

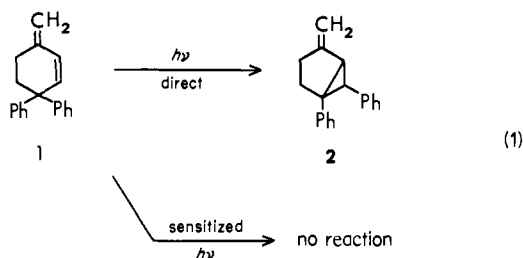
# Multiplicity Control of Reaction Pathways. Mechanistic and Exploratory Organic Photochemistry. LXXIII<sup>1,2</sup>

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**Abstract:** The photochemistry of 5,5-diphenyl-1,3-cyclohexadiene was investigated for comparison with that of 1-methylene-4,4-diphenyl-2-cyclohexene in order to determine the effect of a molecular free rotor on the reaction multiplicity. In contrast to the 4,4-diphenyl diene, whose triplet proved totally unreactive, the 5,5-diene triplet rearranged smoothly *via* a di- $\pi$ -methane mechanism. This difference is attributed to a free rotor effect in which the exocyclic methylene group dissipates excitation energy of the 4,4-diene triplet while the constrained 5,5-diene has no comparable free rotor available. The triplet di- $\pi$ -methane products were shown to be the stereoisomeric *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene and *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene. The singlet excited state of the 5,5-diene led primarily to 1,1-diphenyl-1,3,5-hexatriene with minor formation of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene. The investigation was continued with a study of the photochemistry of the *cis* and *trans* 5,6-bicyclic olefins as well as the *cis*- and *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexenes. In the case of the 5,6-bicyclic olefins both rearrangement to the 4,5-bicyclic olefins and stereoisomerization were encountered while the 4,5-bicyclic olefins gave only rearrangement to the 5,6-bicyclic olefins. The *cis*-*trans* isomerization of the 5,6-bicyclic olefins had two potential pathways, namely (a) internal three-ring bond fission and reclosure with inversion and (b) cleavage of an external bond with group rotation and reclosure. Formation of the 4,5 isomers was *a priori* possible either by internal bond fission and diradical recombination allylically or by a 1,3-sigmatropic rearrangement. By resolution and study of the optically active 5,6-bicyclic olefins it was possible to elucidate the mechanisms used by the excited singlet and triplet states. There was observed a preference for the triplet to undergo external bond fission and single bond rotation with reclosure to give stereoisomerization. In contrast the singlet excited states showed  $\sigma$  preference for involvement of the internal three-ring bond; and it was demonstrated that a 1,3-sigmatropic concerted process was primarily utilized. Thus, mechanisms observed were 1,1-antarafacial, 1,3-suprafacial, 1,3-antarafacial, and 1,1-suprafacial rearrangements, with either inversion or retention of the migrating group being preferred in each case. Evidence was adduced that the forward and backward reaction routes involve nonintersecting potential energy surfaces. A generalization proved useful—that triplet excited states can approach product most rapidly by spatial separation of two odd-electron moieties with an approach to a double doublet configuration while singlet excited states can approach product best by ground state-excited state mixing *via* symmetry allowed processes having points where ground and excited state energy surfaces are close.

Previously we investigated the photochemistry of 1-methylene-4,4-diphenyl-2-cyclohexene (**1**) and found that its rearrangement to the bicyclo[3.1.0] product (**2**) derived exclusively from the singlet with a dramatic lack of reactivity of the triplet.<sup>3</sup> Additionally, there was evidence<sup>4</sup> for utilization of singlet excited states and lack of triplet reactivity in the di- $\pi$ -methane rearrangement of acyclic 1,4-dienes. In the case of 1-methylene-4,4-diphenyl-2-cyclohexene (**1**) the lack of triplet reactivity was ascribed<sup>2</sup> to a "free rotor" effect wherein twisting of the exocyclic methylene group led to rapid radiationless decay of the triplet (*cf.* eq 1). For the acyclic systems direct



(1) For paper LXXII of the series, note H. E. Zimmerman and R. D. Little, *J. Amer. Chem. Soc.*, **94**, 8258 (1972).

(2) For a preliminary report of the photochemistry of 5,5-diphenyl-1,3-cyclohexadiene, note H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

(3) (a) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (b) *ibid.*, **89**, 5971 (1967).

(4) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

experimental support was obtained that such free rotation actually did occur in the triplet excited states.<sup>5</sup> In contrast the di- $\pi$ -methane rearrangement of bicyclic systems seemed to prefer utilization of the triplet.<sup>6</sup>

Thus the generalization was drawn<sup>4</sup> that acyclic di- $\pi$ -methanes rearrange by way of the singlet excited states while the bicyclics utilize the triplet; note Table I. That the photochemical behavior of the mono-

**Table I.** Correlation of Multiplicity with Acyclic *vs.* Bicyclic Di- $\pi$ -methane Structure<sup>4</sup>

	Acyclic	Bicyclic
Singlet	Efficient	Inefficient
Triplet	Inefficient	Efficient

cyclic diene **1** paralleled that of the acyclic dienes rather than the bicyclic ones seemed to derive from the presence of the exo-methylene free rotor. One of the

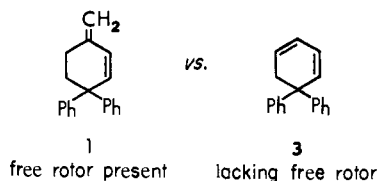
(5) (a) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); (b) *ibid.*, **92**, 1409 (1970).

(6) These bicyclic di- $\pi$ -methane reactants are represented by barrelene,<sup>7</sup> benzobarrelene,<sup>8</sup> and the naphthobarrelenes;<sup>9</sup> however, numerous additional examples are to be found in the literature.

(7) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

(8) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(9) H. E. Zimmerman and C. O. Bender, *ibid.*, **92**, 4366 (1970); **91**, 7516 (1969).



first goals of the present research was to ascertain if this was indeed the case.

The approach selected was a study of the endocyclic analog **3** which differs from **1** primarily in lacking the exocyclic free rotor. Additionally, from preliminary studies<sup>2</sup> there was evidence that the photochemistry of diene **3** led to stereoisomeric 5,6-diphenylbicyclo[3.1.0]-2-hexenes (**4a,b**). Exploratory investigation indicated unusual and intriguing photochemistry of these compounds; and, thus the present study was designed to include this bicyclic photochemistry. Furthermore initial results and thoughts on possible mechanisms suggested the utility of having these bicyclic isomers available optically resolved.

## Results

**Exploratory Photochemistry. 5,5-Diphenyl-1,3-cyclohexadiene.** The preparation of the diphenyl diene **3** had been noted in the literature by Dauben<sup>10</sup> and the general procedure proved quite satisfactory. Exploratory photolyses of diphenyl diene **3** were carried out using acetone, xanthone, and benzophenone sensitizers in *tert*-butyl alcohol solvent. This exploratory work employed both 450-W Hanovia apparatus as well as our Black Box<sup>11</sup> apparatus. From these runs one primary photoproduct predominated, this melting at 59.0–59.5°. This was shown to be *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a**) (*vide infra*). In addition to the main reaction product there were formed two products isomeric with **4a** and a benzophenone adduct when this ketone was used as the sensitizer. One of the isomeric products, mp 72–73°, was found to be *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4b**) and the other isomer proved (note below) to be *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene, a known<sup>12</sup> compound. In a typical run, photolysis of 0.332 g of **3** yielded 0.242 g of *trans* 5,6-bicyclic olefin **4a**, 0.017 g of *trans* 4,5-bicyclic olefin **5a**, and 0.006 g of *cis* 5,6-bicyclic olefin **4b**.

In contrast to the sensitized runs, direct photolysis of 5,5-diphenyl-1,3-cyclohexadiene (**3**) gave predominantly 1,1-diphenyl-1,3,5-hexatriene (**6**). However, *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene was obtained additionally in small quantities. Typically, from a 0.27-g run there was obtained 0.144 g of triene **6** and 0.014 g of bicyclic olefin **4a**.

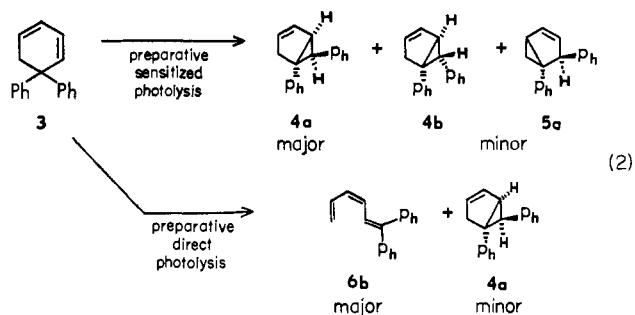
The qualitative photochemical reactivity of 5,5-diphenyl-1,3-cyclohexadiene is outlined in eq 2.

**Structure Elucidation of Photoproducts from Diphenyl Diene 3.** The structures of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a** and **4b**) were established unambiguously by synthesis from the known<sup>13</sup> *trans*-

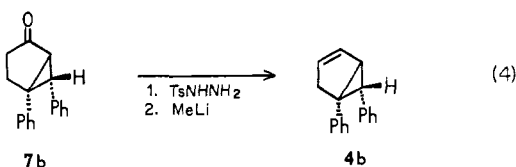
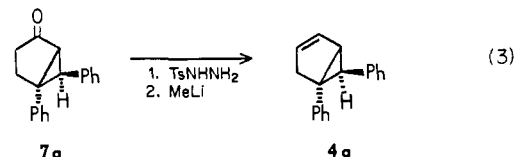
(10) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

(11) (a) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3662 (1971); (b) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).

(12) (a) J. Swenton, A. Crumrine, and T. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970). It is noted that the present study is complementary to that of Swenton. By mutual agreement emphasis was placed on different aspects. (b) J. Swenton and A. Wexler, *ibid.*, **93**, 3068 (1971). (c) We acknowledge with thanks receipt of an nmr spectrum of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene from Dr. Swenton.



and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexenes (**7a** and **7b**), respectively. For these conversions the Dauben method<sup>10</sup> for conversion of ketones to olefins was employed.



In the case of the remaining isomer obtained on sensitized photolysis, it appeared that this was most likely either *trans*- or *cis*-4,5-diphenylbicyclo[3.1.0]-2-hexene (**5a** or **5b**). These compounds were obtained from the extended pyrolysis of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a**) as described by Swenton<sup>12b,c</sup> and the remaining photoproduct proved to be *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene (**5a**).

The structure of the last photochemical product, 1,1-diphenyl-1,3,5-hexatriene (**6**), derived both (a) from the nmr, which revealed six vinyl hydrogens and ten aromatic protons, and (b) from Lemieux oxidation<sup>14</sup> to give benzophenone. That the initial photoproduct was the *cis* isomer of **6** (*i.e.*, **6b**) was suggested by an nmr change on iodine treatment which corresponded to downfield shift of an area of two protons and thus formation of the *trans* stereoisomer **6a**.

**Quantum Yield Determinations of the Photochemical Rearrangement of 5,5-Diphenyl-1,3-cyclohexadiene.** The determination of the quantum yields for the direct and sensitized irradiations posed difficulties which typify pitfalls common to quantitative photochemistry. Thus in the direct irradiation of 5,5-diphenyl diene **3** the formation of the strongly absorbing triene product **6** meant that runs to high conversion risked artificially low quantum yields. This problem was avoided by selection of a filter corresponding to a region where the relative optical density problem was minimized and by running to differing extents of conversion and extrapolating to zero time. In sensitized runs it was important to avoid secondary reaction and to make certain that light was totally absorbed by the sensitizer.<sup>15</sup>

(13) H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964).

(14) (a) R. Lemieux and E. v. Rudloff, *Can. J. Chem.*, **33**, 1701 (1955); (b) M. E. Wall and S. Serota, *J. Org. Chem.*, **24**, 741 (1959).

(15) A summary of some of the factors important in design of quantitative photochemical experiments can be found in ref 11b and 16.

(16) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

Table II. Quantum Yield/ Determinations for Photolysis of 5,5-Diphenyl Diene 3

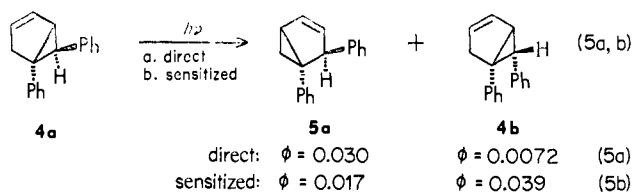
Run	[3], <i>M</i>	[Sensitizer], ( <i>M</i> )	Convsn, %	Quantum yields <sup>a</sup>			
				$\phi(6)$	$\phi(4a)$	$\phi(4b)$	$\phi(5a)$
DQ-1 <sup>d</sup>	0.0029		14	0.35	0.039	<0.001	<0.001
DQ-2 <sup>d</sup>	0.0012		24	0.32	0.045	<0.001	<0.001
DQ-3 <sup>d</sup>	0.0014		41	0.26	0.046	<0.001	<0.001
DQ-4 <sup>d</sup>	0.0011		60	0.24	<i>g</i>	<0.001	<0.001
DBQ-1 <sup>b,c</sup>	0.0017	Benzophenone <sup>e</sup> (0.0075)	24	<0.001	0.16	<i>g</i>	<i>g</i>
DBQ-2 <sup>b,c</sup>	0.0024	Benzophenone <sup>e</sup> (0.0082)	82	<0.001	0.15	0.0077	0.0040
DXQ-1 <sup>c</sup>	0.0076	Xanthone <sup>e</sup> (0.0049)	23	<0.001	0.20	0.0046	0.018
DXQ-2 <sup>c</sup>	0.0060	Xanthone <sup>e</sup> (0.0047)	43	<0.001	0.19	0.0069	0.021

<sup>a</sup>  $\phi(6)$  refers to efficiency of formation of 1,1-diphenyl-1,3,5-hexatriene,  $\phi(4a)$  refers to efficiency of formation of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi(4b)$  refers to efficiency of formation of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi(5a)$  refers to efficiency of formation of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene. <sup>b</sup> Oxetane by-product observed. <sup>c</sup> *tert*-Butyl alcohol solvent. <sup>d</sup> Cyclohexene solvent. <sup>e</sup> >99% light absorbed by sensitizer. <sup>f</sup> Black Box apparatus. <sup>g</sup> Not determined.

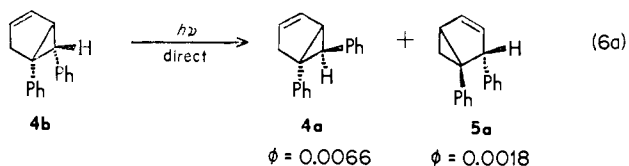
Table II summarizes both direct and sensitized quantum yield determinations.

**Exploratory and Quantitative Photolysis of the *trans*- and *cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexenes.** Exploratory runs were made using both the 450-W immersion apparatus and also the Black Box apparatus.<sup>11</sup> Direct photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a**) was found to give rise to both *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene (**5a**) and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4b**). Quantum yield determinations were run in the Black Box apparatus using 250–310-nm solution filters. The efficiencies obtained are given in eq **5a** and roughly parallel the relative product distributions in exploratory runs.

In contrast to the direct photolysis, xanthone sensitized irradiation of the *trans* 5,6-bicyclic olefin **4a** afforded mainly *cis* bicyclic olefin **4b** with smaller amounts of the *trans* 4,5-bicyclic olefin **5a**. These results along with the observed quantum yield are shown in eq **5b**.

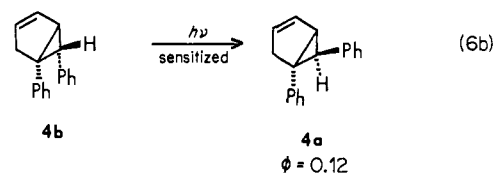


In the case of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4b**) direct irradiation led principally to *trans* 5,6-bicyclic olefin **4a** and additionally to *trans* 4,5-bicyclic olefin **5a**. This is depicted in eq **6a** along with the quantum yields obtained.

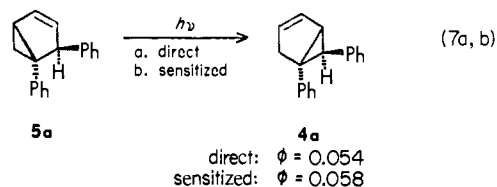


When xanthone sensitization was employed no 4,5-bicyclic product was obtained and the *trans* 5,6-bicyclic olefin **4a** was the only product. This reaction is outlined in eq **6b** along with the quantum yield.

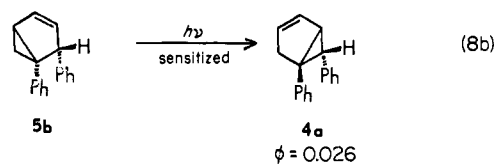
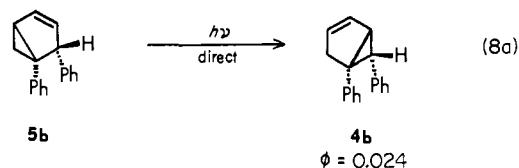
**Exploratory and Quantitative Photolyses of the *trans*- and *cis*-4,5-Diphenylbicyclo[3.1.0]-2-hexenes.** For these runs the Black Box apparatus with 250–310-nm solution



filters was employed. Both direct and sensitized irradiations of the *trans* 4,5-bicyclic olefin **5a** led to formation of the single product *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a**) (note eq **7a** and **7b**). In contrast, the



direct and sensitized photolyses of *cis* 4,5-bicyclic olefin **5b** afforded different results. The direct irradiation gave exclusively *cis* 5,6-bicyclic olefin **4b** while the sensitized reaction gave only the *trans* 5,6-bicyclic olefin **4a**. This is given in eq **8a** and **8b**.



**Preparation of Optically Active *trans*- and *cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** At this point in the research it became clear that the interconversions of the bicyclic olefins could proceed *via* several mechanistically discrete processes. Our previous study<sup>17</sup> on the photochemical stereoisomerization of the *cis*- and *trans*-5,6-diphenylbicyclic ketones **7a** and **7b** suggested the utility of optically active reactants and products. Thus attention was turned towards preparation of resolved

(17) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).

Table III. Stereochemistry of Cis-Trans Isomerization of the 5,6-Diphenyl Olefins

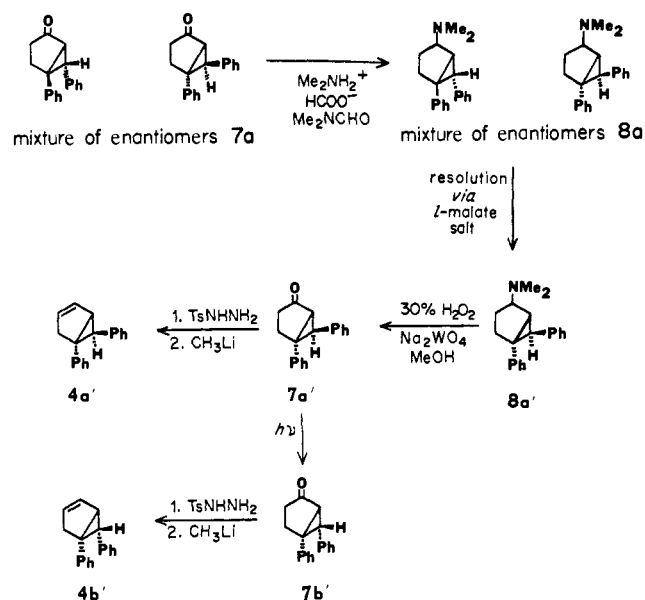
React.	Conditions	$[\alpha]_D^{25}$ of recov react.	$[\alpha]_D^{25}$ of prod	Prod racem, %	Recov react. racem, %	Retent of C-5 config in prod, %
4a'	Direct	+3020	+2100	5.0	0.5	97.5
4a'	Sensitized	+3010	+2070	6.3	0.6	96.9
4b'	Direct	+2150	+1835	39.4	2.6	80.3
4b'	Sensitized	+2190	+2880	5.0	1.0	97.5

<sup>a</sup> Value given for specific rotation of trans olefin 4a' at 278 nm and for cis olefin 4b' at 292 nm.

*trans*- and *cis*-5,6-diphenyl bicyclic olefins 4a and 4b. Ideal starting materials were the optically active *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanones (7a' and 7b'). Not only were these readily obtained by the method of Zimmerman, Hancock, and Licke<sup>17</sup> but additionally the method provided enantiomers of the 5,6-diphenyl bicyclic olefins 4a and 4b with identical configurations at C-5. The critical step of photochemical conversion of optically active trans ketone 7a' to optically active cis ketone 7b' is known<sup>17</sup> to proceed with complete retention of configuration at C-5 and inversion at C-6.

The optically active ketones were converted to the corresponding optically active 5,6-diphenyl bicyclic olefins 4a' and 4b' using the Dauben reaction.<sup>10</sup> This sequence is outlined in Chart I. Optical purity was

Chart I. Synthesis of Optically Active *trans*- and *cis*-5,6-Diphenyl Bicyclic Olefins



supported by isolation of the enantiomeric optically active amine 8'' from the mother liquors of the resolution leading to 8'; after recrystallization, this had equal but opposite rotation. In addition each optically active compound utilized was crystallized to constant rotation.

The rotations of 4a' and 4b' were positive in the 250–600-nm range and thus this synthesis provided the information that *cis*- and *trans*-5,6-diphenyl bicyclic olefins with the same rotation had the same C-5 configuration but C-6 inverted.

**Photolysis of the Optically Active 5,6-Diphenyl Bicyclic Olefins.** Photolysis of the optically active olefins gave the same product distributions observed in case of the inactive reactants (*vide supra*). However, here the rotations of the products were determined.

Additionally, ORD curves were obtained in order to ascertain that there was no contribution due to optically active contaminants.

It was found that in the *cis*-*trans* isomerizations of the 5,6-diphenyl bicyclic olefins 4a and 4b the preferential stereochemistry was retention of configuration at C-5. Thus, in direct and sensitized irradiations of the *trans* reactant 4a complete retention of stereochemistry at C-5 was observed, as was the case also with sensitized irradiation of the *cis* isomer 4b to give 4a. However, in the direct irradiation of *cis* isomer 4b to give 4a, 40% racemization resulted. These results are listed in Table III.

### Interpretative Discussion

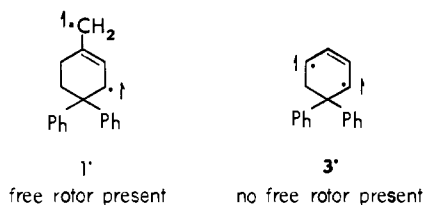
**Mechanism of the Photochemistry of 5,5-Diphenyl-1,3-cyclohexadiene.** The most striking aspect of the photochemistry of the diphenyl diene 3 is the different behavior on direct photolysis compared with sensitization. The formation of 1,1-diphenyl-1,3,5-hexatriene (6) only on direct irradiation provides evidence that this electrocyclic process occurs by way of the singlet excited state of 3.

The predominant conversion of diphenyl diene 3 to the bicyclic olefins 4a, 4b, and 5a on sensitized photolysis indicates these products arise from rearrangement of the triplet excited state of diphenyl diene 3. That some bicyclic product (*i.e.*, 4a) was found in the direct irradiation leaves unproven whether this is formed from the singlet excited state as well, since 4a could theoretically arise either from the singlet or from triplet formed by some intersystem crossing from the singlet.

We note that the formation of 1,1-diphenyl-1,3,5-hexatriene (6b) involves a process in which all delocalized electrons are distributed throughout the molecular system during reaction. In contrast, the triplet process can be seen to proceed *via* a phenyl bridged biradical in which the two odd electrons are formally separated.<sup>18</sup> This observation can be generalized and is discussed below; however for the present it is sufficient to note that it is the electrocyclic process which is favored by the singlet excited state.

Focusing attention on the triplet reaction, we find the observed reactivity of 5,6-diphenyl-1,3-cyclohexadiene (3) to be in dramatic contrast with unreactive triplet of 1-methylene-4,4-diphenyl-2-cyclohexene (1) mentioned earlier in the introduction. The main structural difference of the present 5,5-diphenyl diene 3 is the absence of the exo methylene free rotor (=CH<sub>2</sub>); note 3\* *vs.* 1\*. Thus the idea of triplet energy dissipation

(18) This terminology is convenient but inexact since for most systems under consideration all electrons are really permuted in either case. A more rigorous statement would differentiate between cases where in the singly occupied MO's there is relatively even weighting of AO's from the different parts of the system compared with cases where the AO's in each singly occupied MO are heavily concentrated in one end or the other of the system.



by presence of such potential molecular free rotors accords with this evidence.

A comment is needed to clarify just what mechanism is utilized for energy dissipation and to comment on the relative effectiveness of free rotors in dissipating singlet *vs.* triplet excitation energy. A consideration of the torsional frequency, or energy, for ethylene reveals that with a fundamental of *ca.* 800  $\text{cm}^{-1}$  (*i.e.*, 2.3 kcal per vibrational level), an extremely high vibrational state of the electronic ground state would have to be reached to dissipate the *ca.* 59 kcal/mol electronic excitation energy of a transoid diene triplet (*i.e.*, the triplet of  $1^*$ ). That this is possible is seen in the following. Examination of the energy of ethylene electronic states *vs.* angle of twist, as calculated by Mulliken<sup>19</sup> and by Shavitt<sup>20</sup> and depicted in Figure 1,<sup>21</sup> does indicate crossing of ground state and first triplet excited state potential energy surfaces but not the first singlet excited state. This suggests that the ground state ethylenic well, corresponding to torsion, should have torsional vibrational states reaching the energy of the first triplet and allowing adiabatic conversion of  $T_1$  to  $S_0$ . Hence exceedingly high quantum number vibrations, seemingly inaccessible from the ground state, may well facilitate intersystem crossing from the triplet. We note that the excited singlet state potential energy surface does not cross the ground state and conversion to ground state should be less efficient. Still another difference between the singlet and triplet energy dissipation arises as a consequence of the spin difference and is discussed more generally below.

Thus it is seen that unconstrained  $\pi$  bonds provide a unique molecular feature for rapid destruction of excited triplets.

**Mechanism of the Photochemistry of the Bicyclic Olefins. Multiplicity.** The first point which is striking is the difference in behavior of the 5,6-bicyclic olefins **4a** and **4b** in direct irradiations *vs.* sensitized ones. The simplest rationale is that the direct runs give reactions arising from the first excited singlet  $S_1$  while the sensitized runs give product from the first triplet  $T_1$ .

Nevertheless, one has to worry about the possibility that some of the product from direct irradiation really derives from  $T_1$  with  $T_1$  being formed by intersystem crossing. That the efficiencies for some products are lower in direct runs *vs.* sensitized ones is not proof against this, since intersystem crossing might merely be inefficient.

However, there is some evidence to support the simple rationale. Thus in the irradiation of trans 5,6-bicyclic olefin **4a** the sensitized run (eq 5b) defines the behavior of  $T_1$  as giving rise to a ratio of *ca.* 2:1 **4b vs.** **5a** prod-

(19) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(20) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).

(21) Similarly, an SCF-CI calculation including the  $\sigma$  system has been described by N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 4427 (1971), and predicts preferred twisting of the terminal methylene of triplet butadiene.

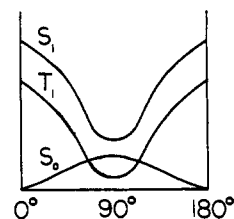


Figure 1. Potential energies of  $S_0$ ,  $S_1$ , and  $T_1$  *vs.* angle of twist for olefins.

uct. In the direct runs (eq 5a), with **4b** being formed with an efficiency of 0.0069, one would expect only half of this value for the efficiency of formation of trans 4,5-bicyclic product **5a** if both **5a** and **4b** came from  $T_1$ . However, the efficiency of formation of trans 4,5-bicyclic product **5a** is  $\phi = 0.029$  and ten times as great as it would be if  $T_1$  were the sole reacting state. Hence, minimally we can conclude that  $S_1$  is primarily responsible for the observed photochemistry. We note that this argument is really a version of the "fingerprint" method of identifying excited states as outlined by us earlier.<sup>22</sup>

Similarly, in the reaction of the cis 5,6-bicyclic olefin, if all of the direct irradiation product (eq 6a) derived from  $T_1$ , then this would signify that the trans 4,5-bicyclic olefin **5a** would be formed with *ca.* one-third the efficiency relative to trans 5,6-bicyclic product **4a**. However, the sensitized run (eq 6b) gave only the trans 5,6-bicyclic product **4a**; **5a** would have been detected in anything approaching  $1/20$ th of the main product **4a**. Thus the direct run does not involve appreciable triplet photochemistry.

In general then it appears that poor intersystem crossing and rapid singlet reactivity are responsible for the different photochemistry observed in direct and sensitized runs and that we are indeed seeing  $S_1$  reactivity in the direct runs and  $T_1$  behavior in the sensitized ones.

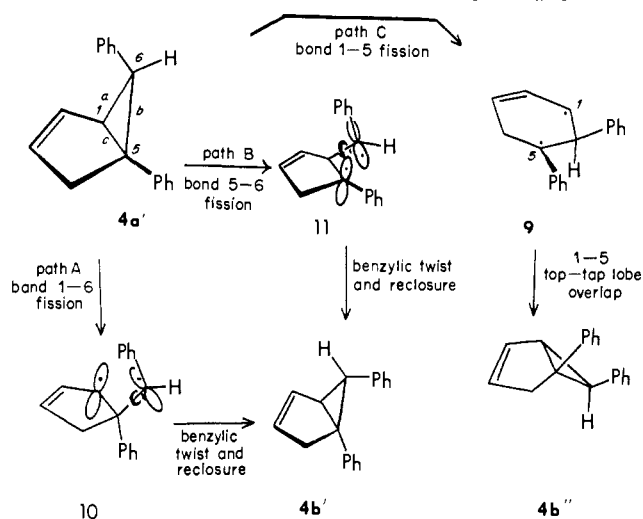
A second general trend is the tendency for the singlet photochemistry to lead to the 1,3-sigmatropic rearrangements interconverting the 5,6 and 4,5 isomers contrasted with a tendency for the triplet to give cis-trans isomerization. This is best considered in connection with the individual mechanisms.

**Stereochemistry of the Cis-Trans Isomerizations.** One intriguing but difficult point in considering the cis-trans isomerization mechanisms was the fact that this could arise, *a priori*, from involvement of either the internal three-ring bond c or of one of the external three ring bonds (a or b). Thus, for example, the conversion of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**4a**) to the cis 5,6-bicyclic olefin **4b** might arise by either paths A, B or C of Chart II.

Inspection of Chart II, however, reveals that if one begins with one enantiomer of the trans 5,6-bicyclic olefin, for example, **4a'**, mechanism C affords enantiomer **4b''** of the cis 5,6-bicyclic olefin product while out-of-plane fission mechanisms A and B lead to enantiomer **4b'** of product. Thus, the out-of-plane bond fission mechanisms A and B do not disturb the configuration at C-5 but do invert the configuration at C-6; the converse is true of the internal bond fission mechanism C. For the reverse reaction, namely con-

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

Chart II. Possible Mechanisms of Cis-Trans Isomerization



version of cis to trans 5,6-bicyclic olefin, the same stereochemical correlation exists.

Hence by utilization of optically active cis and trans 5,6-bicyclic olefins, and determining the extent to which the configuration at C-5 had been retained or inverted, it was possible to establish the relative amounts of the internal bond fission *vs.* external bond fission mechanisms. The details of runs on optically active reactants have already been described; the resulting mechanistic conclusions are tabulated in Table IV. It is seen that

Table IV. Extent of Internal *vs.* External Bond Fission Mechanisms in Stereoisomerization

Reactant	Multiplicity	External bond fission	Internal bond fission
Trans 5,6-olefin	Singlet	97.5	2.5
Trans 5,6 olefin	Triplet	96.9	3.1
Cis 5,6 olefin	Singlet	80.3	19.7
Cis 5,6 olefin	Triplet	97.5	2.5

the preferred mechanism in all stereoisomerizations involves fission of the external bonds (mechanisms A and B). The two alternatives, A and B, are really not different in kind and no attempt seemed necessary to distinguish between these. The preference for these mechanisms seems a result of the better overlap of the  $\pi$  systems with the  $\sigma$  orbitals comprising bonds a and b relative to c. For example, fission of bond b allows scission with overlap of the ever lengthening  $\sigma$  bond b with both phenyl groups during the entire process. For bond c fission, overlap is initially poor due to the near orthogonality of this bond's orbitals with the double bond. Nevertheless, the singlet excited state of the cis 5,6-bicyclic olefin does proceed with significant usage of mechanism C.

From Table IV and the above discussion, one might conclude that external bond fission predominates heavily in all cases. It should be recognized that Table IV has dissected the data to include only fissions leading to cis-trans isomerization. Table V considers the total amount of internal *vs.* external bond fission with both stereoisomerization and sigmatropic rearrangement being included, and gives for each excited state the ratio  $k_{\text{ext}}/k_i$  where  $k_i$  is the rate of internal bond

Table V. Total Amounts of Internal *vs.* External Bond Fission

Reactant	Multiplicity	Percentage reaction with internal bond involvement		
		Sigmatropic rearr.	Stereoisom <sup>a</sup>	$k_{\text{ext}}/k_i$
4a	Singlet	81	0.05	0.2
4a	Triplet	30	2	2.1
4b	Singlet	21	16	1.7
4b	Triplet	0	2	49.0

<sup>a</sup> The overall percentage is equal to the product of the percentage of reaction which is stereoisomerization and the fraction of isomerization occurring by internal bond fission.

fission and  $k_{\text{ext}}$  is the rate of external bond fission which leads to reaction. These constants will not include the bond cleavage which is followed by return to starting material.

Another interesting conclusion is possible from the results. It is seen that the partitioning between mechanisms in the conversion of the cis 5,6-bicyclic olefin singlet to trans product is not the same as that for conversion of the trans 5,6-bicyclic olefin singlet to cis product. This is another striking example demonstrating that microscopic reversibility is an argument which cannot be applied to photochemical interconversion of two different molecules. This result derives from the fact that in very few photochemical reactions is the excited state of product an intermediate in the mechanism. Thus the initially formed species in one direction, namely the excited state of reactant, is not a species which is on the reaction coordinate in the reverse reaction. This point has been made in a somewhat different way by us earlier.<sup>17</sup>

#### Mechanisms of the 1,3-Sigmatropic Rearrangements.

The gross mechanism of the interconversion of the 5,6-bicyclic olefin stereoisomers 4a and 4b with the 4,5-bicyclic olefin stereoisomers 5a and 5b is easier than the cis-trans stereoisomerizations to discuss, since the mechanism necessarily must involve cleavage of the internal bond (*i.e.*, bond c in Chart II). However, a more subtle problem concerns the existence of two possible mechanisms differing only in degree of bond fission during rearrangement. Thus, the sigmatropic rearrangement of trans 5,6-bicyclic olefin 4a to trans 4,5-bicyclic olefin 5a has the *a priori* possibility of proceeding *via* a concerted 1,3-sigmatropic process or the alternative of going by way of a discrete biradical (*i.e.*, species 9) as depicted for path C in Chart II.

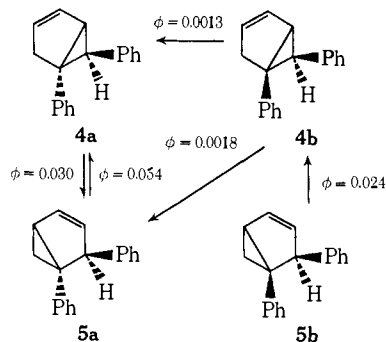
Such mechanistic possibilities have to be considered individually for the singlet and the triplet processes. These processes along with stereoisomerization are summarized in Chart III (A and B), and it is seen that the behavior does depend on multiplicity.

Additionally, in considering the mechanisms of the internal bond sigmatropic processes, we should compare the results of Swenton<sup>12b</sup> in which interconversions of 4a, 4b, 5a, and 5b were observed thermally. In these studies, two benzylic-allylic biradicals corresponding to 9 were suggested as intermediates with one having a cis and the other a trans conformation.<sup>23</sup>

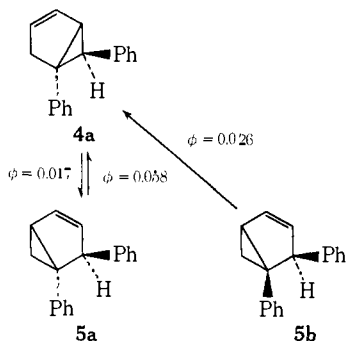
(23) (a) See also W. von E. Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963), for evidence supporting two conformationally distinct species in the thermal chemistry of thujene. (b) Note ref 12b. In this study the alternative mechanism of external bond fission for stereoisomerization was not excluded. Also, the thermolyses of the cis 5,6-

Chart III. Singlet and Triplet Rearrangements Involving Internal Bond Fission<sup>a</sup>

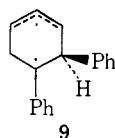
A. Singlets:



B. Triplets:



<sup>a</sup> Contributions due to external bond fission are excluded.



Comparison with the thermal rearrangements is possible only for the interconversion of the trans bicyclic olefins **4a** and **5a** where the ground state kinetic behavior was studied.<sup>23b</sup> Such a comparison does show the same tendency for the trans isomers to interconvert, in both thermal and photochemical processes, rather than to lead to any cis product. But beyond this, the hypothesis proposed for the ground state interconversions does not seem applicable to the photochemical results. Specifically, to the extent that both cis structural isomers, namely cis 5,6-bicyclic olefin **4b** and cis 4,5-bicyclic olefin **5b**, give rise to a cisoid conformer of biradical **9** as suggested for the ground-state chemistry, this biradical would have to behave identically, independent of which cis isomer gave rise to it.

Looking first at the singlet processes depicted in Chart IIIA, we note this not to be the case. The cis 4,5-bicyclic olefin **5b** gives exclusively the cis 5,6-bicyclic olefin **4b** while **4b** gives the two trans bicyclic olefins **4a** and **5a**.

Proceeding to the triplet behavior outlined in Chart IIIB, we find that *cis*-4,5-bicyclic olefin **5b** gives only one (*i.e.*, **4a**) of the two trans bicyclic olefin isomers; hence the behavior of any species derived from internal bond opening of the triplet is still different from any observed from either of the two cis singlets.

This means that there would have to be three different cisoid biradicals, one derived from each of the cis

olefin gave the thermodynamic distribution suggesting that the partition observed may not reflect the kinetics for this isomer. This makes comparison incomplete.

bicyclic olefin singlets and one derived from the triplet of *cis* bicyclic olefin **5b**.

Similarly, the different product distributions starting with trans reactants compared with *cis* isomers provide further evidence against a single species such as biradical **9** common to all reactants, *cis* and *trans*.

Thus, either one or two biradical species will not account for all of the photochemistry observed. In particular, the results exclude a biradical as an intermediate for the singlet photochemistry, even with the assumption of two conformations.

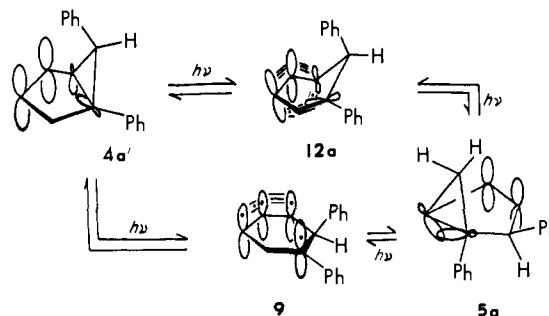
With a common biradical species excluded as an intermediate for all the singlet processes, a concerted mechanism seems most reasonable for the 1,3-sigmatropic rearrangements. This conclusion is not extended to the *cis*-*trans* isomerization (*e.g.*, **4b** to **4a**) for reasons discussed below.

In contrast, the results obtained for the triplet rearrangement (note IIIB) prove consistent with a single allylic biradical intermediate such as **9** which closes preferentially to give *trans* 5,6-bicyclic olefin **4a**. That *trans* 4,5-bicyclic olefin **5a** is formed from *trans* 5,6-bicyclic olefin **4a** but not from *cis* 4,5-bicyclic olefin **5b** is not inconsistent with the biradical mechanism, since the efficiency of each reaction consists of a product of the efficiency of biradical formation multiplied by a partition factor reflecting the tendency to close to give the observed product. In the present instance the observed formation of *trans* 4,5-bicyclic olefin **5a** from *trans* 5,6-bicyclic olefin **4a** would have to arise from a very efficient biradical formation from *trans* 5,6-bicyclic olefin **4a** rather than a facile closure to *trans* 4,5-olefin **5a**. With inefficient closure to *trans* 4,5-olefin **5a**, the formation of essentially exclusively *trans* 5,6-olefin **4a** from *cis* 4,5-olefin **5b** is consistent with the biradical mechanism.

**Molecular Details of the Rearrangement and Stereoisomerization Processes.** It is helpful to note that all of the rearrangements and stereoisomerization processes can be categorized as formal 1,1-sigmatropic or 1,3-sigmatropic rearrangements. These may proceed suprafacially or antarafacially on the allyl  $\pi$  system and with either retention or inversion of configuration of the migrating group.

Thus, in the case of the interconversion of *trans* 5,6-olefin **4a** and *trans* 4,5-olefin **5a** one can picture the process as proceeding *via* an intermediate species **12** (note Chart IV). Such a rearrangement is clearly a

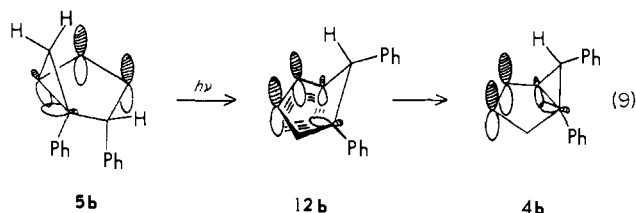
Chart IV. Two Alternative Mechanisms for the 1,3-Sigmatropic Shift *Trans* 5,6-Bicyclic Olefin and *Trans* 4,5-Bicyclic Olefin



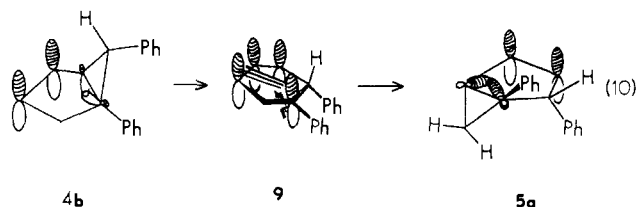
1,3-sigmatropic suprafacial rearrangement in that only one face of the allylic system is bonded to the benzylic center at C-5. It proceeds with retention of configura-

tion of the migrating C-5 benzylic center. The alternative version proceeding *via* the allylic biradical **9** really differs only in flattening out of the  $\pi$  system and can still be considered with the same designation. From the discussion of the preceding section it is seen that such an allylic biradical is an acceptable intermediate in the triplet rearrangement processes but allylic biradical **9** cannot be the ubiquitous intermediate in the singlet reactions. Hence both pathways seem to be used depending on the multiplicity.

Similarly, the singlet conversion of *cis* 4,5-bicyclic olefin **5b** to *cis* 5,6-bicyclic olefin **4b** can be envisaged as proceeding by a 1,3-suprafacial rearrangement with retention of configuration at C-5. That the *cis* stereochemistry is not lost is consistent and in favor of the concerted mechanisms. This is pictured in eq 9.



These reactions can be seen to involve a cyclic array of four orbitals with zero or an even number of sign inversions and thus be said to consist of a Hückel basis set orbital array. With the four delocalized electrons in the  $\pi$  and  $\sigma$  bonds involved in the reaction, the process is ground state forbidden but excited state allowed.<sup>24</sup> The Woodward-Hoffmann rules predict the same allowedness.<sup>25</sup> The singlet photochemistry of *cis* 5,6-bicyclic olefin **4b** contrasts with the previous examples in that it is the one singlet which proceeds *via* a 1,3-antarafacial rearrangement as pictured in eq 10. Since the geometry of the reacting molecule is



very close to totally flattened out at half-reaction, one might enquire if the mechanism can be said to be concerted; it is true that the geometry of the allylic biradical **9** is attained at half-reaction. However, to the extent that the singlet species **9** is not an energy minimum and that its formation and reaction are not separate in time, then one may envisage the singlet rearrangement of **4b** to **5a** as concerted.<sup>26</sup> The utilization of this 1,3-antarafacial rearrangement with C-5 inversion seems a consequence of the steric phenyl-phenyl interaction which would be incurred if rearrangement proceeded to give the *cis* 4,5-bicyclic olefin **5b**. This parallels the ground-state thermodynamics which have been observed<sup>12b</sup> and where **5b** is of high energy. An interesting conclusion results, and this

(24) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

(25) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(26) The suggestion has been made that concerted process is one in which the sub portions of the molecular change overlap in time.<sup>27</sup>

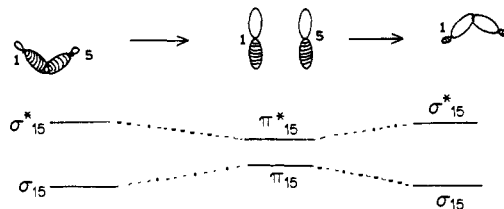
(27) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

is that these singlet reactions do not tend to lead to the ground-state products with minimum excited-state-ground-state energy separation. Rather excited state energetics seem controlling. Finally, we note that the singlet reaction is again an allowed one. Thus the reacting species consists of an array of four orbitals in a cyclic array with zero or an even number of sign inversions (depending on choice of the basis set of orbitals) and can be categorized as Hückel.<sup>24</sup> Such a reaction is ground state forbidden with the four delocalized electrons present in the  $\pi$  bond and  $\sigma$  bond participating. The Woodward-Hoffmann approach again comes to an identical conclusion.

Attention is now turned to reactions which may be termed 1,1-sigmatropic rearrangements. These are the stereoisomerization reactions and they proceed by two basic mechanisms. Accordingly, the internal bond fission-rebonding process can be considered a 1,1-sigmatropic rearrangement proceeding antarafacially at both carbons (or equivalently, antarafacially at one and with inversion at the other). This process is seen most substantially in the stereoisomerization of the singlet excited state of *cis* 5,6-olefin **4b** (note Table IV) where the reaction to give the *trans* 5,6-olefin **4a** proceeds *ca.* 20% by the internal bond fission mechanism. The utilization of this process only by this isomer can again be ascribed to the van der Waals phenyl-phenyl repulsions encountered in the simplest alternative available, namely a 1,3-suprafacial sigmatropic rearrangement to give *cis* 4,5-olefin **5b**; the stereoisomerization by internal bond fission seems then to occur by default.

The correlation diagram for the antara-antara 1,1-sigmatropic rearrangement is given in Chart V. It can

Chart V. MO Transformation Involved in an Antara-antara 1,1-Sigmatropic Rearrangement



be seen that the intermediate orbitals are  $\pi$  like and approach degeneracy only to the extent that carbons 1 and 5 can separate appreciably. The process is energetically unfavorable when  $\sigma_{15}$  is initially doubly occupied as in the ground state but favorable for the excited species.

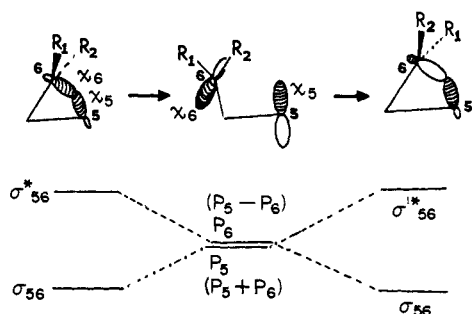
The second type of 1,1-sigmatropic rearrangement is the suprafacial process with inversion at the benzylic center C-6 (or supra-antara). Focussing attention on the total amount of external bond fission (*i.e.*, note Table V) we conclude that this process is most characteristic of the triplet excited states. The process is electronically different than the 1,1-antara-antara process deriving from internal bond fission and can be pictured as in Chart VI.

Interestingly, the correlation diagram involves a real crossing and degeneracy at half-reaction. It is paralleled by the situation for the twisting of ethylenes as discussed by Eyleth.<sup>28</sup> This supra-antara situation differs from that of the antara-antara process. The

(28) E. M. Eyleth, *Photochem. Macromol., Proc. Symp.*, 167 (1970).



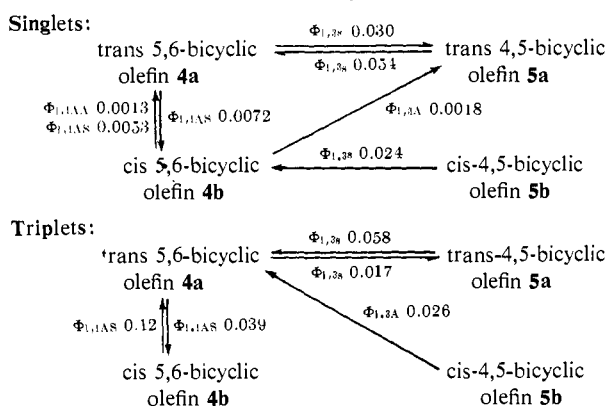
Chart VI. MO Transformation Involved in a Supra-Antara 1,1-Sigmatropic Rearrangement



degeneracy here is enforced by symmetry orthogonality of the basis orbitals  $\chi_5$  and  $\chi_6$ , which is not the case for the antara-antara process.

Finally, hitherto the stereoisomerization and rearrangement processes have been dissected for clarity of discussion. These are combined in Chart VII to allow

Chart VII. Pathways Utilized by Bicyclic Olefins



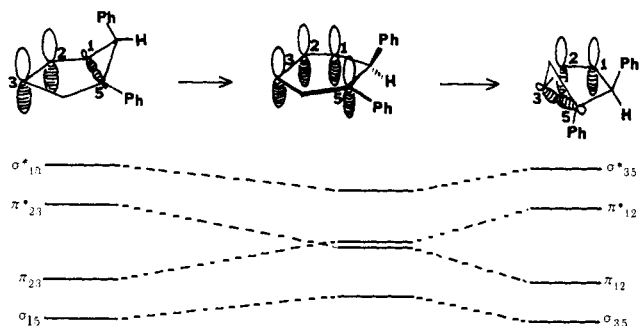
an overall view of the relative importance of the various mechanisms.

#### Correlation of Reaction Pathways with Multiplicity.

In the present study there is a greater tendency for the triplet to react with fission of the external bond relative to the corresponding singlet. Conversely, the excited singlet tends to give more of the internal bond fission than the corresponding triplet. This can be seen in Table V.

When it is recognized that external bond fission can lead to a geometrically orthogonal triplet biradical while internal bond fission affords an approximately square Hückel cyclobutadienoid array (*vide supra*) of orbitals (note Chart VIII), the results can be understood.

Chart VIII. MO Transformation Involved in a 1,3-Suprafacial Sigmatropic Rearrangement



Thus, the orthogonal triplet is a near approach to a double doublet (*i.e.*, biradical) in which the odd elec-

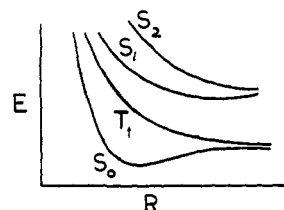


Figure 2. Variation of state energy of a two-center system with separation.

trons are as separated as permitted by molecular geometry, and spin relaxation with intersystem crossing to the ground state is facilitated. The Hückel array does not lead to such a double-doublet approach to product since it lacks the orbital spatial separation.

Conversely, the Hückel array is uniquely suited to allow a near degeneracy of ground and singlet excited states with the same array of four basis orbitals involved in both of the degenerate MO's. This will afford good spatial overlap of ground and excited states and the maximum possibility for internal conversion to ground state at the crossing point by vibronic admixture of ground state configuration with the excited singlet one. Hence, odd electron separation is ideal for facile triplet reactivity and spatial overlap of the two electrons optimizes singlet processes.

The same general question has been considered by Slater<sup>29</sup> in connection with the hydrogen molecule problem. Here both the first triplet excited state and the ground state correlate with the covalent dissociated state while the singlet excited state and the second excited singlet correlate with an ionic dissociated state. For fission of a nonpolar bond, dissociation to an ionic state is effectively forbidden.

The interesting associated point is that more energy is gained initially by dissociation of a triplet than of the corresponding first excited singlet. But this is true only as long as the geometric change is adiabatic (*i.e.*, without change in electronic configuration); thus, in Figure 2 one notes that the downward slope for  $T_1$  is indeed greater than for  $S_1$ . For small changes in geometry, such as a small bond stretching, there is a greater energy gain for the triplet than for the singlet. However, for conversion all the way to ground state  $S_0$ ,  $S_1$  is of higher energy than  $T_1$  initially and has a greater overall energy gain. Hence whether  $T_1$  or  $S_1$  will be more reactive in dissociative processes will depend on where along the reaction coordinate the rate limiting portion of the process occurs. Also, early in the process,  $S_1$  is on a potential energy surface correlating with an ionic stretched state and thus tightly bound species are preferred.

In the present instance, it is seen that the triplet does prefer to undergo homolytic fission and the singlet does prefer the cyclic, concerted species where electron separation is minimized. Actually, for the cyclic array there should be cyclic delocalization energy favoring proximity of orbitals so that the Slater diagram needs to be modified quantitatively to give minima for  $S_1$  and  $T_1$  as well as  $S_0$ .

Such a correlation seems more general. Thus, the

(29) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill, New York, N. Y., 1963, p 67.

of *cis* trans isomerization of olefins (such as piperylene<sup>30c</sup> seems to be most characteristic of triplets. The singlet photochemistry of barrelenes<sup>7-8</sup> involves cycloaddition while the triplet affords a biradical intermediate as part of the di- $\pi$ -methane rearrangement. The electrocyclic opening of 5,5-diphenyl-1,3-cyclohexadiene (3) uses the singlet while the triplet gives rise to phenyl migration *via* a phenyl bridged species with odd electrons modestly separated.<sup>30b</sup> The acyclic di- $\pi$ -methanes give a concerted rearrangement from the singlet<sup>5</sup> but double bond isomerization from the triplet.<sup>5</sup> These are a few of the examples found.

### Experimental Section<sup>31</sup>

**4,4-Diphenylcyclohex-2-en-1-one** was prepared in 72% yield by the condensation of diphenylacetaldehyde and methyl vinyl ketone according to the method of Zimmerman, Keese, Nasielski, and Swenton.<sup>32</sup>

**Tosylhydrazone of 4,4-Diphenylcyclohex-2-en-1-one.** To a stirred solution of 24.8 g (0.100 mol) of 4,4-diphenylcyclohex-2-en-1-one in 100 ml of tetrahydrofuran were added 18.6 g (0.100 mol) of tosylhydrazine and 0.25 ml of concentrated hydrochloric acid. The stirred solution was refluxed for 1.0 hr. Concentration of solvent and addition of ether induced crystallization of 38.5 g (92.5%) of the tosylhydrazone as pale yellow needles, mp 184–192°. Recrystallization from tetrahydrofuran–ether gave a constant melting point of 191.0–192.5°. The spectral characteristics were: ir (CHCl<sub>3</sub>) 3.42, 6.28, 6.72, 6.92, 7.13, 7.24, 7.51, 8.60, 9.60, 14.30, and 15.77  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\tau$  2.1–3.0 (complex mult, 14 H), 3.42 (1 H, *J* = 10 cps), 3.71 (1 H, *J* = 10 cps), 7.5–7.9 (mult, 7 H).

Anal. Calcd for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: C, 72.12; H, 5.77; N, 6.73. Found: C, 71.88; H, 5.93; N, 6.66.

**5,5-Diphenyl-1,3-cyclohexadiene.**<sup>33</sup> To a solution of 20.0 g (0.0482 mol) of the above tosylhydrazone in 250 ml of benzene was added dropwise, with stirring under nitrogen, 80 ml of 1.6 *M* (0.128 mol) *n*-butyllithium in hexane. After the mixture was stirred at room temperature for 0.5 hr, the excess butyllithium was destroyed by the slow addition of water. The aqueous phase was extracted with 70% benzene–hexane; the combined extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to leave 16 g of a dark oil. Chromatography on a 4  $\times$  100 cm silica gel column (Davison, grade 950, 60–200 mesh) slurry packed in hexane and elution in 500-ml fractions with 2 l. of hexane, 2 l. of 5% benzene–hexane, 2 l. of 20% benzene–hexane, and 8 l. of 10% ether–hexane gave: fraction 1, nil; 2, 0.847 g of unidentified yellow solid; 3–4, nil; 5–13, 1.708 g, product diene and an unidentified impurity; 14–22, 7.485 g (70%), 5,5-diphenyl-1,3-cyclohexadiene, mp 56–58°; 23–29 1.970 g, overlap; 30–47, 2.715 g of a dark, unidentified oil.

The diene was recrystallized from hexane to give white crystals, mp 58.5–59.5°. The spectral characteristics were: ir (CHCl<sub>3</sub>) 3.26, 3.32, 3.38, 3.40, 6.02, 6.27, 6.70, 6.92, 8.22, 9.68, and 14.35  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\tau$  2.90 (singlet, 10 H), 3.78–4.35 (multiplet, 4 H), 7.22 (doublet, 2 H, *J* = 2.5 cps); uv (ethanol)  $\lambda$  267 nm ( $\epsilon$  3860),  $\lambda$  260 (4280).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>: C, 93.06; H, 6.94. Found: C, 92.89, H, 6.93.

**Exploratory Photolysis of 5,5-Diphenyl-1,3-cyclohexadiene.** A solution of 271 mg (1.16 mmol) of 5,5-diphenyl-1,3-cyclohexadiene in 500 ml of *tert*-butyl alcohol was purged with nitrogen for 1.0 hr before photolysis, and continuously during photolysis. The cooled, stirred solution was irradiated for 1.0 hr through a Pyrex filter sleeve with a 450-W Hanovia medium-pressure mercury lamp. Solvent removal *in vacuo* gave 340 mg of a light yellow oil.

The photolysate was subjected to reverse phase liquid–liquid partition chromatography on a 3  $\times$  200 cm column of polystyrene–

divinylbenzene copolymer (2% cross-linked, 100–200 mesh)<sup>34</sup> which had been slurry packed in the upper phase from 1:1 methanol–cyclohexane; the lower phase from this system was the eluent. Elution in 40-ml fractions gave: fractions 64–71, 31 mg, *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene and 5,5-diphenyl-1,3-cyclohexadiene; 72–74, 44 mg, overlap containing diene and triene; 75–84, 144 mg, 1,1-diphenyl-1,3,5-hexatriene.

The minor photoproduct was separated from the starting diene by chromatography of fractions 64–71 on a 1  $\times$  30 cm silicic acid column (100–200 mesh) slurry packed in hexane. Elution with hexane in 10-ml fractions gave: fractions 1–4, nil; 5–6, 14 mg, *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene; 7, nil; 8–10, 22 mg, 5,5-diphenyl-1,3-cyclohexadiene.

***cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexanones** were prepared by the photolysis of 20.00 g (80.6 mmol) of 4,4-diphenylcyclohex-2-en-1-one in 700 ml of purified benzene for 21.5 hr with a Hanovia 450-W medium-pressure lamp. The photoproducts<sup>18</sup> were separated by silica gel chromatography to give 14.18 g (71%) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone and 2.597 g (11%) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanone.

**Solvents.** Cyclohexane and dodecane were washed with 30% fuming sulfuric acid, water, and saturated aqueous sodium bicarbonate, dried, and distilled from calcium hydride. Benzene was treated similarly with concentrated sulfuric acid. *tert*-Butyl alcohol was distilled from calcium hydride immediately prior to use.

***trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene** was prepared utilizing the generalized procedure of Dauben.<sup>10</sup> A solution of 28.41 g (0.1145 mol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone, 22.737 g (0.1221 mol) of tosylhydrazine, and 0.25 ml concentrated hydrochloric acid in 200 ml of tetrahydrofuran was heated, with stirring, to reflux. After 15 min, 500 ml of benzene was added, and the tetrahydrofuran and water were removed by azeotropic distillation.

The tosylhydrazone solution was cooled in an ice bath under nitrogen and slowly treated with 105 ml of 2.4 *M* (0.252 mol) methyl lithium in ether. After reaction at room temperature for 1.25 hr, slow addition of water was followed by extraction with 50% hexane–benzene. The organic phase was washed with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to give 31.4 g of a yellow oil.

The oil was chromatographed on a 4.8  $\times$  50 cm silicic acid column (200–325 mesh) slurry packed in 2.5% ether–hexane. Elution with 1300 ml of hexane gave 25.27 g of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene as a pale yellow crystallizing oil, mp 53–58°. The oil was dissolved in a minimum volume of methanol and crystallized 19.12 g (75%) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, mp 59.0–59.5°. Further recrystallization from ethanol gave an analytical sample, mp 59.0–59.5°. The spectral properties were: ir (CHCl<sub>3</sub>) 3.26, 3.32, 3.43, 6.02, 6.25, 6.70, 6.91, 7.40, 7.61, 9.32, 9.62, 14.35, and 15.90  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\tau$  2.81 and 2.93 (partially resolved singlets, 10 H), 4.18 (mult, 1 H), 4.83 (mult, 1 H), and 7.0–7.8 (mult, 4 H).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>: C, 93.06; H, 6.94. Found: C, 93.01; H, 6.84.

***cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexene** was prepared in a procedure analogous to the above, using 5.88 g (23.7 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanone, 4.55 g (24.4 mmol) of tosylhydrazine, 0.15 ml of concentrated hydrochloric acid, and 50 ml of tetrahydrofuran. The solution was refluxed for 1.0 hr, the solvent replaced with benzene, as above, and the cooled solution under nitrogen treated with 25 ml of 2.4 *M* (60.0 mmol) methyl lithium in ether. The usual work-up gave 8.6 g of an orange oil. Chromatography on a 3  $\times$  200 cm silicic acid column, 100–200 mesh, slurry packed in 1% ether–hexane and elution with hexane in 40-ml fractions gave: fractions 1–22, nil; fractions 23–63, 3.1479 g (58%) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene as a crystallizing oil. The olefin was recrystallized from ethanol to a constant melting point of 72–73°. The spectral properties were: ir (CHCl<sub>3</sub>) 3.25, 3.31, 3.37, 3.41, 3.43, 6.03, 6.26, 6.69, 7.48, 7.92, 8.15, 8.31, 9.15, 9.31, 10.30, 11.10, and 14.30  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\tau$  2.98 (mult, 10 H), 3.84 (mult, 1 H), 4.40 (d of t, 1 H), 7.10 (mult, 2 H), 7.36 (mult, 1 H), and 8.13 (d, 1 H).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>: C, 93.06; H, 6.94. Found: C, 92.99; H, 6.82.

**Characterization of 1,1-Diphenyl-1,3,5-hexatriene.** The spectral properties were: ir (CHCl<sub>3</sub>) 3.25, 3.27, 3.33, 3.42, 5.55, 6.04, 6.21, 6.28, 6.72, 6.94, 7.40, 9.32, 9.71, 10.00, 10.41, 11.05, 14.37, and 15.65  $\mu$ ; 100-Mc nmr  $\tau$  2.73 (s, 10 H), 2.8–3.2 (m, 2 H), centered at

(34) We thank the Dow Chemical Co., Midland, Mich., for a generous gift of this material.

(30) (a) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1142 (1962). (b) One would expect odd electron delocalization through  $\sigma$  bonds in the phenyl bridged species and the separation is oily partial.

(31) All melting points were taken on a hot-stage apparatus and are corrected.

(32) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(33) The preparation of this compound has been previously reported by W. C. Dauben, *et al.*,<sup>10</sup> without spectral data, physical properties or experimental details.

3.9 (m, 2 H), centered at 4.75 (m, 2 H); uv (ethanol)  $\lambda_{\max}$  316 nm ( $\epsilon$  18,200).

*Anal.* Calcd for  $C_{18}H_{16}$ : C, 93.06; H, 6.94. Found: C, 92.72; H, 6.71.

A Lemieux oxidation<sup>14</sup> was performed using 92.4 mg (0.40 mmol) of triene, 10 ml of dioxane, 10 ml of benzene, 20.2 mg (0.13 mmol) of potassium permanganate, 690.1 mg (3.21 mmol) of sodium metaperiodate, 166 mg of anhydrous potassium carbonate, and 20 ml of water stirred vigorously for 4 hr. Separation of benzene phase, extraction with benzene of aqueous phase, washing with water, drying, and concentration *in vacuo* gave 83.4 mg of crude oxidation product. Chromatography on silica gel gave 35.7 mg (53%) of benzophenone.

The stereochemistry was established as *cis* by isomerization with a catalytic amount of iodine to the more stable *trans* isomer. The nmr of the isomerized compound was similar to that of the *cis* except for a downfield shift of *ca.* 0.4 of the multiplet centered previously at  $\tau$  3.9. Similarly, the uv spectrum showed enhanced absorption at slightly longer wavelength ( $\lambda_{\max}$  320 nm ( $\epsilon$  23,400)).

**Exploratory Sensitized Photolysis of 5,5-Diphenyl-1,3-cyclohexadiene.** A solution of 0.372 g (0.0016 mol) of 5,5-diphenyl-1,3-cyclohexadiene, 2.911 g (0.0169 mol) of benzophenone (recrystallized from ethanol five times) and 700 ml of *tert*-butyl alcohol was degassed with nitrogen for 1.0 hr. The solution was photolyzed with a 450-W Hanovia medium-pressure mercury lamp through a filter solution in an immersion well. The filter solution consisted of 40.0 g of copper sulfate pentahydrate, 315.0 g of nickelous sulfate hexahydrate, 600.0 g of cobalt sulfate heptahydrate, and 47.0 g of potassium nitrate in 1.0 l. of water. This solution transmits light from 310 to 370 nm, with the maximum at 340 nm. The stirred solution was irradiated for 20 min. Solvent removal gave 3.273 g of yellow crystallizing oil. Partial removal of benzophenone was accomplished by vacuum sublimation at 30–50° (0.01 mm) for 12 hr. The residue was submitted to the reverse phase liquid-liquid partition chromatography system described above. Elution in 40-ml fractions gave: fractions 14–20, 75 mg, yellow alcohols; 21–30, 75 mg, benzopinacol; 35–46, 1.803 g, benzophenone; 65–70, 14 mg, *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene; 71–90, 222 mg, *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene and *ca.* 15% unreacted diene; and 91–104, 85 mg, oxetane.

Further separation of the *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene from the remaining unreacted diene was accomplished by chromatography on silica gel a sbefore to give 192 mg of isolated pure photoproduct.

The results of other runs are: run 2, 380 mg of diene, 10-min irradiation, to give 38% conversion, 5 mg of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 79 mg of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, and 41 mg of oxetane, with total recovery of 90%; run 3, 310 mg of diene, 15-min irradiation, to give 80% conversion, 13.2 mg of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 147 mg of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, and 85 mg of oxetane, with total recovery of 85%.

**Acetone-Sensitized Photolysis of 5,5-Diphenyl-1,3-cyclohexadiene.** A solution of 332 mg of 5,5-diphenyl-1,3-cyclohexadiene in 700 ml of acetone (reagent grade, distilled from anhydrous calcium sulfate) was degassed with nitrogen for 1.0 hr and photolyzed through a Pyrex filter sleeve with a Hanovia 450-W medium-pressure lamp for 32 min. Solvent removal *in vacuo* gave 340 mg of a yellow oil.

The photolysate was subjected to the liquid-liquid chromatography system described above to give 14.1 mg (4.2%) of recovered diene, 5.6 mg (1.7%) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 242.5 mg (73%) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, and 16.8 mg (5.1%) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene.

**Photolysis Apparatus for Quantum Yields.** The Black Box irradiation apparatus<sup>11</sup> used a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector. The light was filtered through a cell containing three water-cooled compartments. The photolysis cell contained two identical compartments, each 12 cm in diameter with a 5-cm optical path and aliphatic epoxy (uv transparent and nonfluorescent) cemented quartz faces. The cells were equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, and nitrogen inlet. An actinometer cell was situated perpendicular to the main optical path to receive the light from a beam splitter consisting of a quartz plate mounted at 45° to the light path. This side cell was used to monitor light input. Before and during irradiation vanadous-purified nitrogen<sup>36</sup> was bubbled through the photolysis solution.

**Actinometry.** Each determination required three runs: (1) actinometer solution in the main sample cell and in the side cell, (2) reactant solution in the main cell and actinometer solution behind the main cell and in the side cell, and (3) actinometer solution in the main cell and the side cell. In runs 1 and 3 the ratio of transmitted light to reflected light was determined, and this ratio along with the amount of light reflected during run 2 was used to calculate the lamp output during run 2. The amount of light transmitted to the back cell was subtracted from this value to obtain the net light absorption. Potassium ferrioxalate actinometry was employed.<sup>36</sup>

**Filter Solutions.** Two filter solution systems were used. Filter I: cell 1, containing 1.0 M (262.86 g/l.) nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, containing 0.8 M (224.88 g/l.) cobalt sulfate heptahydrate in 5% sulfuric acid; and cell 3, containing 0.0001 M (0.0315 g/l.) bismuth chloride in 10% hydrochloric acid. The uv transmission of this filter was 250–310 nm, with a maximum at 280 nm. Filter II: cell 1, containing 78.8 g/l. of nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, containing 250 g/l. of cobalt sulfate heptahydrate in 5% sulfuric acid; and cell 3, containing 24.8 g/l. of stannous chloride dihydrate in 10% hydrochloric acid. The uv transmission of this filter was 315–365 nm with a maximum transmission at 336 nm.

**Quantum Yields for Direct Photolysis of 5,5-Diphenyl-1,3-cyclohexadiene.** Dilute solutions of *ca.* 0.001 M 5,5-diphenyl-1,3-cyclohexadiene were irradiated in cyclohexane using filter I on the Black Box. Photolyzed solutions were concentrated *in vacuo* and then subjected to chromatography as above on two columns: a 3 × 250 cm column of polystyrene beads (*vide supra*) and a 3 × 200 cm column of SilicAR CC-7 (100–200 mesh) slurry packed in hexane and eluted with hexane.

Data for individual quantum yields are listed as follows: mass starting material; light input; total conversion; mass of 1,1-diphenyl-1,3,5-hexatriene, quantum yield of triene; mass of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene; quantum yield of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene.

**DQ-1.** 5,5-Diphenyl-1,3-cyclohexadiene, 510 mg (2.20 mmol); 0.68 mEinstein; 14% conversion; 56.0 mg (0.241 mmol) of 1,1-diphenyl-1,3,5-hexatriene,  $\phi = 0.35$ ; 6.2 mg (0.0267 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.039$ .

**DQ-2.** 5,5-Diphenyl-1,3-cyclohexadiene, 201 mg (0.865 mmol); 0.52 mEinstein; 24% conversion; 38.1 mg (0.164 mmol) of 1,1-diphenyl-1,3,5-hexatriene,  $\phi = 0.32$ ; 5.4 mg (0.0232 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.045$ .

**DQ-3.** 5,5-Diphenyl-1,3-cyclohexadiene, 250 mg (1.076 mmol); 1.20 mEinsteins; 41% conversion; 71.5 mg (0.308 mmol) of 1,1-diphenyl-1,3,5-hexatriene,  $\phi = 0.26$ ; 13.0 mg (0.0560 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.056$ .

**DQ-4.** 5,5-Diphenyl-1,3-cyclohexadiene, 189 mg (0.814 mmol); 1.20 mEinsteins; *ca.* 60% conversion; 92.0 mg (0.396 mmol) of 1,1-diphenyl-1,3,5-hexatriene;  $\phi = 0.24$ ; *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene not determined.

**Quantum Yields for Sensitized Photolysis of 5,5-Diphenyl-1,3-cyclohexadiene.** Dilute solutions of *ca.* 0.002 M 5,5-diphenyl-1,3-cyclohexadiene were irradiated in *tert*-butyl alcohol using filter II on the Black Box. Xanthone or benzophenone was used as sensitizer. The photolyzed solutions were concentrated *in vacuo* and the products isolated by chromatography of the photolysate on two columns: a 3 × 250 cm column of polystyrene beads (*vide supra*) and a 3 × 200 cm column of SilicAR CC-7 (100–200 mesh) slurry packed in hexane and eluted with hexane.

Data for individual quantum yields are listed as follows: mass of 5,5-diphenyl-1,3-cyclohexadiene; sensitizer; mass of sensitizer; light input; total conversion; mass of products (individually) and quantum yields of products.

**DBQ-1.** 5,5-Diphenyl-1,3-cyclohexadiene, 292 mg (1.257 mmol); benzophenone, 1.30 g (7.64 mmol); 1.84 mEinsteins; 24% conversion; 66.9 mg (0.288 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.16$ ; 10.3 mg (0.0256 mmol) of oxetane,  $\phi = 0.014$ .

**DBQ-2.** 5,5-Diphenyl-1,3-cyclohexadiene, 428 mg (1.84 mmol); benzophenone, 1.43 g (7.64 mmol); 8.94 mEinsteins; 82% conversion; 309.0 mg (1.33 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.15$ ; 16.0 mg (0.069 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0077$ ; 8.3 mg (0.036 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0040$ .

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

(36) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956)

**DXQ-1.** 5,5-Diphenyl-1,3-cyclohexadiene, 1.321 g (5.69 mmol); xanthone, 0.722 g (3.68 mmol); 5.74 mEinsteins; 23% conversion; 268.4 mg (1.16 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.20$ ; 6.1 mg (0.026 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0046$ ; 23.9 mg (0.103 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.018$ .

**DXQ-2.** 5,5-Diphenyl-1,3-cyclohexadiene, 1.045 g (4.50 mmol); xanthone, 0.694 g (3.54 mmol); 8.20 mEinsteins; 43% conversion; 365.2 mg (1.57 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.19$ ; 13.2 mg (0.057 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0069$ ; 39.9 mg (0.172 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.021$ .

***trans*- and *cis*-4,5-Diphenylbicyclo[3.1.0]-2-hexene.** These compounds were obtained<sup>12b</sup> by the pyrolysis of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene in refluxing dodecane under nitrogen. The products were isolated by successive chromatography on columns of SilicAR and polystyrene beads (*vide infra*).

**Optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone** was obtained from the racemic compound by conversion to 2-*N,N*-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, resolution *via* the malate salt, and oxidation of the resolved amine to optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone using the procedure described by Zimmerman, Hancock, and Licke.<sup>17</sup>

**Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanone** was obtained by the photolysis of optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone in benzene<sup>17</sup> to low conversion. Chromatography on silica gel gave optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanone.

**Optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene** was prepared from the optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone (recrystallized to constant specific rotation and melting point) using a procedure identical with that described above for the preparation of the racemic compound.

The purified olefin had the same spectral properties and melting point as the racemic compound, and had a strong positive rotation in the range 250–600 nm, with maxima at 278 nm ( $[\alpha]_D^{278} = +3030^\circ$  (concentration 0.00041 g/ml, EtOH) and 268 nm ( $[\alpha]_D^{268} = +2800^\circ$  (concentration 0.00041 g/ml, EtOH)).

*Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>: C, 93.06; H, 6.94. Found: C, 93.03; H, 7.04.

**Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene** was prepared from the optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanone (recrystallized to constant specific rotation and melting point) using a procedure identical to that described above for the preparation of the racemic compound.

The purified olefin had the same spectral properties and melting point as the racemic compound and had a strong positive rotation in the range 250–600 nm, with a maximum at 292 nm ( $[\alpha]_D^{292} = +2210^\circ$  (concentration 0.00013 g/ml, EtOH)).

*Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>: C, 93.06; H, 6.94. Found: C, 92.84; H, 7.04.

**Direct Photolysis of *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** Dilute solutions of ca. 0.002 *M* were irradiated in *tert*-butyl alcohol using filter I on the Black Box. The photolyzed solutions were concentrated *in vacuo* and the products isolated by chromatography on a 3 × 250 cm column of polystyrene beads.

Data for individual runs are listed as follows: mass of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene; light input; total conversion; mass of products (individually), and quantum yields of products.

**TDQ-1.** *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene, 416.3 mg (1.79 mmol); 2.70 mEinsteins; 12% conversion; 5.6 mg (0.024 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0089$ ; 19.1 mg (0.082 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.030$ .

**TDQ-2.** *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene, 842.3 mg (3.62 mmol); 12.51 mEinsteins; 16% conversion; 21.0 mg (0.090 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0072$ ; 87.5 mg (0.377 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.030$ .

**Sensitized Photolysis of *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** Dilute solutions of ca. 0.002 *M* were irradiated in *tert*-butyl alcohol using filter II on the Black Box. Xanthone sensitization (ca. 0.002 *M*) was employed. The photolyzed solutions were concentrated *in vacuo* and the products isolated by chromatography on a 3 × 250 cm column of polystyrene beads.

Data for individual runs are listed as follows: mass of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene; mass of xanthone; light input; total conversion; mass of products (individually); and quantum yields of products.

**TXQ-1.** *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene, 436.0 mg

(1.88 mmol); xanthone, 633.0 mg (3.23 mmol); 2.63 mEinsteins; 15% conversion; 25.2 mg (0.108 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.041$ ; 11.1 mg (0.0478 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.018$ .

**TXQ-2.** *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene, 874.0 mg (3.76 mmol); xanthone, 633.5 mg (3.23 mmol); 2.65 mEinsteins; 7% conversion; 23.9 mg (0.103 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.039$ ; 10.6 mg (0.0456 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.017$ .

**Direct Photolysis of *cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** The procedure followed was identical with that employed in the direct photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, described above. Data for individual runs are tabulated as follows: mass of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene; light input; total conversion; mass of products (individually); and quantum yields of products:

**CDQ-1.** *cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexene, 526.7 mg (2.26 mmol); 21.03 mEinsteins; 13% conversion; 33.3 mg (0.144 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0068$ ; 10.5 mg (0.0452 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0021$ .

**Sensitized Photolysis of *cis*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** A solution of 188.9 mg (0.813 mmol) of *cis*-diphenylbicyclo[3.1.0]-2-hexene and 464.8 mg (2.37 mmol) of xanthone in 750 ml of *tert*-butyl alcohol was photolyzed in the Black Box, using filter II, with 2.88 mEinsteins of light. The photolysate was concentrated *in vacuo* and chromatographed on a 3 × 250 cm column of polystyrene beads to give 63.9 mg (0.274 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene ( $\phi = 0.095$ ) and 115.0 mg (61%) of recovered *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene.

**Direct Photolysis of *trans*-4,5-Diphenylbicyclo[3.1.0]-2-hexene.** A solution of 225.2 mg (0.969 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene in 750 ml of *tert*-butyl alcohol was photolyzed with the Black Box, using filter I, with 5.52 mEinsteins of light. The photolysate was concentrated *in vacuo* and chromatographed on a 3 × 250 cm column of polystyrene beads to give 69.0 mg (0.297 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene ( $\phi = 0.054$ ) and 146.0 mg (65%) of recovered *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene.

**Sensitized Photolysis of *trans*-4,5-Diphenylbicyclo[3.1.0]-2-hexene.** A solution of 226.9 mg (0.977 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene and 674.5 mg (3.44 mmol) of xanthone in 740 ml of *tert*-butyl alcohol was photolyzed using the Black Box and filter II, with 4.14 mEinsteins of light. The photolysate was concentrated *in vacuo* and chromatographed on a 3 × 250 cm column of polystyrene beads to give 55.8 mg (0.0240 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene ( $\phi = 0.058$ ) and 139.9 mg (62%) of recovered *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene.

**Direct Photolysis of *cis*-4,5-Diphenylbicyclo[3.1.0]-2-hexene.** A solution of 308.0 mg (1.32 mmol) of *cis*-4,5-diphenylbicyclo[3.1.0]-2-hexene in 750 ml of *tert*-butyl alcohol was photolyzed using the Black Box and filter I with 16.64 mEinsteins of light. The photolysate was concentrated *in vacuo* and chromatographed on a 3 × 250 cm column of polystyrene beads to give 94.0 mg (0.404 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene ( $\phi = 0.024$ ) and 204.3 mg (66%) of recovered *cis*-4,5-diphenylbicyclo[3.1.0]-2-hexene.

**Sensitized Photolysis of *cis*-4,5-Diphenylbicyclo[3.1.0]-2-hexene.** A solution of 122.4 mg (0.53 mmol) of *cis*-4,5-diphenylbicyclo[3.1.0]-2-hexene and 580.0 mg (2.96 mmol) of xanthone in 750 ml of *tert*-butyl alcohol was photolyzed using the Black Box and filter II with 3.84 mEinsteins of light. The photolysate was concentrated *in vacuo* and chromatographed on a 3 × 250 cm column of polystyrene beads to give 22.8 mg (0.098 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene ( $\phi = 0.026$ ) and 97.6 mg (80%) of recovered *cis*-4,5-diphenylbicyclo[3.1.0]-2-hexene.

**Photolysis of Optically Active *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]-2-hexene.** The optically active compounds were photolyzed under conditions identical to those described above for the racemic compounds. The products were isolated similarly by chromatography on polystyrene beads, and as a further precaution against contamination by impurities the isolated materials were chromatographed a second time on a 1 × 35 cm column of SilicAR CC-7, slurry packed in and eluted with hexane. The complete ORD spectra of the products and recovered starting materials were taken. The results of these spectra are given in Table III. Data for individual runs are as follows: starting material and mass; sensitizer employed (if any) and mass; light input; total conversion; mass of products (individually); and quantum yields of products:

**O. A. TDQ-1.** Optically active *trans*-5,6-diphenylbicyclo[3.1.0]-

2-hexene, 909.4 mg (3.90 mmol); 17.57 mEinsteins; 23% conversion; 118.4 mg (0.510 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.029$ ; 24.1 mg (0.121 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.0069$ .

**O. A. TXQ-1.** Optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 599.9 mg (2.58 mmol); xanthone, 488.8 mg (2.49 mmol); 7.19 mEinsteins; 27% conversion; 61.0 mg (0.262 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.017$ .

**O. A. CDQ-1.** Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 327.3 mg (1.41 mmol); 18.32 mEinsteins; 23% conversion; 27.9 mg (0.120 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-

2-hexene,  $\phi = 0.0066$ ; 7.8 mg (0.0337 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.00183$ .

**O. A. CXQ-1.** Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 366.8 mg (0.158 mmol); xanthone, 488.8 mg (2.49 mmol); 4.21 mEinsteins; 34% conversion; 119.1 mg (0.513 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene,  $\phi = 0.12$ .

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## Organic Photochemistry. XIV. Photocycloaddition of Alkyl Ketones to Conjugated Dienes<sup>1</sup>

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**Abstract:** The photocycloaddition of acetone to 1,3-butadiene (**1**), isoprene (**8**), 2,3-dimethyl-1,3-butadiene (**16**), and 2,5-dimethyl-2,4-hexadiene (**17**) leads in each case to oxetanes. For the dienes **1** and **8**, photosensitized dimerization of the diene is also an important reaction. Photolyses of mixtures of 2-pentanone and **1** give oxetanes in competition with the products from the singlet state photoelimination reaction of 2-pentanone. A mechanism of oxetane formation is proposed in which singlet excited ketone attacks a ground-state diene molecule to give a singlet complex with charge-transfer character. The complex decays to ground-state reactants or reacts to give oxetane. Quantum yield studies and kinetic analysis suggest a rate constant of  $1 \times 10^9 M^{-1} \text{sec}^{-1}$  for singlet complex formation from acetone and **17**. Acetone fluorescence quenching data support such a mechanism and also enable rate constants for singlet quenching to be determined. The oxetanes **21** and **22** from 2-pentanone and **1** are cleaved stereospecifically by acid to give the 4-methyl-1,3-heptadienes **23** and **24**, respectively.

The photocycloaddition reaction of carbonyl compounds with olefins to form oxetanes,<sup>3</sup> although discovered some 60 years ago,<sup>4</sup> is a topic of current preparative<sup>5</sup> and mechanistic<sup>6</sup> interest. There are two distinct mechanisms for photocycloaddition, depending on the electron density at the olefinic double bond. For electron-rich olefins, addition generally proceeds through attack of the  $n\pi^*$  carbonyl compound on ground-state olefin; whether the reaction is singlet or triplet (or both) depends on the competing reactions (e.g., intersystem crossing, triplet quenching) undergone by the carbonyl excited states. The triplet addition appears to involve a long-lived 1,4-biradical with time for bond rotations before ring closure.<sup>6a,7</sup> The singlet mechanism of addition, however, proceeds through a singlet complex, and thence *via* a concerted or very

short-lived 1,4-biradical pathway with insufficient time for such bond rotations.<sup>6b,7,8</sup> For electron-deficient olefins, the photocycloaddition involves attack of the singlet excited carbonyl compound on the olefin to give a singlet complex<sup>1,9</sup> in which an electron appears to have been transferred from the carbonyl  $n\pi^*$  state to the olefin. This complex can react stereospecifically to give oxetane or collapse to reactants. Furthermore, the orientation of the oxetane product may no longer be that expected from the intermediacy of the "most stable biradical,"<sup>6a,9b</sup> but can be rationalized from a molecular orbital study of the *concerted* approach of reactants.<sup>9d,10</sup>

A factor which may limit the efficiency of oxetane formation is the possibility of energy transfer from the excited carbonyl compound to the olefin. Generally, when such a triplet energy transfer process becomes exothermic, it may occur at a rate approaching diffusion-controlled. Examples are known in which the photocycloaddition product is formed in competition with the products arising from triplet energy transfer.<sup>3b</sup> This triplet energy transfer mechanism should be particularly favorable for conjugated dienes, since dienes have much lower triplet energies than monoolefins (e.g., butadiene,  $E_T = 60$  kcal/mol; ethylene,

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