Run II-04. Starting triene (1.100 g, 4.52 mmol); 5.003 g (27.5 mmol) of benzophenone; 740 ml of *tert*-butyl alcohol; filter A; 27°; 6.63 mEinsteins; no photoproduct; 1.055 g (4.34 mmol) of unreacted triene; conversion, 4%; $\Phi_{\text{disappearance}} = 0.028$.

Run II-05. Starting triene (234.2 mg, 0.960 mmol); 5.1714 g (27.6 mmol) of benzophenone; 740 ml of *tert*-butyl alcohol; filter B; 34°; 4.32 mEinsteins; no bicyclic photoproduct; 208.5 mg (0.854 mmol) of unreacted triene; conversion, 11%; $\Phi_{\text{disappearance}}$ 0.025.

Photoreduction of Benzophenone.[38] A solution of 8.37 g (46.0 mmol) of benzophenone and 2.76 g (15.0 mmol) of benzhydrol in 230 ml of *tert*-butyl alcohol was degassed with purified nitrogen[30] for 30 min. The solution was stirred and photolyzed for 1.5 hr with a Hanovia 450-W medium-pressure mercury lamp filtered through Pyrex. After reaction was complete, 3.50 g of benzpinacol was filtered from the crude reaction, and the filtrate was concentrated and chromatographed on a 4 × 100 cm column slurry packed with deactivated[39] silicic acid in 50% chloroform–benzene. Fractions 1–50 were eluted with 1:1 chloroform–benzene and 51–154 with chloroform. Elution in 50-ml fractions gave: fractions 21–27, 661 mg, benzpinacol; fraction 28, 139 mg, overlap; fractions 29–70, 5.76 g, benzophenone; fractions 121–134, 0.250 g, benzhydrol; fractions 135–154, 1.01 g, complex mixture. In summary, there was obtained a total of 4.16 g of benzpinacol.

Quenching of the Photoreduction of Benzophenone. This experiment was carried out exactly as the previous one except for added triene, using 8.37 g (46.0 mmol) of benzophenone, 2.76 g (15.0 mmol) of benzhydrol, and 0.561 g (2.30 mmol) of 1-methylene-4,4-diphenylcyclohexadiene. In this case no benzpinacol crystallized from the reaction mixture, and chromatography, as described in the last experiment, afforded 0.464 g of 1-methylene-4,4-diphenylcyclohexadiene, 0.147 g of benzpinacol, and 8.42 g of benzophenone.

Calculations. The general configuration interaction procedure previously described by us was employed.[26] The valence state ionization potential of carbon of −11.16 eV was used for the C-2p Coulomb integral. The carbon–carbon resonance integral was taken as −2.92 eV for nearest neighbors and as −0.0048 for 1,3 related carbons. Other resonance integrals are tabulated in Table II. The necessary repulsion integrals were taken from Parisier and Parr[40] with interpolation where necessary.

Acknowledgment. Support of this research by the National Science Foundation, National Institutes of Health Grant No. GM07487, and the U. S. Army Research Office (Durham) is gratefully acknowledged, as are Predoctoral NASA and NIH fellowships to D. F. J. and J. M. M.

---

(38) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(39) The packing material was Mallinckrodt SilicAR CC-107 100–200 mesh which was prepared by slurrying in water and then drying at 60° for 17 hr.

(40) R. Parisier and R. B. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

Slither Motion of Divalent Carbon on π Systems in Photochemical Rearrangements. Exploratory and Mechanistic Organic Photochemistry. LXIV[1,2]

Howard E. Zimmerman,* Daniel F. Juers, John M. McCall, and Barbara Schröder

Contribution from the Department of Chemistry, the University of Wisconsin, Madison, Wisconsin 53706.

Received October 6, 1970

Abstract: The present paper gives full details of the new photochemical rearrangement in which 2-methylenebicyclo[3.1.0]-3-hexenes are converted into spiro[2.4]-4,6-heptadienes and other products. Both reactants and products in the reaction are formal adducts of a divalent carbon species to a fulvene moiety, and the conversion of the bicyclo[3.1.0]-3-hexenes into spiro products can be understood as involving the migration of C-6 about the periphery of the π system. 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene was found to give 1,1-dimethylspiro-[2.4]-4,6-heptadiene and 1-methylene-4,4-dimethylcyclohexadiene. In this case, the *gem*-dimethyl carbon slithers in both directions along the π system of a fulvene ring. Irradiation of the stereoisomeric 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexenes led stereospecifically to the *syn*- and *anti*-1,5-diphenylspiro[2.4]-4,6-heptadienes, with the *cis*-bicyclic diene giving the syn isomer and the *trans*-bicyclic diene affording the anti product. Additionally, the trans reactant gave the 2,4-, 2,5-, 3,5-, and the 3,4-diphenyltoluenes. The various products arise from slithering to different points along the π system. Quantum efficiencies were determined and are discussed in terms of reaction mechanism. The slither rearrangements were found to be processes of the singlet excited state. The triplet excited state of the diphenyl bicyclic dienes led to stereoisomerization rather than rearrangement. The slither rearrangement is discussed in molecular orbital terms using a concept of local symmetry.

The present research began with the observation, reported by us earlier,[3] that the photolysis of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene afforded a product of interest. Initial evidence suggested that a deep-seated rearrangement had occurred, and thus a new type of photochemical transformation was promised.

In continuing our efforts, we decided to study not only the stereoisomeric 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexenes (**1**) but also 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**2**).

Results

Exploratory Photochemical Efforts. Our initial photolyses were run using the "black box" apparatus

---

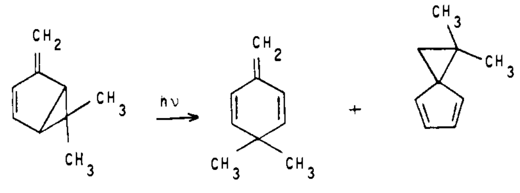
(1) For paper LXIII of the series see H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971).

(2) Part of the present results was reported in preliminary form: H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **92**, 3474 (1970); this communication was erroneousy listed as LVII rather than LVIII.

(3) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

described by us earlier;[4] 250–305-nm solution filters were used. It was found that irradiation of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**2**) in pentane, ethyl ether, or *tert*-butyl alcohol afforded, in each case, two products. These were nicely separated by preparative vpc, and were found to be formed in approximately equal amounts.

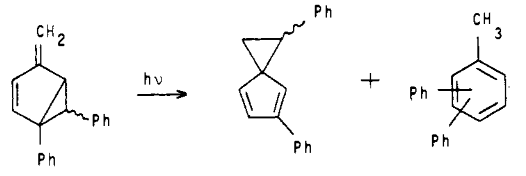
The faster moving component in the vpc separation proved to be the known 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**3**).[1] The product with longer retention time was a colorless liquid shown by elemental analysis and its nmr spectrum to be isomeric with starting material. The nmr spectrum (*vide infra*) led to tentative assignment as 1,1-dimethylspiro[2.4]-4,6-heptadiene (**4**). Hence the reaction can be formulated as



(1)

2 3 4

Similar efforts beginning with 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1b**) in *tert*-butyl alcohol led to observation of a single product isolated using liquid–liquid partition chromatography. Nmr analysis led to the tentative structural identification of the product as a stereoisomer of 1,5-diphenylspiro[2.4]-4,6-heptadiene (**5**). On analogous irradiation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1a**), the same spiroheptadiene product **5** was encountered along with a compound whose nmr spectrum suggested that this new product was a stereoisomer (*i.e.*, **5a**). In addition, four diphenyltoluene isomers were encountered and separated by reverse-phase liquid–liquid partition chromatography. In low conversion runs, these constituted about 11% of the product mixture and the ratio of the stereoisomeric spiroheptadienes (**5a** and **5b**) proved to be a function of extent conversion (*vide infra*). Hence this photochemical transformation is seen to be similar to that of the dimethyl bicyclic diene **2**; the reaction is depicted in eq 2.



(2)

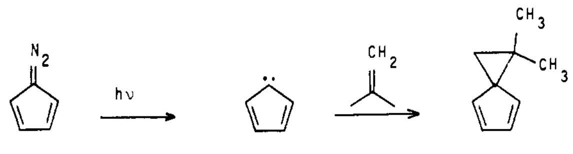
1 5 12-15 (from 1a only)

For preparative purposes, 1,5-diphenylspiro[2.4]-4,6-heptadiene (**5**) could be prepared especially conveniently starting with 1-methylene-4,4-diphenylcyclohexadiene (**11**) which gives[1] 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1**) as the primary product of irradiation which photolyzes further to diphenylspiroheptadiene **5**.

Structure Elucidation of Unknown Product from 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. As noted above, the unknown photolysis product **4**, obtained from irradiation of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**2**), analyzed as C_9H_{12}. This is isomeric with photochemical reactant **2**. The nmr of product **4** provided initial structural evidence. A sharp singlet integrating for six hydrogens at τ 8.60 suggested the presence of two equivalent methyl groups. Similarly, two equivalent hydrogens were found to absorb at τ 8.26 as an unsplit peak; this was attributed to an isolated methylene group. Additionally, a typical A_2B_2 pattern at τ 3.65 corresponded to an isolated group of two sets of symmetrically disposed vinyl hydrogens. Chemical shifts and coupling constants obtained by simulation (*vide infra*) of this A_2B_2 pattern when considered with the equivalent methyl groups and the unsplit methylene suggested a spiro[2.4]-4,6-heptadiene system.[5]

Furthermore, the ultraviolet spectrum of photoproduct **4** exhibited a maximum at 228 (ϵ 7200) and a shoulder at 257 nm (ϵ 2100) and was remarkably similar to that reported[6] for similar spiro[2.4]heptadienes. Note, for example, the 228- (ϵ 5600) and 257-nm shoulder (ϵ 2500) reported[6] for 1-butylspiro[2.4]heptadiene.

Conclusive evidence for the structure of the photoproduct **4** derived from its synthesis is outlined in eq 3. This utilized the addition of photochemically generated cyclopentadienylidene[6,7] (**7**) to isobutylene. To demonstrate the lack of rearrangement of the carbene adduct, it was ascertained that the same product was formed when a Pyrex filter was used to ensure absorption of light only by diazocyclopentadiene reactant. The synthetic material was identical with photoproduct **4**, thus identifying **4** as 1,1-dimethylspiro[2.4]-4,6-heptadiene.



(3)

6 7 4

Structure Elucidation of Products from the Diphenyl Bicyclic Diene. Attention was first turned toward the stereoisomeric photoproducts **5a** and **5b**. The nmr showed, most importantly, that for each of the stereoisomers there were two sets of three protons, and that for both stereoisomers the two sets were uncoupled as determined by double resonance. Determination of coupling constants was possible both by first-order analysis and by spin decoupling. From the nmr, it was clear that one set consisted of three vinyl hydrogens in the sequence –CH=CHC(Ph)=CH– or –CH=CHCH=C(Ph)–. The ultraviolet spectrum, which had a peak at 249 nm (ϵ 6820), was more consistent with the first formulation.[8]

The second set of hydrogens absorbed at higher field in the nmr and seemed reasonably ascribed to the structural arrangement $-CH_2CH(Ph)-$. That this grouping is part of the three ring of a spiro[2.4]heptadiene was

---

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

[5] Deshielded cyclopropyl protons in this spirodiene system have been discussed before; *e.g.*, K. Bangert and V. Boekelheide, *Tetrahedron Lett.*, 1119 (1963), and R. A. Clark and R. A. Fiato, *J. Amer. Chem. Soc.*, **92**, 4737 (1970).

[6] R. A. Moss, *J. Org. Chem.*, 31, 3296 (1966).

[7] W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958).

[8] For 1-phenyl-1,3-butadiene, λ_{max} 308.3 nm; Y. Hirshberg, E. Bergmann, and F. Bergmann, *J. Amer. Chem. Soc.*, 72, 5120 (1950).

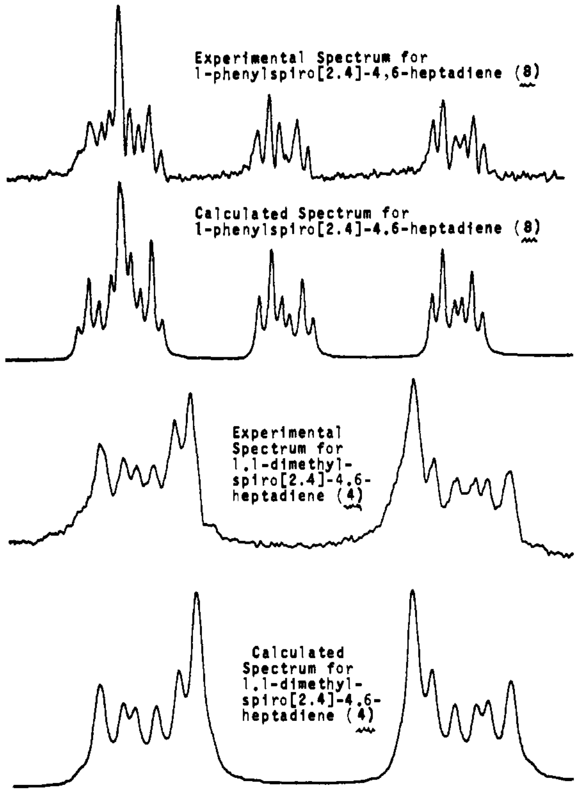
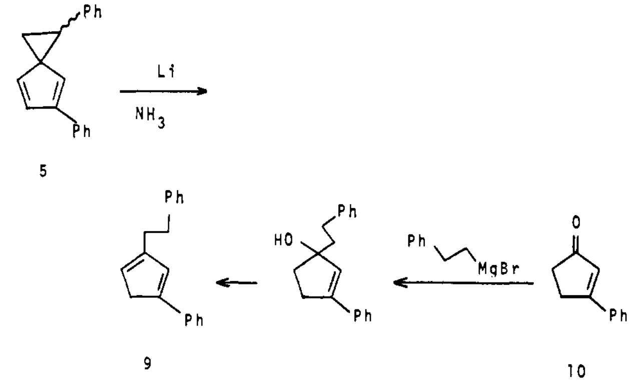


Figure 1. Observed and calculated 100-MHz nmr spectra of the vinyl region of model spiro[2.4]-4,6-heptadienes **4** and **8**.

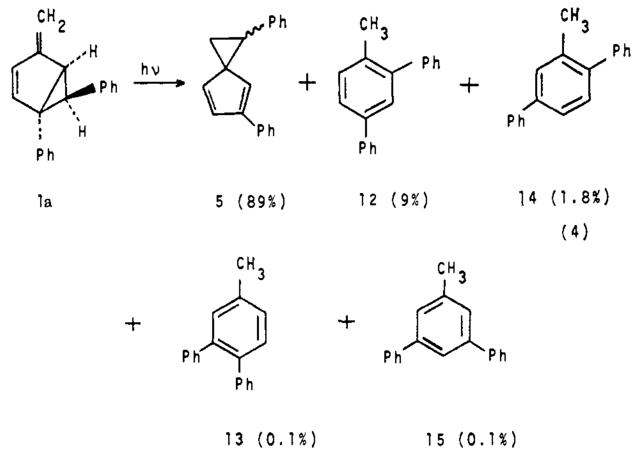
suggested by the lack of coupling between this and the phenylbutadienyl system. Also, the pattern observed was found to agree with the nmr spectrum observed for independently synthesized 1-phenylspiro[2.4]-4,6-heptadiene (**8**). Details of the nmr are given in the Experimental Section.

Final confirmation of structure was obtained from a lithium–liquid ammonia three-ring fission reaction patterned after the findings of Alder.[9] This led to 1-phenyl-3(or 4)-β-phenethylcyclopentadiene (**9**)[10] which was independently synthesized. The degradation and synthesis of degradation product **9** are delineated in Chart I.

Chart I. Proof of Structure of 1,5-Diphenylspiro[2.4]-4,6-heptadiene



As noted above, four diphenyltoluene isomers were obtained from the photolysis of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1a**); attention was turned next to identification of these. The isomers were shown by independent synthesis to be 2,4-diphenyltoluene (**12**), 3,4-diphenyltoluene (**13**), 2,5-diphenyltoluene (**14**), and 3,5-diphenyltoluene (**15**). Details are given in the Experimental Section and the syntheses are outlined in Chart II. Equation 4 outlines the distribution of isolated photoproducts.



Stereochemical Assignments. In order to establish which of the two diphenyl bicyclic diene photoproducts was *anti*-1,5-diphenylspiro[2.4]-4,6-heptadiene (**5a**) and which was *syn*-1,5-diphenylspiro[2.4]-4,6-heptadiene (**5b**), the nmr spectra were compared with those of model compounds, and with computer-simulated nmr spectra.

The problem of stereochemistry seemed soluble if it could be determined whether the three-ring phenyl group had a shielding or deshielding effect on the terminal vinyl protons of the cyclopentadiene ring. For this purpose, 1-phenylspiro[2.4]-4,6-heptadiene (**8**) and 1,1-dimethylspiro[2.4]-4,6-heptadiene (**4**) were used as models.

Computer simulation[11] provided a convenient approach to determining the required chemical shifts. The coupling constants and chemical shifts which gave a good fit were readily found; note Figure 1 and Table I.

Table I. Nmr Parameters for the Vinyl Protons of the Spirodienes

Chemical shift or coupling constant assignment[a]	Spirodiene **5a**[b]	Spirodiene **5b**[b]	Spirodiene **4**[c]	Spirodiene **8**[c]
4	τ 3.76[e]	τ 4.07[d]	τ 3.90	τ 3.97[e]
5			τ 3.68	τ 3.67[e]
6	τ 3.33[d]	τ 3.28[e]	τ 3.68	τ 3.72[d]
7	τ 4.18[d]	τ 3.87[e]	τ 3.90	τ 4.26[d]
4,5			5.5 Hz	5.5 Hz
4,6	2 Hz	2 Hz	1.5 Hz	1.8 Hz
4,7	2 Hz	2 Hz	2.0 Hz	1.8 Hz
5,6			2.0 Hz	1.75 Hz
5,7			1.5 Hz	1.8 Hz
6,7	5 Hz	5 Hz	5.5 Hz	5.0 Hz

[a] See Figure 2 for numbering. [b] Determined by first-order analysis. [c] Determined by computer simulation. [d] Syn to three-ring phenyl. [e] Anti to three-ring phenyl.

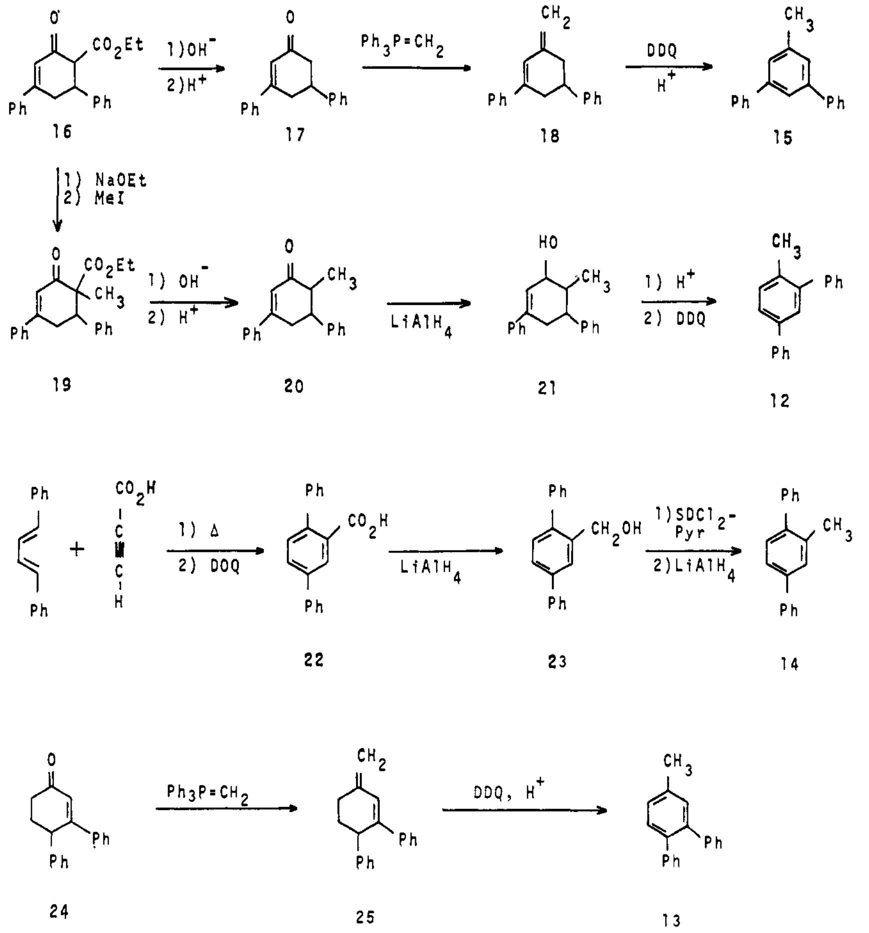
---

(9) K. Alder, H. J. Ache, and F. Flock, *Chem. Ber.*, **93**, 1888 (1960).

(10) The mode of synthesis did not distinguish double bond isomers. However, this was not critical for structure elucidation.

(11) (a) Changes of τ 0.01 in chemical shifts will appreciably alter the calculated spectrum. Coupling constants were determined to ±0.1 Hz. (b) Using a Digital Equipment Corp. PDP-8/I computer. (c) The program used was a modified version of a program written by D. Juers, R. Boettcher, V. J. Hull, and H. E. Zimmerman available from Digital Equipment Computers Users Society #8-194.

Chart II. Synthesis of Photochemical Diphenyltoluenes



Reference to Table I reveals that the vinyl hydrogens at C-4 and C-7 (note Figure 2 for numbering) in 1-phenylspiro[2.4]-4,6-heptadiene (**8**) absorb at τ 3.97 and 4.26 while the corresponding protons in the non-phenyl-bearing model 1,1-dimethylspiro[2.4]-4,6-heptadiene (**4**) absorb at τ 3.90. While one of the absorptions is virtually unaffected (τ 3.90 for model **4** *vs.* 3.97 for model **8**) by phenyl substitution in the three-membered ring, the other absorption is shifted upfield substantially (τ 3.90 for model **4** *vs.* 4.26 for model **8**). This τ 0.36 shift to higher field can be ascribed to shielding of the closer vinyl hydrogen by the proximate three-ring phenyl group. The pertinent data and argument are summarized in Figure 2.

To make use of this effect, the vinyl protons in the stereoisomeric 1,5-diphenylspiro[2.4]-4,6-heptadienes (**5**) were assigned on the basis of coupling constant data. Thus, in one stereoisomer, the vinyl absorptions occur (note Table 1) at τ 3.87 and 4.07. In this stereoisomer, the τ 4.07 peak appears as a triplet, and first-order analysis revealed a small coupling constant of 2 Hz with each of two hydrogens. The τ 3.87 absorption which appeared as a doublet of doublets (J = 5 Hz and J = 2 Hz) can then be deduced as due to the vinyl proton at C-7 since the adjacent proton at C-6 would provide the larger coupling observed. The absorption having only small coupling constants must then be due to the styryl proton at C-4 which has no adjacent protons.

Analogous reasoning led to identification of the τ 3.76 absorption in the other isomer as the styryl peak (*i.e.*, H-4) and the τ 4.18 peak as being due to hydrogen at C-7. Note Table I for a summary of these data.

With the vinyl hydrogens now identified, an assignment of stereochemistry is readily derived from ascertaining which vinyl hydrogen is shielded and which one unaffected for each isomer. Thus, of the two styryl hydrogens absorbing at τ 4.07 and 3.76, the higher field one must be syn to the three-ring phenyl group. This assignment is confirmed by examination of the chemical shifts of the C-7 protons. Here the proton absorbing at τ 3.87 must be anti to the three-ring phenyl group, and the hydrogen absorbing at τ 4.18 must be syn to the phenyl group on the three ring. These mutually consistent observations lead to the conclusion that the stereoisomer with the τ 3.87 and 4.07 peaks must be *syn*-1,5-diphenylspiro[2.4]-4,6-heptadiene (**5b**), and the com-

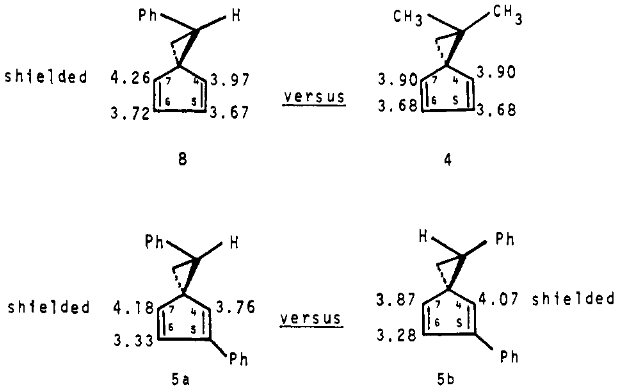


Figure 2. Proton assignments in the spirodienes.

pound with τ 3.76 and 4.18 absorptions is *anti*-1,5-diphenylspiro[2.4]-4,6- heptadiene (**5a**) (note Figure 2).

Reaction Efficiencies. Determination of the quantum yields was a point of interest in itself and a necessity for multiplicity studies (*vide infra*). Quantum yields were determined using both the "black box" apparatus as well as an optical bench designed for organic photochemistry (note Experimental Section for details). Ferrioxalate actinometry[12] was used throughout. The quantum yields are summarized in Tables II and III. It is seen that the reaction to give the spiroheptadienes is modestly efficient.

Table II. Quantum Yield for Photolysis of 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**2**)

Run	Added reagent	Light input, mEinstein/mmol[h]	Conversion, %	Quantum yields	
				Spiro **4**[f]	Triene **3**[g]
I-01[a,d]	None	0.349	3.1	0.040	0.038
I-02[c,d]	None	0.460	3.5	0.040	0.036
I-03[a,d]	None	0.166	1.4	0.043	0.039
I-04[b,e]	Benzophenone	7.62	41.2	<0.0001	<0.0001

[a] Photolysis in pentane. [b] Photolysis in *tert*-butyl alcohol. [c] Photolysis in ether. [d] Microapparatus, 250 nm. [e] Microapparatus, 350 nm. [f] In millimoles of 1,1-dimethylspiro[2.4]-4,6-heptadiene (**4**) per millieinstein of light captured. [g] In millimoles of 1-methylene-4,4-dimethylcyclohexadiene (**3**) per millieinstein of light captured. [h] In sensitized runs, benzophenone absorbed over 99% of the light.

Table III. Quantum Yield for Photolysis of 2-Methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1**)

Run[a,b]	Starting material	Light input, mEinstein/mmol	Conversion %	Syn: anti ratio	Quantum yields	
					Spiro **5**[c]	Diphenyltoluenes[d]
II-01	*trans*-**1a**	1.580	24.3	0.667	0.037	0.0056
II-02	*trans*-**1a**	0.731	12.3	0.423	0.040	0.0062
II-03	*trans*-**1a**	0.466	8.7	0.394	0.038	0.0042
III-01	*cis*-**1b**	0.830	28.9[e]	9.0	0.066[e]	0.001[e]
III-02	*cis*-**1b**	0.725	12.9	62.0	0.082	0.0007

[a] Photolysis in *tert*-butyl alcohol at 33°. [b] Filter transmission 250–305 nm. [c] In millimoles of 1,5-diphenylspiro[2.4]-4,6-heptadiene (**5**) per millieinstein of light captured. [d] In total millimoles of diphenyltoluenes per millieinstein of light captured. [e] Insoluble thermal product in this run makes this figure inaccurate.

Multiplicities. Benzophenone (E_T = 68.8 kcal/mol) was selected for sensitization studies because of its rapid singlet decay rate and efficient intersystem crossing. Its triplet energy promised to be more than sufficient for effective energy transfer. Conditions were selected to ensure triplet but not singlet transfer.[13] However, neither in the case of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**2**) nor the 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene stereoisomers **1a** and **1b** was the normal photochemical reaction detectable. The triplet of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene gave no unimolecular product. Interestingly, the triplet of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene isomerized to its cis isomer with a quantum efficiency of 0.28. The steady state proved to be totally on the side of the cis isomer as shown by the lack of reactivity of the cis triplet.[14] Note the Experimental Section for details on quantum yield determinations.

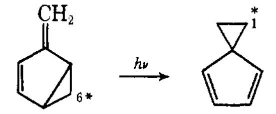
In view of the differing photochemical behavior of the bicyclic diene triplets compared to the unimolecular rearrangements observed for these compounds on direct irradiation, it is possible to ascribe the unimolecular rearrangements to the singlet excited state.

Singlet Reaction Stereochemistry. It appeared that reaction stereochemistry would be a powerful tool in elucidating the mechanism of the rearrangement depicted in eq 1 and 4. Hence, the stereochemistry of the rearrangement of the *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]-3-hexenes **1a** and **1b** was investigated. It was found that direct irradiation of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1b**) gave stereospecifically *syn*-1,5-diphenylspiro[2.4]-4,6-heptadiene (**5b**). In contrast, the irradiation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene did not proceed totally stereospecifically although there was a marked preference for the anti product **5a** (anti:syn ratio 3.12 ± 0.17).

The stereospecificities were determined by extrapolation of the stereoisomer ratios to zero time. This was necessary due to slow photochemical interconversion of the spiro stereoisomer. For the extrapolation, least-squares treatments using both first-order and second-order curves were employed. Their close agreement (*i.e.*, 2.95 and 3.29) justifies confidence in the extrapolation.

Interpretative Discussion

Gross Reaction Mechanism. In discussing the reaction mechanism, we must rationalize a most unusual molecular transformation. Inspection of the molecular change (note eq 1 and 4) reveals that the reaction involves C-6 of the 2-methylenebicyclo[3.1.0]-3-hexene skeleton becoming C-1 of the spiro[2.4]-4,6-heptadiene product. This is tantamount to transposition of a divalent carbon atom (*i.e.*, C-6 in the bicyclic diene) from one end of a butadiene moiety to the other end. Rearrangement mechanisms are pictured in more conventional qualitative valence bond terms in Chart III.



(5)

Two basically different mechanisms are outlined. One of these[19,20] involves three-ring opening and re-

---

[12] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. B*, **140**, 470 (1953).

[13] For a discussion of the methodology, see H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966), footnote 9.

[14] The stereochemical relationships here are reminiscent of previously observed 5,6-diarylbicyclo[3.1.0]hexanes in general, generated from both $n-\pi^*$ [15-17] and $\pi-\pi^*$ [18] excited states. The endo (*i.e.*, trans) isomers are preferred kinetically in the formation of the ring system though they equilibrate photochemically to give equivalent or excess amounts of the exo (*i.e.*, cis) product. This statement is also consistent with the results of our previous paper[1] in which the photolysis of 1-methylene-4,4-diphenylcyclohexadiene was described as leading preferentially to 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene.

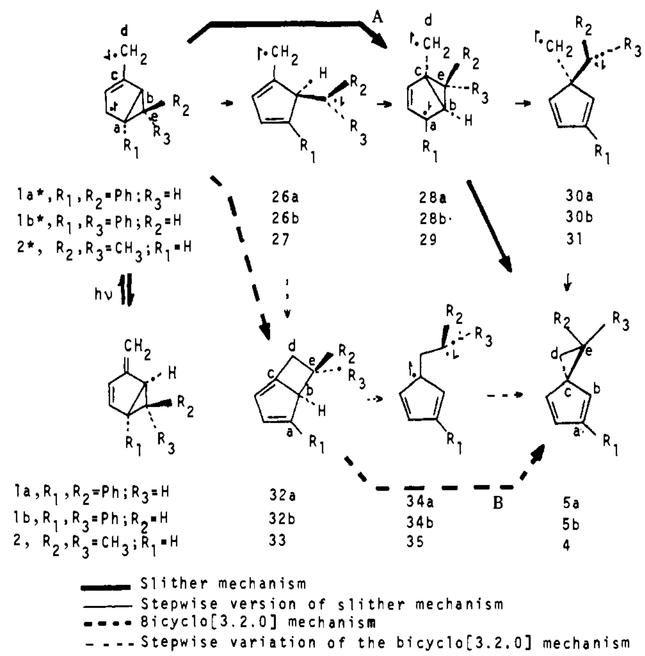
[15] H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964).

[16] (a) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968); (b) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).

[17] H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968).

[18] H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

Chart III. Valence Bond Representation of Possible Pathways in the Photolysis of 2-Methylenebicyclo[3.1.0]-3-hexene



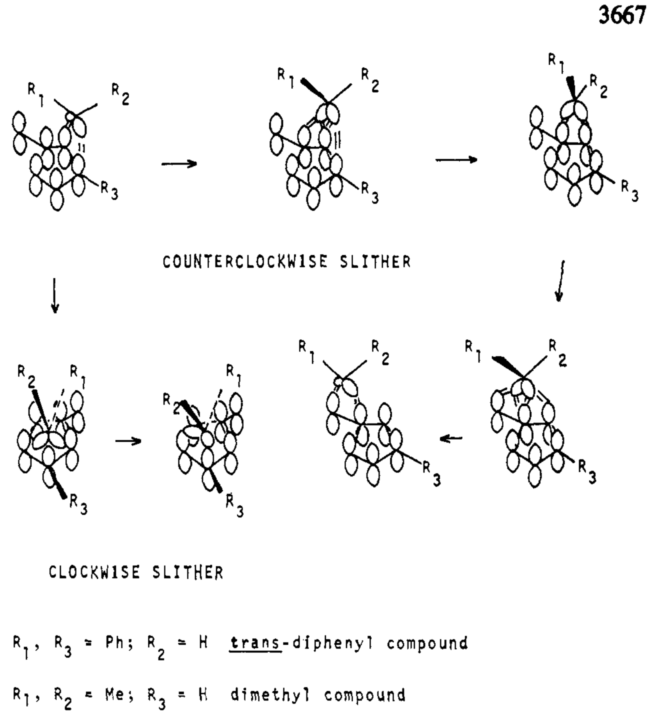


Figure 3. Geometry of the slither migration.

closure to give bicyclo[3.2.0]-1,3-heptadiene intermediate **32** or **33** as shown in Chart III. A second step, thermal or photochemical, is then required to complete the rearrangement. This pathway is denoted by the arrows ---> in Chart III. The reaction as pictured involves a photochemical suprafacial 1,5 migration of carbon e from carbon a to carbon d with inversion of configuration at the migrating carbon. The second step involves a similar 1,5-suprafacial migration of carbon e from carbon b to carbon c but with retention of configuration. The stereochemistry selected for **32** or **33** is based on the assumption that the first step is an excited state process. Such a 1,5 migration must occur with inversion to be an allowed process.[21] The second step would seem most likely to be thermal in order to give the observed product stereochemistry in an allowed process.[21,22]

The second of the two basic mechanisms proceeds through a series of slither type motions (note slither mechanism A in Chart III) in which the original carbon e moves from carbons a and b of a four-carbon sequence (*i.e.*, a, b, c, and d in Chart III) to the central two (*i.e.*, b and c). This affords species **28** or **29**. Similar motion from atoms b and c to the terminal atoms c and d gives rise to spiro products **4** or **5**. Opened biradical species **26** or **27** and **30** or **31** can be envisioned as intermediates along this route (note Chart III).

It is now necessary to consider each of the two basic mechanisms to determine how each accommodates observation. Regarding the "bicyclo[3.2.0] mechanism," there seems to be strong evidence against this route, especially as a unique pathway. Although the bicyclic [3.2.0] intermediate **32** or **33** was not detected, this provides little evidence, since **32** or **33** might further rearrange readily. More cogently, this mechanism fails to account for the less than total stereospecificity in the irradiation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**1a**) contrasted with the stereospecificity of the cis isomer **1b** (*vide supra*). This lack of stereospecificity would require an *ad hoc* rationale in which *trans*-diphenyl bicyclic diene rearranged by two mechanisms, the first involving one inversion and one retention of configuration and the second mechanism requiring two inversions or two retentions. Equally worrisome, the bicyclo[3.2.0] mechanism does not allow for formation of the four diphenyltoluenes. Likewise, the bicyclo[3.2.0] mechanism fails to account for 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**3**) except by again invoking an unrelated mechanism for formation of this product.

In contrast, the slither mechanism will accommodate the three major points which the bicyclo[3.2.0] mechanism fails to explain. These are formation of diphenyltoluenes, lack of stereospecificity in photorearrangement of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene, and formation of 1-methylene-4,4-dimethylcyclohexadiene from 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. Chart IV and Figure 3 picture in detail the slither process in the case of the irradiation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene.

From Chart IV, it is seen that the particular diphenyltoluene formed depends on where the migrating divalent carbon stops. It is also seen that except for the

---

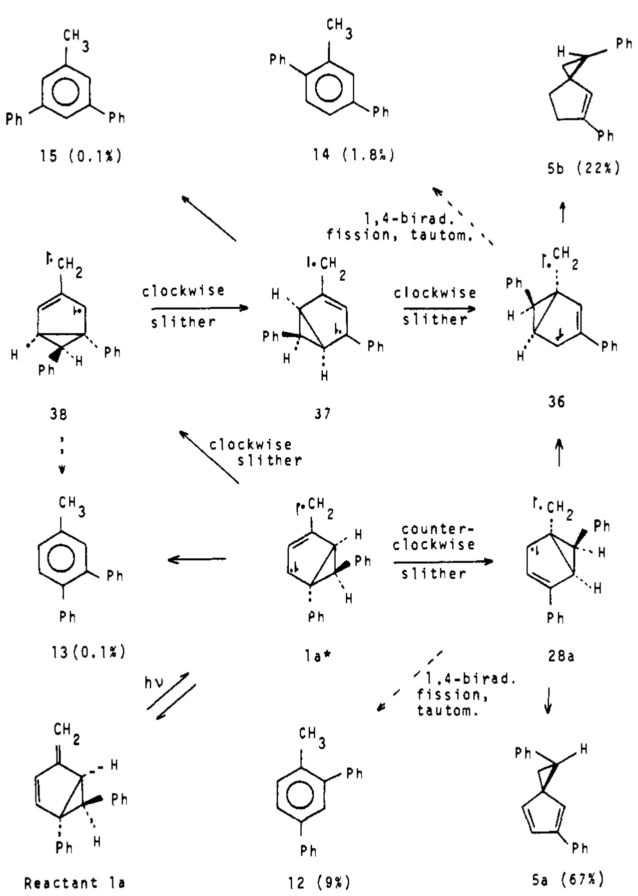
(19) H. E. Zimmerman, 13th Reaction Mechanisms Conference, Santa Cruz, Calif., June 23–26, 1970; H. E. Zimmerman, University of Manchester Institute of Technology, Photochemical Symposium, Manchester, April 21–22, 1970.

(20) Recently this mechanism has been proposed by N. K. Hamer and M. Stubbs,[21,22] *Chem. Commun.*, 1013 (1970). These authors have repeated part of our studies[2,3] and have studied a further analog. The stereochemistry suggested by these authors for the rearrangement of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene qualitatively agrees with that reported by us both presently and in our preliminary communication.[2] However, these researchers appear to have obtained decreased stereospecificity due to prolonged photolysis and resultant product equilibration.

(21) (a) To be excited-state allowed this cyclic array of six orbitals involving six electrons must have an odd number of sign inversions (Möbius). Conversely, to be ground-state allowed, this array must have an even number of sign inversions (*i.e.*, Hückel);[22] (b) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(22) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

Chart IV. Mechanism of Photorearrangement of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene



pathway leading to 3,5-diphenyltoluene (**15**),[23] the final endocyclic bond fission involves a cyclopropyldicarbinyl diradical simply opening the central bond. This is a well-known process[24] for electronically unexcited diradicals of this type.


(6)

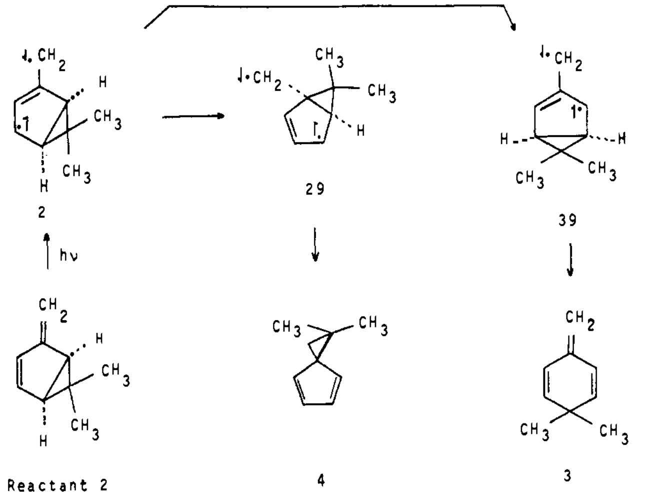
In the case of the excited state, the further migration of the central carbon atom is known to occur as observed in the di-π-methane rearrangement while the diradical is still electronically excited.[26,27] Thus, continued migration around the fulvene ring structure can be expected as long as the molecule remains electronically excited, and internal bond fission with consequent toluene formation is expected when demotion to ground state occurs.

The finding that 2,4-diphenyltoluene is the major toluene formed is of special interest since it provides direct structural evidence for species **28a**. This species corresponds to partial migration around the ring, as has been postulated (*vide supra* and note Chart III) to lead onward to the *anti*-1,5-diphenylspiro[2.4]-4,6-heptadiene. The formation of 2,5-diphenyltoluene as the next most abundant toluene is of interest since it provides evidence for slither of the benzylic moiety around the ring in the opposite direction.[28]

It remains to discuss the dependence of the stereochemistry of the reaction to 1,5-diphenylspiro[2.4]-4,6-heptadiene upon the reaction course. At this point it should be noted that in the slither mechanism the diradical species **26a**, **26b**, **30a**, and **30b** cannot be discrete intermediates since stereochemistry would then be lost. The slither process requires that the endo phenyl group in 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene remains endo throughout the reaction and the exo phenyl group in reactant 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene remains exo. This is reminiscent of an analogous slither process described by us earlier in another connection.[29] As long as the spiro products are formed by a counterclockwise slither around the ring (note Chart IV for designation of counterclockwise) and out onto the exocyclic double bond, the mechanism predicts formation of syn spiro product **5b** from *cis*-diphenyl bicyclic diene **1b** and anti spiro product **5a** from *trans*-diphenyl bicyclic diene **1a** as observed experimentally. This mechanism also accommodates the 25% syn product formed in the case of *trans*-diphenyl bicyclic diene **1a** since this will result from a minor amount of clockwise migration to reach the exocyclic double bond.[28] In contrast, the *cis*-bicyclic diene **1b** rearranges stereospecifically to *syn*-1,5-diphenylspiro[2.4]-4,6-heptadiene (**5b**). This differing behavior is readily understood by noting that clockwise slither in the case of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene requires that two bulky phenyl groups pass one another. Consequently, counterclockwise motion to give only syn spiro product is expected and in fact observed.

Finally, the slither mechanism accommodates the rearrangement of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene to 1,1-dimethylspiro[2.4]-4,6-heptadiene and 1-methylene-4,4-dimethylcyclohexadiene. Chart V depicts the slither process in this system in

Chart V. Rearrangement of 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene to 1-Methylene-4,4-dimethylcyclohexadiene and 1,1-Dimethylspiro[2.4]-4,6-heptadiene



---

[23] In this case, it seems likely that 2-methylene-4,6-diphenylbicyclo[3.1.0]-3-hexene reacts further photochemically under reaction conditions with formation of 3,5-diphenyltoluene or regeneration of the slither system.

[24] Generally,[25] such 1,4-biradical-like systems, when generated thermally, tend to afford 1,4-dienes rather than vinylcyclopropanes.

[25] For a leading reference see J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, 91, 777 (1969); unpublished work of H. E. Zimmerman and R. J. Boettcher.

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

[27] H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1407 (1970).

[28] Product **14** may also derive by slither from species **28a** past the exocyclic position to species **36**. In view of the stereochemical differences between cis and trans isomers of bicyclic diene **1**, we feel this explanation is less likely.

[29] H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).

valence bond terms. In this system, slither occurs with almost equal efficiency in either direction. This can be attributed to relative freedom of motion when bulky substituents are not present on the five-membered ring as in the diphenyl case (*vide supra*).

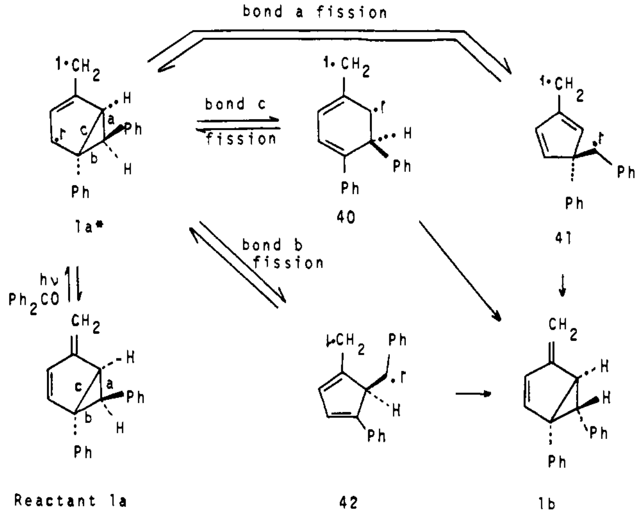
Hence, in contrast to the bicyclo[3.2.0] mechanism, the slither mechanism accounts for the variety of products formed and the reaction stereochemistry with a single hypothesis.

Reaction Efficiencies. The quantum efficiencies for formation of spiro[2.4]heptadiene product are in the range of 0.04–0.08. Previously, the point has been made that photochemical reactions with efficiencies of 0.05 or better tend to be synthetically useful.[30] This fits the present reaction where product is formed smoothly.

The similarity of the quantum efficiencies for the diphenyl and dimethyl bicyclic trienes is interesting from a mechanistic viewpoint. The quantum yields of spiro photoproducts are 0.04 from *trans*-diphenyl bicyclic diene reactant **1a**, 0.083 from *cis*-diphenyl bicyclic diene **1b**, and 0.041 from dimethyl bicyclic diene **2**. When all of the slither processes are included, the quantum efficiency for rearrangement becomes 0.080 in the dimethyl series and remains essentially unchanged for the diphenyl examples cited above (note Tables II and III). The fact that the presence of phenyl substituents does not enhance the reaction efficiency is consistent with a slither process in which the divalent carbon is intimately bonded to the π system at all times, and little free valence requiring stabilization is left on the fulvene ring or the migrating carbon.

The Triplet Photochemistry. A striking aspect of this study is the stereoisomerization and lack of slither rearrangement exhibited by the triplet excited state of 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene. The triplet stereoisomerization seems most reasonably interpreted on the basis of either exocyclic or endocyclic three-ring bond fission as shown in Chart VI. One of these species, **42**, is identical except for multiplicity with that considered in stepwise formulation of the slither process (note **26** in Chart III). Free rotation of such diradical intermediates and reclosure with intersystem crossing lead to the observed stereoisomeric product. The very high quantum yield of 0.28 for isomerization of trans to cis provides evidence for the facility of such three-ring opening processes by way of the triplet.[31,32]

Chart VI. Triplet Stereoisomerization of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene



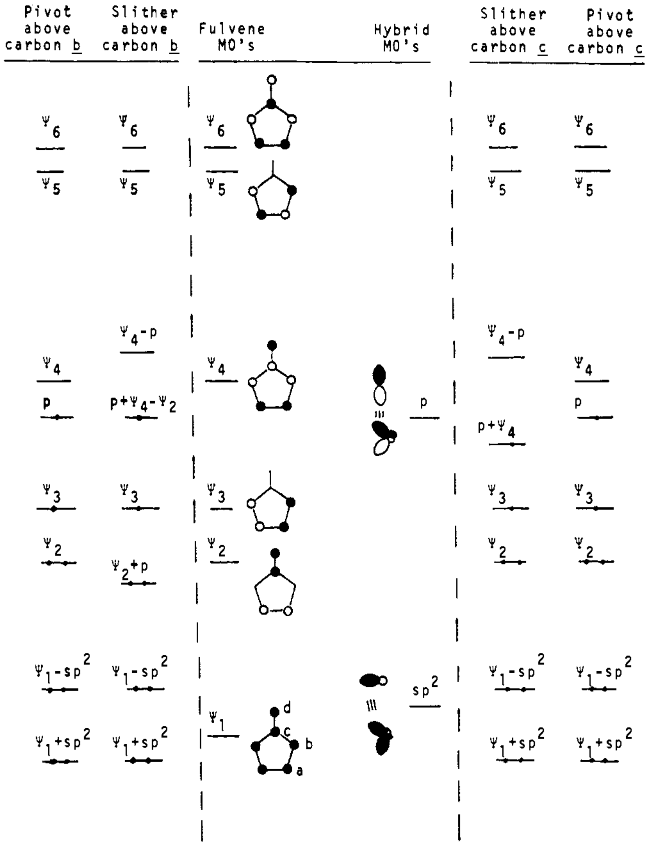


Figure 4. Molecular orbital perturbations in slither and pivot processes.

Hence, we can conclude that the slither processes in which all electrons are part of the same delocalized system throughout the rearrangement is favorable only for the singlet in which electrons are paired.

MO Rationale. One approach in considering the molecular orbital interpretation of the reaction is to discuss the problem in terms of the separated fulvene and carbenoid moieties as shown in Figure 4.

The present discussion depends on the realization that only as carbenoid C-6 is directly above each carbon atom of the fulvene moiety is the reaction stereochemistry, pivot[29] or slither, determined. The total energy corresponding to the orbitals considered as involved in the reaction can be estimated by a perturbation treatment in which the energy of interaction is considered as a function of pivot *vs.* slither geometry for each extent of reaction and point on the fulvene system. Each species along the reaction coordinate where C-6 is above a fulvene carbon can thus be treated separately.

In determining such perturbation interaction, we note that the p orbital of C-6 is locally antisymmetric if a slither process is being followed, since the two lobes with different signs will be projected toward the two

---

[30] H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970). This is because, with lower quantum yields, solvent decomposition tends to compete with product formation. Furthermore, multiple product and secondary irradiation become increasingly troublesome.

[31] H. E. Zimmerman and T. W. Flechtner, *ibid.*, **92**, 7178 (1970).

[32] Facile triplet-sensitized cis–trans isomerization indicates the lack of a free rotor effect[1] as a primary mode of deactivation of the excited state. See H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970).

carbons adjacent to the point of attachment on the fulvene ring. If pivot stereochemistry is being followed, then the p orbital is locally symmetric since only one lobe overlaps with the two adjacent carbon orbitals. When the adjacent carbons have the same sign, there is locally symmetric environment; with different signs there is local antisymmetry. Only when the local symmetry of the fulvene MO under consideration and the p orbital are the same is there bonding interaction.

The reaction begins with carbon six bonded to carbons a and b as shown in Figure 4; the first stereochemical choice appears when C-6 is directly above carbon b. We need now to consider interaction of those MO's which contain different numbers of electrons, since this interaction will lead to decrease in energy of the lower one containing extra electrons and will afford net molecular stabilization.

With C-6 above carbon b, it is seen that both Ψ_2 and Ψ_4 are locally antisymmetric at carbon b and may interact heavily with a slither p orbital. This results in Ψ_2, containing two electrons, going down in energy and the p orbital being "repelled" by both the higher energy Ψ_4 and the lower energy Ψ_2 and thus being relatively unaffected. In the comparable pivot geometry, no locally symmetric MO's of relatively similar energy are available as is needed for appreciable interaction. Hence slither geometry is preferred.

With C-6 above carbon c and the p orbital lobes being aimed toward carbons b and d, we see Ψ_4 locally antisymmetric and mixes with the slither p orbital. No locally symmetric MO's are close in energy and only the slither stereochemistry leads to stabilization, this being due to the one electron containing the p orbital going down in energy and the vacant Ψ_4 going up.

The same conclusion of preference for slither geometry results for clockwise migration with C-6 above carbon a. Additionally, we note that the reason for lack of stabilization in the pivot process is that only the very low-energy MO Ψ_1 is locally symmetric around the molecule and that this interacts to a lesser extent with the much higher energy p orbital. Finally, truncated one-electron calculations on the various bicyclic species containing both the fulvene and the carbenoid fragment and using only the orbital set shown in Figure 4 indicate that the total delocalized electron energy is indeed preferred for slither over pivot geometry as suggested by the above perturbation discussion.

Generality of the Slither Rearrangement. In addition to our own examples, similar rearrangements have been reported for a triphenylbicyclo[3.1.0]-3-hexene[20] discussed earlier and a permethylated bicyclo-[3.1.0]-3-hexene reported very recently by Hart.[33] Additionally, there are a number of examples[34] of irradiation of bicyclo[3.1.0]-3-hexenes where toluenes are obtained as products; these also may proceed by the same basic mechanism. In any case it is seen that the slither rearrangement process promises to be a broadly applicable photochemical reaction.

Experimental Section[35]

2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. The method of synthesis was described previously.[1] Methylenetriphenylphosphorane (32 mmol) was prepared in hexane from 17.3 g (48.13 mmol) of methyltriphenylphosphonium bromide and 14.3 ml (32 mmol) of a 2.25 *M* solution of *n*-butyllithium in hexane. Subsequent addition of 0.884 g (7.25 mmol) of 6,6-dimethylbicyclo[3.1.0]-3-hexen-2-one[1] and isolation of product afforded 0.140 g (16%) of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene.

Photolysis Apparatus and Equipment. The light source for the macro photolysis apparatus was a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter. The light was filtered by a cell containing three water-cooled compartments. These compartments (2.4 cm thick and 12 cm in diameter) were separated by gasketed quartz disks.

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. In some runs, an actinometer cell (26 mm i.d. × 10 cm optical path) was situated perpendicular to the main optical path to receive the light from a beam splitter consisting of a 4.6 × 4.6 × 0.2 cm 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[36] was bubbled through the photolysis solution.

Micro photolyses were conducted on an L-shaped optical bench in aliphatic epoxy-cemented quartz-faced thermostated cells 26 mm i.d. × 10 cm optical path, under deoxygenated nitrogen[36] with stirring. One actinometer cell was situated perpendicular to the main optical path to receive the light from a beam splitter identical with that described above. The light source used was an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator which had a bandwidth at half-height of 7.3 nm/mm slit width.

Actinometry. The basic procedure was independent of the apparatus used. Each determination required three runs: (1) actinometer solution in the main sample cell; (2) reactant solution in the first cell and actinometer in the second; and (3) actinometer solution in the main sample cell. Lamp outputs, determined during runs 1 and 3, were averaged and used to calculate light available to the sample during run 2. When the beam splitter was used, its transmission to reflection ratio was determined by the addition of a side cell of actinometer solution in runs 1 and 3. This ratio was used to calculate available light from the light deflected by the beam splitter to the side cell during run 2. Available light was corrected for light transmitted to the second cell during run 2. Potassium ferrioxalate actinometry was employed.[12]

Filter Solutions. For the preparation of filter solutions for the macro apparatus, nickel sulfate hexahydrate and cobalt sulfate heptahydrate were used in 10% sulfuric acid for filters A and B and 5% sulfuric acid for filters C and D. Stannous chloride dihydrate and bismuth trichloride were each used in 10% hydrochloric acid. Filter transmission was measured in a cell containing three 2.4-cm optical path compartments balanced against a 7.2-cm cell containing water.

Filter A: cell I, 90.0 g of nickel salt/l.; cell II, 200 g of cobalt salt/l.; cell III, 10.2 g of tin salt/l.; transmission (275–365 nm, max at 315 nm) 220–275 nm, 0%; 292 nm, 30%; 315 nm, 60%; 342 nm, 30%; 365–400 nm, 0%.

Filter B: cell I, 26.3 g of nickel salt/l.; cell II, 112.5 g of cobalt salt/l.; cell III, 22.5 g of tin salt/l.; transmission (315–385 nm) 220–315 nm, 0%; 330 nm, 16%; 325 nm, 28%; 360 nm, 25%; 385–400 nm, 0%.

Filter C: cell I, 263 g of nickel salt/l.; cell II, 526 g of cobalt salt/l.; cell III, 0.03 g of bismuth salt/l.; transmission (235–315 nm and 320–355 nm) 220–235 nm, 0%; 270 nm, 40%; 315–320 nm, 0%; 330 nm, 14%; 355–400 nm, 0%.

Filter D: cell I, 526 g of nickel salt/l.; cell II, 210 g of cobalt salt/l.; cell III, 0.12 g of bismuth salt/l.; transmission (250–305 nm, 337–355 nm) 220–250 nm, 0%; 267 nm, 30%; 280 nm, 50%; 292 nm, 30%; 305–337 nm, 0%; 345 nm, 5%; 355–400 nm, 0%.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene. The photolysis of 11.3 g (45.7 mmol) of 1-methylene-4,4-diphenylcyclo-

---

[33] H. Hart and T. Tabata, *Tetrahedron Lett.*, 4929 (1969). In this work, concurrent with our own efforts,[2] we considered intermediates of the type 28a. In those cases aromatization did not occur since no simple hydrogen tautomerization process leading to aromatic products was available.

[34] (a) M. Rey, U. A. Huber, and A. S. Dreiding, *ibid.*, 3583 (1968); (b) H. Hüther and H. A. Brune, *Z. Naturforsch. B*, 23, 1616 (1968).

[35] All melting points were taken on a hot-stage apparatus checked with known compounds.

[36] L. Meites, *Anal. Chem.*, 20, 984 (1948).

hexadiene[1] with 61.9 mEinsteins of light as described earlier[1] afforded a total of 1.258 g of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene. A solution of 273 mg (1.12 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene and 5.473 g (3.00 mmol) of benzophenone in 750 ml of *tert*-butyl alcohol was irradiated through filter B (315–385 nm) in the black box photolysis apparatus with 11.4 mEinsteins of light.[37] The photolysate was concentrated and chromatographed on a column of 100–200 mesh polystyrene beads 2% cross-linked with divinylbenzene as copolymer. The beads were prepared by washing with chloroform, drying, and soaking with a stationary phase (saturated solution of methanol in cyclohexane). They were then slurry packed into a 3.5 × 200 cm column using the mobile phase (saturated solution of cyclohexane in methanol). The excess stationary phase was washed off the column with the mobile phase, and the column was eluted with mobile phase. The eluent was monitored at 254 nm, and 40-ml fractions were collected: fractions 28–47, 5.293 g (97%), benzophenone; fractions 54–70, 187 mg (68.5%), 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; fractions 71–79, 54 mg, a 1:1 mixture of trans starting material to 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene. Material prepared in this way was identical with that previously obtained in the photolysis of 1-methylene-4,4-diphenylcyclohexadiene.[1]

Exploratory Photolysis of 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. A solution of 204.9 mg (1.71 mmol) of the dimethyl bicyclic diene in 730 ml of anhydrous ether was irradiated through filter C (235–315 nm) using the black box apparatus. Before and during photolysis, the solution was stirred and swept with vanadous-purified nitrogen.[36] Light absorbed was 13.6 mEinsteins and conversion was 35%. Analytical vpc (15% Carbowax on 60–80 Chromosorb W, 0.25 in × 25 ft, 90° column) showed two photoproducts in approximately equal amounts with retention times identical with those of 1-methylene-4,4-dimethylcyclohexadiene and 1,1-dimethylspiro[2.4]hepta-4,6-diene (retention times 26 and 41 min, respectively). These photoproducts were isolated by vpc (15% Carbowax on 60–80 Chromosorb W, 0.38 in × 18 ft, 90°). Comparison of their ir, nmr, and uv spectra to those of independently prepared triene and spiro compounds confirmed their identities as 1-methylene-4,4-dimethylcyclohexadiene[1] and 1,1-dimethylspiro[2.4]hepta-4,6-diene (*vide infra*). 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (retention time 21 min on analytical column described above) was collected and shown to be unchanged by photolysis.

1,1-Dimethylspiro[2.4]-4,6-heptadiene. The general procedure of Moss[6] for the preparation of spiro[2.4]-4,6-heptadienes was followed. A pentane solution of diazocyclopentadiene[38] was prepared by reaction of 10.0 g (53 mmol) of *p*-toluenesulfonyl azide,[39] 3.20 g (48.5 mmol) of cyclopentadiene, and 3.8 g (45 mmol) of diethylamine. This solution was photolyzed in a quartz vessel with 100 ml of isobutylene with a GE H100A38-4/T ultraviolet source. The major volatile product, 1,1-dimethylspiro[2.4]-4,6-heptadiene, was isolated by preparative vpc on an apiezon column at 100°. The same reaction product was obtained when diazocyclopentadiene was photolyzed with isobutylene in a Pyrex vessel.

The spectral data were: ir ($CHCl_3$) 6.8, 6.95, 7.26, 7.35, 8.65, 9.0, 9.2, 9.32, 9.75, 10.4, 11.55, and 12.12 μ; nmr ($CDCl_3$) τ 3.40–3.90 (m, 4 H, vinyl A_2B_2), 8.26 (s, 2 H, $-CH_2-$), 8.60 (s, 6 H, methyls); $\lambda_{max}^{95\%\ \text{ethanol}}$ 228 (ϵ 7190) and 257 nm shoulder (ϵ 2100); mass spectrum (70 eV) *m/e* (rel intensity) 120 (16), 106 (6), 105 (61), 91 (16), 79 (22), 78 (16), 77 (21), 51 (19), and 41 (19).

Anal. Calcd for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 90.29; H, 10.03.

Quantum Yields. Irradiation of 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. Dilute solutions (0.004–0.01 *M*) of the dimethyl bicyclic diene were irradiated on the micro apparatus to low conversion. The sample absorbed more than 95% of available light. No change in the optical density of photolysate was observed during photolysis. Analysis for 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene, 1,1-dimethylspiro[2.4]-4,6-heptadiene, and 1-methylene-4,4-dimethylcyclohexadiene was accomplished on a Carbowax vpc column using either *p*-xylene or mesitylene as an internal standard. Data for individual quantum yield runs are listed as follows: mass starting material, added reagent (if any), solvent, wavelength, light input, mass of unreacted starting material, conversion, and mass balance. The mass and quantum yield for each product isolated are then given.

Run I-01. Starting diene (23.3 mg, 0.194 mmol); 38 ml of pentane; 250–270 nm; 0.0677 mEinstein; 21.1 mg (0.175 mmol) of starting diene; conversion, 3.1%; mass balance, 96.0%.

1-Methylene-4,4-dimethylcyclohexadiene (0.306 mg, 0.00255 mmol); $\Phi = 0.038$.

1,1-Dimethylspiro[2.4]-4,6-heptadiene (0.321 mg, 0.00268 mmol); $\Phi = 0.040$.

Run I-02. Starting diene (18.9 mg, 0.158 mmol); 38 ml of ether; 250–270 nm; 0.0729 mEinstein; 18.4 mg (0.153 mmol) of starting diene; conversion, 3.5%; mass balance, 100%.

1-Methylene-4,4-dimethylcyclohexadiene (0.320 mg, 0.00267 mmol); $\Phi = 0.036$.

1,1-Dimethylspiro[2.4]-4,6-heptadiene (0.350 mg, 0.00291 mmol); $\Phi = 0.040$.

Run I-03. Starting diene (37.0 mg, 0.308 mmol); 40 ml of pentane; 250–270 nm; 0.0511 mEinstein; 36.6 mg (0.305 mmol) of recovered starting diene; conversion, 1.4%; mass balance, 100%.

1,1-Dimethylspiro[2.4]-4,6-heptadiene (0.350 mg, 0.00291 mmol); $\Phi = 0.040$.

1-Methylene-4,4-dimethylcyclohexadiene (0.240 mg, 0.00200 mmol); $\Phi = 0.039$.

1,1-Dimethylspiro[2.4]-4,6-heptadiene (0.265 mg, 0.00221 mmol); $\Phi = 0.043$.

Run I-04. Starting diene (50.3 mg, 0.419 mmol); 84 mg (0.46 mmol) of benzophenone; 40 ml of *tert*-butyl alcohol; 350 nm; 3.186 mEinsteins; 42.2 mg (0.352 mmol) of recovered starting diene; conversion, 41.2%; $\Phi_{disapp} = 0.054$.

No monomeric photoproducts were observed.

Exploratory Photolysis of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene. A solution of 102 mg (0.418 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene in 70 mol of *tert*-butyl alcohol was swept 30 min with purified nitrogen.[36] The solution was then photolyzed 10 min with a Hanovia 450-W medium-pressure mercury lamp filtered through Vycor (cut off below 220 nm).

The photolysate was concentrated and chromatographed on a 2.5 × 150 cm column dry packed with 250 g of Celite (Eagle-Picher Co., Celatom FW-80) bearing 103 ml of the lower phase of a solvent system consisting of 1000 ml of cyclohexane, 400 ml of *N*,*N*-dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water. The packed column was equilibrated with the upper phase of the solvent system at 28.5° before the photolysate was applied. The column was eluted with the upper phase of the solvent system, the eluent was monitored at 270 nm, and 20-ml fractions were collected. The fractions were worked up by washing with water, drying, and concentrating: fractions 24–27, 63 mg, mixture of starting material and diphenyl toluenes; fractions 28–30, 21 mg, 1,5-diphenylspiro[2.4]-4,6-heptadiene.

High-Conversion Photolysis of 1-Methylene-4,4-diphenylcyclohexadiene. When preparing large quantities of the *trans*-bicyclic diene photoproducts, it was convenient to generate the bicyclic diene *in situ* by photolysis of 1-methylene-4,4-diphenylcyclohexadiene[1] as described below.

A 2.04-g (8.36 mmol) sample of 1-methylene-4,4-diphenylcyclohexadiene was photolyzed in four similar batches. Each sample was dissolved in 110 mol of *tert*-butyl alcohol, swept with purified nitrogen,[36] photolyzed 1 hr with a 450-W Hanovia medium-pressure mercury lamp through a Vycor filter, concentrated, and chromatographed as described above on a 4.5 × 150 cm Celite liquid–liquid partition chromatography column. Elution in 40-ml fractions gave: fractions 26–32, mixture of the starting diphenyltriene, *trans*-bicyclic diene, and diphenyltoluenes; fractions 33–36, 1,5-diphenylspiro[2.4]-4,6-heptadiene. The corresponding fractions from each run were combined to yield a total of 1.238 g of the first peak which contained the impure starting material and 358 mg (18%) of the second peak, 1,5-diphenylspiro[2.4]-4,6-heptadiene. This spiro compound could be further purified by reverse-phase liquid–liquid partition chromatography on polystyrene beads as described above. Traces of column residues from the polystyrene bead chromatography were most conveniently removed by rechromatography on deactivated silicic acid (Mallinckrodt silicAR CC-107 100–200 mesh slurried with water and allowed to dry 12 hr at room temperature).

---

[37] Preparative photolyses were performed in the same manner as outlined previously in the section on actinometry except that only one actinometry run was performed, and neither a side cell nor a back cell was employed during sample photolysis.

[38] T. Weil, *J. Org. Chem.*, **28**, 2472 (1963).

[39] W. Doering and C. H. Depuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

The spectral data of the 1,5-diphenylspiro[2.4]-4,6-heptadiene mixture were: ir ($CHCl_3$) 3.22 (sh), 3.24 (sh), 3.31, 3.40, 3.49 (sh), 6.23, 6.62 (sh), 6.69, 6.90, 7.76, 8.47, 9.10, 9.21, 9.32, 9.70, 9.87, 9.98, 10.21, 12.13, and 14.45 μ; $\lambda_{max}^{dioxane}$ 249 nm (ϵ 6820); nmr of the syn isomer (100 MHz, CCl_4) τ 2.5–3.0 (m, 10 H, arom), 3.28 (d of d, 1 H, vinyl, J = 2, 5 Hz), 3.87 (d of d, 1 H, vinyl, J = 2, 5 Hz), 4.07 (t, 1 H, vinyl, J = 2 Hz), 6.88 (t, 1 H, benzylic, J = 8 Hz), 7.78 (d of d, 1 H, cyclopropyl, J = 8, 5 Hz), and 8.02 (d of d, 1 H, cyclopropyl, J = 8, 5 Hz). The peaks of the anti isomer (present to a lesser extent) were: τ 3.33 (d of d, 1 H, vinyl, J = 5, 2 Hz), 3.76 (t, 1 H, vinyl, J = 2 Hz), and 4.18 (d of d, 1 H, vinyl, J = 5, 2 Hz). The rest of the absorptions overlapped exactly with the major isomer.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.11; H, 6.83.

The complex mixture peak from the original liquid–liquid chromatography (*vide supra*) was separated by reverse-phase liquid–liquid chromatography on polystyrene beads as described above. The mixture was chromatographed in two batches, and corresponding peaks were combined before work-up: fractions 58–72, 363 mg (18%), 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; fractions 74–81, 120 mg (6%) of 1-methylene-4,4-diphenylcyclohexadiene; fractions 84–99, 384 mg, a mixture of diphenyltoluenes.

Column residues were removed from the toluene mixture by sublimation, 90° (0.1 mm). Nmr analysis revealed 81% 2,4-diphenyltoluene, 15% 2,5-diphenyltoluene, 2% 3,4-diphenyltoluene, and 2% 3,5-diphenyltoluene in the mixture. A 112-mg portion of the sublimed material was subjected to rechromatography on the polystyrene bead column: fractions 86–92, 2 mg, 3,4-diphenyltoluene as shown by nmr comparison with authentic material; fractions 93–97, 11 mg, 1:1 mixture of 2,4- and 2,5-diphenyltoluene; fractions 98–101, 42 mg, 5:1 mixture of 2,4- to 2,5-diphenyltoluene; fractions 102–105, 41 mg, material which, after sublimation, 65° (0.1 mm), gave material that was identical (ir and nmr) with authentic 2,4-diphenyltoluene; fractions 106–113, 12 mg of a mixture containing 20% of 3,5-diphenyltoluene (determined by nmr) and 80% of 2,4-diphenyltoluene; fractions 93–97 from this chromatography were subjected one more time to the polystyrene bead column; fractions 92–97, 4 mg of material which, upon sublimation, was identical (ir and nmr) with authentic 2,5-diphenyltoluene.

Exploratory Photolysis of 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene. All photochemical runs on this compound were conducted in such a way that quantum yield data could be determined. Therefore, note quantum yield section below.

Reduction of 1,5-Diphenylspiro[2.4]hepta-4,6-diene. After the manner of Alder, Ache, and Flock,[9] 25 ml of ammonia was condensed into a solution of 145 mg (0.594 mmol) of 1,5-diphenylspiro[2.4]-4,6-heptadiene in 4 ml of ether. To this mixture, 14 mg (2 mg-atoms) of lithium was added and the mixture stirred at reflux for 1 hr. After 2.0 g of ammonium chloride has been added, the ammonia was allowed to evaporate. The residue was dissolved in 150 ml of water and 150 ml of ether. The organic layer was washed with water and saturated sodium chloride solution, dried, concentrated to 2 ml, and cooled. The resulting precipitate was filtered to yield 52 mg (37%) of 1-phenyl-3(or 4)-β-phenethylcyclopentadiene, mp 110–112°, after recrystallization from ether. This material was identical (melting point, ir, nmr, uv) with authentic material (*vide infra*).

1-Phenyl-3(or 4)-β-phenethylcyclopentadiene. To a solution of 0.99 g (6.25 mmol) of 3-phenylcyclopentenone[40] in 50 ml of anhydrous ether was added 25 ml of a 0.25 M (6.25 mmol) ethereal solution of β-phenethylmagnesium bromide which was prepared from 2.33 g (12.5 mmol) of β-phenethyl bromide and 1.3 g (0.054 g-atom) of magnesium. This addition was done slowly under nitrogen. The mixture was stirred at reflux for 1 hr and poured into ice water. After 6.0 g of ammonium chloride had been added, the layers were separated, and the organic layer was concentrated. The residue was sublimed, 125° (0.005 mm). The sublimed material was triturated with cold ether, treated with Norit, and recrystallized from ether to yield 217 mg (14%) of 1-phenyl-3(or 4)-β-phenethylcyclopentadiene, mp 109–111°.

The spectral data were: ir ($CHCl_3$) 3.26, 3.32, 3.41, 6.25, 6.70, 6.90, 7.28, 9.31, 9.70, 11.00, 11.27, and 14.50 μ; $\lambda_{max}^{dioxane}$ 313 nm (ϵ 15,100); nmr ($CDCl_3$) τ 2.4–3.0 (m, 10 H, arom), 3.27 (br s, 1 H, vinyl), 3.80 (br s, 1 H, vinyl), 6.78 (br s, 2 H, cyclopentadienyl aliphatic), and 7.20 (br s, 4 H, allylic and benzylic).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.47; H, 7.36.

1,5-Diphenyl-4-methyl-4-carbethoxycyclohexen-3-one. 1,5-Diphenyl-4-carbethoxycyclohexen-3-one[41] (2.90 g, 9.07 mmol) was added to a solution of sodium ethoxide prepared from 452 mg (19.6 mg-atoms) of sodium in 50 ml of absolute ethanol which had been freshly distilled from a 10% solution of sodium ethoxide in commercial absolute ethanol. The mixture was stirred under nitrogen until the keto ester had dissolved. Then 5 ml of methyl iodide was added, and the solution was refluxed for 2.5 hr with 2-ml portions of methyl iodide being added at 30-min intervals. The reaction mixture was cooled and diluted with water, and was ether extracted. The organic extracts were water washed, dried, and concentrated. The residue was crystallized from 95% ethanol to yield 2.22 g (73%) of 1,5-diphenyl-4-methyl-4-carbethoxycyclohexen-3-one, mp 85–87°.

The spectral data were: ir ($CHCl_3$) 3.34, 3.40, 5.81, 6.04, 6.20, 6.35, 6.68, 6.90, 7.05, 7.27, 7.40, 7.50, 7.90, 8.70, 9.05, 9.80, 11.00, 11.35, 11.65, and 14.45 μ; nmr ($CDCl_3$, 100 MHz) τ 2.36–2.88 (m, 10 H, arom), 3.46 (d, 1 H, vinyl, J = 2 Hz), 5.92 (q, 2 H, $-OCH_2$, J = 7 Hz), 6.34 (d of d of d, 1 H, allylic, J = 2, 11, 17 Hz), 6.72 (d of d, 1 H, benzylic, J = 4, 11 Hz), 7.09 (d of d, 1 H, allylic, J = 4, 17 Hz), 8.67 (s, 3 H, methyl), and 8.86 (t, 3 H, methyl, J = 7 Hz).

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 79.21; H, 6.64.

1,5-Diphenyl-4-methylcyclohexen-3-one. A solution of 1.67 g (5.00 mmol) of 1,5-diphenyl-4-methyl-4-carbethoxycyclohexen-3-one and 2.28 g (40.8 mmol) of potassium hydroxide was refluxed for 16.5 hr in 50 ml of 95% ethanol and 50 ml of water. Then 7.5 ml of 33% sulfuric acid was added, and the mixture was refluxed an additional 1.25 hr. After cooling, the reaction mixture was diluted with water and ether was extracted. The organic phase was dried, concentrated, and sublimed, 130° (0.1 mm). The sublimed material was triturated with cold hexane to yield 0.918 (70%) of 1,5-diphenyl-4-methylcyclohexen-3-one, mp 59.5–68.5°.

The spectral data were: ir ($CHCl_3$) 3.23, 3.25, 3.32, 3.40, 3.47, 6.04, 6.20, 6.35, 6.70, 6.90, 7.30, 7.41, 7.63, 8.49, 8.95, 9.11, 9.32, 9.71, 11.34, and 14.46 μ; nmr (CCl_4, 100 MHz) τ 2.4–2.9 (m, 10 H, arom), 3.44 (s, 1 H, vinyl), 6.80–7.20 (m, 3 H, benzylic and allylic), 7.20–7.66 (m, 1 H, α keto), and 9.08 (d, 3 H, methyl, J = 7 Hz).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.90; H, 6.82.

1,5-Diphenyl-4-methylcyclohexen-3-ol. To a solution of 699 mg (2.67 mmol) of 1,5-diphenyl-4-methylcyclohexen-3-one in 100 ml of dry ether, 500 mg (13.2 mmol) of lithium aluminum hydride was added. The mixture was stirred under nitrogen for 2.5 hr. Then 21 ml of ethyl acetate was added cautiously, and the stirring was continued for an additional 15 min. The mixture was poured into 250 ml of water, and 125 ml of ether was added along with sufficient dilute sulfuric acid to dissolve aluminum hydroxide. The ether layer was water washed, dried, concentrated, and sublimed, 100° (0.1 mm), to yield 717 mg (101%) of 1,5-diphenyl-4-methylcyclohexen-3-ol, mp 56–59° after crystallization from carbon tetrachloride.

The spectral data were: ir ($CHCl_3$) 2.79, 2.93, 3.25, 3.27, 3.33, 3.38, 3.92, 3.52, 6.25, 6.69, 6.88, 7.30, 9.31, 9.67, 9.82, 10.01, 11.30, and 14.42 μ; nmr (CCl_4) τ 2.55–3.03 (m, 10 H, arom), 3.83 (s, 1 H, vinyl), 5.76–6.18 (m, 1 H, OCH), 6.18–6.49 (s, 1 H, OH), 7.33–7.61 (m, 3 H, allylic and benzylic), 7.93–8.40 (m, 1 H, cyclohexyl), and 9.12 (d, 3 H, methyl, J = 6 Hz).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.25; H, 7.75.

2,4-Diphenyltoluene. A solution of 462 mg (1.75 mmol) of 1,5-diphenyl-4-methylcyclohexen-3-ol and 80 mg (0.47 mmol) of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed for 2.25 hr under a Soxhlet extractor which had calcium chloride in the extractor thimble. Then 452 mg (1.99 mmol) of dichlorodicyanoquinone was added. After an additional 45-min reflux, the reaction mixture was poured into 100 ml of 10% sodium hydroxide containing 2.0 g of sodium sulfite. The benzene layer was washed with water, dried, concentrated, and sublimed, 100° (0.1 mm), to yield 344 mg (80.7%) of 2,4-diphenyltoluene.

The spectral data were: ir (neat) 3.27, 3.30, 3.39, 3.42, 3.50, 6.25, 6.76, 6.94, 7.20, 9.31, 9.74, 9.90, 11.20, 12.12, 12.99, 13.20, and 14.35 μ; nmr (CCl_4) τ 2.55–3.05 (m, 13 H, arom) and 7.82 (s, 3 H, methyl).

---

[40] V. Brosche and W. Menz, *Chem. Ber.*, **41**, 190 (1908).

[41] R. Connor and D. Andrews, *J. Amer. Chem. Soc.*, **56**, 2713 (1934).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.55; H, 6.51.

3,4-Diphenylcyclohexenone. Following the procedure of Zimmerman and Hancock,[18] 19.6 g (0.100 mol) of deoxybenzoin and 8.15 ml (0.100 mol) of methyl vinyl ketone were condensed in the presence of potassium hydroxide to yield 13.63 g (63%) of 3,4-diphenylcyclohexenone.

6-Methylene-2,3-diphenylcyclohexene. This material was obtained in 93% yield by the reaction of methylenetriphenylphosphorane prepared from 4.32 g (13.1 mmol) of triphenylmethylphosphonium bromide and 5 ml of 2 *M* (10 mmol) *n*-butyllithium with 2.00 g (8.07 mmol) of 3,4-diphenylcyclohexenone as described earlier.[18]

3,4-Diphenyltoluene. A solution of 503 mg (2.05 mmol) of 6-methylene-2,3-diphenylcyclohexene, 501 mg (2.21 mmol) of dichlorodicyanoquinone, and 55 mg (0.32 mmol) of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed 45 min. The reaction mixture was poured into aqueous 10% sodium hydroxide and sodium sulfite. The benzene layer was water washed, dried, and concentrated to yield 403 mg (80.5%) of 3,4-diphenyltoluene, mp 85–86°, when sublimed at 75° (0.1 mm).

The spectral data were: nmr (CCl_4) τ 2.76–3.08 (m, 13 H, arom) and 7.65 (s, 3 H, methyl).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.15; H, 6.57.

3,5-Diphenylcyclohex-2-enone. 1,5-Diphenyl-4-carbethoxycyclohexen-3-one[41] (3.385 g, 10.50 mmol) was added to a solution of 1.18 g (21.0 mmol) of potassium hydroxide in 90 ml of ethanol and 90 ml of water. The solution was heated at 80° for 17 hr under nitrogen. The reaction mixture was then acidified by addition of 42 ml (42 mmol) of 1 *M* sulfuric acid, and this solution was heated at 90° for 1 hr. After extraction with methylene chloride, the organic phase was washed with water and dried. Concentration afforded 2.858 g of crystals which were recrystallized from chloroform and hexane to give 1.917 g (74%) of 3,5-diphenylcyclohexenone, mp 89–90°. A sample for analysis was recrystallized again and sublimed at 100° (0.1 mm).

The spectral data were: ir ($CHCl_3$) 3.3, 6.05, 7.10, 7.7, 7.95, 9.0, and 9.75 μ; nmr ($CDCl_3$) τ 2.4–2.9 (m, 10 H, arom), 3.45 (br s, 1 H, vinyl), 6.85–7.90 (m, 5 H, aliphatic).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.09; H, 6.45. Found: C, 87.07; H, 6.52.

1-Methylene-3,5-diphenylcyclohex-2-ene. Methylenetriphenylphosphorane was prepared by dropwise addition of 4.1 ml (10.8 mmol) of 2.67 *M* *n*-butyllithium to a slurry of 5.10 g (14.4 mmol) of methyltriphenylphosphonium bromide in 190 ml of anhydrous ether. After stirring under nitrogen for 0.5 hr, 1.801 g (7.19 mmol) of 3,5-diphenylcyclohex-2-enone dissolved in 50 ml of benzene was added. After refluxing for 3.5 hr, the reaction mixture was filtered through magnesium sulfate, water washed, dried, and concentrated. The residue was chromatographed on a 3.0 × 35 cm column, slurry packed with silica gel; the column was eluted with 5% ether–hexane. Concentration of the first 500 ml of eluent afforded 1.48 g (83%) of 1-methylene-3,5-diphenylcyclohex-2-ene, mp 75–76°.

The spectral data were: ir (KBr) 3.32, 3.45, 6.28, 6.72, 6.95, 7.95, 9.75, 11.2, 13.25, and 14.35 μ; nmr ($CDCl_3$) τ 2.50–2.85 (m, 10 H, arom), 3.32 (broad s, 1 H, –HC=), 5.00 (s, 1 H, *exo*-methylene), 5.05 (s, 1 H, *exo*-methylene), 7.18–7.55 (m, 5 H, aliphatic).

Anal. Calcd for $C_{19}H_{18}$: C, 92.68; H, 7.32. Found: C, 92.50; H, 7.51.

3,5-Diphenyltoluene. A solution of 0.444 g (1.80 mmol) of 1-methylene-3,5-diphenylcyclohex-2-ene, 0.455 g (2.00 mmol) of dichlorodicyanoquinone, and 40 mg of *p*-toluenesulfonic acid in 20 ml of benzene was refluxed 1 hr. The reaction mixture was then poured into a basic solution of sodium bisulfite, washed with water, and concentrated. The crude reaction mixture was chromatographed with 5% ether–hexane on a 3.0 × 35 cm silica gel column slurry packed with 5% ether–hexane. Concentration of the first 700 ml of eluent afforded 303 mg (69%) of 3,5-diphenyltoluene. The material was further purified by sublimation, 110° (0.5 mm), mp 102–103°.

The spectral data were: ir (KBr) 3.32, 3.45, 6.3, 7.0, 7.15, 9.4, 9.8, 11.6, 13.25, and 14.4 μ; nmr (CCl_4) τ 2.40–2.90 (m, 13 H, arom), 7.81 (s, 3 H, methyl).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.15; H, 6.62.

2,5-Diphenylbenzyl Alcohol. A solution of 0.137 g (0.50 mmol) of 2,5-diphenylbenzoic acid[42] in 10 ml of ether was added dropwise to a stirred suspension of 0.062 g (1.67 mmol) of lithium aluminum hydride in 20 ml of ether. The solution was refluxed under nitrogen for 30 min. After destroying excess LAH with ethyl acetate, the solution was water washed, dried, and concentrated. The residue was chromatographed on a 3.0 × 20 cm silica gel column slurry packed and eluted with 20% ether–hexane to afford 43 mg (50.5%) of pure 2,5-diphenylbenzyl alcohol which was further purified by sublimation, 100° (0.1 mm), mp 105–106°.

The spectral data were: ir ($CHCl_3$) 2.78, 2.90, 3.28, 3.35, 6.78, 7.25, 8.50, 9.35, 9.75, 9.92, 11.15, 11.95, and 14.35 μ; nmr ($CDCl_3$) τ 2.30–2.90 (m, 13 H, arom), 5.6 (s, 2 H, benzylic), and 7.8 (s, 1 H, –OH).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.60; H, 6.16. Found: C, 87.69; H, 6.15.

2,5-Diphenyltoluene. The method of Corey for reduction of benzyl alcohols was employed.[43] A solution of 0.244 g (0.984 mmol) of 2,5-diphenylbenzyl alcohol and 0.313 g (1.97 mmol) of sulfur trioxide–pyridine complex was stirred under nitrogen at 0° for 10 hr. Then, 0.374 g (9.84 mmol) of lithium aluminum hydride was added and the reaction mixture was stirred at 0° for 1 hr and at 25° for 4 hr. After adding 2.5 ml of aqueous 10% sodium hydroxide, the reaction mixture was filtered and concentrated. The crude product was chromatographed on a 2.2 × 60 cm silica gel column, slurry packed and eluted with 5% ether–hexane. The first 600 ml afforded, after concentration, 102 mg (44.5%) of pure 2,5-diphenyltoluene. A sample was purified for analysis by sublimation, 110° (0.5 mm), mp 103–104°.

The spectral data were: ir (CS_2) 3.28, 3.33, 3.45, 6.3, 7.08, 9.35, 9.78, 9.95, 11.38, 12.08, 13.3, 13.9, and 14.35 μ; nmr (CCl_4) τ 2.40–2.85 (m, 13 H, arom) and 7.70 (s, 3 H, methyl).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.29; H, 6.65.

1-Phenylspiro[2.4]-4,6-heptadiene. This material was prepared as previously described from photochemical generation of cyclopentadienylidene in the presence of styrene.[6]

The spectral data were: nmr (100 MHz, CCl_4) τ 2.88 (s, 10 H, arom), 3.62–3.78 (m, 2 H, vinyl), 3.94–4.04 (m, 1 H, vinyl), 4.22–4.34 (m, 1 H, vinyl), 6.82 (t, 1 H, benzylic, $J = 8$ Hz), 7.84 (d of d, 1 H, cyclopropyl, $J = 4, 8$ Hz), and 8.10 (d of d, 1 H, cyclopropyl, $J = 4, 8$ Hz).

Quantum Yields. 2-Methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene. Dilute solutions of 0.0005–0.005 *M* 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene were irradiated in *tert*-butyl alcohol. In runs on the macro apparatus, no filter decay was observed. Small (<10%) changes in optical density were not corrected. Runs to various conversions were extrapolated to 0% conversion as detailed in the Results. Photolyzed solutions were concentrated *in vacuo*. The residues from runs II-01, II-02, II-03, III-01, and III-02 were chromatographed by direct-phase liquid–liquid partition chromatography (*vide supra*). The second peak from these chromatographies contained 1,5-diphenylspiro[2.4]-4,6-heptadiene, and the relative amount of syn and anti stereoisomers was determined by nmr. The quantum yield of the combined spiro products was determined gravimetrically by weighing appropriate fractions and correcting for column bleed of 0.03 mg per fraction. The first peak from these chromatographies and the residues from runs II-04 and III-03 were chromatographed by reverse-phase liquid–liquid chromatography on polystyrene beads (*vide supra*). The first peak (when present) contained benzophenone. The second peak from this chromatography contained bicyclic diene. The third peak (when present) contained 1-methylene-4,4-diphenylcyclohexadiene (*vide infra*). The fourth peak (when present) contained the diphenyltoluene mixture. Peaks from this chromatogram were identified by nmr, and the quantum yields were determined gravimetrically by weighing appropriate fractions and correcting for a column bleed of 0.13 mg per fraction. 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene was sublimed immediately prior to use due to thermal decomposition. A troublesome impurity in 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene was 1-methylene-4,4-diphenylcyclohexadiene. However, in run II-03, this impurity was carefully removed by chromatography, and, in this case, none of this compound was detected in the photomixture. Consequently, 1-methylene-4,4-diphenylcyclohexadiene was not a photoproduct of 2-methylene-*trans*-5,6-diphenylbicyclo-[3.1.0]-3-hexene.

---

(42) W. Ried and K. H. Boenninghausen, *Anal. Chem.*, **639**, 61 (1961).

(43) E. J. Corey and K. Achiwa, *J. Org. Chem.*, **34**, 3667 (1969).

Data for individual quantum yields are listed as follows: mass of starting material, added reagent if any, volume of *tert*-butyl alcohol solvent, apparatus, filter or wavelength, temperature, amount of light absorbed, mass of unreacted starting material, and per cent conversion. The mass, composition, and quantum yield for each product isolated are then given.

Run II-01. Starting material was 597.3 mg (2.447 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 3.91 mEinsteins; 452.9 mg (1.856 mmol) of unreacted *trans*-bicyclic diene; conversion, 24.3%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (35.0 mg, 0.143 mmol), syn:anti ratio was 0.667, $\Phi = 0.0366$.

Diphenyltoluenes (5.3 mg, 0.022 mmol), $\Phi = 0.0056$.

Run II-02. Starting material was 598.3 mg (2.452 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 1.79 mEinsteins; 524.0 mg (2.148 mmol) of unreacted *trans*-bicyclic diene; conversion, 12.3%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (17.5 mg, 0.0715 mmol), syn:anti ratio was 0.423, $\Phi = 0.0401$.

Diphenyltoluenes (2.7 mg, 0.011 mmol), $\Phi = 0.0062$.

Run II-03. Starting material was 1.028 g (4.213 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 1.96 mEinsteins; 938.9 mg (3.848 mmol) of unreacted *trans*-bicyclic diene; conversion, 8.66%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (18.4 mg, 0.0754 mmol), syn:anti ratio was 0.394, $\Phi = 0.0384$.

Diphenyltoluenes (2.0 mg, 0.0082 mmol), $\Phi = 0.0042$.

Run II-04. Starting material was 38.0 mg (0.156 mmol) of 2-methylene-*trans*-5,6-dipehylbicyclo[3.1.0]-3-hexene; 734.0 mg (4.033 mmol) of benzophenone; 40 ml; micro; 350 nm; 33°; 0.198 mEinstein; 26.5 mg (0.109 mmol) of unreacted *trans*-bicyclic diene; conversion, 28.9%.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (12.5 mg, 0.0512 mmol), $\Phi = 0.259$. After correction for energy transfer to product, $\Phi = 0.28$.

Run III-01. Starting material was 35.0 mg (0.143 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 40 ml; micro; 270 nm; 33°; 0.187 mEinstein; 24.9 mg (0.102 mmol) of unreacted *cis*-bicyclic diene; conversion, 28.9% (insoluble thermal product in this run makes this figure high).

1,5-Diphenylspiro[2.4]-4,6-heptadiene (3.0 mg, 0.0123 mmol), greater than 90% syn isomer, $\Phi = 0.066$ (this figure is low due to light scatter caused by the insoluble thermal product mentioned above).

Run III-02. Starting material was 95.6 mg (0.392 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 0.284 mEinstein; 83.3 mg (0.341 mmol) of unreacted *cis*-bicyclic diene; conversion, 12.9%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (5.8 mg, 0.024 mmol), greater than 98% syn, $\Phi = 0.082$.

Run III-03. Starting material was 12.0 mg (0.0492 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 738.3 mg (4.057 mmol) of benzophenone; 40 ml, micro; 350 nm; 33°; 0.0709 mEinstein; 12.1 mg (0.053 mmol) of unreacted *cis*-bicyclic diene; 0%.

No photoproducts were observed.

Acknowledgment. Support of this research by the National Science Foundation, National Institutes of Health Grant No. GM07487, and the U. S. Army Research Office (Durham) is gratefully acknowledged, as are predoctoral NASA and NIH fellowships to D. F. J. and J. M. M.

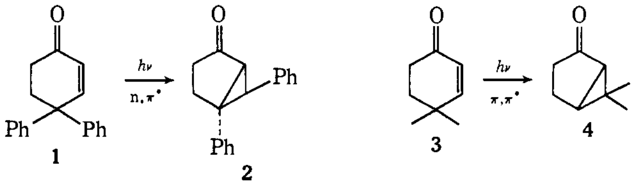
The Photochemistry of 4-Methyl-4-phenyl-2-cyclohexenone. The Effect of Solvent on the Excited State[1]

William G. Dauben,* Wayne A. Spitzer,[2a] and Michael S. Kellogg[2b]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received June 25, 1970*

Abstract: The photochemistry of 4-methyl-4-phenyl-2-cyclohexenone (**5**) was studied in a variety of solvents. In aprotic, nonpolar solvents, irradiations of **5** gave 5-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**6**) and 4-methyl-3-phenyl-2-cyclohexenone (**7**), photoproducts of the type attributed to an n,π^* triplet reaction. In the protic polar solvents, irradiation of **5** gave **6** and **7**, as well as *exo*-6-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**8**), 6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**9**), and *endo*-6-methyl-*exo*-6-phenylbicyclo[3.1.0]hexan-2-one (**10**), with **8–10** predominating. These latter products are of the type favored in π,π^* triplet reactions. The results are attributed to a bringing together (or perhaps an inversion) of the n,π^* and π,π^* triplet energy levels on going from nonpolar to polar solvents.

It is well established that 4,4-disubstituted 2-cyclohexenones can undergo a variety of reactions upon photoexcitation. The choice of reaction pathway followed by such compounds appears to be dependent upon the nature of the substituents at the 4 position and upon the character (n,π^* or π,π^*) of the low-lying triplet. For example, the 1,2-phenyl migration and rearrangement of the disubstituted-cyclohexenone **1** to give the bicyclo[3.1.0]hexan-2-one (**2**) is thought to occur from the n,π^* triplet excited state,[3,4] whereas skeletal rearrangements such as **3** to **4**[5] have been attributed to the π,π^* triplet excited state.[6]



In order to evaluate these suggestions, the photochemistry of 4-methyl-4-phenyl-2-cyclohexenone (**5**)

---

(1) This work was supported, in part, by Grant No. AM-00709, National Institute of Arthritis and Metabolic Diseases, U.S. Public Health Service, and the Hoffmann-LaRoche Foundation.

(2) (a) National Institutes of Health Predoctoral Fellow, 1967–1970; (b) National Institutes of Health Predoctoral Fellow, 1969–present.

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

(4) H. E. Zimmerman and K. G. Hancock, *ibid.*, 90, 3749 (1968).

(5) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(6) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 52, 971 (1969).