminary aspects of the study, synthesizing photochemical dicyanomethylene reactant **2** and running initial photolyses.

(31) (a) All melting points were determined using a calibrated hot-stage apparatus. Mass spectra were obtained using an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained using a JEOL MH-100, Varian T-60, or Bruker WH-270 spectrometer. High-pressure liquid chromatography was performed on a Waters Model ALC-100 liquid chromatograph employing a LDC 254-nm UV detector which was calibrated for the relative responses of detected compounds and standards. Vapor phase chromatography was performed on a Varian Aerograph Series 2100 instrument employing a flame ionization detector which was calibrated for the relative responses of the detected compound and standard. Column chromatography was performed on either silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) or basic alumina (Fisher Scientific, adsorption grade, 80–200 mesh) packings mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored by a hand-held UV lamp. Preparative thin layer chromatography was performed using MN-Kieselgel G-UV-254 silica gel. (b) For preparations which are similar to one another, the first example is given in detail. For full details in the related cases see ref 31c. (c) D. R. Diehl, Ph.D. Thesis, University of Wisconsin, Madison, 1978.

(32) J. W. ApSimon, J. W. Hooper, and B. A. Laishes, *Can. J. Chem.*, **48**, 3064 (1970).

(33) H. E. Zimmerman and R. T. Klun, *Tetrahedron*, **34**, 1775 (1978).

(34) H. E. Zimmerman, F. X. Albrecht, and M. Haire, *J. Am. Chem. Soc.*, **97**, 3726 (1975).

(35) H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.*, **90**, 3749 (1968).

(36) H. E. Zimmerman and D. J. Sam, *J. Am. Chem. Soc.*, **88**, 4905 (1966).

(37) (a) This compound has been previously reported prepared by phenylcuprate addition to 2-phenylcyclohexenone.[12b] No experimental details or physical data were given. (b) N. Arumugam and P. Shenbagamerthi, *Tetrahedron Lett.*, 2251 (1972).

(38) H. E. Zimmerman, T. R. Welter, D. Tartler, and R. A. Bunce, unpublished results.

(39) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).

(40) H. E. Zimmerman and R. L. Swafford, unpublished results.

(41) H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **91**, 5307 (1969).

(42) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 133.

(43) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", 2nd ed., Academic Press, New York.

(44) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(45) (a) A preliminary photolysis of this molecule was performed by Gary E. Keck while in this research group. (b) G. E. Keck private communication.

(46) (a) Quantum yields checked by 100-MHz NMR integration agreed with those determined by vapor phase chromatography. (b) Additionally, the quantum yield for run 4 was checked by high-pressure liquid chromatography using one $8 \times \frac{1}{4}$ in. column packed with 5–10-μ porous silica gel beads and eluted with 0.02% anhydrous ether in anhydrous hexane. The quantum yield value was 0.044.

(47) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(48) (a) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Molecules", McGraw-Hill, New York, 1949.

(49) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

(50) (a) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, 1975, Chapter 5. (b) Reference 49. (c) Matrix elements between doubly excited configurations themselves were derived, ref 50d. (d) H. E. Zimmerman and M. G. Steinmetz, unpublished results.

(51) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(52) K. Nishimoto and L. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

(53) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(54) (a) O. Kennard, Ed., "Molecular Structures and Dimensions", Vol. A1, Unwin Brothers, Cambridge, England, 1972; (b) G. Favinni, F. Zuccarello, and G. Buimi, *J. Mol. Struct.*, **3**, 385 (1969); J. E. Lambert, R. E. Carhart, and P. W. R. Corfield, *Chem. Commun.*, 999 (1968); (c) R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **18**, 932 (1965); (d) W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).

(55) (a) S_0 energies before configuration interaction are used to obtain excitation energies since calculations using only singly and doubly excited configurations tend to give excessive ground-state stabilization.[30b,c] (b) Note the same finding by E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533 (1976). (c) See also ref 18d,e.

Regiochemical Control in Dihydrophenanthrene Synthesis. A Photochemical Total Synthesis of Juncusol

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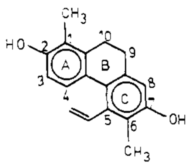
Abstract: Three approaches are described toward the total synthesis of juncusol, 1,6-dimethyl-5-vinyl-2,7-dihydroxy-9,10-dihydrophenanthrene (**1**), a cytotoxic constituent of the needlerush *Juncus roemerianus*. Wittig condensation of the phosphonium salt derived from 2-methyl-3-methoxybenzyl bromide with 3-methoxy-4-methyl-5-cyanobenzaldehyde gave the mixture of *E* and *Z* cyanostilbenes **13**. Reduction of this mixture gave the corresponding diarylethane, which failed to undergo oxidative aryl-aryl cyclization. Photocyclization of the above stilbenes proceeded readily to give a 7:1 ratio of the two expected phenanthrenes in which the unwanted 7-cyano regioisomer **17** predominated. The Ziegler modification of the Ullmann coupling was used to prepare the symmetrical dialydehyde **43**, which was converted by Wittig reagent to the vinyl aldehyde **44** and ultimately reduced to key intermediate **47**. Photocyclization of the latter gave the dihydrophenanthrene alcohol **48** which was converted via the aldehyde **46**, Wittig homologation, and demethylation to juncusol. The overall yield of the latter from 2-methyl-3-methoxybenzaldehyde is 18% over ten steps; the route provides the first total synthesis of this natural product.

Introduction

During their search for antileukemic constituents of the extract of the needlerush (*Juncus roemerianus*), Miles et al. isolated a crystalline $C_{18}H_{18}O_2$ phenol, juncusol, having cytotoxic activity against the NCI 90 KB human epidermoid carcinoma of the nasopharynx test system (ED_{50} = 0.3 μg/mL).[1] The structure of juncusol was established by these investigators as the 9,10-dihydrophenanthrene **1** by single-crystal X-ray diffraction analysis of its diacetate.

Juncusol (**1**), like its congener juncunol (**2**),[2] differs from most other 9,10-dihydrophenanthrene phytoalexins[3] such as orcinol (**3**), logoglossol (**4**), and hircinol (**5**) in having alkyl and vinyl substituents on the carbocyclic nucleus. For this reason the efficient and regioselective total synthesis of juncusol is not a trivial exercise. Although substances **3, 4,** and **5** are synthetically accessible through conventional phenanthrene chemistry followed by catalytic reduction of the 9,10 double bond,[4] such an approach may not be feasible for juncusol. Thus the selective catalytic hydrogenation of the 9,10 double bond is often



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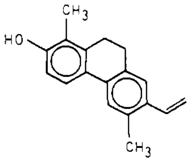

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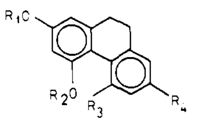

3 $R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = OH$

4 $R_1 = R_2 = CH_3$, $R_3 = OH$, $R_4 = H$

5 $R_1 = R_4 = H$, $R_2 = CH_3$, $R_3 = OH$

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