(15) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).
(16) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).
(17) M. Oda, Y. Kayama, and Y. Kitahara, *Tetrahedron Lett.*, 2019 (1974).
(18) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).
(19) O. Mancera, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953).
(20) M. Oda and Y. Kitahara, *Tetrahedron Lett.*, 3295 (1969).
(21) A small explosion occurred when the reaction was performed at room temperature as described in ref 20.
(22) T. Nozoe, S. Seto, S. Itô, M. Sato, and T. Katona, *Proc. Jpn. Acad.*, **28**, 488 (1952).
(23) S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Lett.*, 4151 (1966).
(24) S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *J. Org. Chem.*, **34**, 520 (1969).

Generality of the Photochemical Bicycle Rearrangement. Exploratory and Mechanistic Organic Photochemistry[1,2]

Howard E. Zimmerman* and Timothy P. Cutler

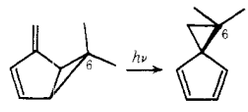
Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

Received December 5, 1977

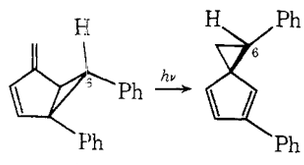
The generality of the slither, or bicycle, rearrangement has been examined in three new systems: 2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (**5**), 3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (**6**), and 3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene (**7**). In each case endo and exo stereoisomers were studied. The photochemistry of these systems consisted of slither rearrangements in which carbon-6, with its two sp^5 three-ring orbitals, bicycles around the five-ring and also out onto the exocyclic methylene group. The stereospecific slithering process is termed "bicycling", since C-6 moves stereospecifically around the five-ring with the sp^5 orbitals acting as "wheels". With the wheels staying on the five-ring and exocyclic bonds, the endo group remains endo and the exo group at C-6 remains exo. Counterclockwise bicycling is shown to be preferred to clockwise bicycling (with the molecule drawn following the convention in the text). Evidence is presented in the case of diphenyl bicyclic olefin for a minor pathway permitted for the endo but not exo stereoisomer. This involves counterclockwise bicycling just past the *exo*-methylene group followed by backup onto this exo moiety to give the stereoisomer of the major spiro product. In the benzo examples, bicycling over the π system of the benzo moieties is shown to be inhibited. SCF–CI calculations were carried out for the reacting species along the excited state surface leading toward product. This surface curves downward until a cyclopropyl diradical structure is reached, at which point an approach to the ground-state surface is encountered. Correlation diagram treatments were derived as well. Finally, a concept of dissection of electronic excitation into components around the molecule was introduced. This involved a **ΔP** matrix giving the change in bond orders of the excited state vs. the ground state. The treatment allows one to determine which molecular motions lead to a mutual approach of excited and ground states and predicts reaction pathways.

Introduction

Previously we have described the photochemical rearrangement of 6,6-dimethyl- and 5,6-diphenyl-substituted 2-methylenebicyclo[3.1.0]hex-3-enes (1 and **2**, respectively) to give spiro[2.4]hepta-4,6-diene products (**3** and **4**).[3] The reaction was shown to proceed via the excited singlet and to be stereospecific in the one case with stereochemistry (note eq 1).



1 3 (1a)



2b 4b (1b)

The reaction is one in which carbon-6 slithers, or bicycles, along the surface of a fulvene π system, retaining stereochemistry in such a way that the endo group at C-6 remains endo and the exo group remains exo. The reaction stereochemistry can be envisaged as involving two sp^5 hybrid orbitals bonding C-6 to the five-ring, these orbitals constituting "bicycle wheels". As the forward wheel rolls along the five-ring, the inside (endo) handlebar remains inside the five-ring and the exo one remains outside.

Because of the intriguing nature of this new reaction, we wished to explore its generality, its limitations, and structural effects governing the reaction course. Also, our single photon counting technique for determining excited singlet rate constants[4] provided a way to ascertain the reaction facility as a function of structure.

The systems selected for study were 2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (**5**), 3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (**6**), and 3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene (**7**). These promised to provide information on the generality of the reaction as a function of structure and also indicate if the reaction still occurred with benzo substitution. Additionally, the compounds were selected so that fluorescence emission could be used to monitor excited-state decay.

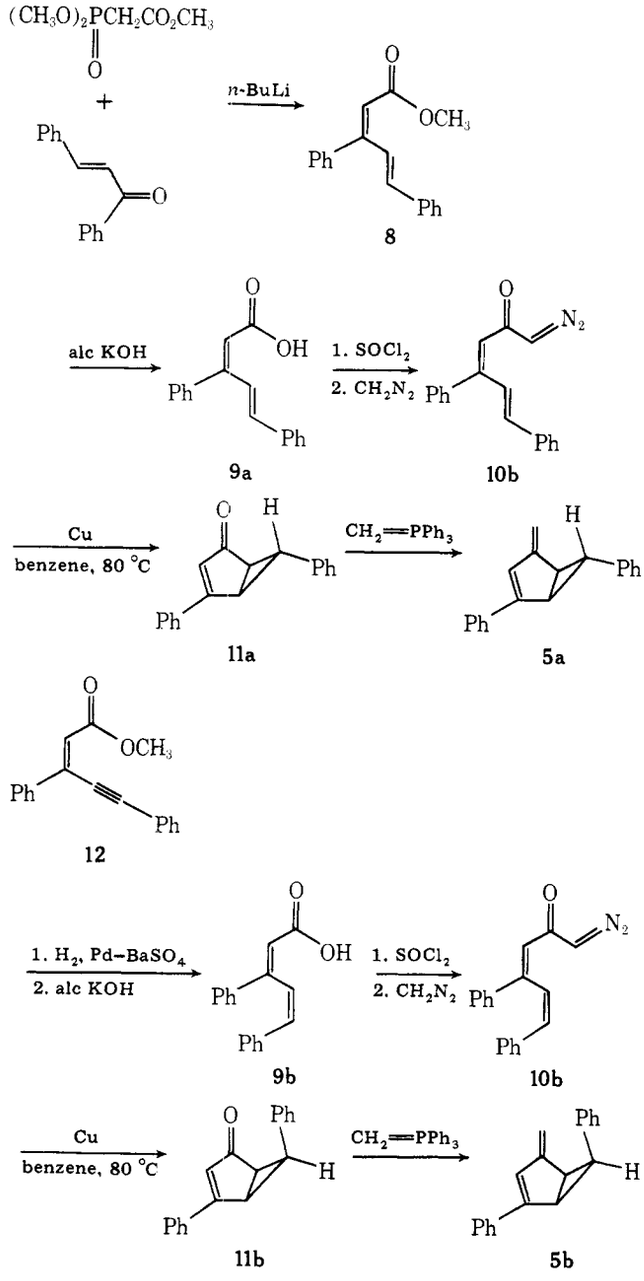
Synthesis of Reactants and Potential Photoproducts. The synthesis of the exo and endo isomers of diphenyl diene **5** (i.e., **5a** and **5b**)are shown in Scheme I; synthesis of the exo and endo isomers of benzo phenyl bicyclic olefins **6a** and **6b** and the corresponding anisyl analogues **18a** and **18b** are shown in Scheme II.

One novel feature of our synthetic efforts is the intramolecular cyclization of the α,β:γ,δ-unsaturated diazoketones (e.g., **10a,b**). Another is the three-ring formation by reaction of dimethylsulfoxonium methylide with methyleneindene π bonds to form **20a** and **22a** (note Scheme III).

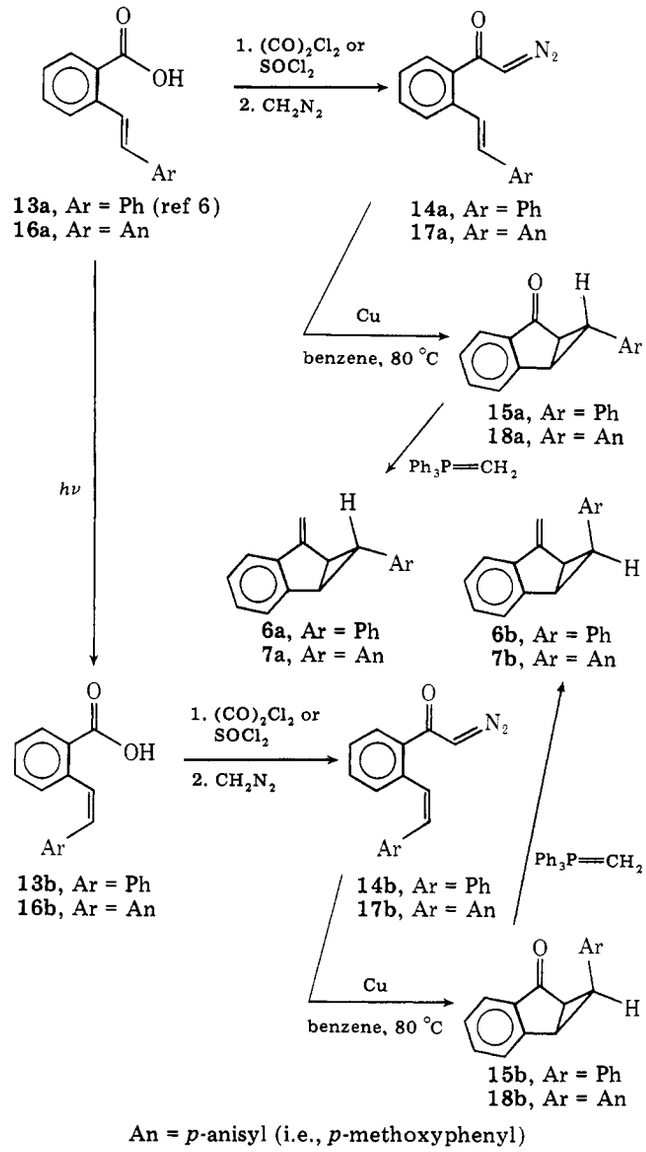
With the photochemical reactants in hand, it proved stra-

0022-3263/78/1943-3283$01.00/0

Scheme I. Synthesis of Photochemical Reactants 5a and 5b

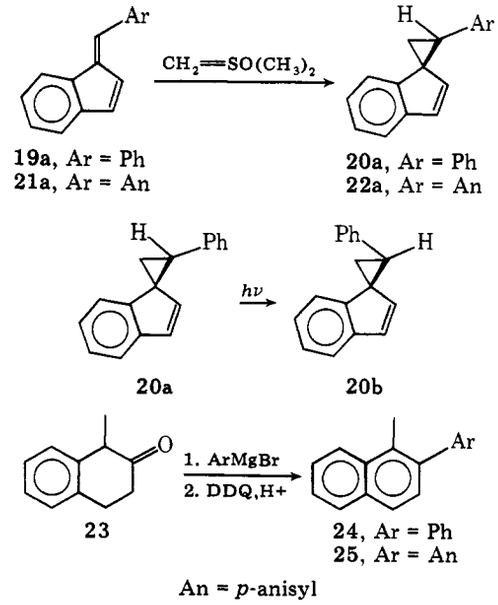


Scheme II. Synthesis of Photochemical Reactants 6a, 6b, 7a, and 7b



An = *p*-anisyl (i.e., *p*-methoxyphenyl)

Scheme III. Synthesis of Potential Photoproducts



An = *p*-anisyl

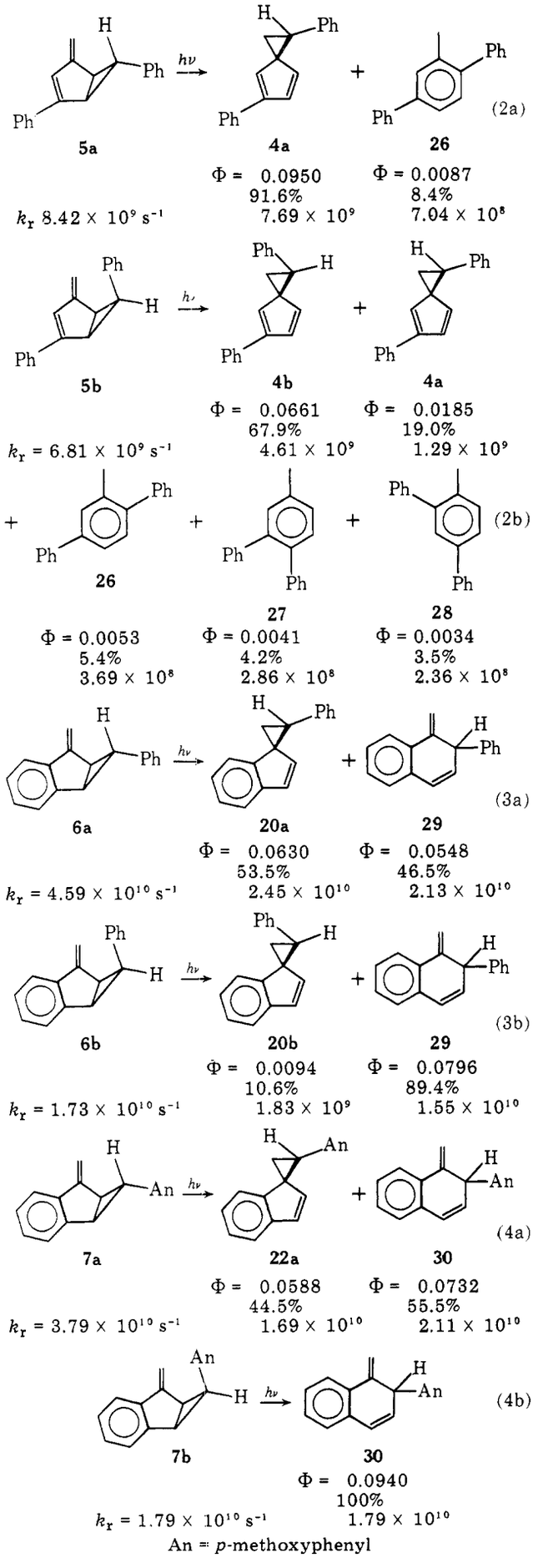
tegic to obtain some of the more likely photoproducts. In this we were guided by the reaction course previously described.[3] These efforts are outlined in Scheme III.

The photochemical products derived from the stereoisomeric diphenyl dienes **5a** and **5b** seemed likely to be known compounds already investigated in our previous study of the 5,6-diphenyl bicyclic dienes **2a** and **2b.**

Results

Exploratory Photochemistry. Irradiation of *exo*-diphenyl diene **5a** afforded the known[3] *anti*-1,5-diphenylspiro[2.4]-hepta-4,6-diene (**4a**) as the major product along with 2,5-diphenyltoluene as a very minor product. Note eq 2a in Scheme IV. Thus the reaction is analogous to that observed in our earlier investigations.[3] Irradiation of the stereoisomeric *endo*-diphenyl diene **5b** led to a more complex product assortment (eq 2b, Scheme IV). Despite the high conversion and the expectation that product stereoisomers might interconvert, there was a slight excess of the syn isomer of the 1,5-diphenyl spiro diene **4b.** Thus, there were early indications of stereospecificity in the rearrangement, as expected from

Scheme IV. Quantum Yields and Kinetic Product Distributions[a-d]



[a] Quantum yields and kinetic product distributions are given below each compound. Extrapolated values for diphenyl diene **5b**. [b] Rates associated with the total reaction are given for each starting material and individual rates of reaction to each product are given under product mixture compositions and are in s^{-1}. [c] In preparative irradiations 1-methyl-2-phenylnaphthalene was also isolated from **6a** and **6b** (eq 3a and 3b). [d] Quantum yield expected error limits are ±5%; rate limits are 20%.

our previous studies. As noted in eq 2b of Scheme IV, in addition to the two spiro products (i.e., **4a** and **4b**) there were formed minor amounts of 2,5-diphenyltoluene (**26**), 3,4-diphenyltoluene (**27**) and 2,4-diphenyltoluene (**28**).

Photolysis of *exo*-benzo phenyl bicyclic olefin **6a** afforded as the major product the *anti*-spiroindene **20a** (see Scheme IV, eq 3a and Scheme III) and two further products. One of these was the 1-methyl-2-phenylnaphthalene (**24**) anticipated and synthesized (vide supra). The other, product **29**, proved to be isomeric with starting material. This labile compound was found to be readily converted to the methylphenyl naphthalene **24** either by heating in refluxing benzene or on treatment with acid. The NMR spectrum revealed the presence of an exocyclic methylene group and also a styryl vinyl group. Both of these were adjacent to a single, benzylic methine. The spectral data, coupled with the rearrangement to methylphenylnaphthalene **24**, indicated 1-methylene-2-phenyl-1,2-dihydronaphthalene as the structure of the compound **29**.

Photolysis of the corresponding *endo*-benzo phenyl bicyclic olefin **6b** proved qualitatively similar. Note eq 3b of Scheme IV. However, here the syn isomer **20b** of spiroindene was formed. Also, now the major product was the methylenedihydronaphthalene **29**.

Irradiation of the corresponding benzo anisyl bicyclic olefins **7a** and **7b** proved remarkably parallel to that of the phenyl relatives (note eq 4a and 4b of Scheme IV), except that no spiro product could be found in the case of the photolysis of the *endo*-anisyl isomer **7b**.

Kinetic Product Distributions, Quantum Yields, and Multiplicity Determinations. It was of interest to determine the kinetic distribution of products. Also quantum efficiencies were desired. Finally, we wished to determine if the bicycle, or slither, reaction was a singlet process in these cases, as in the examples we studied earlier.[3]

Quantum yields were determined using the organic chemist's microbench[7] described earlier. Runs were made to varying conversions below 10% until limiting values were obtained. Analysis was by high-pressure liquid chromatography. Where very minor products were obtained, their distribution was taken from NMR analysis of higher conversion runs. In the case of *endo*-diphenyl diene **5b** it was especially necessary to check the kinetic distribution and quantum yields by extrapolation to zero conversion. The quantum yield proved only a mild function of time at the low conversions (note Experimental Section and Figure 1). However, the partitioning between stereoisomers and the stereospecificity proved more dependent on the extrapolation, as seen in Figure 1.

Quantum yields are summarized in Scheme IV and included in Table I. Details are to be found in the Experimental Section.

The quantum yields allow one to obtain the kinetic distribution of products percentage-wise, and this information, too, is included in Scheme IV.

Finally, in order to determine reaction multiplicity, sensitized irradiations were carried out. Both *m*-methoxyacetophenone and benzophenone sensitizers were used; the latter was used in the quantum yield determinations. It was observed that the endo compounds (i.e., **5b, 6b,** and **7b**) stereoisomerized to give the corresponding exo isomers **5a, 6a,** and

Table I. Direct and Sensitized Quantum Yields

compd	registry no.	conditions	quantum yields[a] spiro product(s)	nonspiro product(s)	reactant isomerization	spiro/nonspiro ratio
5a	66374-26-3	direct	0.0950	0.0087	<0.0003	10.92
		sensitized	<0.0003	<0.0003	<0.0003	
5b	66511-75-9	direct	0.0847	0.0129	<0.0003	6.56
		sensitized	0.0003	0.0003	0.159	
6a	66374-27-4	direct	0.0630	0.0548	<0.001	1.15
		sensitized	<0.001	<0.001	<0.001	
6b	66511-76-0	direct	0.0094	0.0796	<0.001	0.118
		sensitized	<0.001	<0.001	0.117	
7a	66374-28-5	direct	0.0588	0.0732	<0.001	0.803
		sensitized	<0.001	<0.001	<0.001	
7b	66511-77-1	direct	<0.001	0.0940	<0.001	<0.01
		sensitized	<0.001	<0.001	0.126	

[a] Quantum yields are extrapolated to zero conversions. Except for endo diene **5b** the dependence on extent conversion proved minor. Error limits ±5%.

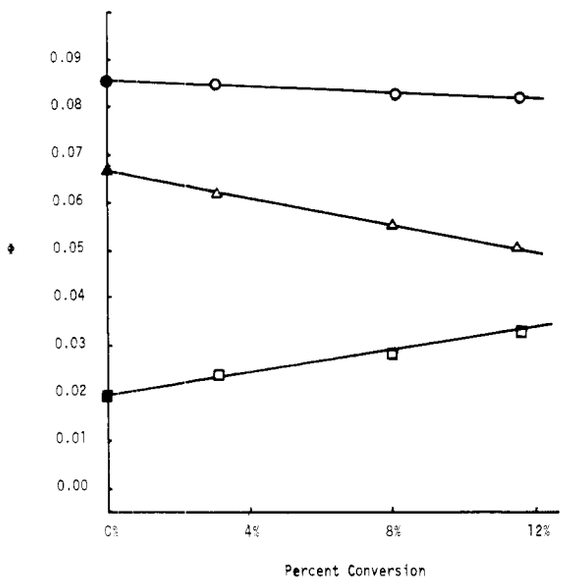


Figure 1. Plot of quantum yields of 1,5-diphenylspiro[2.4]hepta-4,6-diene (**4a,b**) from *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]-hex-3-ene (**5b**) vs. percent conversion: ○, total formation of **4a** and **4b**; △, formation of **4b**; □, formation of **4a**. Darkened symbols on the ordinant indicate the extrapolated values.

7a. However, no bicycle rearrangement products could be found. The exo stereoisomers proved to be unreactive in the sensitization experiments. The sensitization results are included in Table I. Where no reaction was observed, upper limits are set.

It can be seen that the bicycle rearrangement occurs in direct irradiations and not from the triplets when independently generated. This means that the rearrangements are singlet processes.

Determination of Excited Singlet Rearrangement and Decay Rates. It was of considerable interest to determine the excited singlet rearrangement rate in order to ascertain if this was a function of structure. The method we have described earlier[4] has proven especially useful.[8,9] This involves single photon counting using an on-line minicomputer as a multichannel analyzer and also for effective deconvolution by an iterative convolution technique.

In our hands,[10] simulated deconvolution can give singlet decay rates (i.e., k_{dt}'s) and lifetimes (i.e., τ's) with an uncertainty of ±16 ps. Thus, rates as rapid as 2×10^{10} s^{-1} (i.e., a lifetime of 50 ps) may be measured with a 32% error. The k_{dt}'s obtained are used along with quantum yields (i.e., the ϕ_r's) to give the desired excited singlet rate constants (the k_r's) as given in the equation

$$k_r = \phi_r k_{dt} \tag{5}$$

Unfortunately, often the decay constants are faster than 2×10^{10} s^{-1} and one would like to obtain the still faster rate constants without an excessive increase in relative error. For this our method of magic multipliers[4] is of utility. This depends on the often observed increase in excited-state lifetime and fluorescence quantum yield at lower temperatures. With an increased lifetime and decreased rate of decay, an excited state decay too rapid to measure at room temperature quite often becomes accessible at 77 K. The ratio of intensities of emission at 77 K and room temperature (e.g., 293 K) is readily measurable. This ratio is our magic multiplier and is given by the equation

$$M = \phi_f^{77}/\phi_f^{rt} = k_{dt}^{rt}/k_{dt}^{77} \tag{6a}$$

Transposition as in the equation

$$k_{dt}^{rt} = M k_{dt}^{77} \tag{6b}$$

allows us to obtain the desired, rapid room temperature rate of decay.

The excited-state rates of decay, lifetimes, magic multipliers, and reaction rates are collected in Table II. Also, the room temperature reaction rate constants are included in Scheme IV.

Interpretative Discussion

Occurrence and Generality of the Bicycle Rearrangement. The reaction presently under study is a special case of the walk rearrangement, for which both thermal[11] and photochemical[12] examples are known. Two stereochemical courses are possible for these reactions in the case of bicyclo[*n*.1.0] systems. In one, the endo group becomes exo and vice versa. This is termed a "pivot mechanism". In the other the endo group remains endo and the exo group stays exo. Previously we have termed this a "slither reaction",[3,11c,12] but a "bicycle mechanism" is more descriptive (vide infra). Thus there are two variants of the rearrangement.

The photochemical rearrangement presently described involves the three-ring carbon of a 2-methylenebicyclo[3.1.0]hex-3-ene walking around the five-ring and also out onto the exocyclic π bond. Only a few examples of this reaction are known. In addition to the three examples of our previous study[3] described above, only two other examples have been observed.[13]

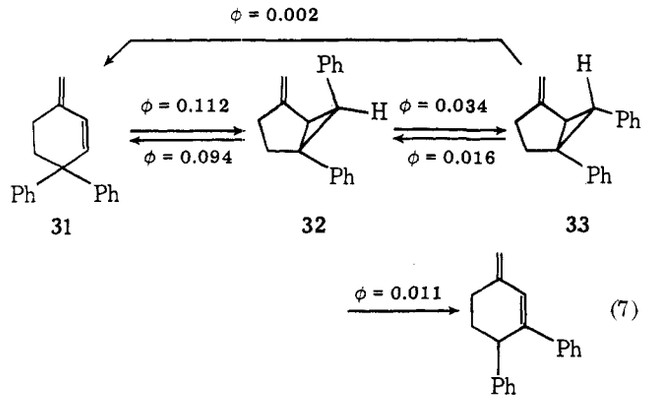
Hence, the present study provides needed evidence that the

Table II. Summary of Singlet Rates and Lifetimes[a]

compd	M	temp, K	τ, ps	$^1k_{dt}$, s^{-1}	^1k_r, s^{-1}
5a	42	293	12.4	8.09×10^{10}	8.42×10^9
		77	516	1.94×10^9	
5b	36	293	14.4	6.97×10^{10}	6.81×10^9
		77	524	1.91×10^9	
6a	100	293	2.57	3.89×10^{11}	4.59×10^{10}
		77	256	3.90×10^9	
6b	91	293	5.13	1.95×10^{11}	1.73×10^{10}
		77	468	1.91×10^9	
7a	120	293	3.47	2.88×10^{11}	3.79×10^{10}
		77	415	2.41×10^9	
7b	114	293	5.27	1.90×10^{11}	1.79×10^{10}
		77	601	1.66×10^9	

[a] Error limits ±20% for rates.

reaction is, indeed, general. It is seen that benzo derivatives (i.e., **6** and **7**) of the basic 2-methylenebicyclo[3.1.0]hex-3-ene system also give the rearrangement. This is relevant, since the same general system, minus the endocyclic double bond, does not give the rearrangement, but rather other photochemistry[14] as shown in eq 7.



(7)

The Overall Reaction Mechanism. The first point of interest is the formation of toluenes (note eq 2a and 2b), as well as methylnaphthalenes and their 1-methylenedihydronaphthalene precursors (note eq 3a, 3b, 4a, and 4b). In our previous work we noted[3] that these can be construed as reaction mechanism "markers", telling where the reacting molecule has been mechanistically. This point can be seen by inspection of Scheme V, which gives a mechanism in terms of traditional organic resonance structures. Here the main bicycle steps are depicted with heavy arrows. The toluene derivatives can be seen to derive from biradical species along this main reaction pathway. In each case a Grob fragmentation of a 1,4-biradical is involved. The toluenes thus can be seen to provide support for the biradical species postulated, and these products trace the topology of the migration of the PhCH moiety as it traverses the molecule.

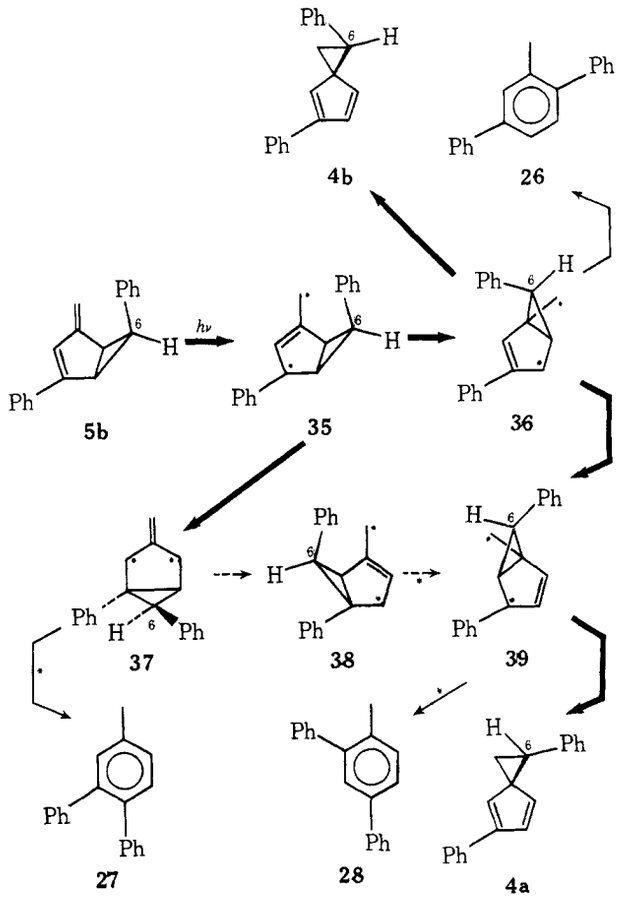
It is of some interest to note that a number of the species in Scheme V were shown to be involved in our previous study[3] beginning with the excited state of 2-methylene-5,6-diphenylbicyclo[3.1.0]hex-3-ene (**2**). The pathways utilized in that study[3] are marked in Scheme V.

The reaction mechanism in the cases of the benzo analogues is similar and discussion is deferred for pinpointing differences.

Reaction Stereospecificity. The first point to be noted is that the reaction is stereospecific as in our previous work[3] and in agreement with that of Hamer and Stubbs.[13a] Thus, the *endo*-aryl group assumes a product configuration in which the aryl group is oriented in the same direction as in the reactant.[15]

This excludes a mechanism involving complete three-ring

Scheme V. Mechanism for Rearrangement of *endo*-Diphenyl Diene **5b**

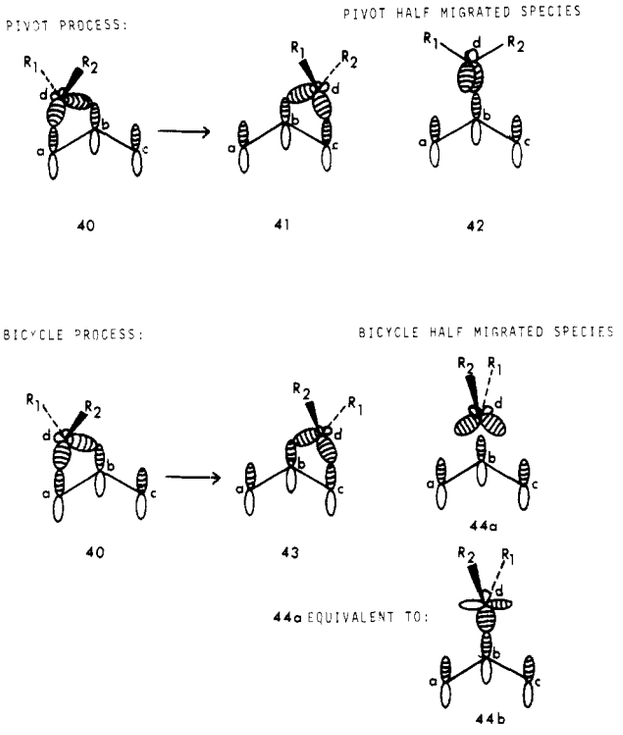


(▬) Main bicycle pathways. (—) 1,4-Biradical Grob side routes. (- -) Potential but unlikely pathways in present study. (*) Pathways shown in ref 3 to be utilized in the photochemistry of 2-methylene-5,6-diphenylbicyclo[3.1.0]-hex-3-ene.

fission to give phenylcarbene plus 3-phenylfulvene (or benzofulvene), followed by readdition of the carbene to the exocyclic methylene double bond. Although, it is seen that all products derive from these two fragments, nevertheless the reaction stereospecificity rules out such a mechanism. A carbene plus fulvene pair would not remember the stereochemistry of reactant, and the same product configuration would result from either of two stereoisomeric reactants.

Scheme V presents an overall reaction mechanism. In this we have depicted the experimentally observed reaction stereochemistry without rationalization. Thus, the transforma-

Scheme VI. Two Stereochemical Mechanisms for Carbenoid Migration



tion of excited state **35** to **36** has been shown as proceeding with the *endo*-phenyl remaining endo. This is tantamount to inversion of configuration[16] at the benzylic carbon (i.e., C-6 of the bicyclic system). Similarly, the conversion of bicyclic biradical **36** to bicyclic biradical **39** and the conversion of bicyclic excited state **35** to bicyclic biradical **37** are shown with the same inversion stereochemistry. Also the same is true of the final formation of the spiro three-rings of the products **4a** and **4b.**

A parallel reaction course is envisaged for the *exo*-diphenyl diene rearrangement except that the phenyl group at C-6 remains exo. For the benzo derivatives, again, the same reaction stereochemistry accounts for the observed products.

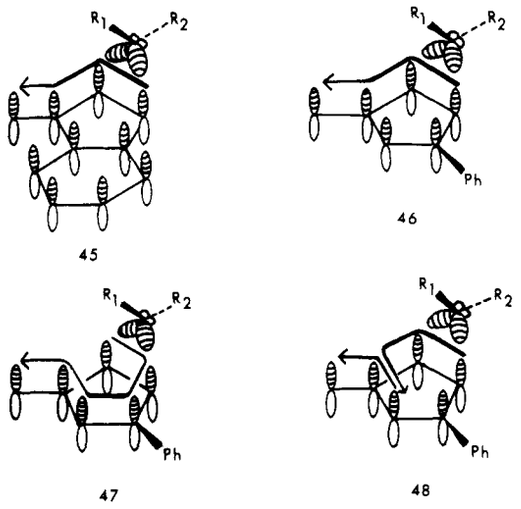
However, we have not justified the preference for this reaction stereochemistry. Years ago[12b] we noted a preference for such stereochemistry in the case of the santonin to lumisantonin conversion and more recently[11d] we have further analyzed the possible stereochemistry in such rearrangements. We termed the two alternatives pivot and slither mechanisms. Thus, in such rearrangements the migrating carbon has two stereochemical options as it moves from a set of two carbons (e.g., a and b) to the next set (i.e., b and c). The two mechanisms are depicted in Scheme VI. In each the a,b,d three-ring of species **40** is lost and converted into the b,c,d three-ring as in species **41** or **43.**

As a result of pivoting about bond b–d, the pivot process can be seen to reverse the endo and exo relationships of groups R_1 and R_2. Conversely, the slither, or bicycle, process can be seen to keep the endo group R_2 endo and to maintain the exo group R_1 as exo.

It is instructive to inspect the species at half reaction. In the pivot species **42** there is a σ bond due to b–d overlap while the hybrid orbital at center d overlaps with the orbitals at a and c.

For the bicycle mechanism, there are two quantum mechanically equivalent representations for the half reaction species; these are **44a** and **44b.** The first, **44a,** is clearly related to starting and final species (i.e., **40** and **43**) except with intermediate positioning. Carbon d has two sp^5 hybrid orbitals. The second, **44b,** superficially appears different in that it

Scheme VII. Topology of Bicycling (i.e., Slithering) on the Fulvene Systems



consists of a p orbital at center d and also has an sp^2 hybrid orbital. It can be seen to appear to maintain σ bond b–d while undergoing inversion of configuration at center d by virtue of using both lobes of its p orbital.

We have noted before[11d] that two such representations are truly equivalent.[17,18] An easy way to follow the stereochemistry of the bicycle mechanism is to consider the two sp^5 orbitals as front and rear wheels of a bicycle which then rolls along the pathway of a π system. The two groups R_1 and R_2 are positioned as handlebars of a bicycle, and thus in bicycling around a ring the endo handlebar, or group, remains endo and the exo one stays exo.

Inspection of the six examples presently described, including three sets of endo and exo stereoisomers, reveals that the bicycle (or slither) mechanism very simply accommodates the experimental stereochemistry of endo reactant giving syn product and exo reactant giving anti product.[15] In the cases of the benzo phenyl and anisyl bicyclic olefins **6** and **7** the bicycling carbon does so in a counterclockwise[19] direction. The same is true for the *exo*-diphenyl diene **5a.** In the case of the *endo*-diphenyl diene **5b** the major kinetic product **4b** again arises from counterclockwise bicycling. The bicycling (or slither) topology is depicted in Scheme VII.

The alternative to the bicycle mechanism consists of a series of pivot processes. It can be seen that two pivot steps of the kind depicted in Scheme VI leave an endo group (e.g., R_2) endo and an exo group (e.g., R_1) exo; this is the same outcome the bicycle mechanism affords. Thus any reaction consisting of an even number of pivot steps is stereochemically equivalent overall to a reaction resulting from the bicycle alternative.

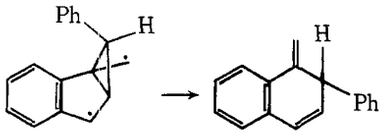
However, a clue to the solution of this problem was found in our earlier observation that the endo isomer **2a**[3b] led to enhanced Grob fragmentation of the diradical intermediate species with formation of toluene byproducts. Thus, it seemed likely that diradical species derived from the endo isomer were more likely to undergo such internal bond fission (i.e., Grob fragmentation[20]) where there was steric relief of strain deriving from *endo*-phenyl–five-ring interaction. Fragmentation of the cyclopropyl diradicals in the bicyclo[3.1.0]hexane framework results in flattening of the peripheral six-ring to give a 1-methylene-2,4-cyclohexadiene system.

The present study tested (1) the generality of the endo tendency to Grob fragment and (2) the effect of a strategically placed fused benzo group to enhance the *endo*-phenyl steric interaction.

Thus, after *one* step to give a diradical species **58b,** a difference between the bicycle and pivot processes does exist.

Table III. Quantum Efficiencies for Bicyclic Dienes 1 and 2[3]

compd	registry no.	conditions	quantum yields: spiro product(s)	quantum yields: nonspiro product(s)	quantum yields: reactant isomerization
1	29443-86-5	direct	0.041	0.038	
		sensitized	0.0001	0.0001	
cis-**2b**	33823-63-1	direct	0.082	0.0007	
		sensitized			0.001
trans-**2a**	29444-92-6	direct	0.039	0.0053	
		sensitized			0.28



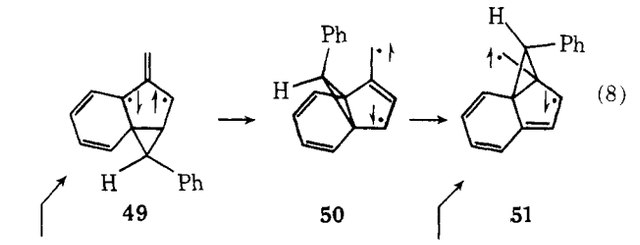
58b (endo) **29**

From endo reactant the bicycle process affords endo diradical, while the pivot process leads to exo diradical. The exo reactants would afford exo diradicals as **36a** and **58a** in a bicycle process but endo diradicals in a pivot mechanism. To the extent that steric factors are indeed involved, the bicycle mechanism would lead to an excess of Grob fragmentation starting with endo reactants, while the pivot mechanism would lead to an excess of fragmentation from the exo reactants.

Experimentally the same preference for the endo reactant to give toluene byproducts was indeed encountered with the total toluene product yield being greater from endo reactant, hence, signifying that this is a general trend. More dramatically, in the case of the benzo analogues, the Grob fragmentation became the predominant reaction course for the endo reactants. This predominance may arise because of greater localization of the two odd electrons as a result of fusion of the benzo ring in place of a double bond.

One point of interest is the formation of the minor reaction products in the photolysis of *endo*-diphenyl diene **5b.** In the case of the minor spiro diene **4a,** there are two possibilities. Note Schemes V and VII. The first possibility is that this product arises from clockwise bicycling around the five-ring (**35–37–38–39–4a** in Scheme V). It would make sense that only the endo isomer might undergo such a process, since in the exo isomer, two (bulky) phenyl groups would have to pass one another in such a mechanism. The exo isomer rearranges with no competing minor stereochemical course. The difficulty with this mechanism of clockwise bicycling is that it passes through species **38** (note Scheme V) which, in the absence of ad hoc specifications, should be the excited state of *trans*-2-methylene-5,6-diphenylbicyclo[3.1.0]hex-3-ene (**2a**). The singlet energy (115 kcal/mol) of this species is higher than that of reactant **5b** (94 kcal/mol) which has an added phenyl group at the end of a butadiene moiety. Thus any mechanism passing through this excited state (i.e., **38**) is energetically unreasonable. If **38** were ground state at this point in the mechanism, it would not proceed further, and no *trans*-2-methylene-5,6-diphenylbicyclo[3.1.0]hex-3-ene (**2a**) was observed in our studies. The second and more reasonable possibility is a counterclockwise overshoot plus backup mechanism (**35–36–39–42** in Scheme V or **48** in Scheme VII).

Another point of interest is the complete reaction stereospecificity for the benzo aryl bicyclic olefins **6** and **7** contrasted with the incomplete stereospecificity of the diphenyl bicyclic diene **5.** Reference to the structures and mechanisms in Scheme V written for the diphenyl bicyclic diene **5** reveals that utilization of either the clockwise bicycle mechanism or the counterclockwise overshoot plus backup leads to disruption of benzo aromaticity.[21] Note, for example, structures such as



(8)

49 **50** **51**

clockwise mechanism

counter-clockwise overshoot path

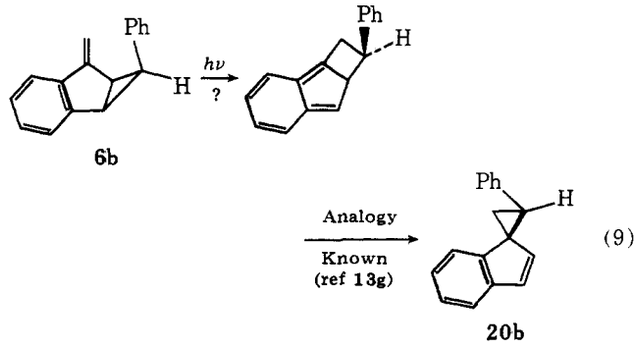
49, 50, and **51.** This leaves counterclockwise bicycling without overshoot as the preferred reaction pathway in this case.

Significance of Quantum Efficiencies and Excited Singlet Rates. To begin our discussion, we note that there is a strikingly small spread of reaction efficiencies of the various methylenebicyclic[3.1.0] systems studied (note Scheme IV and Table I), if one includes the total product distribution. Reference to our previous studies[3] (note Table III) reveals that the 2-methylene-6,6-dimethylbicyclo[3.1.0]hex-3-ene (**1**) and the 2-methylene-5,6-diphenylbicyclo[3.1.0]hex-3-enes (**2a** and **2b**) react with similar order of magnitude efficiencies. Thus all quantum yields of disappearance range from 0.04 to 0.13.

Along similar lines, we note (see Table II and Scheme IV) a remarkably small spread in the excited-state rate constants.

This suggests relatively little stabilization by the aryl groups present, whether on the migrating carbenoid carbon or substituted on the remainder of the system. Discussion of this point is deferred for consideration of the reaction electronics.

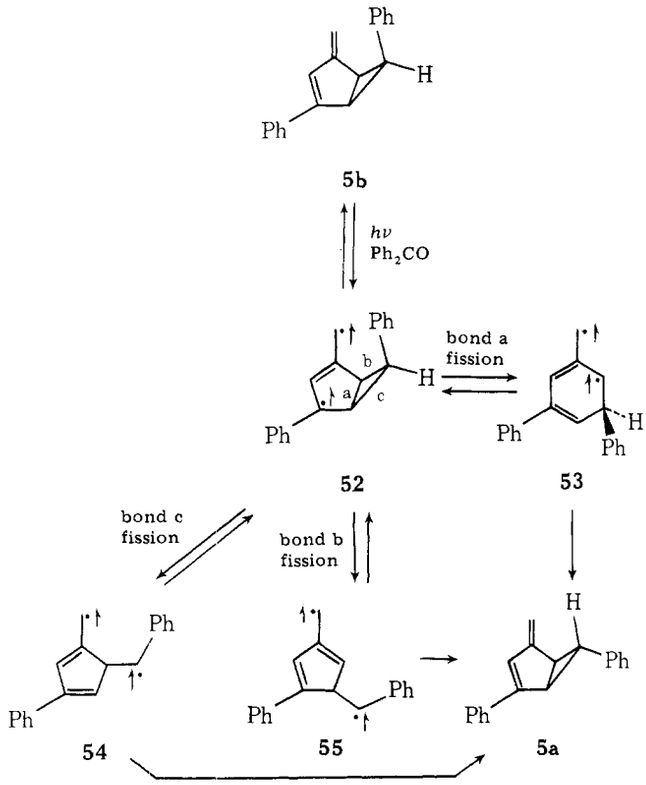
Additionally, a major conclusion which derives from our observations is that an intriguing alternative mechanism considered by Hamer and Stubbs[13a] can be ruled out. Applied to the benzo cases presently studied the mechanism predicts loss of aromaticity of the benzo ring; this is shown in eq 9.



(9)

Thus, one would expect a major inhibition of the reaction efficiency and rate for the benzo analogues, and this is not observed.

Scheme VIII. Mechanism of Stereoisomerization of Triplet Bicyclic Diene



Reaction Multiplicity. Since the slither, or bicycle, rearrangement proceeds on direct irradiation but not on sensitized photolysis, this rearrangement can be seen to be a singlet process. Conversely, endo–exo isomerization of the bicyclic and benzo bicyclic olefins occurs only on sensitization, where the triplet is generated independently. This signifies that the stereoisomerization process is preferred by the triplet, but unfavorable from the singlet.

For the triplet stereoisomerization three possible bonds may be involved—a, b, or c. This is illustrated in Scheme VIII for the case of diphenyl bicyclic diene **5**; the cases of benzo bicyclic olefins **6** and **7** are parallel. In each case, after three-ring fission opening, free rotation and reclosure affords the observed stereoisomer. While there is no experimental evidence in this case, in the example of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one triplets[22] it is an out of plane bond (here b or c) which is opened in preference as a consequence of better overlap with the π system.

The preference of the triplet for this bond fission and stereoisomerization and its reluctance to undergo the bicycle reaction is discussed subsequently in connection with our MO treatment of the reactions. However, we note for the time being that there is a tendency for hydrocarbon triplets to undergo such bond fission as has been observed in the stereoisomerization of *cis*- and *trans*-4,5-diphenylbicyclo[3.1.0]-hex-2-enes,[23] since triplets can minimize energy more readily than excited singlets by such bond fission[23,24] to afford diradicals.[25] Conversely, concerted processes such as the bicycle or slither rearrangement tend to prefer the S_1 state as noted earlier.[23,24]

Theoretical

The Concept of Electronic Excitation Distribution; The ΔP Matrix and Its Variants. An index which we have found exceptionally intriguing and useful is ΔP_{rt} representing the change in bond order between atoms r and t on electronic excitation.[26a] Such an element can be derived as a difference in ground- and excited-state bond orders obtained from sophisticated (e.g.) SCF–CI calculations or, in a simpler SCF or Hückel approximation, just as a difference in bond orders of two MO's such as k and l, where k is the MO losing the electron and l is the MO receiving it on electronic excitation. The **ΔP** matrix is a convenient way of storing these elements; the element in row r and column t gives the change in bond order between atomic or hybrid orbitals r and t on excitation.

Thus, certain of the elements will be negative, indicating that on excitation the molecule has become more antibonding at these sites. Other elements will be positive, indicating that the sets of orbitals corresponding to the indices r and t have become more bonding in the excited state relative to the ground state. Still other elements will be zero or nearly zero, indicating that excitation has not perturbed the wave function at these molecular sites.

Hence it is possible to point to portions of the molecule where electronic excitation has had little or no effect and to note other portions of the molecule where the excitation energy is heavily concentrated, as evidenced by large changes in bond orders. Similarly, one can use the diagonal elements of the **ΔP** matrix which represent changes in electron densities at atoms resulting from electronic excitation.

As an example, one might envisage a molecule containing a 1-phenylbutadiene moiety and a separated phenyl chromophore. Inspection of the **ΔP** matrix shows that the elements corresponding to overlap of orbitals of the isolated benzene ring are zero, while those of the phenylbutadiene moiety are nonzero. This fits intuitive expectation that only the lower energy phenylbutadiene moiety will be excited in (e.g.) S_1. If saturated portions of the molecule were included, as in an extended Hückel or CNDO calculation, these portions would be found to be minimally affected by excitation.

Bond orders are related to energy contributions, but to obtain these where different hybridizations are encountered it is convenient to multiply each bond order term by $[H_{rt} + F_{rt}]$. (H_{rt} and F_{rt} are the matrix elements between orbitals r and t using one-electron and SCF energy operators.[26b]) This corrects for changes in S character and overlap. The resulting terms will have the reverse sign of the ΔP_{rt} matrix elements and are termed $\Delta E'_{rt}$, where $\Delta E'_{rt} = \Delta P_{rt}[H_{rt} + F_{rt}]$. The $\Delta E'_{rt}$ terms can be construed to be local contributions to the total electronic excitation energy. Contributions due to nuclear–nuclear repulsion are neglected for convenience, and for simplicity a ground-state $[H_{rt} + F_{rt}]$ is used, since we use the matrix for only semiquantitative purposes.

Thus, the use of the **ΔP** and **ΔE′** matrices involves inspection of these to note where there are large positive or negative elements and where there are zero or nearly zero elements. Small elements tell us that these local bonds are not appreciably excited independent of which type matrix we use. This leads us to the concept of local degeneracies, that is, sites of the molecule where the ground and excited states (or, more naively, highest bonding and lowest antibonding MO's) have equal energy and bond order contributions. However, it is important to note that while a negative ΔP_{rt} matrix element signifies a local increase in antibonding, the corresponding $\Delta E'_{rt}$ matrix element will be positive and signifies an increase in local electronic bond energy (i.e., for the bonding between orbitals r and t). Similarly, where a positive ΔP_{rt} occurs and thus indicates an increase in bonding between orbitals r and t on excitation, a negative $\Delta E'_{rt}$ element will result and will indicate an energy lowering (i.e., stabilization) resulting from overlap r–t.

The preceding thus describes an approach to defining the effect of electronic excitation on bonding at different sites around the molecule and also the partition of the excitation energy. Applications of the method to the systems at hand are presented below.

Migration and Redistribution of Electronic Excitation

during Reaction. Once one has developed a method for discussion of the distribution of electronic excitation in photochemical reactants, the inviting possibility suggests itself that one can follow the redistribution of this excitation as the excited-state molecule traverses the reaction coordinate. While in most photochemical reactants one generally can identify classical chromophores where excitation is likely to be concentrated, this is not invariably the case in a reacting species where bonds are in the process of being formed and broken. Additionally, there is the question whether groups which are viewed merely as substituents, such as phenyl and other aryl moieties, remain ground state in character as the reaction progresses. This should vary from case to case, and the method at hand allows one to follow the $\Delta\mathbf{P}$ and $\Delta\mathbf{E}'$ matrices along the reaction coordinate. Finally, one might inquire whether there is a relationship between the distribution of the local energy contributions (i.e., the $\Delta E'_{rt}$ matrix elements, or alternatively the ΔP_{rt} matrix elements) and the reaction course.

The approach of following migration of electronic excitation during reaction is applied to the photochemistry of the present study. This application is postponed in order to allow complete presentation of the theoretical concepts.

Local Degeneracies, Squelching the ΔP's, Probing for the Ground-State Surface by Molecular Distortion, and Conversion of Electronic into Vibrational Energy. With the concept of the two matrices indicating which portions of a molecule are endowed with electronic excitation and to what extent, the question arises whether we can find molecular changes (e.g., bond stretching, twisting, etc.) which are capable of converting electronically excited sites of the molecule into unexcited sites. This is equivalent to effecting local degeneracies. Dissipation of local excitation and enforcing a local degeneracy can be effected by squelching the ΔP_{rt} or $\Delta E'_{rt}$ matrix element corresponding to that portion of the molecule.

If a ΔP_{rt} element is negative (i.e., the corresponding $\Delta E'_{rt}$ element is positive), this local excitation can be reduced by diminishing the overlap corresponding to the excited bond. We might consider stretching the bond, or alternatively, twisting it. If the ΔP_{rt} element is positive (and $\Delta E'_{rt}$ is negative), then we need to compress the bond and increase the overlap.[27]

By such molecular distortions we are, in effect, converting electronic excitation into vibrational energy. In some cases this corresponds to converting π system electronic excitation into σ bond vibrational energy.

Thus we have a mechanism for dissipating electronic energy into vibrational energy by local distortions.[28] The very rapid rate of vibrational energy equilibration postulated by the RRKM theory[29] suggests that one or two such distortions can dissipate energy subsequently to all available modes of vibration of the molecule. Thus a local leak of electronic excitation should be enough.

Distortion along one geometric coordinate leads to diminished electronic excitation and thus an approach of ground and electronically excited-state potential energy surfaces. The near degeneracy, however, is at a geometry corresponding to an upper vibrational state of the molecular ground state. For a photochemical reaction involving a very extended reaction coordinate, corresponding to a complex series of molecular reorganizations, our ΔP_{rt} will predict only a short distance along this coordinate and successive species must be treated in the same way.

Applications to the Present Case. As a beginning, to determine what electronic effects were controlling the bicycle reaction, we carried out SCF–CI calculations. At the SCF level it was possible to inspect the MO eigenfunctions for qualitative understanding; and, with configuration interaction one could be more certain which excitations were involved. Overall bond orders and energies were derived from the total calculations, which included both singly and doubly excited configurations. For details note the section on Calculations. For the basis sets utilized note Figure 2. Our calculations were done on starting bicyclic diene **56** with one phenyl group at carbon-6 as a most appropriate model. Calculations were also carried out on the corresponding spiro product **60,** on the cyclopropyldicarbinyl diradical intermediate **58** (i.e., exo isomer of **36** without the C-4 phenyl group), and on the two 1,3-diradicals **57** and **59** (note also Figure 3). Also calculations were carried out on the benzo analogue, however, without the C-6 phenyl group (i.e., on **61**); the biradical **62,** derived from one bicycle step, was studied. Finally, the bicyclic diene **63,** having a phenyl group on the diene system, and the derived 1,4-biradical **64** (one bicycle step) were investigated. The basis set numbering for systems **56–60** are depicted explicitly in Figure 2. Similar numbering was used for **61–64** with the benzo basis orbitals indicated in Figure 2.

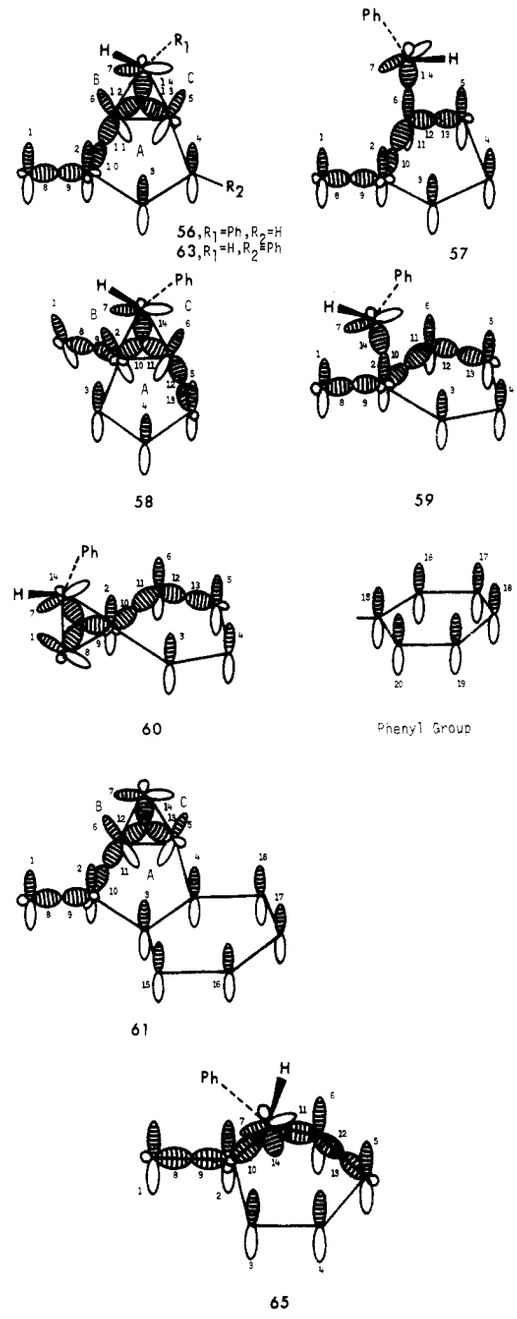


Figure 2. Basis sets for SCF–CI calculations.

Table IV. Distribution of Electronic Excitation in Bicyclic Olefins 56, 61, and 63

bond	phenyl bicyclic diene 56[a]		bond	benzo bicyclic olefin 61[b]		bond	phenyl bicyclic diene 63[c]	
r,t	ΔP_{rt}	$\Delta E'_{rt}$	r,t	ΔP_{rt}	$\Delta E'_{rt}$	r,t	ΔP_{rt}	$\Delta E'_{rt}$
1,2	−0.2620	2.3052	1,2	−0.1754	1.5487	1,2	−0.2401	2.1096
2,3	0.1624	−1.0808	2,3	0.1150	−0.7603	2,3	0.1950	−1.3076
2,6	0.0856	−0.0399	2,6	0.0310	−0.1041	2,6	0.0297	−0.0998
3,4	−0.2382	2.0939	3,4	−0.1103	0.7794	3,4	−0.3307	2.8506
4,5	0.1186	−0.4153	4,5	0.0840	−0.2848	4,5	0.0500	−0.1721
2,12	0.0313	−0.0790	2,12	0.0086	−0.0217	2,12	0.0108	−0.0271
4,13	0.0454	−0.1164	4,13	0.0182	−0.0498	4,13	0.0165	−0.0419
7,15	0.1281	−0.7178	3,15	−0.1184	0.8400	4,15	0.1893	−1.0881
15,16	−0.0969	0.6932	15,16	−0.1720	1.2520	15,16	−0.1234	0.8788
16,17	0.0390	−0.2839	16,17	−0.0500	0.3617	16,17	0.0355	−0.2588
17,18	−0.0462	0.3344	17,18	−0.0840	0.6090	17,18	−0.0595	0.4303
18,19	−0.0581	0.4213	4,18	−0.1850	1.3385	18,19	−0.0670	0.4857
19,20	0.0414	−0.3008				19,20	0.0406	−0.2952
15,20	−0.0869	0.6227	5,6	−0.0254	0.1694	15,20	−0.1203	0.8582
			5,12	−0.0047	0.0211			
5,6	−0.0234	0.1543	6,13	0.0024	−0.0108	5,6	−0.0195	0.1300
5,12	−0.0041	0.0183	12,13	0.0001	−0.0019	5,12	−0.0010	0.0045
6,13	0.0020	−0.0090				6,13	0.006	−0.0027
12,13	0.0003	−0.0057	6,7	−0.0186	0.1236	12,13	−0.0011	0.0210
			6,14	−0.0046	0.0205			
6,7	−0.0880	0.5834	7,12	−0.0122	0.0544	6,7	−0.0253	0.1680
6,14	0.0003	−0.0013	12,14	0.0018	−0.0344	6,14	−0.0028	0.0125
7,12	−0.0355	0.1577				7,12	−0.0089	0.0397
12,14	0.0024	−0.0457	5,7	−0.0433	0.2874	12,14	0.0013	−0.0248
			5,14	−0.0139	0.0620			
5,7	−0.0930	0.6044	7,13	−0.0100	0.0456	5,7	−0.0278	0.1842
5,14	−0.0095	0.0416	13,14	−0.0026	0.0497	5,14	−0.0063	0.0281
7,13	−0.0357	0.1589				7,13	−0.0091	0.0406
13,14	−0.0014	0.0267				13,14	−0.0002	0.0038

[a] Registry no.: 66374-29-6. [b] Registry no.: 65680-45-7. [c] Registry no.: 66374-30-9.

Excitation Localization in the Reactant Excited States. The first application of the ideas expressed above was determination of the distribution of electronic excitation in the reactant bicyclic diene. In view of the size of the system of interest (i.e., diphenyl bicyclic diene **5**), two slightly truncated models were used. These were monophenyl-substituted bicyclic dienes **56** and **63.** Selected ΔP_{rt} matrix elements for these two excited singlets are given in Table IV.

It is seen that appreciable ΔP_{rt} matrix elements are found mainly for butadiene and phenylbutadiene portions of the molecule. This corresponds to one's intuitive feeling that low-energy chromophores are selectively excited. Thus, for example, the C-6 phenyl group is only slightly perturbed on electronic excitation.

A lesser but real amount of excitation is found in the three-ring bond orbital system and also the overlapped pair 4–5. This can be seen independent of whether we look at ΔP_{rt} or $\Delta E'_{rt}$ matrix elements.

The case of the benzo bicyclic olefin **61** (note Table IV again) has appreciable elements corresponding mainly to the styryl moiety.

Diffusion of Electronic Excitation during Reaction. Utilization of ΔP_{rt} and $\Delta E'_{rt}$ Values in Following Flow and Reaction Course. Turning now to the excited-state rearrangements, we note that as the reaction proceeds, electronic excitation energy no longer is concentrated in the original diene moiety or in any single portion of the molecule. Thus, in species **57, 58,** and **59** electronic excitation has diffused throughout the system. This can be seen in Table V where the appreciable ΔP_{rt} elements are spread throughout the molecular system. The same general conclusion is reached using the $\Delta E'_{rt}$ elements except that here some larger concentrations of excitation energy are found. Interestingly, the C-6 phenyl group is seen to be only slightly excited from inspection of the $\Delta E'_{rt}$ elements. Another point of interest concerns the bond order and energy elements corresponding to 5–7 vs. 2–7 overlap in species **57.** ΔP_{57} is quite negative in contrast to ΔP_{27}, which is slightly positive. A negative ΔP_{rt} suggests that the bonding should be weakened, while a positive ΔP_{rt} indicates that strengthening the bond should help the reaction. This is precisely what happens as the molecule proceeds bicycling along the reaction coordinate at this point. The corresponding argument, based on the **ΔE′** matrix, shows that $\Delta E'_{57}$ is very positive, while $\Delta E'_{27}$ is slightly negative. Thus it is the "high energy bond" which is selectively broken in proceeding onward to product.

These results fit the generalization that overlaps corresponding to negative ΔP_{rt} elements or positive $\Delta E'_{rt}$ elements need to be diminished to obtain photochemical reaction, while overlaps corresponding to positive ΔP_{rt} elements or negative $\Delta E'_{rt}$ elements need to be increased for reaction. If such overlap changes lead toward a photochemical reaction product, then successful photochemistry is expected. If the overlap changes do not lead toward a product, or lead away from a possible product, then the reaction is forbidden.

Interestingly, ΔP_{57} diminishes in absolute value by the time species **58** is reached. Another point of interest is that inspection of the **ΔE′** matrix shows that the original butadiene excitation is still present, although considerably diminished. Also, the ΔP_{rt} and $\Delta E'_{rt}$ elements tend to diminish as the 1,4-cyclopropyldicarbinyl diradical **58** is approached.

Still another point is seen in the matrices corresponding to the initial excited state **56.** For each of the three cyclopropane bonds, a, b, and c, four overlaps are involved. Due to different overlaps and S character it would not be permissible to sum bond order contributions; however, summing the $\Delta E'_{rt}$ elements is reasonable. Reference to Table IV reveals that the sum of energy contributions (i.e., the $\Delta E'_{rt}$'s) for the in-plane bond a is lowest of all, and we do not expect this bond to be stretched or broken. In fact, no 3,5-diphenyltoluene product

Table V. Redistribution of Electronic Excitation along the Reaction Coordinate

bond	56		bond	57[a]		bond	58[b]		bond	59[c]	bond	60[d]
r,t	ΔP_{rt}	$\Delta E'_{rt}$	r,t	ΔP_{rt}	$\Delta E'_{rt}$	r,t	ΔP_{rt}	$\Delta E'_{rt}$	r,t	ΔP_{rt}	r,t	ΔP_{rt}
1,2	−0.2620	2.3052	1,2	−0.0976	0.8173	1,2	−0.116	0.8271	1,2	0.0101	2,3	0.0615
2,3	0.1624	−1.0808	2,3	0.0681	−0.4666	2,3	0.0209	−0.0733	1,7	−0.3671	2,6	0.0658
2,6	0.0856	−0.0399	2,6	0.0086	−0.0535	3,4	−0.0063	0.0502	1,14	0.0002	3,4	−0.3169
3,4	−0.2382	2.0939	2,7	0.0114	−0.0531	3,10	−0.0076	0.0212	2,3	−0.0257	4,5	0.2147
4,5	0.1186	−0.4153	2,14	0.0213	−0.0691	4,5	0.0083	−0.0654	2,6	0.0196	5,6	−0.3190
2,12	0.0313	−0.0790	3,4	−0.1393	1.1678	5,6	−0.0866	0.3737	3,4	−0.0121		
4,13	0.0454	−0.1164	4,5	0.1125	−0.8119	5,11	0.0157	−0.0408	4,5	−0.1430	1,2	−0.0702
			5,6	−0.0119	0.0799				5,6	−0.0670	1,9	0.0113
5,6	−0.0234	0.1543	5,7	−0.2735	1.6038	2,6	0.0506	−0.3067	6,7	0.0047	2,8	−0.0116
5,12	−0.0041	0.0183	5,14	0.0469	−0.1460	2,11	0.0167	−0.0692	6,14	0.0163	8,9	0.0015
6,13	0.0020	−0.0090	6,7	0.0151	0.0000	6,10	0.0021	−0.0095	7,8	−0.0042		
12,13	0.0003	−0.0057	6,14	−0.0011	0.0157	10,11	0.0012	−0.0229	7,9	−0.0511	1,7	−0.1340
			7,10	−0.0138	0.0550				7,10	0.0407	1,14	0.0378
6,7	−0.0880	0.5834	7,11	0.0360	−0.1179	2,7	−0.0324	0.1899	7,11	0.0094	7,8	0.0244
6,14	0.0003	−0.0013	7,12	−0.0714	0.2803	2,14	0.0188	0.0780			8,14	−0.0069
7,12	−0.0355	0.1577	7,13	−0.0041	0.0163	7,10	0.0019	0.0083				
12,14	0.0024	−0.0459				10,14	−0.0009	0.0172			2,7	−0.0594
											2,14	−0.0166
5,7	−0.0930	0.6044				6,7	−0.0245	0.1593			7,9	0.0084
5,14	−0.0095	0.0416				6,14	0.0343	−0.1440			9,14	−0.0026
7,13	−0.0357	0.1589				7,11	0.0189	−0.0794				
13,14	−0.0014	0.0267				11,14	−0.0122	0.2345				

[a] Registry no.: 66374-31-0. [b] Registry no.: 66374-32-1. [c] Registry no.: 66374-33-2. [d] Registry no.: 13189-30-5.

was encountered. The second bond, bond b (the one closer to the *exo*-methylene moiety), is seen in Table IV to have less excitation energy than the more remote bond c. The consequent expectation of selective fission of bond c is realized in our bicycle mechanism (vide supra). One expects the rear wheel of the bicycle to have more excitation energy than the forward wheel for forward motion.

It is noted that in species **58** the reverse is true, and that bond c has less excitation energy than bond b. While in the excited state of a reactant, relative bond excitation energies and excitation bond orders should lead the excited state forward; for such an intermediate species as **58** the significance of a tendency to move forward vs. backwards on the hypersurface is less meaningful, since few reactions have unit efficiency and reversibility at intermediate stages of the reaction is possible. On the other hand, other information suggests that at this point along the reaction coordinate we are no longer dealing with the excited state and hence the excitation properties are not meaningful.

Finally, we note that in the excited singlet of spiro product **60** excitation is heavily concentrated in the traditional chromophore, this being the diene moiety.

SCF MO Correlation Diagrams for the Bicycle Reaction and State Reaction Energetics. MO correlation diagrams were derived from the SCF portion of the calculations. Correlations were checked, not only for the species described above, but also by interpolation between these. The correlations of interest for the bicycle rearrangement of 2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene, as a suitable but reasonably sized model, are depicted in Figure 3a. The qualitative nature of these correlations was found to be the same for the benzo analogue lacking the C-6 phenyl group. Hence it is reasonable to take the correlations as characteristic of the basic rearrangement.

It was of interest to compare the rearrangement in a dihydro system lacking the endocyclic π bond of the reactant. This is shown in Figure 3b. This corresponds to conversion of one vinylcyclopropane to an isomeric vinylcyclopropane by way of an intermediate cyclopropyldicarbinyl diradical. Thus the first step is the reverse of the last stage of a di-π-methane rearrangement and the last step is the same as the corresponding part of the di-π-methane rearrangement mechanism.[30] Ex-

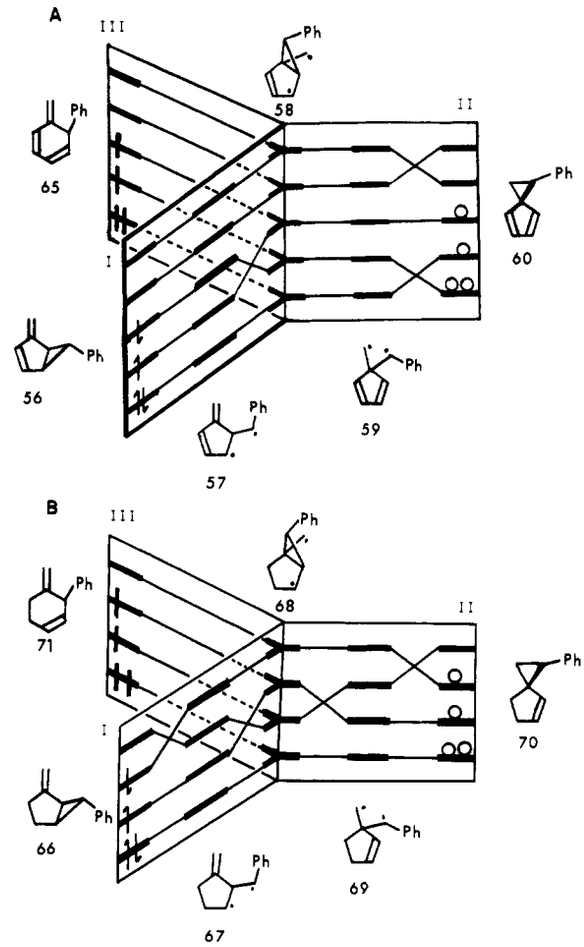


Figure 3. (a) SCF MO correlation diagram for the bicycle rearrangement. (b) SCF MO correlation diagram for the potential bicycle rearrangement of 2-methylene-6-phenylbicyclo[3.1.0]hexane.

perimentally, it is known from our earlier efforts[14] that such simple vinylcyclopropanes give different photochemistry (for example, note the vinylcyclopropane in eq 7). Since the alternative photochemistry is of efficiency comparable to the

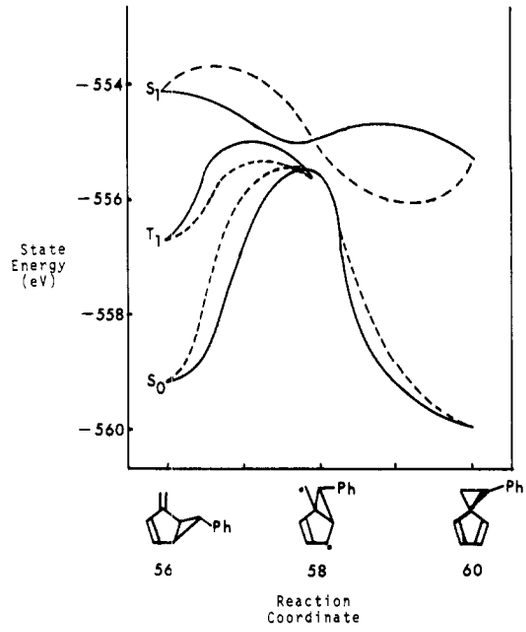


Figure 4. Rearrangement energetics for S_0 and S_1: pivot mechanism (- - -), slither or bicycle (—). Triplet surface available only between species **56** and **58**.

bicycle process, the absence of bicycling cannot be attributed to its being overshadowed by more efficient processes; and bicycling must be inherently unfavorable.

Inspection of Figure 3a, starting with bicyclic diene reactant **56**, reveals a photochemically allowed process in which loss of excitation occurs just prior to reaching the cyclopropyldicarbinyl diradical **58**. It is also seen that conversion of the ground-state configuration of **58** to triene **65** and spiroheptadiene **60** is ground-state allowed, while any reversion to bicyclic diene is ground-state forbidden.

Also of interest is consideration of the excited state of the bicycle product. We see that the excited state of spiroheptadiene **60** has only a forbidden pathway back to bicyclic diene **56** and triene **65**. This fits the experiment in which only cis–trans isomerization was observed from the spiroheptadiene products.

Now we turn to the matter of the role of the second double bond in the bicycle reaction of the 2-methylenebicyclo[3.1.0] systems, especially in view of the known[14] lack of bicycling experimentally. Inspection of the correlation diagram for the dihydro system in Figure 3b shows that two of the three bridges (i.e., I and II) do differ from those of the bicyclic diene correlation diagram as shown in Figure 3a. The conversion of vinylcyclopropane **66** to either of the potential products, vinylcyclopropane **70** or di-π-methane type diene **71**, is excited-state forbidden. In each case an upper excited state is generated along the reaction coordinate. This is related to the lack of general reversibility of the di-π-methane rearrangement.[30] Conversely, starting with the di-π-methane system **71** an excited state can proceed in allowed fashion to the vinylcyclopropane products **66** and **70**.

Finally we consider the overall state energetics along the reaction coordinate using our SCF–CI calculations. The results are depicted in Figure 4 and include both bicycle and pivot processes. Interestingly, the pivot process reveals an early barrier before the cyclopropyldicarbinyl diradical stage is reached. Conversely, the bicycle process is exothermic in S_1 and finally reaches a point along the reaction coordinate where a near degeneracy with S_0 is obtained. This agrees with our $\Delta E'$ and ΔP matrix treatment.

A final interesting aspect deals with the T_1 potential energy surface derived from our SCF–CI calculations. The results are included in Figure 4. This shows that the bicycle reaction of the triplet is appreciably endothermic in its early stages, while opening of bond C with pivoting is much less so. Also, the surface for opening with pivoting intersects the S_0 pivot surface, thus providing a facile route for the observed stereoisomerization.

Conclusion

The bicycle, or slither, rearrangement has thus far[31] proven relatively specific to the systems studied. Nevertheless, the reaction has proven itself unusually general in these systems and promises considerable synthetic utility. With regard to the theoretical treatment of the reaction, we note that the concept of localization and delocalization of electronic excitation, along with the ΔP and $\Delta E'$ matrix treatment, needs to be tested further, but is proving of considerable generality in our experience.

Experimental Section[32]

Methyl (*E,E*)-3,5-Diphenyl-2,4-pentadienoate. The corresponding ethyl ester has been described,[33] without experimental detail, as being prepared by a procedure analogous to that detailed as follows. To a solution of 5.00 g (27.5 mmol) of trimethyl phosphonoacetate in 100 mL of 1,2-dimethoxyethane was added 18.3 mL of 1.5 M *n*-butyllithium (27.5 mmol) dropwise. After stirring 15 min, 5.73 g (27.5 mmol) of *trans*-chalcone in 75 mL of 1,2-dimethoxyethane was added dropwise. The mixture was then refluxed under nitrogen for 20 h, cooled, poured into water, and ether extracted. The extracts were dried and concentrated in vacuo to yield 6.81 g of yellow oil which was chromatographed on a 3 × 130 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 2% ether in hexane. Elution in 250-mL fractions gave: fractions 1–12, nil; fractions 13–16, 4.01 g (55%) of methyl (*E,E*)-3,5-diphenyl-2,4-pentadienoate as a colorless oil.

The spectral data were: IR (thin film) 3.24, 3.25, 3.30, 3.38, 5.86, 6.20, 6.30, 6.37, 6.71, 6.90, 6.98, 7.32, 7.66, 7.76, 7.95, 8.28, 8.40, 8.59, 9.33, 9.90, 10.26, 10.99, 11.63, 12.95, 13.26, 14.28, 14.50 μm; NMR ($CDCl_3$) τ 1.46 (d, 1 H, J = 16 Hz, γ-vinyl), 2.46–2.88 (m, 10 H, arom), 3.01 (d, 1 H, J = 16 Hz, δ-vinyl), 4.21 (s, 1 H, vinyl), 6.26 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.72; H, 6.33.

(*E,E*)-3,5-Diphenyl-2,4-pentadienoic Acid. A mixture of 3.50 g (13.2 mmol) of methyl (*E,E*)-3,5-diphenyl-2,4-pentadienoate and 10.00 g (178 mmol) of potassium hydroxide in 125 mL of methanol was refluxed for 4 h, cooled, and poured into water. The solution was acidified to methyl orange with 10% hydrochloric acid and ether extracted. The extracts were water washed, dried, and concentrated in vacuo to yield 3.34 g (101%) of crystalline crude acid, mp 126–138 °C. Recrystallization from ethanol gave 3.16 g (96%) of colorless crystals of (*E,E*)-3,5-diphenyl-2,4-pentadienoic acid, mp 140–142 °C (lit.[33] mp 142–144 °C).

The spectral data were: IR (KBr) 3.27, 3.42, 3.62, 3.72, 3.85, 5.99, 6.20, 6.33, 6.39, 6.71, 6.90, 7.09, 7.75, 7.93, 8.20, 9.70, 10.19, 10.25, 10.87, 11.56, 12.99, 13.30, 14.28, 14.60 μm; NMR (acetone-d_6) τ 1.2 (s, 1 H, $-CO_2H$), 1.39 (d, 1 H, J = 17 Hz, γ-vinyl), 2.30–2.80 (m, 10 H, arom), 3.27 (d, 1 H, J = 17 Hz, δ-vinyl), 4.05 (s, 1 H, vinyl).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.61; H, 5.69.

(*E,E*)-1-Diazo-4,6-diphenyl-3,5-hexadien-2-one. Using the general procedure for the *E,Z* isomer,[32b] the acid chloride was prepared from 2.16 g (8.63 mmol) of (*E,E*)-3,5-diphenyl-2,4-pentadienoic acid and 1.43 g (12.0 mmol) of thionyl chloride in 30 mL of anhydrous benzene. Treatment of the acid chloride in 10 mL of anhydrous benzene with diazomethane prepared from 4.68 g (13.1 mmol) of EXR-101 and 25 mL of 33% potassium hydroxide led to 1.72 g (72%) of (*E,E*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one as a yellow oil isolated after chromatography.

The spectral data were: IR (thin film) 3.24, 3.25, 3.30, 3.44, 4.76, 5.51, 6.21, 6.37, 6.76, 6.90, 7.33, 7.46, 8.62, 8.76, 9.43, 9.71, 10.38, 13.33, 14.88 μm; NMR ($CDCl_3$) τ 1.28 (d, 1 H, J = 16 Hz, γ-vinyl), 2.40–2.80 (m, 10 H, arom), 3.32 (d, 1 H, J = 16 Hz, δ-vinyl), 4.12 (s, 1 H, vinyl), 4.60 (s, 1 H, $-CN_2H$); mass spectrum (calcd for $C_{18}H_{14}N_2O - N_2$, 246.104491) *m/e* 246.10354.

***exo*-4,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one.** As in the general cyclization procedure[32b] described for the endo isomer, from 1.00 g of copper bronze, 100 mL of anhydrous benzene, and 1.60 g (5.83

mmol) of (*E,E*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one in 25 mL of benzene, there was obtained after chromatography and recrystallization from 95% ethanol 912 mg (63.6%) of colorless crystals, mp 136–137 °C.

The spectral data were: IR (KBr) 3.27, 3.30, 3.42, 5.93, 6.25, 6.32, 6.40, 6.70, 6.91, 7.41, 7.86, 8.47, 9.79, 10.10, 11.34, 11.47, 13.02, 13.16, 14.49 μm; NMR ($CDCl_3$) τ 2.30–3.00 (m, 10 H, arom), 4.00 (s, 1 H, vinyl), 6.98 (t, 1 H, J = 4 Hz, benzyl cyclopropyl), 7.30–7.48 (m, 2 H, cyclopropyl); mass spectrum (calcd for $C_{18}H_{14}O$, 246.104491) *m/e* 246.10305.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.80; H, 5.70.

***exo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene.** To a stirred suspension of 2.33 g (6.52 mmol) of methyltriphenylphosphonium bromide in 75 mL of anhydrous ether under nitrogen was added 4.50 mL of 1.45 M *n*-butyllithium (6.52 mmol) in hexane. After stirring 15 min, 574 mg (2.33 mmol) of *exo*-4,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 30 mL of anhydrous ether was added dropwise. The mixture was stirred 2 h, poured into water, and ether extracted. The extracts were dried and concentrated in vacuo to yield 591 mg of residue which was chromatographed on a 2 × 40 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 100-mL fractions gave: fraction 1–2, nil; fractions 3–5, 551 mg (96%) of crystalline *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene, mp 96–98 °C. Recrystallization from 95% ethanol gave 506 mg (88%) of colorless crystals, mp 97–98 °C.

The spectral data were: IR ($CHCl_3$) 3.25, 3.27, 3.30, 3.33, 6.17, 6.25, 6.71, 6.92, 6.97, 7.46, 8.26, 8.50, 8.93, 9.34, 9.72, 11.43, 11.76, 14.53, 15.15 μm; NMR ($CDCl_3$) τ 2.36–2.56 (m, 2 H, *o*-vinyl arom), 2.60–3.00 (m, 8 H, arom), 3.73 (s, 1 H, vinyl), 4.91 (s, 2 H, exocyclic methylene), 7.20 (d of d, 1 H, J = 3, 6 Hz, cyclopropyl), 7.41 (d of d, 1 H, J = 3, 6 Hz, cyclopropyl), 8.90 (t, 1 H, J = 3 Hz, benzyl cyclopropyl); UV (95% EtOH) 231 nm (ε 23 500), 237 (ε 28 000), 303 (ε 22 000); mass spectrum (calcd for $C_{19}H_{16}$, 244.12520) *m/e* 244.12479.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.38; H, 6.69.

Methyl (*Z*)-3,5-Diphenylpent-2-en-4-ynoate. This ester was prepared by the method of Wiley and Staples[5] from benzoylphenylacetylene[34] and methyl bromoacetate.

Methyl (*E,Z*)-3,5-Diphenyl-2,4-pentadienoate. A solution of 1.89 g (7.20 mmol) of methyl (*Z*)-3,5-diphenylpent-2-en-4-ynoate in 75 mL of methanol was stirred over 609 mg of 5% palladium on barium sulfate poisoned with 0.25 mL of synthetic quinoline under 1 atm of hydrogen. When 190 cm^3 [7.62 mmol at 19 °C (730 Torr)] of hydrogen was consumed the mixture was filtered, poured into 5% hydrochloric acid, and extracted with ether. The ether extracts were washed with water, dried, and concentrated in vacuo to yield 1.86 g (98%) of methyl (*E,Z*)-3,5-diphenyl-2,4-pentadienoate as a colorless oil.

The spectral data were: IR ($CHCl_3$) 3.27, 3.31, 3.39, 5.85, 6.25, 6.30, 6.37, 6.71, 6.92, 6.99, 7.46, 7.84, 8.40, 8.64, 9.96, 11.52, 12.99, 14.43 μm; NMR ($CDCl_3$) τ 2.46–3.04 (m, 11 H, arom and vinyl), 3.15 (d, 1 H, J = 12 Hz, α-styryl), 3.76 (s, 1 H, vinyl), 6.28 (s, 3 H, CO_2CH_3); mass spectrum (calcd for $C_{18}H_{16}O_2$, 264.11503) *m/e* 264.11456.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.51; H, 5.94.

(*E,Z*)-3,5-Diphenyl-2,4-pentadienoic Acid. A mixture of 4.12 g (15.6 mmol) of methyl (*E,Z*)-3,5-diphenyl-2,4-pentadienoate and 5.00 g (89.0 mmol) of potassium hydroxide in 100 mL of methanol was refluxed for 2 h, cooled, and poured into water. The solution was acidified to methyl orange with 10% hydrochloric acid and ether extracted. The ether extracts were water washed, dried, and concentrated in vacuo to yield 3.83 g of crude crystalline acid, mp 131–140 °C. Recrystallization from methanol gave 3.56 g (91%) of (*E,Z*)-3,5-diphenyl-2,4-pentadienoic acid as colorless crystals, mp 145–147 °C.

The spectral data were: IR ($CHCl_3$) 3.27, 3.32, 3.76, 3.88, 5.97, 6.25, 6.31, 6.37, 6.71, 6.92, 7.07, 7.52, 7.81, 8.16, 8.35, 8.93, 9.30, 9.74, 10.00, 10.36, 10.93, 11.49, 11.90 μm; NMR (acetone-d_6) τ 2.32–3.04 (m, 11 H, arom and vinyl), 3.16 (d, 1 H, J = 12 Hz, α-styryl), 3.68 (s, 1 H, vinyl); mass spectrum (calcd for $C_{17}H_{14}O_2$, 250.09943) *m/e* 250.09873.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.70; H, 5.68.

(*E,Z*)-1-Diazo-4,6-diphenyl-3,5-hexadien-2-one. A mixture of 2.77 g (11.1 mmol) of (*E,Z*)-3,5-diphenylpentadienoic acid and 2.48 g (20.9 mmol) of thionyl chloride in 50 mL of anhydrous benzene was refluxed under nitrogen for 1.5 h, cooled, and concentrated in vacuo. The residue was dissolved in 10 mL of anhydrous benzene and added dropwise to excess distilled ethereal diazomethane prepared from 5.62 g (15.7 mmol) of EXR-101 (70% *N,N'*-dimethyl-*N,N'*-dinitroterephthalamide in mineral oil) and 30 mL of 33% potassium hydroxide. After 1 h, the excess diazomethane was removed under a stream of nitrogen and the solution was concentrated in vacuo to yield 3.04 g of residue which was chromatographed on a 2.5 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in 10% ether in hexane and eluted with 20% ether in hexane. Rapid chromatography was possible and necessary. Elution in 250-mL fractions gave: fractions 1–4, nil; fractions 5–6, 655 mg of (*E,E*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one as determined by NMR; fraction 7, 206 mg of a ~1:1 mixture of (*E,E*)- and (*E,Z*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one as determined by NMR; fractions 8–10, 577 mg (19%) of (*E,Z*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one as a yellow oil which was pure as determined by NMR.

The spectral data were: IR (thin film) 3.27, 3.31, 4.81, 5.87, 6.10, 6.21, 6.41, 6.72, 6.92, 7.27, 8.76, 9.17, 9.30, 9.69, 13.05, 13.26, 13.50, 14.51 μm; NMR ($CDCl_3$) τ 2.40–3.05 (m, 11 H, arom and vinyl), 3.24 (d, 1 H, J = 12 Hz, vinyl), 4.16 (s, 1 H, vinyl), 4.42 (s, 1 H, $-CHN_2$); mass spectrum (calcd for $C_{18}H_{14}N_2O - N_2$, 246.10446) *m/e* 246.10245.

***endo*-4,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one.** To a stirred suspension of 500 mg of copper–bronze (LUCO, No. 16, 99.5% copper, Leo Uhlfelder Co., Mt. Vernon, N.Y.) in 25 mL of anhydrous benzene heated in a 60 °C bath was added dropwise 520 mg (1.90 mmol) of (*E,Z*)-1-diazo-4,6-diphenyl-3,5-hexadien-2-one in 10 mL of benzene. The mixture was refluxed under nitrogen for 1 h, cooled, filtered through Celite, and concentrated in vacuo to yield 535 mg of residue which was chromatographed on a 2.5 × 45 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 250-mL fractions gave: fractions 1–3, nil; fraction 4, 42 mg of unidentified oil; fraction 5, 102 mg of *exo*-4,6-diphenylbicyclo[3.1.0]hex-3-en-2-one as determined by NMR: fractions 6–7, 151 mg of *endo*-4,6-diphenylbicyclo[3.1.0]hex-3-en-2-one as a semisolid. Recrystrallization from 95% ethanol gave 122 mg (26%) of pure product as colorless crystals, mp 151–153 °C.

The spectral data were: IR (KBr) 3.27, 3.30, 3.43, 5.92, 6.25, 6.32, 6.70, 6.88, 7.79, 8.43, 9.22, 9.79, 10.12, 11.50, 11.90, 13.26, 14.39 μm; NMR ($CDCl_3$) τ 2.44–3.05 (m, 10 H, arom), 3.82 (s, 1 H, vinyl), 6.84–7.18 (m, 2 H, cyclopropyl), 7.44 (dd, 1 H, J = 5, 8 Hz, benzyl cyclopropyl); mass spectrum (calcd for $C_{18}H_{14}O$, 246.10446) *m/e* 246.10366.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73; Found: C, 87.91; H, 5.77.

***endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene.**[32b] From 670 mg (1.88 mmol) of methyltriphenylphosphonium bromide in 40 mL of anhydrous ether under nitrogen, 1.30 mL of 1.45 M *n*-butyllithium (1.88 mmol), and 220 mg (0.893 mmol) of *endo*-4,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 15 mL of anhydrous ether chromatography gave 167 mg of crude *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene as a brown solid, mp 131–142 °C. Recrystallization from 95% ethanol gave 131 mg (60%) of pure product as colorless crystals, mp 153 °C.

The spectral data were: IR ($CHCl_3$) 3.25, 3.30, 3.32, 6.17, 6.25, 6.72, 6.91, 8.36, 9.32, 9.75, 11.46, 14.44, 15.15 μm; NMR ($CDCl_3$) τ 2.65–3.10 (m, 10 H, arom), 3.96 (s, 1 H, vinyl), 7.05 (d of d, 1 H, J = 6, 7.5 Hz, cyclopropyl), 7.25 (broad d of d, 1 H, J = 6, 8.5 Hz, cyclopropyl), 7.49 (d of d, 1 H, J = 7.5, 8.5 Hz, cyclopropyl); UV (95% EtOH) 224 nm (ε 21 400), 235 (ε 22 700), 298 (ε 19 500); mass spectrum (calcd for $C_{19}H_{16}$, 244.12520) *m/e* 244.12479.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.46; H, 6.76.

(*E*)-2-Stilbenecarboxylic Acid. This compound was prepared according to the method of Booth and Turner[6] from 3-(phenylmethyl)-1(3*H*)-isobenzofuranone.[35]

(*E*)-3,4-Benzo-1-diazo-6-phenyl-3,5-hexadien-2-one. By the general procedure for diazo ketones described above,[32b] reaction of (*E*)-2-stilbenecarboxylic acid with 1.77 g (14.9 mmol) of thionyl chloride in 25 mL of anhydrous benzene, followed by treatment with distilled diazomethane from 9.36 g (26.2 mmol) of EXR-101 and 50 mL of 33% potassium hydroxide, afforded 2.47 g (83%) of (*E*)-3,4-benzo-1-diazo-6-phenyl-3,5-hexadien-2-one as a deep yellow oil which was pure by NMR analysis and used directly in the next preparation.

The spectral data were: IR (thin film) 3.22, 3.27, 4.78, 5.65, 6.25, 6.71, 6.78, 6.91, 7.43, 8.16, 8.26, 8.77, 9.90, 10.43, 11.43, 13.18, 13.53, 14.49, 14.92 μm; NMR ($CDCl_3$) τ 2.30–2.90 (m, 10 H, arom and vinyl), 3.04 (d, 1 H, J = 16 Hz, vinyl), 4.54 (s, 1 H, CHN_2); mass spectrum (cold inlet) (calcd for $C_{16}H_{12}N_2O$, 248.09496) *m/e* 248.09496.

***exo*-3,4-Benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one.** Using the usual cyclization procedure,[32b] 2.00 g of copper–bronze in 60 mL of anhydrous benzene and 2.31 g (9.30 mmol) of (*E*)-3,4-benzo-1-diazo-6-phenyl-3,5-hexadien-2-one in 10 mL of benzene were reacted to afford, after chromatography and recrystallization from 95% eth-

anol, 1.37 g (67%) of *exo*-3,4-benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one as colorless crystals, mp 124–125 °C (lit.[36] mp 127–127.5 °C).

The spectral data were: IR (KBr) 3.27, 3.30, 3.42, 5.90, 6.25, 6.70, 6.82, 7.81, 8.05, 8.35, 8.77, 9.12, 9.98, 11.88, 11.98, 12.82, 13.16, 13.33, 14.39 μm; NMR ($CDCl_3$) τ 2.20–3.00 (m, 9 H, arom), 6.80 (d of d, 1 H, J = 3, 5 Hz, cyclopropyl), 7.22 (d of d, 1 H, J = 3, 5 Hz, α-carbonyl cyclopropyl), 7.44 (t, 1 H, J = 3 Hz, benzyl cyclopropyl); mass spectrum (calcd for $C_{16}H_{12}O$, 220.08865) *m/e* 220.08881.

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.06; H, 5.53.

***exo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene.** Using the general procedure above,[32b] 2.75 g (7.70 mmol) of methyltriphenylphosphonium bromide in 160 mL of anhydrous ether under nitrogen, 5.13 mL of 1.50 M *n*-butyllithium (7.70 mmol), and 849 mg (3.85 mmol) of *exo*-3,4-benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one in 25 mL anhydrous ether gave, after chromatography, 665 mg (79%) of desired olefin, mp 130–133 °C. Recrystallization from 95% ethanol gave 612 mg (73%) of *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene as colorless crystals, mp 135 °C.

The spectral data were: IR (KBr) 3.27, 3.32, 3.42, 6.25, 6.71, 6.90, 7.22, 8.33, 8.70, 9.35, 9.72, 11.07, 12.12, 13.25 μm; NMR ($CDCl_3$) τ 2.20–3.05 (m, 9 H, arom), 4.48 (s, 1 H, exocyclic methylene), 4.76 (s, 1 H, exocyclic methylene), 7.10 (d of d, 1 H, J = 3, 6 Hz, cyclopropyl), 7.20–7.40 (m, 1 H, cyclopropyl), 8.16 (t, 1 H, J = 3 Hz, cyclopropyl); UV (*t*-BuOH) 210 nm (ε 24 600), 239 (ε 27 100), 290 (ε 2870), 300 (ε 2220); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10855.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.46; H, 6.50.

(*Z*)-2-Stilbenecarboxylic Acid. A solution of 4.00 g (17.6 mmol) of (*E*)-2-stilbenecarboxylic acid in 500 mL of benzene was purged with purified nitrogen[37] for 1 h and then irradiated with continuing purging for 8.0 h through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo to yield 3.95 g of colorless solid, mp 144–146 °C. Recrystallization from benzene afforded 3.57 g (89%) of (*Z*)-2-stilbenecarboxylic acid, mp 147 °C (lit.[38] mp 145–146.5 °C).

The spectral data were: IR ($CHCl_3$) 3.27, 3.33, 3.47, 3.77, 3.94, 5.92, 6.27, 6.41, 6.71, 6.94, 7.12, 7.69, 7.88, 8.20, 8.33, 9.30, 10.87 μm; NMR (acetone-d_6) τ 1.96–2.10 (m, 1 H, $-CO_2H$), 2.64 (m, 10 H, arom and vinyl), 3.42 (d, 1 H, J = 12 Hz, vinyl).

(*Z*)-3,4-Benzo-1-diazo-6-phenyl-3,5-hexadien-2-one. With the general procedure above for diazo ketones,[32b] from 1.02 g (4.56 mmol) of (*Z*)-2-stilbenecarboxylic acid, 856 mg (7.25 mmol) of thionyl chloride in 25 mL of anhydrous benzene, distilled diazomethane from 3.88 g (10.9 mmol) of EXR-101, and 20 mL of 33% potassium hydroxide there was obtained 1.05 g (93%) of (*Z*)-3,4-benzo-1-diazo-6-phenyl-3,5-hexadien-2-one as a deep yellow oil which was pure by NMR analysis.

The spectral data were: IR (thin film) 3.22, 3.26, 3.29, 3.38, 4.76, 5.81, 6.17, 6.63, 6.67, 6.90, 7.38, 7.75, 8.20, 8.73, 9.82, 11.36, 12.73, 13.05, 14.28 μm; NMR ($CDCl_3$) τ 2.30–3.02 (m, 9 H, arom), 3.12 (d, 1 H, J = 12 Hz, vinyl), 3.36 (d, 1 H, J = 12 Hz, vinyl), 4.34 (s, 1 H, $-CHN_2$); mass spectrum (calcd for $C_{16}H_{12}N_2O - N_2$, 220.08881) *m/e* 220.08909.

***endo*-3,4-Benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one.**[32b] From 1.00 g of copper–bronze in 25 mL of anhydrous benzene and 941 mg (3.79 mmol) of (*Z*)-3,4-benzo-1-diazo-6-phenyl-3,5-hexadien-2-one in 10 mL of benzene there was obtained from chromatography 374 mg (45%) of *endo*-3,4-benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one as a colorless oil.

The spectral data were: IR (KBr) 3.30, 3.33, 5.87, 6.23, 6.69, 6.80, 6.92, 7.63, 7.76, 7.91, 8.30, 8.47, 9.05, 9.35, 10.81, 10.99, 11.36, 12.12, 12.90, 13.16, 14.29 μm; NMR ($CDCl_3$) τ 2.34–3.02 (m, 9 H, arom), 6.52–6.88 (M, 2 H, cyclopropyl), 7.16 (d of d, 1 H, J = 5, 9 Hz, cyclopropyl); mass spectrum (calcd for $C_{16}H_{12}O$, 220.08881) *m/e* 220.08911.

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.29; H, 5.49.

***endo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene.**[32b] From 4.61 g (12.96 mmol) of methyltriphenylphosphonium bromide in 75 mL of anhydrous ether, 8.61 mL (12.9 mmol) of 1.5 M *n*-butyllithium in hexane, and 949 mg (4.31 mmol) of *endo*-3,4-benzo-6-phenylbicyclo[3.1.0]hex-3-en-2-one in 25 mL of anhydrous ether chromatography gave 864 mg (92%) of *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene as colorless crystals, mp 142–144 °C. Recrystallization from 95% ethanol gave 812 mg (86%) of product as colorless crystals, mp 144–145 °C.

The spectral data were: IR ($CHCl_3$) 3.27, 3.33, 3.42, 6.12, 6.25, 6.70, 6.81, 6.94, 8.33, 8.93, 9.35, 9.76, 10.81, 11.43, 12.82, 14.49, 15.15 μm; NMR ($CDCl_3$) τ 2.42–3.18 (m, 9 H, arom), 4.52 (s, 1 H, exocyclic methylene), 4.71 (s, 1 H, exocyclic methylene), 6.94 (d of d, 1 H, J = 6, 8 Hz, cyclopropyl), 7.14 (broad d of d, 1 H, J = 6, 8.5 Hz, cyclopropyl), 7.44 (d of d, 1 H, J = 8, 8.5 Hz, benzyl cyclopropyl); UV (cyclohexane) 238 nm (ε 24 200), 252 (ε 20 100), 286 (ε 5080), 301 (ε 3890); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10963.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.38; H, 6.60.

3-(4-Methoxyphenylmethylene)-1(3*H*)-isobenzofuranone. A mixture of 33.2 g (200 mmol) of 4-methoxyphenylacetic acid, 25.0 g (150 mmol) of phthalic anhydride, and 0.65 g (8.0 mmol) of sodium acetate was heated quickly to 230 °C and the temperature was raised over 3 h to 250 °C. The mixture was cooled and crystallized from 10% benzene–ethanol to yield 21.6 g (57%) of 3-(4-methoxyphenylmethylene)-1(3*H*)-isobenzofuranone as yellow crystals, mp 146–148 °C (lit.[39] mp 147–148 °C).

The spectral data were: IR ($CHCl_3$) 3.33, 3.38, 3.41, 3.45, 3.55, 5.67, 6.02, 6.27, 6.37, 6.64, 6.80, 6.85, 6.94, 7.41, 7.52, 7.69, 7.75, 7.87, 8.00, 8.26, 8.55, 8.66, 9.26, 9.71, 10.20, 11.49, 11.63, 12.20 μm; NMR ($CDCl_3$) τ 2.08–2.64 (m, 6 H, arom), 3.12 (d, 2 H, J = 8 Hz, anisyl), 3.60 (s, 1 H, vinyl), 6.19 (s, 3 H, $-OCH_3$); mass spectrum (calcd for $C_{16}H_{12}O_3$, 252.07864) *m/e* 252.07924.

3-(4-Methoxyphenylmethyl)-1(3*H*)-isobenzofuranone. To a refluxing solution of 18.3 g (72.0 mmol) of 3-(4-methoxyphenylmethylene)-1(3*H*)-isobenzofuranone in 100 mL of 12% potassium hydroxide in water with 2.0 mL of ethanol was added 5.00 g (76.5 mg-atoms) of zinc dust. Refluxing was continued until the mixture was no longer red and the mixture was cooled, filtered, acidified with 10% hydrochloric acid (Congo Red), and extracted with ether. The ethereal extracts were dried and concentrated in vacuo to yield 16.5 g (90%) of nearly colorless crystals, mp 81–85 °C, which were recrystallized from 95% ethanol to yield 15.6 g (85%) of 3-(4-methoxyphenylmethyl)-1(3*H*)-isobenzofuranone as colorless crystals, mp 86–87 °C (lit.[39] mp 87–88 °C).

The spectral data were: IR (KBr) 3.26, 3.30, 3.33, 3.41, 3.52, 5.73, 6.22, 6.32, 6.62, 6.83, 6.94, 7.43, 7.63, 7.69, 7.78, 7.87, 8.06, 8.26, 8.37, 8.44, 8.51, 9.05, 9.39, 9.52, 9.62, 9.90, 10.20, 10.99, 12.24, 12.99, 13.33, 14.39 μm; NMR ($CDCl_3$) τ 2.14–3.02 (m, 6 H, arom), 3.18 (d, 2 H, J = 8 Hz, anisyl, 4.34 (t, 1 H, J = 6 Hz, methine), 6.21 (s, 3 H, $-OCH_3$), 6.82 (t, 2 H, J = 6 Hz, $-CH_2Ar$); mass spectrum (calcd for $C_{16}H_{14}O_3$, 254.09429) *m/e* 254.09422.

(*E*)-4′-Methoxy-2-stilbenecarboxylic Acid. A solution of 15.5 g (60.9 mmol) of 3-(4-methoxyphenylmethyl)-1(3*H*)-isobenzofuranone and 4.80 g (85.5 mmol) of potassium hydroxide in 70 mL of 50% aqueous ethanol was evaporated to dryness at 100 °C. The salt was heated at 100 °C for 1.5 h at 25 Torr and then heated at 200 °C for 4 h at 25 Torr. The cooled residue was taken up in water and the resulting solution was acidified with 10% hydrochloric acid (Congo Red) and extracted with ether. The ethereal extracts were dried and concentrated in vacuo to yield 14.2 g (92%) of crude product, mp 167–176 °C. Recrystallization from methanol gave 13.6 g (88%) of (*E*)-4′-methoxy-2-stilbenecarboxylic acid as colorless crystals, mp 179–180 °C (lit.[39] mp 179–180 °C).

The spectral data were: IR (KBr) 2.92, 3.38, 3.79, 5.58, 6.15, 6.25, 6.41, 6.62, 6.78. 6.85, 7.06, 7.12, 7.69, 7.75, 7.84, 7.94, 8.04, 8.39, 8.52, 8.76, 9.02, 9.28, 9.73, 10.34, 11.05, 11.63, 11.81, 12.15, 12.27, 12.50, 13.34, 13.98, 14.50, 15.00 μm; NMR (acetone-d_6) τ 1.90–3.16 (m, 11 H, arom, vinyl and $-CO_2H$), 6.18 (s, 3 H, $-OCH_3$); mass spectrum (calcd for $C_{16}H_{14}O_3$, 254.09378) *m/e* 254.09429.

(*E*)-3,4-Benzo-1-diazo-6-(4-methoxyphenyl)3,5-hexadien-2-one. Using the general diazo ketone procedure,[32b] from 4.34 g (17.1 mmol) of (*E*)-4′-methoxy-2-stilbenecarboxylic acid, 4.34 g (34.2 mmol) of oxalyl chloride, distilled diazomethane prepared from 9.36 g (26.2 mmol) of EXR-101, and 50 mL of 33% potassium hydroxide there was obtained 4.24 g (89%) of (*E*)-3,4-benzo-1-diazo-6-(4-methoxyphenyl)-3,5-hexadien-2-one as a deep yellow oil which was pure by NMR analysis.

The spectral data were: IR (thin film) 3.22, 3.26, 3.33, 3.38, 3.41, 3.52, 6.25, 6.63, 6.78, 6.85, 6.94, 7.04, 7.43, 7.73, 8.02, 8.53, 8.77, 9.01, 9.72, 9.95, 10.42, 11.05, 11.47, 12.20, 13.14, 13.42, 13.70, 14.38, 15.00 μm; NMR ($CDCl_3$) τ 2.24–3.22 (m, 10 H, arom and vinyl), 4.45 (s, 1 H, $-CHN_2$), 6.23 (s, 3 H, $-OCH_3$); mass spectrum (cold inlet) (calcd for $C_{17}H_{14}N_2O_2$, 278.10552) *m/e* 278.10559.

***exo*-3,4-Benzo-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-en-2-one.**[32b] From 2.04 g of copper–bronze in 50 mL of anhydrous benzene and 4.03 g (14.5 mmol) of (*E*)-3,4-benzo-1-diazo-6-(4-methoxyphenyl)-3,5-hexadien-2-one in 25 mL of benzene chromatography and recrystallization from 95% ethanol gave 1.77 g (49%) of *exo*-3,4-benzo-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-en-2-one as colorless crystals, mp 112–113 °C.

The spectral data were: IR (KBr) 3.27, 3.31, 3.42, 3.51, 5.91, 6.24, 6.62, 6.82, 7.26, 7.65, 7.80, 7.93, 8.06, 8.48, 8.80, 9.11, 9.39, 9.78, 9.98,

11.91, 12.24, 12.97, 13.88, 14.50 μm; NMR ($CDCl_3$) τ 2.24–3.36 (m, 8 H, arom), 6.30 (s, 3 H, $-OCH_3$), 6.94 (d of d, 1 H, J = 3, 5 Hz, cyclopropyl), 7.33 (d of d, 1 H, J = 3, 5 Hz, cyclopropyl), 7.55 (t, 1 H, J = 3 Hz, cyclopropyl); mass spectrum (calcd for $C_{17}H_{14}O_2$, 250.09938) m/e 250.09916.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.77; H, 5.69.

***exo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo-[3.1.0]hex-3-ene.**[32b] From 4.41 g (12.4 mmol) of methyltriphenylphosphonium bromide in 100 mL of anhydrous ether, 8.30 mL of 1.50 M n-butyllithium solution (12.4 mmol), and 1.66 g (6.65 mmol) of *exo*-3,4-benzo-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-en-2-one in 75 mL of anhydrous ether chromatography gave 1.43 g of *exo*-3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene as a colorless oil which crystallized on standing, mp 90–92 °C. Recrystallization from 95% ethanol yielded 1.12 g (68%) of product as colorless crystals, mp 93–95 °C.

The spectral data were: IR ($CHCl_3$) 3.33, 3.42, 6.25, 6.62, 6.85, 7.07, 8.16, 8.33, 8.51, 9.71, 10.81, 11.43 μm; NMR ($CDCl_3$) τ 2.44–3.24 (m, 8 H, arom), 4.48 (s, 1 H, exocyclic methylene), 4.77 (s, 1 H, exocyclic methylene), 6.21 (s, 3 H, $-OCH_3$), 7.16 (d of d, 1 H, J = 3, 5 Hz, cyclopropyl), 7.31 (broad d of d, 1 H, J = 3, 5 Hz, cyclopropyl), 8.20 (t, 1 H, J = 3 Hz, cyclopropyl); UV (cyclohexane) 243 nm (ε 26 600), 248 (ε 25 900), 267 (ε 15 400), 295 (ε 5520); mass spectrum (calcd for $C_{18}H_{16}O$, 248.12011) m/e 248.12060.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.16; H, 6.66.

(*Z*)-4′-Methoxy-2-stilbencarboxylic Acid. A mixture of 2.00 g (7.87 mmol) of (*E*)-4′-methoxy-2-stilbenecarboxylic acid in 500 mL benzene was purged with purified nitrogen[37] for 30 min and then irradiated with continued purging for 4.0 h through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo to yield 2.06 g (103%) of nearly colorless solid residue, mp 156–160 °C. Recrystallization from 20% ethanol in benzene gave 1.77 g of (*Z*)-4′-methoxy-2-stilbencarboxylic acid as colorless crystals, mp 161–162 °C.

The spectral data were: IR (KBr) 2.92, 3.38, 3.79, 5.58, 6.15, 6.25, 6.41, 6.62, 6.78, 6.85, 7.06, 7.12, 7.69, 7.75, 7.84, 7.94, 8.04, 8.39, 8.52, 8.76, 9.02, 9.28, 9.73, 10.34, 11.05, 11.63, 11.81, 12.15, 12.27, 12.50, 13.34, 13.98, 14.50, 15.00 μm; NMR (acetone-d_6) τ 1.92–3.40 (m, 10 H, $-CO_2H$, arom and vinyl), 3.50 (d, 1 H, J = 12 Hz, vinyl), 6.28 (s, 3 H, $-OCH_3$); mass spectrum (calcd for $C_{16}H_{14}O_3$, 254.09429) m/e 254.09378.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.45; H, 5.49.

(*Z*)-3,4-Benzo-1-diazo-6-(4-methoxyphenyl)-3,5-hexadien-2-one. A mixture of 1.45 g (5.70 mmol) of (*Z*)-4′-methoxy-2-stilbenecarboxylic acid and 1.32 g (10.4 mmol) of oxalyl chloride was left for 2 h. Excess oxalyl chloride was removed in vacuo and 10 mL of anhydrous benzene was added. The solution was concentrated in vacuo and the residue was redissolved in 10 mL of anhydrous benzene and added dropwise to excess distilled ethereal diazomethane prepared from 2.81 g (7.9 mmol) of EXR-101 (70% *N,N′*-dimethyl-*N,N′*-dinitrosoterephthalamide in mineral oil) and 15 mL of 33% potassium hydroxide. After stirring 1.5 h at room temperature, the excess diazomethane was removed in vacuo to yield 1.50 g (95%) of (*Z*)-3,4-benzo-1-diazo-6-(4-methoxyphenyl)-3,5-hexadien-2-one as a deep yellow oil which was pure by NMR analysis. This was used in the subsequent step without further purification.

The spectral data were: IR (thin film) 3.25, 3.32, 3.39, 3.52, 4.76, 5.97, 6.21, 6.58, 6.83, 7.35, 7.81, 7.94, 8.47, 8.89, 9.26, 9.33, 9.63, 10.87, 11.90, 13.51, 14.39 μm; NMR ($CDCl_3$) τ 2.32–3.60 (m, 10 H, arom and vinyl), 4.32 (s, 1 H, $-CHN_2$), 6.34 (s, 3 H, $-OCH_3$); mass spectrum (calcd for $C_{17}H_{14}N_2O_2 - N_2$, 250.09938) m/e 250.09960.

***endo*-3,4-Benzo-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-en-2-one.**[32b] From 1.15 g of copper–bronze in 20 mL of benzene and 1.42 g (5.10 mmol) of (*Z*)-3,4-benzo-1-diazo-6-(4-methoxyphenyl)-3,5-hexadien-2-one in 10 mL of benzene 369 mg (29%) of pure product as a colorless oil was obtained by chromatography.

The spectral data were: IR 3.27, 3.30, 3.42, 3.53, 5.88, 6.25, 6.66, 6.82, 7.63, 7.80, 7.91, 8.00, 8.47, 8.97, 9.31, 11.75, 12.74, 12.91, 14.40 μm; NMR ($CDCl_3$) τ 2.20–3.28 (m, 6 H, arom), 3.48 (d, 2 H, J = 8 Hz, *o*-anisyl), 4.48 (s, 3 H, $-OCH_3$), 6.64–7.00 (m, 2 H, cyclopropyl), 7.24 (d of d, 1 H, J = 5, 9 Hz, cyclopropyl); mass spectrum (calcd for $C_{17}H_{14}O_2$, 250.09938) m/e 250.09904.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.68; H, 5.39.

***endo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene.**[32b] From 445 mg (1.25 mmol) of methyltriphenylphosphonium bromide in 25 mL of anhydrous ether, 0.835 mL (1.25 mmol) of 1.50 M n-butyllithium in hexane, and 148 mg (0.591 mmol) of *endo*-3,4-benzo-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-en-2-one in 25 mL of anhydrous ether chromatography afforded 106 mg (72%) of *endo*-3,4-benzo-6-(methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene as a crystalline solid, mp 121–124 °C. Recrystallization from 95% ethanol gave 97 mg (66%) of product as colorless crystals, mp 127 °C.

The spectral data were: IR ($CHCl_3$) 3.28, 3.33, 3.42, 3.51, 6.25, 6.82, 7.08, 7.57, 7.91, 8.33, 8.45, 9.71, 10.13, 11.55, 12.50 μm; NMR ($CDCl_3$) τ 2.52–3.30 (m, 8 H, arom), 4.55 (s, 1 H, exocyclic methylene), 4.68 (s, 1 H, exocyclic methylene), 6.26 (s, 3 H, $-OCH_3$), 6.94 (d of d, 1 H, J = 6, 7.5 Hz, cyclopropyl), 7.12 (broad d of d, 1 H, J = 6, 9 Hz, cyclopropyl), 7.50 (t, 1 H, J = 9 Hz, cyclopropyl); UV (95% EtOH) 242 nm (ε 24 800), 254 (ε 21 000), 280 (ε 7160), 305 (ε 3770); mass spectrum (calcd for $C_{18}H_{16}O$, 248.12011) m/e 248.12060.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.00; H, 6.36.

3-Phenyl-5-(phenylmethylene)-2-cyclopenten-1-one. The compound was prepared by the method of Borsche and Menz[40] from 3-phenyl-2-cyclopentenone.

2-Phenyl-5-(phenylmethylene)-1,3-cyclopentadiene. To a suspension of 500 mg (2.03 mmol) of 3-phenyl-5-(phenylmethylene)-2-cyclopenten-1-one in 25 mL of anhydrous tetrahydrofuran was added 1.45 mL of 1.40 M diisobutylaluminum hydride in hexane dropwise. The mixture was stirred for 30 min, poured into water, and extracted with ether. The ether extracts were washed with water, dried, and evaporated to yield 461 mg of semisolid residue which was chromatographed on a 3 × 50 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 125-mL fractions gave: fractions 1–2, nil; fractions 3–4, 276 mg (59%) of 2-phenyl-5-(phenylmethylene)-1,3-cyclopentadiene as a dark red-orange oil which crystallized on standing, mp 61–68 °C. Recrystallization from 95% ethanol gave 236 mg (50%) of 2-phenyl-5-(phenylmethylene)-1,3-cyclopentadiene as red-orange crystals, mp 72–73 °C.

The spectral data were: IR ($CHCl_3$) 3.27, 3.33, 6.18, 6.27, 6.63, 6.91, 7.30, 7.72, 8.16, 8.33, 9.73, 10.75, 11.43, 12.20, 14.60, 15.15 μm; NMR ($CDCl_3$) τ 2.22–3.12 (m, 13 H, arom and vinyl), 3.54 (d of d, 1 H, J = 2, 6 Hz, vinyl).

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.95; H, 6.11.

1,5-Diphenylspiro[2.4]hepta-4,6-diene. To 100 mg (4.17 mmol) of solid mineral oil free sodium hydride and 1.10 g (5.00 mmol) of solid trimethylsulfoxonium iodide[41] was added cautiously under nitrogen 6.0 mL of anhydrous dimethyl sulfoxide dropwise. After hydrogen evolution had ceased, the mixture was stirred 10 min and then 118 mg (0.512 mmol) of 2-phenyl-5-(phenylmethylene)-1,3-cyclopentadiene in 10 mL of anhydrous Me_2SO was added dropwise. After stirring 15 min, the mixture was poured into water and extracted with ether. The ether extracts were washed with water and saturated sodium chloride, dried, and concentrated in vacuo to yield 121 mg of residue which was chromatographed in a 1 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 3% ether in hexane. Elution in 50-mL fractions gave: fractions 1–2, nil; fractions 3–4, 9.72 mg of 1:1 mixture of *syn*- and *anti*-1,5-diphenylspiro[2.4]-hepta-4,6-diene as a colorless oil. The spectral data were identical with those reported previously.[3a]

1-(Phenylmethylene)-1*H*-indene. This compound was prepared by the method of Kresze, Henkel, and Goetz[42] from indene and benzaldehyde.

***anti*-2-Phenylspiro[cyclopropane-1,1′-[1*H*]indene].** To a dry mixture of 100 mg (4.17 mmol) of mineral oil free sodium hydride and 1.10 g (5.00 mmol) of trimethylsulfoxonium iodide was added under nitrogen 6.0 mL of anhydrous dimethyl sulfoxide.[41] After hydrogen evolution had ceased, 100 mg (0.480 mmol) of 1-(phenylmethylene)-1*H*-indene in 5 mL of anhydrous dimethyl sulfoxide was added dropwise. The mixture was stirred for 30 min, poured into water, and extracted with ether. The ether extracts were washed with water and saturated sodium chloride solution, dried, and concentrated in vacuo to yield 97.0 mg of residue, which was chromatographed on a 1 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 50-mL fractions gave: fractions 1–2, nil; fraction 3, 88 mg (84%) of *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] as a crystalline solid, mp 77–79 °C. Recrystallization from 95% ethanol gave 72 mg (69%) of product, mp 79–80 °C.

The spectral data were: IR (KBr) 3.27, 3.32, 3.42, 6.27, 6.71, 6.90, 7.27, 7.30, 7.87, 8.13, 8.33, 8.70, 9.35, 9.71, 9.80, 10.20, 11.11, 11.49, 12.35, 12.82, 13.25, 13.79, 14.39 μm; NMR ($CDCl_3$) τ 2.50–3.10 (m, 9 H, arom), 3.25 (d, 1 H, J = 6 Hz, vinyl), 4.04 (d, 1 H, J = 6 Hz, vinyl), 6.82 (t, 1 H, J = 8 Hz, cyclopropyl), 7.44 (d of d, 1 H, J = 5, 8 Hz, cyclopropyl), 8.06 (d of d, 1 H, J = 5, 8 Hz, cyclopropyl); UV (*t*-BuOH)

210 nm (ε 24 600), 239 (ε 27 100), 290 (ε 2870), 300 (ε 2220); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10909.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.40; H, 6.51.

***syn*-2-Phenylspiro[cyclopropane-1,1′-[1*H*]indene].** A solution of 245 mg (1.12 mmol) of *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 30 min and then irradiated with continued purging for 3.5 h through quartz with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo at 40 °C to yield 249 mg of a yellow oily residue which was chromatographed in portions (30.0 mg) by high-pressure liquid chromatography on a 50 × 0.96 cm silica microsphere[43] column (particle size 10–30 μm). The mixture was eluted with 0.05% acetone in hexane and recycled three times with the final cycle giving: fraction 1, 131 mg of *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene]; fraction 2, 41 mg of a mixture of *syn*- and *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene]; fraction 3, 35 mg of *syn*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] as a colorless oil; fraction 4, 29 mg of a mixture of product and unidentified material.

The spectral data for the syn isomer were: IR (thin film) 3.27, 3.32, 3.40, 6.27, 7.73, 8.21, 8.70, 9.15, 9.35, 9.70, 9.86, 10.20, 11.11, 11.49, 12.82 μm; NMR ($CDCl_3$) τ 2.56–3.02 (m, 9 H, arom), 3.12 (d, 1 H, J = 5 Hz, vinyl), 3.72 (d, 1 H, J = 5 Hz, vinyl), 6.64 (t, 1 H, J = 8 Hz, cyclopropyl), 7.78–8.02 (m, 2 H, cyclopropyl); UV (95% EtOH) 235 nm (ε 26 600), 284 (ε 2470), 296 (ε 2050); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10909.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.81; H, 6.33.

1-(4-Methoxyphenylmethylene)-1*H*-indene. This compound was prepared by the method of Kresze, Henkel, and Goetz[42] from indene and 4-methoxybenzaldehyde.

***anti*-2-(4-Methoxyphenyl)spiro[cyclopropane-1,1′-[1*H*]indene].**[32b] From 100 mg (4.17 mmol) of mineral oil free sodium hydride, 1.10 g (5.00 mmol) of trimethylsulfoxonium iodide,[41] 6.0 mL of anhydrous dimethyl sulfoxide, 166 mg (0.697 mmol) of 1-(4-methoxyphenylmethylene)-1*H*-indene in 5 mL of anhydrous dimethyl sulfoxide, and product chromatography there was obtained 146 mg of *anti*-2-(4-methoxyphenyl)spiro[cyclopropane-1,1′-[1*H*]indene] as a nearly colorless solid, mp 104–112 °C. Recrystallization from 95% ethanol gave 118 mg (68%) of product as colorless crystals, mp 120–121 °C.

The spectral data were: IR (KBr) 3.27, 3.33, 3.42, 6.25, 6.62, 6.69, 6.87, 6.93, 7.25, 7.75, 7.84, 8.00, 8.26, 8.47, 9.11, 9.71, 10.13, 11.98, 12.42, 13.09, 13.25, 14.30 μm; NMR ($CDCl_3$) τ 2.60–3.40 (m, 8 H, arom), 3.25 (d, 1 H, J = 6 Hz, vinyl), 4.07 (d, 1 H, J = 6 Hz, vinyl), 6.18 (s, 3 H, $-OCH_3$), 6.84 (t, 1 H, J = 8 Hz, cyclopropyl), 7.76 (d of d, 1 H, J = 5, 8 Hz, cyclopropyl), 8.04 (d of d, 1 H, J = 5, 8 Hz, cyclopropyl); UV (95% EtOH) 218 nm (ε 22 800), 246 (ε 24 400), 290 (ε 4400), 301 (ε 3170); mass spectrum (calcd for $C_{18}H_{16}O$, 248.12011) *m/e* 248.11914.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.03; H, 6.70.

3,4-Dihydro-1-methyl-2(1*H*)-naphthalenone. This material was prepared by the method of Stille and Wu[44] from 3,4-dihydro-1-methylnaphthalene[45] and *m*-chloroperbenzoic acid.

1-Methyl-2-phenylnaphthalene.[32c] To phenylmagnesium bromide prepared from 270 mg (11.1 mg-atoms) of magnesium turnings and 1.73 g (11.0 mmol) of bromobenzene in anhydrous ether was added 1.76 g (11.0 mmol) of 3,4-dihydro-1-methyl-2(1*H*)-naphthalenone in 5 mL of anhydrous ether. The mixture was stirred for 1 h, 25 mL of 2.4 M hydrochloric acid was added, and the ethereal phase was separated. Standard workup yielded 2.60 g of yellow oil. The product mixture was dissolved in 50 mL of benzene and 2.72 g (12 mmol) of dichlorodicyanobenzoquinone and 65.0 mg (0.377 mmol) of *p*-toluenesulfonic acid were added. The mixture was refluxed for 3 h with a Dean–Stark trap, cooled, and filtered. The filtrate was diluted with ether, washed with 1 N sodium hydroxide, water, and saturated sodium chloride, dried, and concentrated in vacuo to yield 2.39 g of oil, which was chromatographed on a 2.5 × 40 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 100-mL fractions gave in fractions 3–5 1.687 g of 1-methyl-2-phenylnaphthalene as a colorless oil which crystallized on standing, mp 78–80 °C. Recrystallization from methanol gave 1.30 g (54%) of colorless crystals, mp 83–84 °C (lit.[46] mp 80–82 °C).

The spectral data were: IR (KBr) 3.27, 3.31, 3.42, 6.28, 6.70, 6.81, 7.25, 8.01, 8.47, 9.34, 9.74, 9.99, 10.13, 11.59, 12.20, 13.12, 13.42, 14.18 μm; NMR ($CDCl_3$) τ 1.94–3.04 (m, 11 H, arom), 7.47 (s, 3 H, methyl); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10889.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.40; H, 6.66.

1-Methyl-2-(4-methoxyphenyl)naphthalene. To 468 mg (18.2 mg-atoms) of magnesium turnings covered with anhydrous ether was added 0.1 mL of dibromoethane. When reaction was initiated, 3.45 g (18.4 mmol) of 4-bromoanisole in 50 mL of ether was added dropwise. The mixture was stirred for 1 h and 2.95 g (18.4 mmol) of 3,4-dihydro-1-methyl-2(1*H*)-naphthalenone in 10 mL of anhydrous ether was added dropwise. The mixture was stirred for 1 h and 50 mL of 2.4 M hydrochloric acid was added. The ethereal phase was separated, washed with water and saturated sodium chloride, dried, and concentrated in vacuo to yield 4.04 g of yellow oil which was dissolved in 75 mL of benzene. To the benzene solution was added 3.75 g (16.5 mmol) of dichlorodicyanobenzoquinone and 93.4 mg (0.542 mmol) of *p*-toluenesulfonic acid and the mixture was refluxed for 4 h with a Dean–Stark trap. The mixture was cooled and filtered and the filtrate was diluted with ether, washed with 1 N sodium hydroxide, water, and saturated sodium chloride, dried, and concentrated in vacuo to yield 3.33 g of oil which was chromatographed on a 2.5 × 60 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 100-mL fractions gave: fractions 1–8 nil; fractions 9–11, 3.38 g of 1-methyl-2-(4-methoxyphenyl)naphthalene as a crystalline solid, mp 101–114 °C. Recrystallization from 95% ethanol gave 2.94 g (64%) of product as colorless crystals, mp 117–118 °C.

The spectral data were: IR (KBr) 3.28, 3.30, 3.33, 3.38, 3.42, 3.52, 6.23, 6.62, 6.65, 6.84, 6.90, 6.94, 7.25, 7.75, 8.00, 8.06, 8.47, 9.01, 9.66, 10.10, 11.93, 12.15, 12.27, 12.82, 13.25, 14.39 μm; NMR ($CDCl_3$) τ 1.87–3.21 (m, 8 H, arom), 6.24 (s, 3 H, $-OCH_3$), 7.43 (s, 3 H, methyl); mass spectrum (calcd for $C_{18}H_{16}O$, 248.12011) *m/e* 248.11931.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.85; H, 6.47.

Photolysis Equipment for Preparative Irradiations and Quantum Yield Determinations. All direct and sensitized preparative irradiations were performed using a Hanovia 450-W medium-pressure mercury lamp and immersion apparatus or the black box apparatus[7] as specified for each run. All direct and sensitized quantum yield determinations were performed using the microoptical bench[7] employing a Bausch and Lomb Model 33-86-79 monochromator having a 5.4-mm entrance slit and a 3.0-mm exit slit (22-nm half width theoretical band-pass) and an Osram HBO 200-W high-pressure mercury lamp. Light output was monitored using a digital electronic actinometer[47] which employed two 1P28 photomultipliers, a multiplexed voltage to frequency converter, and dual digital counters. This instrument was calibrated prior to each run and each wavelength with ferrioxalate actinometry.[48] The light absorbed in the reaction cell was ascertained by the splitting ratio method described previously.[7]

For photolyses employing the black box, the band-pass was controlled by one of the following filter solution combinations as specified for each run: 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, 4.50×10^{-2} M stannous chloride in 10% hydrochloric acid; transmission, 0% below 285 nm, 45% at 315 nm, 0% above 340 nm; filter B, cell 1, 0.2 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 10% sulfuric acid; 0.2 M stannous chloride dihydrate in 10% hydrochloric acid; transmission, 0% below 315 nm, 28% at 345 nm, 0% above 380 nm.

Exploratory Direct Photolysis of *exo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 500 mg (2.05 mmol) of *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]-hex-3-ene in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 10 h through filter A on the black box apparatus. The photolysate was concentrated in vacuo to yield 503 mg of colorless oil. The light absorbed was 5.51 mEinsteins. The residue was chromatographed in 50-mg portions on a 2.54 × 183 cm column of octadecyl-coated sponge-surfaced glass beads.[49] The column was eluted with 55% acetonitrile–water (v/v) at a flow rate of 10 mL/min and the collected eluate was concentrated in vacuo, diluted with water, and extracted with ether. The ether extracts from each fraction were dried and concentrated individually in vacuo to give: fraction 1, 349 mg of starting material; fraction 2, 119 mg of 1,5-diphenylspiro[2.4]hepta-4,6-diene[3a] as a colorless oil shown by NMR analysis to be ~96% anti isomer; fraction 3, 12 mg of 2,5-diphenyltoluene. The starting material was unchanged (IR, NMR, UV, mp) and the spiroheptadiene photoproduct had spectral data (IR, NMR, UV) identical with that reported previously[3a] as did the 2,5-diphenyltoluene[3a] (IR, NMR, UV, mp).

Exploratory Direct Photolysis of *endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. Product Isolation. A solution

of 500 mg (2.04 mmol) of *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 20 h through filter A on the black box apparatus. The photolysate was concentrated in vacuo to yield 515 mg of light yellow oil. The light absorbed was 12.77 mEinsteins. The residue was chromatographed on a 2.54 × 183 cm column of octadecyl-coated sponge-surfaced glass beads.[49] The column was eluted with 50% acetonitrile–water (v/v) at a flow rate of 18 mL/min and the collected eluate was concentrated in vacuo, diluted with water, and extracted with ether. The ether extracts from individual fractions were dried and concentrated in vacuo to give: fraction 1, 220 mg of starting material; fraction 2, 165 mg of 1,5-diphenylspiro[2.4]hepta-4,6-diene as a colorless oil which was shown by NMR analysis to be ~55% syn isomer; fraction 3, 75 mg of a ~8:1 mixture of spiro photoproduct and diphenyltoluenes as determined by NMR analysis; fraction 4, 24 mg of a ~10:1 mixture of diphenyltoluenes to spiro photoproduct. Fractions 3 and 4 were combined and rechromatographed in 25-mg portions on two serial 1.27 × 183 cm columns of octadecyl-coated sponge-surfaced glass beads.[49] The column was eluated with 50% acetonitrile–water (v/v) at a flow rate of 4 mL/min. The eluate corresponding to individual fractions was treated as above to give: fraction 1, 67 mg of 1,5-diphenylspiro[2.4]hepta-4,5-diene having essentially the same composition as a fraction 2 above; fraction 2, 14 mg of 2,5-diphenyltoluene; fraction 3, 8 mg of 3,4-diphenyltoluene; fraction 4, 6 mg of a mixture of 3,4- and 2,4-diphenyltoluenes; fraction 5, 6 mg of 2,4-diphenyltoluene. Starting material was unchanged (IR, NMR, UV, mp) and spiro photoproduct spectral data (IR, NMR) were identical with that reported previously[3a] and authentic material and the diphenyltoluenes were identical (IR, NMR) with authentic materials.[3a]

Low Conversion Direct Photolysis of endo-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 450 mg (1.84 mmol) of *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 1.0 h through filter A on the black box apparatus. The light absorbed was 0.607 mEinstein. The photolysate was concentrated in vacuo to yield 446 mg of colorless semisolid. Recrystallization of the mixture from ethanol gave 321 mg of crystalline starting material, mp 152–153 °C. The mother liquor was concentrated under nitrogen and chromatographed on a 2.54 × 183 cm column of octadecyl-coated sponge-surfaced glass beads.[49] The column was eluted with 60% acetonitrile–water (v/v) at a flow rate of 15 mL/min and the collected eluate was concentrated in vacuo, diluted with water, and ether extracted. The ether extracts from individual fractions were dried and concentrated in vacuo to yield: fraction 1, 108 mg of starting material; fraction 2, 14 mg (2.8%) of 1,5-diphenylspiro[2.4]hepta-4,6-diene as a colorless oil which was shown by NMR analysis to be 73% syn isomer, $\Phi = 0.0849$. The spiro product was identical in other respects with authentic material (IR, UV).[3a] Diphenyltoluene photoproducts were too small in amount to recover.

Intermediate Conversion Direct Photolysis of *endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 424 mg (1.74 mmol) of *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 3.0 h through filter A on the black box apparatus. The light absorbed was 2.17 mEinsteins. The photolysate was concentrated in vacuo to yield 455 mg of nearly colorless oil which was chromatographed in portions on a 2.54 × 183 cm column of octadecyl-coated sponge-surfaced glass beads.[49] The column was eluted with 55% acetonitrile–water (v/v) at a flow rate of ~15 mL/min and the collected eluate was concentrated in vacuo, diluted with water, and ether extracted. The ether extracts were concentrated in vacuo to yield: fraction 1, 354 mg of starting material; fraction 2, 44.7 mg (10.6%), $\Phi = 0.084$, of 1,5-diphenylspiro[2.4]hepta-4,6-diene as a colorless oil which was shown by NMR analysis to be ~63% syn isomer. Diphenyltoluene photoproducts were not isolated.

Exploratory Sensitized Photolysis of *exo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. A solution of 200 mg (0.818 mmol) of *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene and 5.11 g (28.0 mmol) of benzophenone in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 10 h through filter B on the black box apparatus. The photolysate was concentrated in vacuo to yield 7.23 g of white crystalline residue. The light absorbed was 13.2 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 0.5% ether in hexane. Elution in 250-mL fractions gave: 1–10, nil; 11–12, 203 mg of crystalline starting material unchanged by GC and NMR analysis, mp 96–99 °C. A control mixture containing 0.5% endo isomer was examined under identical conditions and this conversion would have been measurable. Therefore, conversion was <0.5%, $\Phi = <3.0 \times 10^{-4}$.

Sensitized Photolysis of *endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. Quantum Yield. Product Isolation. A solution of 176 mg (0.720 mmol) of *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene and 5.02 g (27.5 mmol) of benzophenone in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 45 min through filter B on the black box apparatus. The photolysate was concentrated in vacuo to 5.20 g of white crystalline solid. The light absorbed was 1.06 mEinsteins. The residue was chromatographed on a 3 × 100 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 0.2% ether in hexane. Elution in 250-mL fractions gave: 1–15, nil; 16–17, 41 mg (0.168 mmol) of *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene which was identical with authentic material (NMR, GC), 23% conversion, $\Phi = 0.159$; 18–19, 138 mg of starting endo isomer unchanged.

Exploratory Direct Photolysis of *exo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 233 mg (1.07 mmol) of *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 67 min through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo at 40 °C to yield 255 mg of a colorless oil. Crystallization of the residue from *tert*-butyl alcohol gave 56.0 mg of starting material and the mother liquor was chromatographed in portions by high-pressure liquid chromatography on a 50 × 0.96 cm silica microsphere column (particle size 10–30 μm).[43] Elution with 0.03% acetone in hexane gave: fraction 1, 53.4 mg of starting material; fraction 2, 9.3 mg of mixture of starting material and 1-methylene-2-phenyl-1,2-dihydronaphthalene; fraction 3, 46.3 mg of an oil consisting of 1-methylene-2-phenyl-1,2-dihydronaphthalene containing ~8% tautomeric 1-methyl-2-phenylnaphthalene as ascertained by NMR; fraction 4, nil; fraction 5, 61.8 mg of *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene]. The *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] was identical (IR, NMR, UV) with independently prepared material.

The spectral data for 1-methylene-2-phenyl-1,2-dihydronaphthalene (incessantly contaminated with 1-methyl-2-phenylnaphthalene) were: IR (thin film) 3.27, 3.30, 3.52, 6.04, 6.25, 6.71, 6.92, 9.73, 10.73, 11.46, 14.40 μm; 270-MHz NMR (acetone-d_6) τ 2.40–3.00 (m, 9 H, arom), 3.36 (d, 1 H, $J = 9.6$ Hz, vinyl), 3.84 (d of d, 1 H, $J = 9.6$, 5.0 Hz, vinyl), 4.46 (d of d, 1 H, $J = 1.8$, 0.92 Hz, exocyclic methylene), 4.88 (d of d, 1 H, $J = 1.5$, 0.92 Hz, exocyclic methylene), 5.56 (d of d of d, 1 H, $J = 5.0$, 1.8, 1.5 Hz, methine); UV (95% EtOH) 284 nm (ϵ 15 400); mass spectrum (calcd for $C_{17}H_{14}$, 218.10955) *m/e* 218.10940.

Exploratory Direct Photolysis of *endo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 209 mg (0.958 mmol) of *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 1.5 h through a 2-mm Pyrex filter with Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo at 40 °C to yield 217 mg of a colorless oil. The residue was chromatographed in 50-mg portions by high-pressure liquid chromatography on a 50 × 0.96 cm silica microsphere column (particle size 10–30 μm).[43] Elution with 0.05% acetone in hexane gave: fraction 1, 102 mg of an oil consisting of 1-methylene-2-phenyl-1,2-dihydronaphthalene containing ~10% tautomeric 1-methyl-2-phenylnaphthalene by NMR analysis; fraction 2, 76.4 mg of starting material; fraction 3, 9.0 mg of starting material containing a trace of spiro photoproduct; fraction 4, 12.1 mg of *syn*-2-phenylspiro[cyclopropane-1,1′-[1*H*[indene]as a colorless oil containing <5% anti isomer by NMR analysis. The methylenedihydronaphthalene photoproduct was identical (IR, NMR, UV) with material obtained from photolysis of the exo isomer. The *syn*-2-phenylspiro[cyclopropane-1,1′-[1*H*]-indene] was identical (IR, NMR, UV) with independently prepared material.

Tautomerization of 1-Methylene-2-phenyl-1,2-dihydronaphthalene. A solution of 71.0 mg (0.325 mmol) of 1-methylene-2-phenyl-1,2-dihydronaphthalene containing ~12% 1-methyl-2-phenylnaphthalene by NMR and 2.5 mg of *p*-toluenesulfonic acid monohydrate (1.31×10^{-2} mmol) in 10 mL of benzene was refluxed for 30 min. The mixture was cooled, poured into water, and ether extracted. The ether extracts were washed with saturated sodium

bicarbonate and water, dried, and concentrated in vacuo to yield 66.2 mg (93%) of crystalline residue, mp 77–80 °C which was entirely 1-methyl-2-phenylnaphthalene by NMR analysis. Recrystallization from methanol gave 46.0 mg of 1-methyl-2-phenylnaphthalene as a colorless crystals, mp 83–84 °C, which were identical (IR, NMR, mp) with independently prepared material.

In an alternate experiment, 56.6 mg (0.259 mmol) of 1-methylene-2-phenyl-1,2-dihydronaphthalene (containing ~15% 1-methyl-2-phenylnaphthalene by NMR) in 10 mL of anhydrous benzene was refluxed for 1.5 h. The mixture was cooled and concentrated in vacuo to yield 55.8 mg of a solid residue, mp 77–79 °C, which was entirely 1-methyl-2-phenylnaphthalene by comparison with independently prepared material (IR, NMR).

Exploratory Sensitized Photolysis of *exo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. A solution of 226 mg (1.04 mmol) of *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene and 3.01 g (20.1 mmol) of 3-methoxyacetophenone in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 2.5 h with a Hanovia 450-W medium-pressure mercury lamp through a 2-mm Pyrex filter and 5 mm of 0.05 M sodium vanadate in 0.05 M sodium hydroxide solution (0% $T < 330$ nm) which was circulated as lamp coolant. The photolysate was concentrated in vacuo at 40 °C to yield 3.34 g of a semisolid which was chromatographed on a 2.5 × 110 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 3% ether in hexane. Elution in 125-mL fractions gave: fractions 1–7, nil; fraction 8, 221 mg of *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene unchanged.

Exploratory Sensitized Photolysis of *endo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. A solution of 240 mg (1.10 mmol) of *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]-hex-3-ene and 3.06 g (20.4 mmol) of 3-methoxyacetophenone in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 0.75 h with a Hanovia 450-W medium-pressure mercury lamp through a 2-mm Pyrex filter and 5 mm of 0.05 M sodium vanadate in 0.05 M sodium hydroxide solution (0% $T < 330$ nm) which was circulated as lamp coolant. The photolysate was concentrated in vacuo at 40 °C to yield 3.41 g of a semisolid which was chromatographed on a 3 × 120 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 0.5% ether in hexane. After elution with 1.95 L of eluate, 75-mL fractions were collected giving: fractions 1–3, 95.0 mg of *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene having spectral properties (NMR, IR) identical with authentic material, mp 95–98 °C; fractions 4–5, 31.0 mg of a ~2:1 mixture of endo and exo isomers as determined by NMR analysis; fractions 6–10, 105 mg of unchanged (NMR, mp) starting endo isomer.

Exploratory Direct Photolysis of *exo*-3,4-Benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 211 mg (0.850 mmol) of *exo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated for 1 h with continued purging through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo at 40 °C to yield 226 mg of a nearly colorless oil which was chromatographed on a 20 × 20 × 0.2 cm preparative alumina (E. Merck, GF-254, Type 60/E) plate eluted twice with 10% ether in hexane. The isolated bands were: band 1 (R_f 0.82), 157 mg of a mixture of starting material and 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene as determined by NMR analysis; band 2 (R_f 0.65), 57.0 mg of *anti*-2-(4-methoxyphenyl)spiro[cyclopropane-1,1′-[1*H*]indene] which was identical (IR, NMR, mass spectrum, mp) to independently prepared material. The residue from band 1 was rechromatographed on a 20 × 20 × 0.2 cm preparative alumina (E. Merck, GF-254, Type 60/E) plate eluted four times with 2% ether in hexane. The isolated bands were: band 1 (R_f 0.79), 48.0 mg of unreacted starting material; band 2 (R_f 0.71), 31.0 mg of a ~3:2 mixture of unreacted starting material and 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene; band 3, 62.0 mg of an oil consisting of 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene containing ~15% tautomeric 1-methyl-2-(4-methoxyphenyl)naphthalene as ascertained by NMR; band 5, 9.1 mg of a mixture of the methylenedihydronaphthalene photoproduct, tautomeric naphthalene, and spiro photoproduct. The *anti*-2-(4-methoxyphenyl)spiro[cyclopropane-1,1′-[1*H*]indene] was identical (IR, NMR, UV) with independently prepared material.

The spectral data for 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene (incessantly contaminated with 1-methyl-2-(4-methoxyphenyl)naphthalene) were: IR (thin film) 3.28, 3.30, 3.33, 3.38, 3.42, 3.52, 6.23, 6.60, 6.62, 6.86, 6.90, 6.94, 7.25, 7.75, 8.00, 8.06, 8.50, 9.20, 9.66, 10.10, 11.93, 12.15, 12.27, 12.82, 13.25, 14.39 μm; NMR ($CDCl_3$) τ 2.48–3.36 (m, 8 H, arom), 3.55 (d, 1 H, J = 9 Hz, vinyl), 3.97 (dd, 1 H, J = 6, 9 Hz, vinyl), 4.58 (s, 1 H, methylene), 5.04 (s, 1 H, methylene), 5.74 (broad s, 1 H, methine); mass spectrum (calcd for $C_{18}H_{16}O$, 248.12011) *m/e* 248.11931.

Exploratory Direct Photolysis of *endo*-3,4-Benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene. Product Isolation. A solution of 197 mg (0.793 mmol) of *endo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 1 h through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp. The photolysate was concentrated in vacuo at 40 °C to yield 213 mg of a pale yellow oil which was chromatographed on a 20 × 20 × 0.2 cm preparative alumina (E. Merck, GF-254, Type 60/E) plate eluted three times with 5% ether in hexane. The isolated bands were: band 1 (R_f 0.85), 82.0 mg of an oil consisting of 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene containing ~23% of tautomeric 1-methyl-2-(4-methoxyphenyl)naphthalene as determined by NMR; band 2 (R_f 0.70), 22.6 mg of an oily mixture of starting material, methylenedihydronaphthalene photoproduct, and tautomeric naphthalene; band 3 (R_f 0.62), 80.0 mg of unreacted starting material. The 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene was identical (IR, NMR) with the product obtained by photolysis of the exo isomer.

Tautomerization of 1-Methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene. A solution of 80.4 mg (0.324 mmol) of 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene [containing <5% 1-methyl-2-(4-methoxyphenyl)naphthalene by NMR analysis] in 25 mL of benzene was refluxed for 2.0 h. The mixture was cooled and concentrated in vacuo to yield 81.2 mg (101%) of crystalline residue, mp 113–117 °C, which was identical (NMR) with independently prepared 1-methyl-2-(4-methoxyphenyl)naphthalene. Recrystallization from 95% ethanol gave 63.0 mg (78%) of pure 1-methyl-2-(4-methoxyphenyl)naphthalene, mp 117–118 °C, which was further related (IR, mp) to independently prepared material.

Exploratory Sensitized Photolysis of *exo*-3,4-Benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene. A solution of 290 mg (1.17 mmol) of *exo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene and 3.00 g (20.0 mmol) of 3-methoxyacetophenone in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 3 h with a Hanovia 450-W medium-pressure mercury lamp through a 2-mm Pyrex filter and 5 mm of 0.05 M sodium vanadate in 0.05 M sodium hydroxide solution (0% $T < 330$ nm) which was circulated as lamp coolant. The photolysate was concentrated in vacuo at 40 °C to yield 3.36 g of solid residue which was chromatographed on a 2.5 × 100 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 5% ether in hexane. Elution in 250-mL fractions gave: fractions 1–9, nil; fractions 10–11, 282 mg of *exo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]-hex-3-ene unchanged.

Exploratory Sensitized Photolysis of *endo*-3,4-Benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene. A solution of 315 mg (1.27 mmol) of *endo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene and 3.02 g (20.1 mmol) of 3-methoxyacetophenone in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[37] for 1 h and then irradiated with continued purging for 30 min with Hanovia 450-W medium-pressure mercury lamp through a 2-mm Pyrex filter and 5 mm of 0.05 M sodium vanadate in 0.05 M sodium hydroxide solution (0% $T < 330$ nm) which was circulated as lamp coolant. The photolysate was concentrated in vacuo at 40 °C to yield 3.36 g of solid residue which was chromatographed on a 2.5 × 110 cm silica gel column (Grace, grade 62, 60–200 mesh) slurry packed in hexane and eluted with 2.5% ether in hexane. After elution with 2.25 L of eluate 125-mL fractions were collected to yield: fractions 1–2, 81.0 mg of *exo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene which was identical with authentic material (IR, NMR, mp); fraction 3, 56.6 mg of a ~3:2 mixture of endo and exo isomers of starting material as determined by NMR; fractions 4–6, 171.2 mg of starting endo isomer unchanged.

Summary of Quantum Yield Results for *exo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. All quantum yield runs were performed on the microoptical bench using 305 ± 22 nm as the irradiation wavelength. The solvent was anhydrous *tert*-butyl alcohol (40 mL) and solutions were purged with purified nitrogen for 1 h prior to and during photolysis. Analysis was by high-pressure liquid chromatography using three serial 1.6 mm × 60 cm columns of octadecyl-coated sponge-surfaced glass beads[49] and eluting at a rate of 0.4 mL/min with 50% aqueous acetonitrile. A 254-nm UV detector was

employed and 4,4′-dimethoxybiphenyl was employed as internal standard.

The data are reported as follows: starting *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (mmol); light absorbed (mEinsteins); 1,5-diphenylspiro[2.4]hepta-4,6-diene photoproduct (mmol), quantum yield; diphenyltoluene photoproduct mixture (mmol), quantum yield, % conversion.

Run 1: bicyclic starting material (9.09×10^{-2} mmol); 3.50×10^{-2} mEinstein; spiro photoproduct (3.36×10^{-3} mmol), $\Phi = 9.60 \times 10^{-2}$; diphenyltoluene ($3.08 \times 10^{-4}$ mmol), $\Phi = 8.80 \times 10^{-3}$; 4.04%.

Run 2: bicyclic starting material (8.44×10^{-2} mmol); 4.92×10^{-2} mEinstein; spiro photoproduct (4.63×10^{-3} mmol); $\Phi = 9.41 \times 10^{-2}$; diphenyltoluene ($4.24 \times 10^{-4}$ mmol); $\Phi = 8.60 \times 10^{-3}$; 5.99%.

Run 3: bicyclic starting material (6.32×10^{-2} mmol); 4.78×10^{-2} mEinstein; spiro photoproduct (4.54×10^{-3} mmol); $\Phi = 9.50 \times 10^{-2}$; diphenyltoluene ($4.26 \times 10^{-4}$ mmol); $\Phi = 8.90 \times 10^{-3}$; 7.86%.

Summary of Quantum Yield Results for *endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene. Quantum yield runs were performed on the microoptical bench using 305 ± 22 nm as the irradiation wavelength and anhydrous *tert*-butyl alcohol (40 mL). The sensitized quantum yield of isomerization is reported under the exploratory photolysis of the starting material (vide supra). Analysis for run 3 was by high-pressure liquid chromatography using three serial 1.6 mm × 60 cm columns of octadecyl-coated sponge-surfaced glass beads[49] and eluting at a rate of 0.4 mL/min with 45% aqueous acetonitrile. A 254-nm UV detector was employed and 4,4′-dimethoxybiphenyl was employed as internal standard. Analysis for runs 1 and 2 was by vapor-phase chromatography using a 0.64 × 150 cm column packed with 5% QF-1 on 100–120 Varaport 30 at 160 °C using 9-methylanthracene as internal standard.

The data are reported as follows: starting *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (mmol); light absorbed (mEinsteins); 1,5-diphenylspiro[2.4]hepta-4,6-diene photoproduct (mmol), quantum yield; diphenyltoluene photoproducts (mmol), quantum yield; % conversion.

Run 1: bicyclic starting material (1.04×10^{-1} mmol); 2.78×10^{-2} mEinstein; spiro photoproducts (2.36×10^{-3} mmol); $\Phi = 8.49 \times 10^{-2}$; diphenyltoluenes ($3.59 \times 10^{-4}$ mmol); $\Phi = 1.29 \times 10^{-2}$; 2.61%.

Run 2: bicyclic starting material (6.65×10^{-2} mmol); 2.94×10^{-2} mEinstein; spiro photoproducts (2.50×10^{-3} mmol); $\Phi = 8.50 \times 10^{-2}$; diphenyltoluenes ($3.73 \times 10^{-4}$ mmol); $\Phi = 1.27 \times 10^{-2}$; 4.32%.

Run 3: bicyclic starting material (7.74×10^{-2} mmol); 4.96×10^{-2} mEinstein; spiro photoproducts (4.19×10^{-3} mmol); $\Phi = 8.45 \times 10^{-2}$; diphenyltoluenes ($6.59 \times 10^{-4}$ mmol); $\Phi = 1.33 \times 10^{-2}$; 6.26%.

Summary of Quantum Yield Results for *exo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. All quantum yield runs were performed on a microoptical bench using 305 ± 22 nm as the irradiation wavelength and anhydrous *tert*-butyl alcohol (40 mL). Analysis was by high-pressure liquid chromatography using a 50 × 0.96 cm silica microsphere[43] column (particle size 10–30 μm) and eluting with 0.03% acetone in hexane. A 254-nm UV detector was employed and biphenyl was employed as internal standard.

The data are reported as follows: starting *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (mmol); light absorbed (mEinsteins); *anti*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] photoproduct (mmol), quantum yield; 1-methylene-2-phenyl-1,2-dihydronaphthalene photoproduct (mmol), quantum yield; % conversion.

Run 1: bicyclic starting material (9.90×10^{-2} mmol); 2.14×10^{-2} mEinsteins; spiro photoproduct (1.34×10^{-3} mmol); $\Phi = 6.26 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (1.16×10^{-3} mmol); $\Phi = 5.42 \times 10^{-2}$; 2.52%.

Run 2. bicyclic starting material (1.04×10^{-1} mmol); 4.23×10^{-2} mEinsteins; spiro photoproduct (2.64×10^{-3} mmol); $\Phi = 6.24 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (2.28×10^{-3} mmol); $\Phi = 5.39 \times 10^{-2}$; 4.73%.

Run 3: bicyclic starting material (1.28×10^{-1} mmol); 7.68×10^{-2} mEinsteins; spiro photoproduct (4.73×10^{-3} mmol); $\Phi = 6.16 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (4.12×10^{-3} mmol); $\Phi = 5.36 \times 10^{-2}$; 6.91%.

Summary of Quantum Yield Results for *endo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene. All quantum yield runs were performed on the microoptical bench. Runs 1–3 used 305 ± 22 nm as the irradiation wavelength. Run 4 used 345 ± 22 nm as the irradiation wavelength and benzophenone as the added sensitizer. In all runs, the solvent was *tert*-butyl alcohol and solutions were purged with purified nitrogen for 1 h prior to and during photolysis. Analysis was by high-pressure liquid chromatography using a 50 × 0.96 cm silica microsphere[43] column (particle size 10–30 μm) and eluting with 0.03% acetone in hexane. A 254-nm UV dectector was employed and biphenyl was employed as internal standard.

The data are reported as follows: starting *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (mmol); added benzophenone, if any (mmol); light absorbed (mEinsteins); *syn*-2-phenylspiro[cyclopropane-1,1′-[1*H*]indene] photoproduct (mmol), quantum yield; 1-methylene-2-phenyl-1,2-dihydronaphthalene photoproduct (mmol), quantum yield; or, isomeric *exo*-3,4-benzo-2-methylene-6-phenyl-bicyclo[3.1.0]hex-3-ene (mmol), quantum yield; % conversion.

Run 1: bicyclic starting material (1.20×10^{-1} mmol); 2.78×10^{-2} mEinsteins; spiro photoproduct (2.60×10^{-4} mmol); $\Phi = 9.40 \times 10^{-3}$; methylenedihydronaphthalene photoproduct (2.20×10^{-3} mmol); $\Phi = 7.91 \times 10^{-2}$; 2.05%.

Run 2: bicyclic starting material (1.08×10^{-1} mmol); 4.77×10^{-2} mEinsteins; spiro photoproduct (4.25×10^{-4} mmol); $\Phi = 8.90 \times 10^{-3}$; methylenedihydronaphthalene photoproduct (3.78×10^{-3} mmol); $\Phi = 7.92 \times 10^{-2}$; 3.89%.

Run 3: bicyclic starting material (1.42×10^{-1} mmol); 6.70×10^{-2} mEinsteins; spiro photoproduct (6.23×10^{-4} mmol); $\Phi = 9.30 \times 10^{-3}$; methylenedihydronaphthalene photoproduct (5.28×10^{-3} mmol); $\Phi = 7.88 \times 10^{-2}$; 4.16%.

Run 4: bicyclic starting material (1.74×10^{-1} mmol); benzophenone sensitizer (2.93 mmol); 4.68×10^{-2} mEinsteins; exo bicyclic diene (5.48×10^{-3} mmol); $\Phi = 0.117$; 3.15%.

Summary of Quantum Yield Results for *exo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene. All quantum yield runs were performed on the microoptical bench using 305 ± 22 nm as the irradiation wavelength and anhydrous *tert*-butyl alcohol (40 mL). Analysis was by high-pressure liquid chromatography using a 50 × 0.96 cm silica microsphere[43] column (particle size 10–30 μm) and eluting with 0.03% acetone and 0.5% ether in hexane. A 254-nm UV detector was employed and benzophenone was employed as internal standard.

The data are reported as follows: starting *exo*-3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene (mmol); light absorbed (mEinsteins); *anti*-2-(4-methoxyphenyl)spiro[cyclopropane-1,1′-[1*H*]indene] photoproduct (mmol), quantum yield; 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene photoproduct (mmol), quantum yield; % conversion.

Run 1: bicyclic starting material (5.20×10^{-2} mmol); 2.01×10^{-2} mEinstein; spiro photoproduct (1.17×10^{-3} mmol); $\Phi = 5.82 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (1.45×10^{-3} mmol); $\Phi = 7.21 \times 10^{-2}$; 5.04%.

Run 2: bicyclic starting material (8.25×10^{-2} mmol); 2.16×10^{-2} mEinstein; spiro photoproduct (1.26×10^{-3} mmol); $\Phi = 5.83 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (1.57×10^{-3} mmol); $\Phi = 7.27 \times 10^{-2}$; 3.43%.

Run 3: bicyclic starting material (1.17×10^{-1} mmol); 2.12×10^{-2} mEinstein; spiro photoproduct (1.25×10^{-3} mmol); $\Phi = 5.90 \times 10^{-2}$; methylenedihydronaphthalene photoproduct (1.56×10^{-3} mmol); $\Phi = 7.35 \times 10^{-2}$; 2.40%.

Summary of Quantum Yield Results for *endo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene. All quantum yield runs were performed on the microoptical bench. Runs 1–3 used 305 ± 22 nm as the irradiation wavelength. Run 4 used 345 ± 22 nm as the irradiation wavelength and benzophenone as the added sensitizer. In all runs, the solvent was *tert*-butyl alcohol. Analysis was by high-pressure liquid chromatography using a 50 × 0.96 cm silica microsphere[43] column (particle size 10–30 μm) and eluting with 0.03% acetone and 0.5% ether in hexane. A 254-nm UV detector was employed and benzophenone was employed as internal standard for runs 1–3. For run 4 the internal standard employed was deoxybenzoin.

The data are reported as follows: starting *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene (mmol); added benzophenone, if any (mmol); light absorbed (mEinsteins); 1-methylene-2-(4-methoxyphenyl)-1,2-dihydronaphthalene photoproduct (mmol); quantum yield; or, isomeric *exo*-3,4-benzo-2-methylene-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-3-ene (mmol); quantum yield; % conversion.

Run 1: bicyclic starting material (1.13×10^{-1} mmol); 3.58×10^{-2} mEinstein; methylenedihydronaphthalene photoproduct (3.33×10^{-3} mmol); $\Phi = 9.30 \times 10^{-2}$; 2.95%.

Run 2: bicyclic starting material (9.10×10^{-2} mmol); 3.37×10^{-2} mEinstein; methylenedihydronaphthalene photoproduct (3.10×10^{-3} mmol); $\Phi = 9.20 \times 10^{-2}$; 3.41%.

Run 3: bicyclic starting material (7.22×10^{-2} mmol); 3.71×10^{-2} mEinstein; methylenedihydronaphthalene photoproduct (3.48×10^{-3} mmol); $\Phi = 9.38 \times 10^{-2}$; 4.83%.

Run 4: bicyclic starting material (9.52×10^{-2} mmol); 4.56×10^{-2} mEinstein; exo bicyclic diene (5.78×10^{-3} mmol); $\Phi = 1.26 \times 10^{-1}$;

6.15%.

Emission Studies. Magic Multipliers.[4] Emission spectra were measured using an Aminco–Kiers spectrofluorimeter equipped with a Hanovia 901C-1 150-W xenon arc lamp. For each compound, the fluorescence spectrum was measured at both 77 and 295 K with solutions having optical densities in the range of 0.8 to 1.8 in 4:1 methylcyclohexane–isopentane under otherwise identical conditions. Magic multipliers were obtained by dividing the integrated emission intensities at 77 K by the integrated emission intensities at 295 K. The average value obtained for each compound was as follows: (1) *exo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene, M = 41.7 (three runs); (2) *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene, M = 36.5 (four runs); (3) *exo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene, M = 99.6 (five runs); (4) *endo*-3,4-benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene, M = 91.2 (four runs); (5) *exo*-3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]-hex-3-ene, M = 120 (four runs); (6) *endo*-3,4-benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene, M = 114 (four runs).

Single Photon Counting. The apparatus and procedure have been described previously.[4,8a] The experiments were run such that data was collected until a minimum of 2000 counts was collected in the highest channel. Data was collected at <3% of the lamp frequency to assure that few double photons were collected. Excitation wavelength ranged from 260 to 275 nm and emission was monitored in the range from 320 to 335 nm with an RCA 8850 photomultiplier. Optical densities were adjusted from 0.8 to 2.0 at the excitation wavelength. The "A value" was used as the measure of the relative fit of the computer calculated decay curve to the experimentally collected curve. The decay rate for each compound was determined to be independent of excitation wavelength, emission wavelength, and sample OD with A value <5%. All runs were performed at 77 K. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, A value.

(1) *exo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene, 516 ps, 1.94×10^9 s^{-1}, six runs, 0.046.

(2) *endo*-2-Methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene, 524 ps, 1.91×10^9 s^{-1}, six runs, 0.049.

(3) *exo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene, 256 ps, 3.90×10^9 s^{-1}, six runs, 0.046.

(4) *endo*-3,4-Benzo-2-methylene-6-phenylbicyclo[3.1.0]hex-3-ene, 468 ps, 2.14×10^9 s^{-1}, six runs, 0.048.

(5) *exo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo-[3.1.0]hex-3-ene, 415 ps, 2.41×10^9 s^{-1}, six runs, 0.045.

(6) *endo*-3,4-Benzo-6-(4-methoxyphenyl)-2-methylenebicyclo[3.1.0]hex-3-ene, 601 ps, 1.66×10^9 s^{-1}, six runs, 0.045.

Calculations. The Pople semiempirical SCF method[17,50] (complete neglect of differential overlap) was used for closed-shell SCF calculations. A configuration interaction treatment was applied to the SCF molecular orbitals including both single and double excitations. For single excitations, the highest six occupied and lowest six unoccupied MO's were used to give 36 configurations; double excitations were selected by a first-order perturbation approach[51,52] from the 325 possible configurations obtained by promoting from the highest five occupied to the lowest five vacant MO's. 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.[53] Standard methods for the reduction of many electron integrals then gave general formulas used to determine matrix elements between configurations.[17,50,53] Matrix elements between doubly excited configurations were then derived.

Standard geometries for bicyclo[3.1.0]hexenyl systems were assumed and found to compare favorably with those reported for the theoretical STO-3G equilibrium geometry for the bicyclo[3.1.0]hexenyl cation.[54] The geometries for the spiro[2.4]hepta-4,6-diene systems were based on the reported MINDO/2 calculation for the ground-state optimized geometry of spiro[2.4]hepta-4,6-diene.[55] Geometries for intermediate species were assumed.

Two electron repulsion integrals were calculated by the Pariser–Parr approach.[56] Resonance integrals were calculated by the Mulliken approximation as employed by Hoffmann,[57] but with K scaled according to the CNDO/S convention of Boyd and Whitehead.[58,59] Nearest neighbor and selected 1,3 resonance integrals were used. Valence state ionization potentials were those described by Hinze and Jaffe.[60]

Calculations were performed with Fortran IV programs[51] on a PDP-11/T55 computer having 32K words of memory. Direct disk access allowed storage and use of the large matrices encountered in configuration interaction calculations.

Acknowledgment. Support of this research by the National Science Foundation and the National Institutes of Health Grant GMO7487 is gratefully acknowledged.

Registry No.—**4a,** 29583-83-3; **4b,** 29444-93-7; **8,** 66374-34-3; **9a,** 66374-35-4; **9a** acid chloride, 66374-36-5; **9b,** 66374-37-6; **9b** methyl ester, 66374-38-7; **10a,** 66374-39-8; **10b,** 66374-40-1; **11a,** 66374-08-1; **11b,** 66511-71-5; **12,** 66374-09-2; **13a,** 5079-90-3; **13b,** 66374-10-5; **14a,** 17563-11-0; **14b,** 66374-11-6; **15a,** 66511-72-6; **15b,** 66511-73-7; **16a,** 66374-12-7; **16b,** 66374-13-8; **17a,** 66374-14-9; **17b,** 66374-15-0; **18a,** 66374-16-1; **18b,** 66511-74-8; **19a,** 5394-86-5; **20a,** 66374-17-2; **20b,** 66374-18-3; **21a,** 2428-41-3; **22a,** 66374-19-4; **23,** 4024-14-0; **24,** 6057-87-0; **25,** 66374-20-7; **26,** 33776-38-4; **27,** 16776-12-8; **28,** 10468-84-5; **29,** 66374-21-8; **30,** 66374-22-9; trimethyl phosphonacetate, 5927-18-4; *trans*-chalcone, 614-47-1; 4-methoxyphenylacetic acid, 104-01-8; 3-(4-methoxyphenylmethylene)-1(3*H*)-isobenzofuranone, 4767-61-7; 3-(4-methoxyphenylmethyl)-1(3*H*)-isobenzofuranone, 66374-23-0; 3-phenyl-5-(phenylmethylene)-2-cyclopenten-1-one, 66374-24-1; 2-phenyl-5-(phenylmethylene)-1,3-cyclopentadiene, 66374-25-2.

References and Notes

(1) (a) This is Paper 115 of our photochemical series; (b) for a preliminary report of this work see H. E. Zimmerman and T. P. Cutler, *J. Chem. Soc., Chem. Commun.*, 232 (1978).
(2) For Paper 114 see H. E. Zimmerman, M. G. Steinmetz, and C. L. Kreil, *J. Am. Chem. Soc.*, **100,** 4146 (1978).
(3) (a) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Am. Chem. Soc.*, **93,** 3662 (1971); (b) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **92,** 3474 (1970).
(4) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96,** 439 (1974).
(5) R. H. Wiley and C. E. Staples, *J. Org. Chem.*, **28,** 3408 (1963).
(6) G. Boothe and A. Turner, *J. Chem. Soc. C*, 668 (1966).
(7) H. E. Zimmerman, *Mol. Photochem.*, **3,** 281 (1971).
(8) (a) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **97,** 3718 (1975); (b) H. E. Zimmerman, F. X. Albrecht, and M. J. Haire, *ibid.*, **97,** 3726 (1975); (c) H. E. Zimmerman and L. M. Tolbert, *ibid.*, **97,** 5497 (1975).
(9) (a) Note also pioneering work by W. Ware.[9b,c] The method in ref 9b used a sum of exponentials with fixed exponents and variable preexponential terms adjusted to fit experiment. The more recent work in ref 9c uses adjustable exponents which then correspond to actual rate constants. Except for the mode of reiteration, the latter method parallels our own technique.[4] (b) W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *J. Phys. Chem.*, **77,** 2038 (1973); (c) M. H. Hui and W. R. Ware, *J. Am. Chem. Soc.*, **98,** 4718 (1976).
(10) H. E. Zimmerman and T. P. Cutler, *J. Chem. Soc., Chem. Commun.*, 598 (1975).
(11) (a) J. A. Berson and M. R. Willcott, *J. Am. Chem. Soc.*, **88,** 2494 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Am. Chem. Soc.*, **89,** 4076 (1967). These early examples involved scrambling of the sp^3-hybridized carbon in tropylidenes. The reaction was envisaged as proceeding by this carbon walking along the periphery of the rest of the system with retention of configuration. We have described a ground-state example in which the nonring carbon walked around a five-ring with inversion of configuration:[11c-e] (c) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88,** 5352 (1966); (d) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90,** 5612 (1968); (e) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91,** 434 (1969). (f) Related examples by Hart[11g] and Winstein[11h] also involve five rings: (g) D. W. Swatton and H. Hart, *ibid.*, **89,** 5076 (1967); H. Hart, T. R. Rogers, and J. Griffiths report a case of inversion of configuration [*J. Am. Chem. Soc.*, **91,** 754 (1969)]; (h) R. F. Childs and S. Winstein also noted a case of inversion [*J. Am. Chem. Soc.*, **90,** 7146 (1968)].
(12) (a) One early example is the type A dienone rearrangement;[12b] however, the actual rearrangement step is really a ground-state process and is described in ref 11c–e as "photochemistry without light": (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83,** 4484 (1961); **84,** 4527 (1962); (c) H. E. Zimmerman and W. Eberbach, *ibid.*, **95,** 3970 (1973); (d) also see ref 3.
(13) (a) N. K. Hamer and M. Stubbs, *Chem. Commun.*, 1013 (1970); (b) T. Tabata and H. Hart, *Tetrahedron Lett.*, 4929 (1969). (c) Also, two examples of toluene formation have been reported which might arise either from a parallel reaction or from a different mechanism involving hydrogen migration:[13d,e] (d) M. Rey, U. A Huber, and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968); (e) H. Hüther and H. A. Brune, *Z. Naturforsch. B,* **23,** 1616 (1968). (f) An interesting alternative mechanism has been presented in ref 13a involving a bicyclo[3.2.0]hepta-1,3-diene intermediate which has been shown[13g] to lead to the spiro product. This alternative mechanism accounts for some but not all of the experimental observations: (g) N. K. Hamer and M. Stubbs, *Tetrahedron Lett.*, 3531 (1972).
(14) H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **91,** 5307 (1969).
(15) The syn and anti designations are a bit arbitrary and depend on substitution in the system under study. In our previous systems[3] the endo isomer gave anti product and exo reactant gave syn product.
(16) The formation of endo isomer from endo precursor actually is inversion of configuration at this one carbon (i.e., C-6), since breaking of one three-ring bond is on the opposite side of C-6 from bonding to this carbon. This nomenclature is a bit confusing, but valid and necessary.
(17) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, N.Y., 1975, Chapter IV.

(18) J. A. Pople, *Q. Rev., Chem. Soc.*, **11**, 273 (1957).
(19) This directionality depends on our arbitrary convention of viewing the molecule from the side having the three-ring projecting above the molecular plane and also on our choice of the enantiomer for discussion.
(20) For a discussion and for references note H. E. Zimmerman, J. Boettcher, N. E. Buehler, G. E. Keck, and M. G. Steinmetz, *J. Am. Chem. Soc.*, **98**, 7680 (1976).
(21) (a) It has been noted by us earlier[21b,c] that often disruption of aromaticity is a factor leading to excited-state activation barriers or to avoidance of pathways involving aromatic rings. In the present instance, avoidance of the benzo π system suggests that this is no longer appreciably excited in the diradical species along the reaction coordinate: (b) H. E. Zimmerman and W. R. Elser, *J. Am. Chem. Soc.*, **91**, 887 (1969); (c) H. E. Zimmerman and D. R. Amick, *J. Am. Chem. Soc.*, **95**, 3977 (1973).
(22) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Am. Chem. Soc.*, **90**, 4892 (1968).
(23) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972).
(24) (a) J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972); (b) J. Michl, "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley, New York, N.Y., 1974, p 301.
(25) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972), have discussed diradicals at length.
(26) (a) H. E. Zimmerman, W. T. Gruenbaum, R. T. Klun, M. G. Steinmetz, and T. R. Welter, *J. Chem. Soc., Chem. Commun.*, 228 (1978); (b) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, N.Y., 1975, note Chapter V.
(27) Obviously, we cannot convert the excited-state wave function into the ground-state one (or the LUMO into the HOMO in the simpler approximation), since the two must remain orthogonal. The two final wave functions will still differ.
(28) Our treatment is reminiscent of that of the more traditional theory of radiationless transitions, which is difficult to utilize practically. For example, note the discussion by B. R. Henry and W. Siebrant in "Organic Molecular Photophysics", J. B. Birks, Ed., Wiley, London, 1973.
(29) K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, N.Y., 1969, Chapter 6.
(30) (a) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); (b) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(31) (a) In our laboratories in unpublished efforts[31b] we have uncovered some extensions of the reaction; (b) H. E. Zimmerman and D. Armesto, unpublished results.
(32) (a) All melting points were determined on 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 or Bruker WH-270 spectrometer. High-pressure liquid chromatography was performed using an LDC 254-nm UV detector which was calibrated for the relative responses of the detected compound and standard. Column chromatography employed Vycor columns such that, with packings containing Sylvania type 2282 phosphor, elution could be monitored with a hand-held UV lamp. (b) For preparations similar to one another, one example is given in detail. For full details in the related cases see ref 32c: (c) T. P. Cutler, Ph.D. Thesis, University of Wisconsin, Madison, 1977.
(33) (a) The synthesis of the corresponding ethyl ester has been described by a similar procedure;[2b] (b) E. Bergman and A. Solomonovici, *Tetrahedron*, **27**, 2675 (1971).
(34) J. Brewbake and J. Napolitano, U.S. Patent 3 409 424 (1968); *Chem. Abstr.*, **70**, 28650f (1969).
(35) W. Treibs and H.-J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).
(36) M. Popovici, V. Ioan, M. Elian, and C. Nenitzecu, *Rev. Roum. Chim.*, **12**, 583 (1967).
(37) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).
(38) D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 475 (1956).
(39) A. Horeau and J. Jaques, *Bull. Soc. Chim. Fr.*, 53 (1948).
(40) V. Borsche and W. Menz, *Ber. Dtsch. Chem. Ges.*, **41**, 190 (1908).
(41) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).
(42) G. Kresze, H.-G. Henkel, and H. Goetz, *Justus Liebigs Ann. Chem.*, **674**, 18 (1964).
(43) H. E. Zimmerman, R. A. Bunce, D. Tartler, and T. R. Welter, unpublished results.
(44) J. K. Stille and C. N. Wu, *J. Org. Chem.*, **30**, 1222 (1965).
(45) J. English and G. Cavaglier, *J. Am. Chem. Soc.*, **65**, 1085 (1943).
(46) J.-P. Quillet and J. Dreux, *Bull. Soc. Chim. Fr.*, 645 (1966).
(47) H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weigt, *Mol. Photochem.*, submitted for publication.
(48) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(49) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Am. Chem. Soc.*, **95**, 2155 (1973).
(50) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.
(51) H. E. Zimmerman and M. G. Steinmetz, unpublished results.
(52) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, **35**, 33 (1974).
(53) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).
(54) W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).
(55) W. W. Schoeller and J. Dahm, *Tetrahedron*, **29**, 3237 (1973).
(56) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
(57) R. Hoffmann, *J. Chem. Phys.*, **39**, 1387 (1963).
(58) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73 (1972).
(59) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. A*, 3579 (1971).
(60) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).

Thioxanthenylidene: A Nucleophilic Carbene[1]

Timothy B. Patrick,* Marjorie A. Dorton,[2] and James G. Dolan

Department of Chemistry, Southern Illinois University, Edwardsville, Illinois 62026

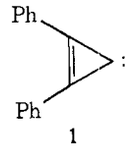
Received March 10, 1978

Photolysis of 9-diazothioxanthene (8) in tetrahydrofuran solution has been used to generate thioxanthenylidene (7). In the presence of cyclohexene, the primary product was the dimer thioxanthenylene. In the presence of dimethyl fumarate and dimethyl maleate, the major products were the carbene adducts **12** and **13**, respectively. The data clearly show that carbene 7 exhibits nucleophilic character. Attempts were made to generate thioxanthenylidene 10,10-dioxide, but its precursor, 9-diazothioxanthene 10,10-dioxide, gave only dimer and products from 1,3-cycloaddition reactions.

The electrophilic nature of a carbene can be attenuated by overlap of its vacant p orbital with electron-donating substituents or by incorporation of the vacant p orbital into an aromatic π system. The carbene can behave as a nucleophile if extensive stabilization of the vacant p orbital is achieved.[3]

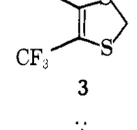
Diphenylcyclopropylidene (**1**)[4] and cycloheptatrienylidene (**2**)[5,6] are prime examples of carbenes that exhibit nucleophilic reactions toward electron-deficient alkenes (e.g., fumaronitrile and dimethyl fumarate). In these systems, the vacant p orbital has been stabilized by incorporation into a carbocyclic aromatic π system.

Heteroatom interactions with carbenic centers are also known. Pertinent to our work are the sulfur-containing car-



1

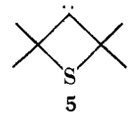

2



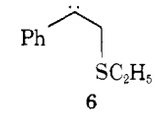
3

$CH_3\ddot{S}\ddot{C}SCH_3$

4



5



6

0022-3263/78/1943-3303$01.00/0