

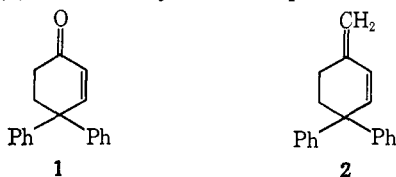
The Di- π -methane Rearrangement of 1-Methylene-4,4-diphenyl-2-cyclohexene and Related Photochemical Processes. Mechanistic and Exploratory Organic Photochemistry. XLV^{1,2}

Howard E. Zimmerman and Gary E. Samuelson

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin. Received February 20, 1969

Abstract: A photochemical transformation was uncovered in which a 1,2 shift of a phenyl group to the terminal carbon of a 1,3-diene occurs. Thus irradiation of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) in cyclohexane was found to afford the stereoisomeric 2-methylene-5,6-diphenylbicyclo[3.1.0]hexanes. The reaction provides a new variation of the di- π -methane rearrangement and is formally analogous to the $n-\pi^*$ rearrangement of 4,4-diaryl-cyclohexenones. However, in contrast to the enone reaction, the present rearrangement was shown to proceed *via* a singlet excited state. In the present instance, the triplet excited state of the 4,4-diphenyldiene (**2**) may be generated but is unreactive, in sharp contrast with the di- π -methane rearrangement of benzobarrelene which reacts *via* a triplet. The present reaction proved to be highly stereoselective with preferential formation of the *trans* stereoisomer of 2-methylene-5,6-diphenylbicyclo[3.1.0]hexane (*ca.* 125:1). Also, the reaction efficiency was found to be enhanced in solvent methanol compared to cyclohexane. The bicyclic products themselves were found to be photochemically interconvertible and also to revert to the 4,4-diphenyldiene. However, the *cis*-bicyclic compound returned to 4,4-diphenyldiene only inefficiently and, in addition, afforded 1-methylene-3,4-diphenyl-2-cyclohexene. Quantum yields were determined for the reactions studied. Molecular details of the reactions, including stereochemistry, are discussed from a mechanistic viewpoint.

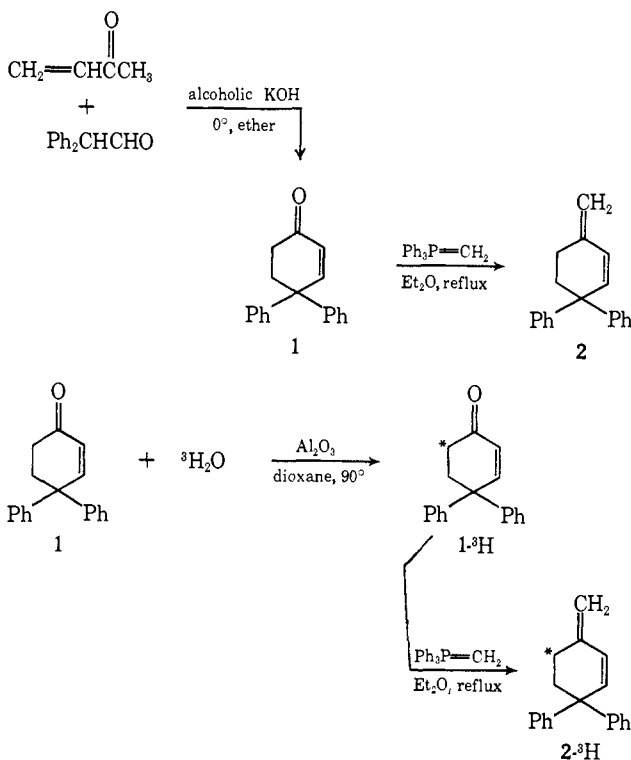
The photochemical rearrangements of 4,4-diaryl-cyclohexenones have been investigated extensively.³⁻⁷ Evidence has been advanced in favor of a mechanism involving aryl migration in a triplet $n-\pi^*$ excited state. An intriguing question concerned the photochemical behavior of molecules of similar structure but lacking an in-plane unshared electron pair and thus having no $n-\pi^*$ excited state. Such a molecule was 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) which is an analog of the much-studied^{3,4,7} 4,4-diphenylcyclohexenone (**1**). Not only was the problem of interest



because of its relationship to enone photochemistry but also the behavior of such diene $\pi-\pi^*$ excited states was of intrinsic concern.

Synthesis of Reactant and Tritium Incorporation. A synthesis of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) was required. Additionally, the material was required with tritium incorporated for quantitative studies planned. Reactant **2** was conveniently prepared by the Wittig reaction of the known³ 4,4-diphenylcyclohexenone (**1**); note Chart I. Tritium was conveniently incorporated at C-6 of 4,4-diphenylcyclohexenone (**1**) by

Chart I. Synthesis of 1-Methylene-4,4-diphenyl-2-cyclohexene and Tritium Incorporation^a



^a * represents tritium label.

base-catalyzed exchange using tritium oxide-alumina in dioxane.⁴ This proved convenient, since tritium was found not to be lost in subsequent operations and also because tritium at C-6 is too remote for secondary isotope effects to be a problem.⁸

(8) In the photochemistry of 4,4-diphenylcyclohexenone itself, tritium at C-6 was shown (ref 4) to lead to the same results as ¹⁴C at C-4, thus establishing the absence of isotope effects.

(1) (a) For paper XLIV of the series, see H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969); (b) paper LXIII: H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969).

(2) Preliminary communication: H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967).

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

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

(5) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

(6) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).

(7) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).

Table I. Spectral Data and Interpretations for Compounds 2, 3, and 4

Compd	Nmr signal, τ	Integration and assignment ^a	Infrared signal, μ	Assignment ^b
2	2.80	10 H, s, aromatic	6.11	C=C stretch
	3.79	2 H, AB quartet, $J = 10$ Hz, -CH=CH-	11.29	=CH ₂ , C-H bend
	5.18	2 H, s, =CH ₂		
3	7.70	4 H, s, -CH ₂ CH ₂ -		
	2.70	10 H, s, aromatic	6.06	C=C stretch
	4.90, 5.20	2 H, br, =CH ₂	11.49, 11.58	=CH ₂ , C-H bend
	7.42	2 H, s, -CH ₂ -		
	7.7-8.3	4 H, m, -CH ₂ - and cyclopropyl CH-CH		
4	2.75-3.40	10 H, m, aromatic	6.05	C=C stretch
	4.95, 5.17	2 H, slightly split s, =CH ₂	11.48	=CH ₂ , C-H bend
	7.46	2 H, AB quartet, $J = 3.8$ Hz, cyclopropyl CH-CH		
	7.57-8.05	4 H, m, -CH ₂ -		

^a R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963; s represents singlet; br, broad singlet; m, multiplet. ^b K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden-Day, Inc., San Francisco, Calif., 1962.

Direct Irradiation of 1-Methylene-4,4-diphenyl-2-cyclohexene. Exploratory Efforts. Initial studies employed a short-wavelength cutoff filter of Vycor and a medium-pressure lamp in an immersion apparatus. It was found that irradiation of 1-methylene-4,4-diphenyl-2-cyclohexene (2) in cyclohexane afforded two primary photoproducts, 3 and 4.

The structures of these products were suggested by the nmr and infrared spectra; note Table I which also includes data for reactant 2.

Firm structural assignments were obtained first by degradation and then by synthesis. The degradation involved reaction with osmium tetroxide followed by lead tetraacetate cleavage of the glycols formed. The degradation products proved to be the known³ bicyclic ketones, *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-

2-one (7 and 8, respectively). This degradation is outlined in Chart II.

The synthesis of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (3) and 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (4) required only the Wittig reaction of the ketones 7 and 8 as depicted also in Chart II.

Hence the photochemical transformation of 1-methylene-4,4-diphenyl-2-cyclohexene (2) may be seen to involve phenyl migration from C-4 to C-3 along with 2,4-bond formation as shown in eq 1.

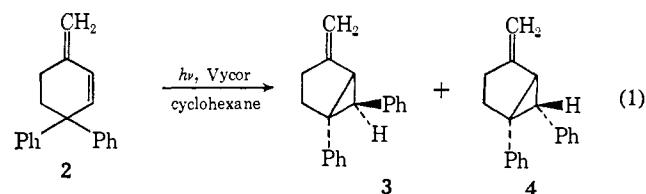
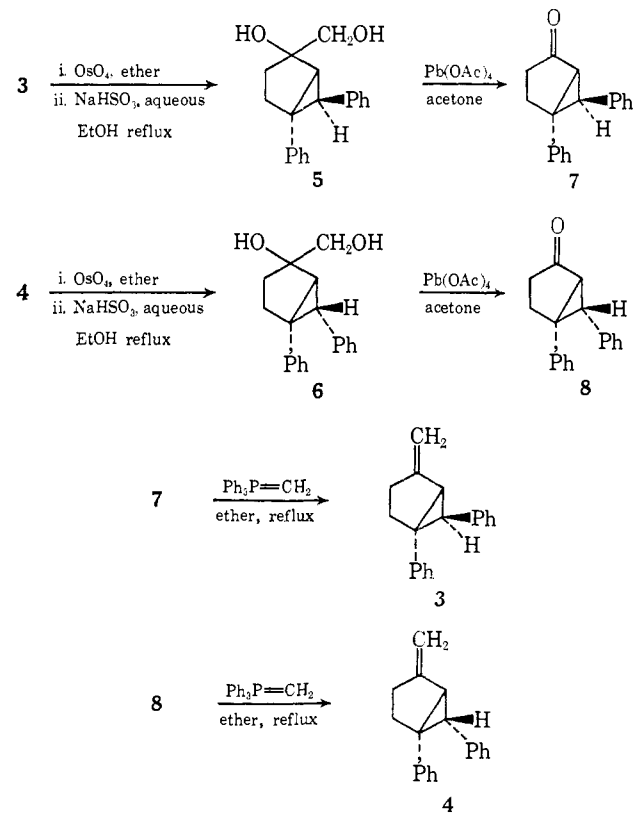
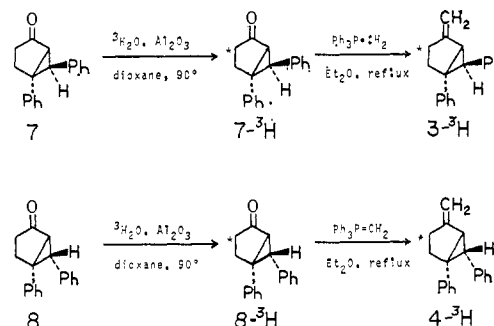


Chart II. Degradation and Synthesis of Photoproducts 3 and 4



In subsequent photolyses, it was found that the ratio of the *cis* to *trans* isomer of product (*i.e.*, 4:3) increased with the extent of photolytic conversion. Nevertheless, it did appear that the *cis* isomer 4 was a primary product (*vide infra*).

Synthesis of Labeled Photoproducts 3 and 4. In order to carry out quantitative studies on the photochemical rearrangements of 2-methylene-*trans*- and 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (3 and 4, respectively), tritium-labeled reactants were required. Such a label was most conveniently introduced using the previously described alumina-catalyzed exchange of tritium oxide with the ketone precursors 7 and 8; note Chart III.

Chart III. Tritium Incorporation in 3 and 4^a

^a *Represents tritium label.

Table II. Quantum Yields of 1-Methylene-4,4-diphenyl-2-cyclohexene Rearrangement

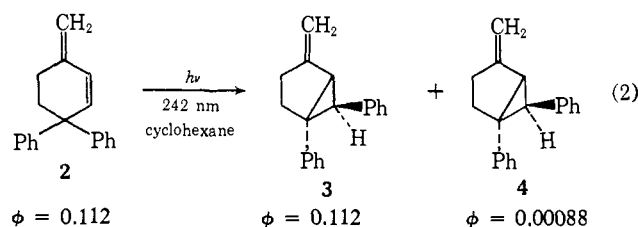
Run ^a	Diene used, mg	Light, mEinstein	Diene recovered, mg ^b	3 ^d	Quantum yields ^c	4 ^e
1	104.0	0.0382	104.5 ± 4.2	0.109 ± 0.004	<i>f</i>	
2	134.0	0.232	133.0 ± 5.3	0.114 ± 0.004	0.00093 ± 0.00007	
3	106.8	0.0905	106.0 ± 4.3	<i>f</i>	0.00083 ± 0.00007	
4 ^p	95.1	0.0432	95.0 ± 3.8	0.0061 ± 0.0004	<i>f</i>	

^a Runs 1-3 at 242 nm in cyclohexane at 24.0°. ^b From isotope dilution analysis. ^c In millimoles per millieinstein. Errors estimated from experimental data. ^d Appearance of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. ^e Appearance of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. ^f Not determined. ^p In neat chlorobenzene, 9.82 M, at 263.5 nm and 24.5°

The Reaction Efficiency. A precise method of product analysis was necessary to determine the quantum efficiency and product ratio in the photochemical rearrangement of **2**. Isotope dilution was selected since it was known⁴ to be accurate at the low conversions desired and would circumvent incomplete chromatographic separation of **2**, **3**, and **4**. In addition, the uncertain stabilities of the olefins during purification suggested the formation of a solid derivative of each which could be more readily purified for specific activity determinations. The method chosen was oxidation to the related ketones using osmium tetroxide followed by sodium metaperiodate since the ketones were known⁴ to be easily recrystallized to constant specific activity.

The general procedure for microdetermination of quantum yields thus involved irradiation of *ca.* 100-mg quantities of radioactive reactant through a Bausch and Lomb monochromator, followed by dilution of aliquots of the solution with known excesses of the inactive components. The diluted mixtures were then oxidized to the corresponding ketones and the resultant activities used to calculate the amounts of products produced or reactant recovered.

Irradiation of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) in cyclohexane at 242 nm afforded **3** and **4** in the ratio of *ca.* 125:1 as determined by isotope dilution analysis. The quantum yields for product appearance and reactant disappearance are given in eq 2 and Table II.



Multiplicity of the Phenyl Migration Reaction. Having uncovered the rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) to give the 2-methylene-5,6-diphenylbicyclo[3.1.0]hexane stereoisomers (**3** and **4**), it was of importance to determine whether a singlet or a triplet excited state of reactant was the rearranging species. As a test, a 2.9×10^{-3} M solution of **2** in benzene with sufficient benzophenone ($E_T = 68.8$ kcal/mole) to absorb >99% of the incident light was irradiated through Pyrex in a quartz immersion apparatus. After 5-hr irradiation, concentration and chromatography yielded 77% recovered **2** and no evidence of photoproducts **3** and **4**.

That energy transfer from benzophenone to diene **2** was occurring was shown by quenching the known⁹

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

triplet reaction of benzophenone with benzhydrol to form benzpinacol. Thus, 8.90×10^{-3} M **2** was found to quench at least 80% of the benzpinacol formation under conditions where the benzophenone was absorbing *ca.* 97% of the incident light.

In a further attempt at triplet sensitization, a 9.9×10^{-3} M solution of **2** in chlorobenzene¹⁰ ($E_T = \sim 82$ kcal/mole and singlet lifetime $< 10^{-9}$ sec)¹¹ was irradiated at 264 nm in the microquantum yield apparatus. Neat chlorobenzene, 9.82 M, was calculated to absorb $96.5 \pm 2.0\%$ of the incident light. The quantum yield for the appearance of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (**3**) was measured by the method of isotope dilution to be 0.0061 mmol/mEinstein; note Table II. This value, *ca.* 5.5% of the direct quantum yield, is within experimental error of the value calculated to arise from direct absorption of light by reactant **2**.

The failure of benzophenone and chlorobenzene to sensitize the rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) to the *trans* and *cis* stereoisomers of 2-methylene-5,6-diphenylbicyclo[3.1.0]hexane (**3** and **4**) suggests that the triplet excited state of **2** is unreactive and that an excited singlet state is probably responsible for the observed rearrangement (*vide infra*).

Photolysis of 1-Methylene-4,4-diphenyl-2-cyclohexene in Methanol. Reports in the literature¹² of proton solvent addition to reactive ground-state intermediates such as bicyclobutanes and *trans* olefins generated by photolysis of dienes and monoolefins prompted investigation of the behavior of diene **2** in methanol. Irradiation of a methanolic solution of **2** with a known amount of light and analysis by nmr disclosed no evidence of methanol addition products. However, a surprising increase in the quantum yield resulted with that for **3** approaching 0.21 mmol/mEinstein.

Interconversion and Photochemical Behavior of the Stereoisomeric 2-Methylene-5,6-diphenylbicyclo[3.1.0]hexanes. Because of the observation mentioned earlier that the *cis:trans* ratio (*i.e.*, **4:3**) in the photolysis of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) increased with increasing extent of conversion, the photochemical behavior of the *trans* and *cis* isomers of 2-methylene-5,6-diphenylbicyclo[3.1.0]hexane was examined.

(10) Chlorobenzene is a convenient, high-energy sensitizer for very low conversion use. In high conversion runs hydrogen chloride formation results.

(11) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

(12) (a) W. G. Dauben and F. G. Willey, *Tetrahedron Lett.*, 893 (1962); (b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (c) W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967); (d) J. Pusset and R. Beugelmans, *ibid.*, 3249 (1967); (e) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **90**, 802 (1968); (f) P. J. Kropp, *ibid.*, **88**, 4091 (1966); (g) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966); (h) P. J. Kropp, *ibid.*, **89**, 3650 (1967); (i) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

Table III. Quantum Yields of Rearrangement of 2-Methylene-*trans*- and 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane

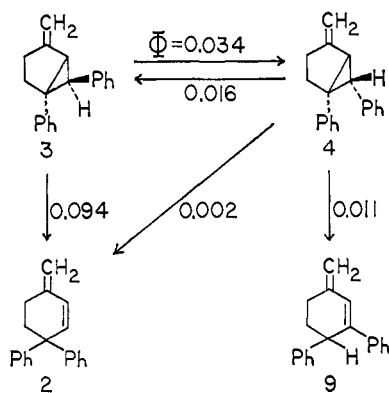
Run ^a	Reactant and wt, mg	Light, mEinstein	Unreacted reactant, ^b mg	Quantum yields, mmole/mEinstein ^c			
				2	3	4	9
1	3, 89.6	0.0950	90.0 ± 3.6	0.0943 ± 0.0039		0.0331 ± 0.0020	
2	3, 96.8	0.0683	98.0 ± 3.9	0.0946 ± 0.0039		0.0361 ± 0.0022	
3	4, 95.4	0.176	92.5 ± 4.6	0.0023 ± 0.0002	0.0162 ± 0.0010		<i>d</i>
4	4, 96.0	0.121	91.8 ± 4.6	<i>d</i>	0.0167 ± 0.0010		0.0107 ± 0.0008
5	4, 99.3	0.106	96.5 ± 4.8	0.0026 ± 0.0003	<i>d</i>		0.0117 ± 0.0009

^a All runs in 39.0 ml of cyclohexane at 242 nm and 25.0°. ^b Isotope dilution analysis; error from data. ^c Quantum yields for appearance of products only; error from experimental data. ^d Not determined.

Exploratory photolysis of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (**3**) and nmr analysis indicated the formation of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) and 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (**4**) in the ratio of *ca.* 2.5:1. No additional products were observed and more extensive photolysis resulted only in the appearance of the products of the *cis* isomer **4** (*vide infra*).

Similar photolysis of the *cis* isomer **4** gave the *trans* isomer **3** and a new product, 1-methylene-3,4-diphenyl-2-cyclohexene (**9**), but no 4,4-diphenyldiene **2**. The structure of **9** was established by synthesis using the Wittig reaction on the known¹³ 3,4-diphenylcyclohex-2-en-1-one.

Owing to the difficulty of separating the product mixtures in the photolyses of **3** and **4**, the method of isotope dilution analysis was again employed, this time using tritiated **3** and **4** as reactants. The quantum yields determined at 242 nm in cyclohexane are summarized in Table III and the over-all course of the reactions is depicted in Chart IV.

Chart IV. Photochemical Reactions of the *trans*- and *cis*-2-Methylene-5,6-diphenylbicyclo[3.1.0]hexanes

Insight into the multiplicity of the excited state involved in the photoisomerization of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (**3**) was provided by sensitization of **3** with acetone.¹⁴⁻¹⁶ Remarkably, no 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) could be detected and the sole product formed appeared to be 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (**4**)

(13) E. C. Dodds, R. L. Huang, W. Lawson, and R. Robinson, *Proc. Roy. Soc. (London)*, **B140**, 470 (1953).

(14) Acetone was chosen since its triplet energy ($E_T = \sim 80$ kcal/mol)¹⁵ should lie sufficiently above that of the bicyclic olefin **3** for triplet transfer to be reasonably efficient. Thus phenylcyclopropane has a triplet energy of *ca.* 81 kcal/mole.¹⁶ In the present instance, the system is more heavily conjugated and should have a still lower triplet energy relative to phenylcyclopropane.

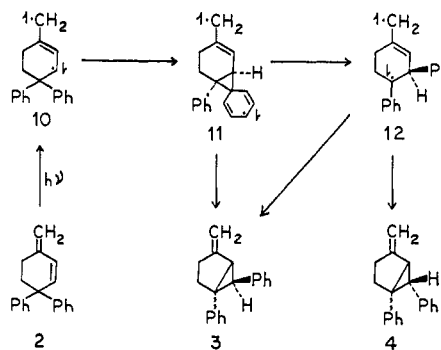
(15) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(16) D. F. Evans, *J. Chem. Soc.*, 2753 (1959).

with an approximate sensitized quantum yield of 0.078 mmol/mEinstein.

Thus, it appears likely that the formation of diene **2** from the *trans* bicyclic olefin **3** occurs *via* a singlet excited state, while the triplet state preferentially isomerizes to the *cis*-bicyclic olefin **4**.

Discussion of Results. Diene Photochemistry. The reaction of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) proceeds in a manner formally analogous to that of 4,4-diphenylcyclohexenone (**1**). However, the similarity is seen to be superficial. One difference is the electronic configuration of the reacting species. While the enone **1** rearranges by way of its triplet $n-\pi^*$ excited state,⁴ the diene **2** has no unshared electrons and hence no $n-\pi^*$ states available. Thus, the reaction may be represented as proceeding through a $\pi-\pi^*$ excited state as shown in Chart V.

Chart V. Rearrangement of 1-Methylene-4,4-diphenyl-2-cyclohexene

A second difference is the multiplicity of the rearranging species. Generation of the triplet of diene **2** (*cf.* 1,3-butadiene, $E_T = 59.6$ kcal/mol)¹⁷ using benzophenone ($E_T = 68.8$ kcal/mol) or chlorobenzene ($E_T = 82$ kcal/mol) sensitization was found to be ineffective in producing the rearrangement of **2** to the bicyclic products **3** and **4**. Since triplet transfer with benzophenone was shown to occur (*i.e.*, by quenching of benzpinacol formation, *vide supra*), it can be concluded that T_1 does not rearrange. The possibility still might exist that a higher triplet of **2** is responsible for the ob-

(17) Thus, D. F. Evans [*ibid.*, 1735 (1960)] has observed a S_0-T_2 transition energy for butadiene of 82.2 kcal/mole and calculated values seem to support this observation.¹⁸

(18) Some calculated values are (T_1 , T_2 , splitting, in kcal/mole) by Sidman¹⁹ (78, 101, 23), Pariser and Parr²⁰ (90, 106, 16), Pullman²¹ (57.5, 85.0, 27.5), and Fain and Matsen²² (61.3, 89.5, 28.2). Thus, although the calculations often give too high values for T_1 , they do agree on the magnitude of the T_1-T_2 separation.

(19) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

(20) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

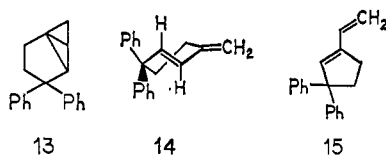
(21) A. Pullman, *J. Chim. Phys.*, **51**, 188 (1954).

(22) J. Fain and F. A. Matsen, *J. Chem. Phys.*, **26**, 377 (1957).

served reaction. However, if we assume that the T_1 - T_2 splitting in **2** is comparable to that of 1,3-butadiene, it would appear that T_2 should be near 82 kcal/mol and therefore should be formed by chlorobenzene sensitization.¹⁷⁻²² This then allows us to rule out a second triplet (*i.e.*, T_2) as the rearranging species. Such a conclusion is of general interest since very often evidence ruling out T_1 as involved in a photochemical reaction still leaves T_2 as well as S_1 as potentially involved excited states. Differentiation between S_1 and T_2 can be quite difficult.

We are then left with the first excited singlet S_1 of diene **2** as responsible for the rearrangement observed upon direct irradiation. Thus, the present reaction joins the class of acyclic and monocyclic olefins which undergo the di- π -methane rearrangement by way of their singlet excited states.²³

We note that the mechanism in Chart V involves reaction of the electronically excited diene **2**. One might inquire whether it is possible that a ground-state bicyclobutane as **13** or a ground-state *trans*-diene **14** might be formed and then proceed onward to product or provide a means of energy dissipation. This is of special concern since it is known^{12a-e} that *s-trans*-dienes can form bicyclobutanes and there is some suggestion that transoid π bonds can form in the case of cyclohexenes.^{12f-i} However, the lack of methanol solvent intervention (*vide supra*) so characteristic of the bicyclobutane photochemistry as well as *s-trans*-cyclohexene irradiations suggests that neither reaction course is presently involved. Additionally, low-temperature irradiations with infrared monitoring as described in the Experimental Section showed no evidence for thermally labile intermediates. Finally, with respect to species



13 being formed reversibly and hence allowing energy dissipation, we note also that species **13** has two modes of opening potentially available. One leads back to diene reactant **2** and the other affords the unobserved five-ring diene **15**. A very strong obstacle to the *trans*-diene **14** being an intermediate is the reaction stereochemistry which affords the *trans*-bicyclic isomer **3**; this is the stereoisomer having the migrated phenyl group lying over the five-ring and *endo*. However, only one phenyl group in the *trans*-diene **14** is close to coplanar with the π system and migration of this group leads to its final orientation as *exo*.

Another aspect which is especially intriguing deals with the reaction stereochemistry which results in the highly stereoselective formation of the *trans*-bicyclic product **3**. This is the same stereochemical pathway found for the corresponding ketone, 4,4-diphenylcyclohexenone (**1**), and the stereochemical results have been discussed.^{4,24} We might inquire initially whether the stereochemistry is a consequence of the "allowedness" of the reaction. Reference to Figure 1 shows that for

(23) H. E. Zimmerman and P. S. Mariano [*J. Amer. Chem. Soc.*, **91**, 1718 (1969)] have commented on the relationship of structure and multiplicity in the di- π -methane rearrangement.

(24) H. E. Zimmerman and R. L. Morse [*ibid.*, **90**, 954 (1968)] described similar results for 4,4,5-triphenylcyclohexenone.

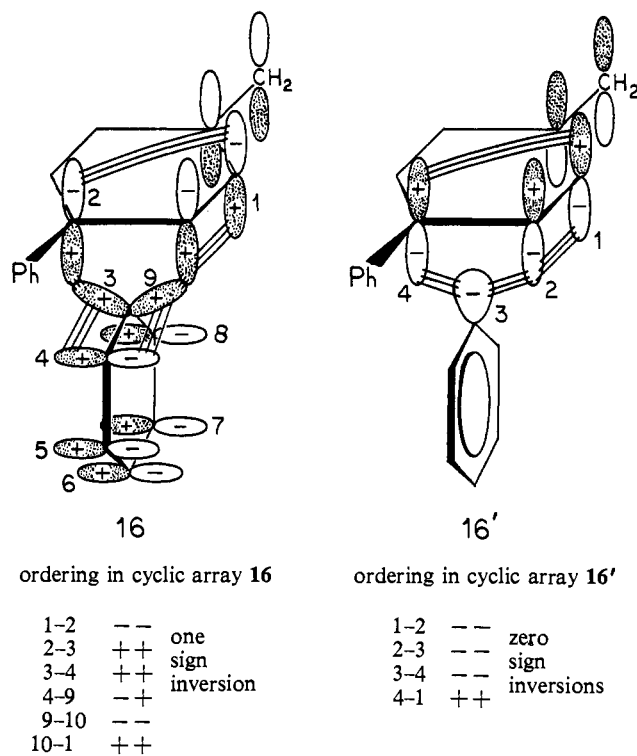
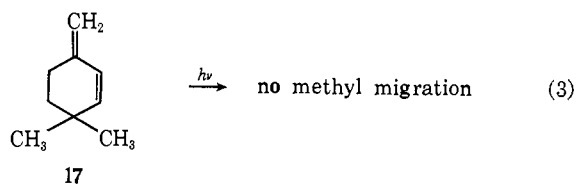


Figure 1. Cyclic array of orbitals in the transition state for phenyl migration. Inclusion of the remaining four phenyl orbitals in **16'** does not alter the evenness or oddness of sign inversions.

migration with inversion at C-4, which affords the observed *endo* product, there are either ten or six orbitals in a cycle which overlap, depending on whether one takes the largest cyclic array of orbitals or the smaller one. However, in each case there are an odd number of sign inversions, and an electronically excited $4N + 2$ electron cyclic system with an odd number of sign inversions is favored (over one with zero or an even number of inversions). Thus the reaction is "allowed." The same result would be deduced if we did not use the π -system orbitals of the migrating phenyl ring but invoked only the orbitals of the phenyl-C-4 σ bond (note **16'**). Fortunately or otherwise, we come to the same prediction of allowedness. However, discussion without inclusion of the phenyl π system is not realistic since the π system seems to be requisite; for example, there is no rearrangement in the case of 1-methylene-4,4-dimethyl-2-cyclohexene (**17**).^{12e} Although



the reaction with inversion at C-4 is allowed, this cannot validly be taken as controlling the inversion process since the retention process has the same number of inversions and is also allowed.^{25, 26}

(25) Such a process would involve overlap of the plus lobes of orbitals 1 and 2 in order to give a *cis* ring fusion.

(26) The same lack of predictive power results in this case from the

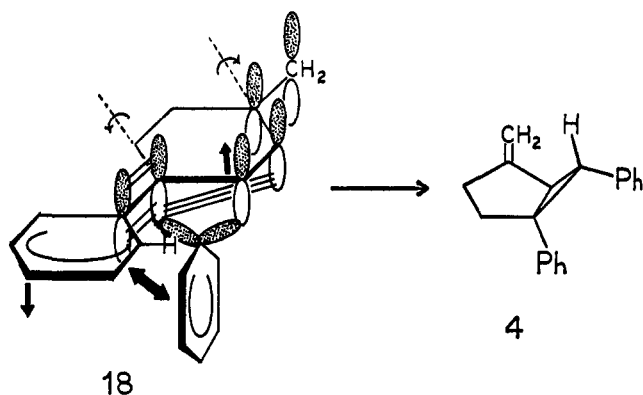


Figure 2. Phenyl-phenyl interaction enforced in the C-4 retention stereochemistry.

Another factor seems to be superimposed on the requirement for allowedness. As was noted in discussion of the stereochemistry of the 4,4-diphenylcyclohexenone rearrangement,⁴ mere van der Waals repulsive forces between freely rotating phenyl groups do not suffice to rationalize preferential *trans*-bicyclic ring structure formation, since the alternative to phenyl-phenyl interaction is phenyl-*endo* five-ring repulsions. However, in the concerted rearrangement process, not only the migrating bridged phenyl is constrained but also the nonmigrating one.²⁷ The nonmigrating phenyl should be oriented to delocalize the odd electron density of the partially rearranged species, and this orientation is precisely one which leads to severe phenyl-phenyl interaction when retention stereochemistry at C-4 is followed. This is depicted in Figure 2 where the C-4 phenyl is seen to twist downward, directly interfering with the migrating aryl group. The alternative inversion stereochemistry leading to *trans*-product **3** does not suffer from this disadvantage and thus is preferred. It may be that the *cis*-product **4** does not come *via* the concerted route but rather by the open biradical **12**.

A final point concerning the rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene (**2**) is noteworthy, namely the doubling of the quantum efficiency of the rearrangement on proceeding from cyclohexane to methanol. When an array of orbitals in a transition state, either in an unexcited or an excited species, is "nonalternant,"²⁹ there is no reason for the electron density to be uniformly distributed and one might anticipate varying degrees of effect by solvent polarity on the reaction rate. The present instance seems to be such a case. From the photochemical viewpoint, this result means that one must be careful in assessing the significance of solvent polarity effects.

"2A + 2A" reasoning described by R. Hoffmann, 12th Reaction Mechanisms Conference, Brandeis University, Waltham, Mass., June 1968. This is not surprising since the "2A + 2A" type reasoning is really another way of counting sign inversions.

(27) In enone photochemistry, evidence has been advanced^{4,24,28} that a nonmigrating aryl group is a prerequisite for the aryl migration process.

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

(29) In the earlier discussion of "allowedness" vs. "forbiddenness" of the rearrangement process, attention was focused on the largest cycle of orbitals of the rearranging moiety and additional overlap was neglected as an approximation. The present description of the system as "nonalternant" derives from our finding several cyclic arrays of odd numbers of orbitals (e.g., 1, 2, and 10); however, this includes some overlap (i.e., 2-10) not discussed in connection with allowedness.

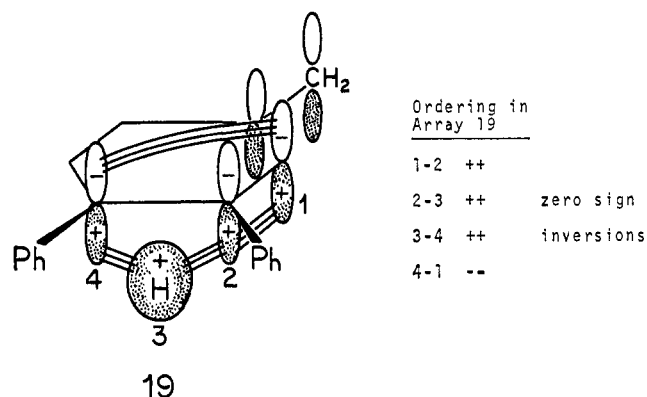


Figure 3. Cyclic array of orbitals in the hydrogen migration reaction.

Discussion of Results. Bicyclic Olefin Photochemistry. The observed interconversions and other reactions of 2-methylene-*trans*- and 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (**3** and **4**) are most easily understood as resulting from three-ring fission in a $\pi-\pi^*$ excited state.³⁰ The reversion of the *trans*-bicyclic olefin **3** to diene **2** contrasted with the inefficiency of such a reaction from the *cis*-isomer **4** is reminiscent of the situation in the photochemistry of 4,4-diphenylcyclohexenone, although the reaction is considerably more efficient in the present hydrocarbon case. The same principle as in the ketone case seems to be prevailing, namely that a photochemical reaction with an inefficient pathway in one direction may well find the same structural disadvantage for the reverse reaction. A mechanistic pathway for these reactions and for the formation of 1-methylene-3,4-diphenyl-2-cyclohexene (**9**) is outlined in Chart VI.

The observed efficiency of the reversion of the *trans*-isomer **3** to diene **2** can best be explained by invoking the same electronically allowed transition state **16** as was proposed in the formation of **3**.^{31,32}

Two reasonable mechanisms are possible for isomerization of the *cis*-isomer **4** to 1-methylene-3,4-diphenyl-2-cyclohexene (**9**). An electronically allowed 4-orbital, 4-electron, cyclic transition state may be involved in this hydrogen migration reaction. Such a transition state is shown in Figure 3. The presence of $4N$ electrons, with zero or an even number of sign inversions, in such a cyclic array would result in the concerted hydrogen migration reaction being allowed in the excited state.

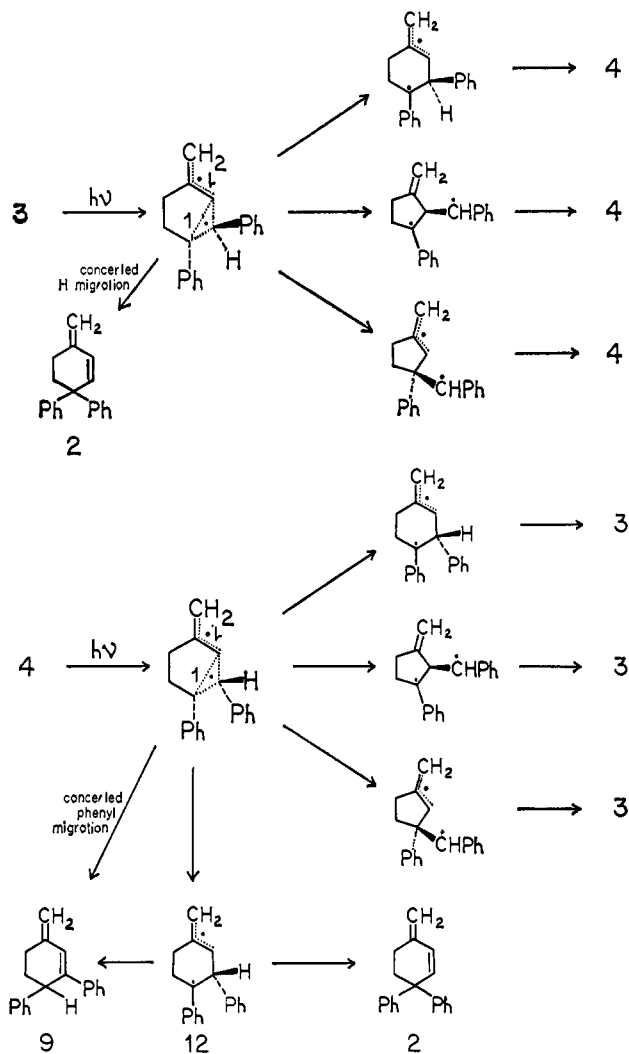
Alternatively, the hydrogen migration reaction responsible for the formation of **9** may be proceeding through an intermediate biradical such as **12**. Of interest is the preferential hydrogen migration relative to phenyl. Previous reports in the literature indicate that preferential hydrogen migration from such a biradical

(30) The excited state may also have $\sigma-\pi^*$ and $\pi-\sigma^*$ character due to overlap of the three ring orbitals with the π system, but all gradations of these descriptions are possible in any single case and a $\pi-\pi^*$ designation is simplest.

(31) The analogous reversion reaction was observed as a very minor reaction course in the photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.³² However, presently the excitation is most likely distributed throughout the three ring, the exocyclic double bond, and the aryl groups in contrast to the ketone where excitation was localized heavily in the carbonyl group.

(32) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968).

Chart VI. Mechanisms of the Bicyclic Olefin Reactions



may be occurring in the photochemistry of 1,1,3,3-tetra-phenylpropene.³³

A final point to be considered is the multiplicity of the bicyclic olefin reaction. The absence of diene 2 in the acetone-sensitized photolysis of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (3) and the observation of only *cis-trans* isomerization define the behavior of independently generated triplet excited state 3*. Accordingly, the phenyl migration process observed in direct irradiation must not proceed *via* the triplet but rather by way of a singlet excited species. Also, that the triplet undergoes stereoisomerization provides permissive, but not necessitative, evidence for the triplet being involved in the *cis-trans* isomerization found in the direct irradiation. The formation of 4 and 3 in the direct irradiation with an efficiency lower than that in the sensitized case may then be due to an inherently less efficient singlet process or reaction from the triplet state after inefficient intersystem crossing.

Experimental Section³⁴

4,4-Diphenylcyclohex-2-en-1-one. Slight modification of the method of Zimmerman, Keese, Nasielski, and Swenton³⁵ gave,

(33) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petersen, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(34) Melting points were obtained on a hot-stage apparatus calibrated with known materials.

in a typical run, a 74% yield of 4,4-diphenylcyclohex-2-en-1-one, mp 93–94° after recrystallization from methanol.

1-Methylene-4,4-diphenyl-2-cyclohexene. To a stirred suspension of 12.15 g (34.0 mmol) of methyltriphenylphosphonium bromide in 230 ml of dry ether under nitrogen was added 15.4 ml (34.0 mmol, 2.19 *M*) of *n*-butyllithium solution. The orange solution was stirred for 15 min followed by dropwise addition of a solution of 7.003 g (28.2 mmol) of 4,4-diphenylcyclohex-2-en-1-one in 120 ml of benzene-ether over a period of 1.5 hr. The heavy, white suspension was refluxed for 3 hr, cooled, diluted with hexane, and filtered. Another portion of hexane was added, and the solution was filtered and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 25 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 250-ml fractions gave: fractions 1–2, 3% ether in hexane, nil; 3–10, 3%, 6.257 g of crude 1-methylene-4,4-diphenyl-2-cyclohexene (90%). Distillation gave pure 1-methylene-4,4-diphenyl-2-cyclohexene as a colorless oil: bp 125–127° (0.05 mm); $\lambda_{\text{max}}^{\text{EtOH}}$ 232 nm (ϵ 31,000), 238 (31,600), 263 sh (1740), and 270 sh (1160); ir (neat) 3.26, 3.30, 3.40, 6.11, 6.24, 6.70, 6.91, 9.70, 10.18, 11.29, 13.29, and 14.30 μ ; nmr (CCl₄) τ 2.80 (s, 10 H, aromatic), AB quartet centered at 3.79 ($\delta_A - \delta_B = 0.19$ ppm, 2 H, $-\text{CH}=\text{CH}-$, $J_{\text{AB}} = 10$ Hz), 5.18 (br s, 2 H, $=\text{CH}_2$), and 7.70 (s, 4 H, ring CH_2).

Anal. Calcd for C₁₅H₁₈: C, 92.63; H, 7.37. Found: C, 92.41; H, 7.69.

Solvent Purification. Cyclohexane for photolysis was purified by stirring for 12 hr with 30% fuming sulfuric acid, washing with water, drying with sodium sulfate, and distilling from phosphorus pentoxide. Benzene used in sensitization experiments with benzophenone was purified by shaking three times with acidic potassium permanganate solution, four times with concentrated sulfuric acid, and three times with aqueous sodium bicarbonate, drying with sodium sulfate, and distilling from phosphorus pentoxide.

Irradiation of 1-Methylene-4,4-diphenyl-2-cyclohexene. A solution of 0.5287 g (2.14 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 775 ml of purified cyclohexane was irradiated for 2 hr under deoxygenated nitrogen³⁶ through a Vycor filter ($\lambda > 220$ nm) with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Uv spectra taken before and after photolysis showed the disappearance of at least 70% of the starting material. The yellow photolysate was concentrated *in vacuo* and chromatographed on a 1.8 × 100 cm column of deactivated silica gel (Davison 950, 60–200 mesh, treated with water, dried at 50°) slurry packed in pentane. Elution in 200-ml fractions gave: fraction 1, pentane, nil; 2–3, pentane, 70 mg of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane; 4, pentane, 209 mg of a ca. 4:1 mixture of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane and 1-methylene-4,4-diphenyl-2-cyclohexene; 5, pentane, 63 mg of a mixture of 1-methylene-4,4-diphenyl-2-cyclohexene and 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane; 6–8, pentane, 58 mg of crystalline 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane; 9–10, 1% ether in pentane, 57 mg of a yellow oil having broad, uncharacterizable nmr absorption; total recovery 86%.

cis- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones were prepared by photolysis of 4,4-diphenylcyclohex-2-en-1-one in benzene according to the method of Wilson and Zimmerman.³

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. To a stirred suspension of 10.41 g (29.2 mmol) of methyltriphenylphosphonium bromide in 250 ml of dry ether was added 13.3 ml (2.19 *M*, 29.2 mmol) of *n*-butyllithium solution under nitrogen. The orange solution was stirred for 15 min and a solution of 6.034 g (24.3 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 100 ml of benzene-ether was added dropwise over 45 min. The heavy, white suspension was refluxed for 4 hr, cooled, diluted with hexane, filtered, and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 25 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 500-ml fractions gave: fraction 1, 2% ether in hexane, nil; 2–5, 2%, 2.762 g of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane; 6, 16%, nil; 7–9, 16%, 0.5783 g of recovered *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one; yield based on reacted ketone, 51%. Sublimation of the hydrocarbon fraction (40°, 0.005 mm) gave pure 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane: mp 38–39°; ir (CS₂) 3.24, 3.26, 3.30, 3.34, 3.40, 3.49, 6.06, 6.24, 8.37, 9.31, 9.72, 10.29, 11.49, 11.58, 12.76, 13.21, 13.52, 13.82 and 14.38 μ ; nmr (CCl₄) τ 2.70 (s, 10 H, aromatic), 4.90 and 5.20 (br s, 2 H, $=\text{CH}_2$),

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

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

7.42 (s, 2 H, ring CH₂), 7.7–8.3 (m, 4 H, ring CH₂ and cyclopropyl CH–CH).

Anal. Calcd for C₁₅H₁₈: C, 92.63; H, 7.37. Found: C, 92.40; H, 7.64.

Nmr and ir spectra were superimposable in all respects on those of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane isolated from the photolysis of 1-methylene-4,4-diphenyl-2-cyclohexene.

Osmium Tetroxide Oxidation of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane.³⁷ *Method A.* A solution of 0.3315 g (1.34 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 40 ml of ether was treated at room temperature with 0.3383 g (1.33 mmol) of osmium tetroxide for 6.5 hr. The solvent was removed and the black residue hydrolyzed by refluxing with 3.0 g of sodium bisulfite for 1.5 hr in 50 ml of 50% ethanol. The solution plus 250 ml of saturated sodium chloride solution was chloroform extracted, and the extract dried, concentrated, and chromatographed on a 2.0 × 71 cm column of silicic acid (Mallinckrodt SilicAR) slurry packed in 10% methanol in chloroform. Elution in 100-ml fractions gave: fractions 1–2, chloroform, 37 mg of yellow oil; 3–10, chloroform, nil; 11–12, 2% methanol in chloroform, nil; 13–15, 2%, 131 mg of 2-hydroxy-2-hydroxymethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (35%). Spectral data for the diol were as follows: ir (CHCl₃) 2.80, sharp, and 2.94 μ, broad OH absorption; nmr (CDCl₃) τ 2.70 (d, 10 H, aromatic), AB quartet centered at 6.42 (*J*_{AB} = 11 Hz, 2 H, –CH₂O), 6.91 (s, 2 H, –OH), and 7.3–8.9 (m, 6 H, ring CH₂ and cyclopropyl –CHCH–).

Oxidative Cleavage of 2-Hydroxy-2-hydroxymethyl-*trans*-5,6-diphenylbicyclo[3.5.0]hexane.³⁸ To a solution of 116 mg (0.47 mmol) of 2-hydroxy-2-hydroxymethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 10 ml of dry acetone was added 0.70 g (1.58 mmol) of lead tetraacetate. The orange mixture was stirred for 3.5 hr, diluted with ether–hexane, and extracted with water, 5% sodium hydroxide, and again with water. The organic layer was dried with sodium sulfate and concentrated yielding 90 mg (88%) of crude *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 73.5–76°. The ketone was recrystallized from ether–hexane to give mp 74.5–75.5° (lit.³ mp 73–74°); mixture melting point undepressed; ir spectrum identical with that of an authentic sample of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane To a stirred suspension of 7.962 g (22.3 mmol) of methyltriphenylphosphonium bromide in 150 ml of dry ether was added 10.4 ml (2.19 *M*, 22.8 mmol) of *n*-butyllithium solution under nitrogen. The orange solution was stirred for 30 min and a solution of 4.800 g (19.4 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 100 ml of benzene–ether was added dropwise over 20 min. The heavy, white suspension was refluxed for 3 hr, cooled, diluted with hexane, and filtered. The filtrate was concentrated *in vacuo* and the crystalline residue chromatographed on a 4.5 × 25 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 500-ml fractions gave: fractions 1–4, 2% ether in hexane, 4.122 g of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane; 5–8, 18%, 57 mg of yellow oil shown to be recovered ketone by ir; yield was 86.5%. Recrystallization of the hydrocarbon fraction from hexane gave pure 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane: mp 104–105°; ir (CS₂) 3.24, 3.26, 3.30, 3.35, 3.40, 3.49, 6.05, 6.24, 7.73, 8.40, 9.20, 9.29, 9.72, 11.48, 12.32, 13.15, 13.92, and 14.35 μ; nmr (CDCl₃) τ 2.75–3.40 (m with sharp singlet at 2.92, 10 H, aromatic), 4.95 and 5.17 (slightly split s, 2 H, =CH₂, *J* = 1.5 Hz), AB quartet centered at 7.46 (2 H, cyclopropyl –CHCH–, *J*_{AB} = 3.8 Hz), 7.57–8.05 (m, 4 H, ring CH₂).

Anal. Calcd for C₁₅H₁₈: C, 92.63; H, 7.37. Found: C, 92.74; H, 7.30.

Nmr and ir spectra were superimposable in all respects on those of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane isolated from the photolysis of 1-methylene-4,4-diphenyl-2-cyclohexene and a mixture melting point was undepressed at 103–104°.

Osmium Tetroxide Oxidation of 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane *Method A.* A solution of 0.500 g (2.03 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 25 ml of ether was treated at room temperature with 1.00 g (3.94 mmol) of osmium tetroxide for 6.5 hr. The solvent was removed and the residue refluxed with 3.0 g of sodium bisulfite in 50 ml of 50% ethanol for 1.5 hr. The solution plus 50 ml of saturated sodium chloride solution was chloroform extracted. The chloro-

form solution was dried and concentrated *in vacuo*. The residue was triturated with chloroform yielding 0.2775 g of white crystals. The remaining oil was chromatographed on a 2.0 × 68 cm column of deactivated silicic acid (Mallinckrodt SilicAR, treated with water, dried at 50°) slurry packed in 10% methanol in chloroform. Elution in 250-ml fractions gave: fraction 1, chloroform, 42 mg of yellow oil shown to be hydrocarbon residue; 2–4, 2% ethanol in chloroform, 195 mg of 2-hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane; and 5–7, 2%, 19 mg of uncharacterized yellow oil. Fractions 2–4 were combined with the crystals obtained previously to give 472 mg (82.5%) of 2-hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane: melting point after recrystallization from ethanol, 186.5–189°; ir (CHCl₃) sharp 2.80 and broad 2.95 μ hydroxyl; nmr (CDCl₃) τ 2.70–3.40 (m, with sharp singlet at 2.91, 10 H, aromatic), 6.25 (s, 2 H, –CH₂O–), 7.45–8.60 (m, 8 H, ring CH₂, cyclopropyl –CHCH–, and 2 –OH).

Anal. Calcd for C₁₅H₂₀O₂: C, 81.39; H, 7.19. Found: C, 81.25; H, 7.15.

Oxidative Cleavage of 2-Hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. To a solution of 150 mg (0.54 mmol) of 2-hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 15 ml of dry acetone was added 450 mg (1.01 mmol) of lead tetraacetate. The orange mixture was stirred at room temperature for 2 hr, diluted with ether–benzene, and extracted with water, 5% sodium hydroxide, and again with water. The organic layer was dried with sodium sulfate and concentrated yielding 128 mg (96%) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 112–113°. Recrystallization from dichloromethane–hexane gave mp 115–116.5° (lit.³ mp 116.5–117.5°), mixture melting point undepressed, and ir spectrum identical with that of an authentic sample of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Benzophenone Sensitization of 1-Methylene-4,4-diphenyl-2-cyclohexene. A solution of 0.5010 g (2.03 mmol) of distilled 1-methylene-4,4-diphenyl-2-cyclohexene and 30.60 g of benzophenone³⁹ in 700 ml of benzene was irradiated 5 hr under deoxygenated nitrogen through a Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. After removal of solvent, the residue was chromatographed on a 4.5 × 73 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 500-ml fractions gave: fractions 1–4, 2% ether in hexane, nil; 5–8, 4%, 0.385 g of 1-methylene-4,4-diphenyl-2-cyclohexene (identified by nmr spectrum); 9–12, 4%, 30.496 g of benzophenone. The benzophenone was recrystallized and the mother liquors were shown to be free of any hydrocarbon photoproducts.

Test for Energy Transfer from Benzophenone to 1-Methylene-4,4-diphenyl-2-cyclohexene. The photochemical reaction of benzophenone with benzhydrol to form benzpinacol, as reported by Hammond, *et al.*,⁹ was used. In irradiation 1, a solution of 7.4973 g (41.2 mmol) of benzophenone and 2.5002 (13.5 mmol) of benzhydrol in 228 ml of *t*-butyl alcohol was irradiated 1 hr under deoxygenated nitrogen through a Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. During irradiation a white solid precipitated out and was filtered off at the end yielding 1.910 g of benzpinacol. The remaining solution was concentrated yielding an additional 1.276 g of solid benzpinacol. The residue was chromatographed on a 4.5 × 75 cm column of silicic acid (Mallinckrodt SilicAR) slurry packed in 50% benzene–chloroform. Elution in 250-ml fractions gave: fractions 1–5, 50% benzene in chloroform, nil; 6–8, 50%, 0.687 g of benzpinacol; 9–14, 50%, 5.271 g of benzophenone. The benzpinacol from the column was combined with that filtered off yielding 3.873 g, mp 188.5–190° (lit.⁹ mp 186°); ir was identical with published spectrum (OH at 2.84 μ).

In irradiation 2, a solution of 7.4965 g (41.2 mmol) of benzophenone, 2.4992 g (13.5 mmol) of benzhydrol, and 0.4998 g (2.02 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 228 ml of *t*-butyl alcohol was irradiated 1 hr under conditions identical with those in irradiation 1. No solid precipitate was observed. After removal of solvent, the residue was chromatographed on a 4.5 × 80 cm column of silicic acid (Mallinckrodt SilicAR) slurry packed in 40% chloroform in benzene. Elution in 100-ml fractions gave: fractions 1–10, 40% chloroform in benzene, nil; 11–15, 40%, 0.4550 g of 1-methylene-4,4-diphenyl-2-cyclohexene (identified by nmr spectrum); 16–19, 40%, 0.472 g of benzpinacol; 20–21, 40%,

(37) J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

(38) P. Tomboulouian, *ibid.*, **26**, 2652 (1961).

(39) Amount of benzophenone calculated to absorb at least 99% of the light using the minimum extinction coefficient at 304 nm.

1.198 g of a mixture of benzophenone and benzpinacol by ir; 22–31, 40%, 6.127 g of benzophenone. Fraction 20 gave 0.047 g of benzpinacol from ethanol and the residue from fractions 20–21 was rechromatographed on a 2.2×115 cm column of silicic acid (Mallinckrodt SilicAR) slurry packed in 35% chloroform in benzene. Elution in 50-ml fractions gave: fractions 1–11, 35% chloroform in benzene, nil; 12–16, 40% 0.089 g of benzpinacol; 17–21, 40%, 0.970 g of benzophenone. Total yield of benzpinacol from irradiation 2 was 0.608 g.

Photolysis of 1-Methylene-4,4-diphenyl-2-cyclohexene to Varying Conversions. Several photolyses were done to determine the approximate *trans:cis* photoproduct ratios for different extents of conversion. Analysis was by nmr integration of the exocyclic methylene regions at *ca.* τ 4.9 and 5.2, the aromatic region, and the signals near τ 7.4.

A solution of 0.514 g (2.08 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 775 ml of cyclohexane was irradiated 1 hr under deoxygenated nitrogen through a Vycor filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. After removal of solvent, nmr analysis showed *ca.* 43% diene remaining. The remainder of the material appeared to be 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane with the *cis* isomer near the limit of detection of the instrument (*ca.* 4%). The ratio of *trans:cis* is thus *ca.* 13:1.

A solution of 0.503 g (2.04 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 750 ml of cyclohexane was irradiated 2 hr in the same apparatus and the solvent removed *in vacuo*. Nmr analysis showed *ca.* 14% diene remaining and a *trans:cis* ratio of *ca.* 5:1.

A solution of 0.430 g (1.75 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 775 ml of cyclohexane was irradiated 6 hr under the same conditions as before. After chromatography on silica gel to remove polymer, the material was subjected to nmr analysis, which showed *ca.* 6% diene remaining. The *trans:cis* ratio of the product formed was *ca.* 3:1.

Osmium Tetroxide Oxidation of 1-Methylene-4,4-diphenyl-2-cyclohexene. Method A. A solution of 0.499 g (2.03 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 50 ml of ether was stirred 5 hr at room temperature with 0.512 g (2.01 mmol) of osmium tetroxide. The solvent was removed and the residue refluxed 1.5 hr with 3.0 g of sodium bisulfite in 50 ml of 50% ethanol. The solution was filtered and extracted with chloroform, and the extracts were dried and concentrated. The residue was chromatographed on a 2.0×70 cm column of deactivated silicic acid (Mallinckrodt SilicAR slurred with water, dried at 50°) slurry packed in 10% methanol in chloroform. Elution in 50-ml fractions gave: fractions 1–2, chloroform, nil; 3–6, chloroform, 410 mg (73%) of 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene, mp 82–100°. Recrystallization from benzene-hexane gave 0.312 g of pure 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene: mp 108–109°; nmr (CDCl₃) τ 2.82 (d, 10 H, aromatic), AB quartet centered at 3.93 (2 H, $-\text{CH}=\text{CH}-$, $J_{AB} = 10$ Hz), 6.52 (s, 2 H, $-\text{CH}_2\text{O}-$), 7.45–8.45 (A₂B₂ overlapping a broad singlet, 6 H, ring CH₂ and 2 OH); ir (CHCl₃) 2.78 and 2.93 μ , hydroxyl absorptions.

Anal. Calcd for C₁₉H₂₀O₂: C, 81.39; H, 7.19. Found: C, 81.37; H, 7.14.

No trace of osmium tetroxide attack on the endocyclic double bond could be found.

Oxidative Cleavage of 1-Hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene. A solution of 120 mg (0.43 mmole) of 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene in 15 ml of dry acetone was stirred 2 hr at room temperature with 450 mg (1.01 mmol) of lead tetraacetate. The mixture was diluted with ether-benzene, washed with water, 5% sodium hydroxide, again with water, dried, and concentrated yielding 99 mg (96.5%) of 4,4-diphenylcyclohex-2-en-1-one. Recrystallization from ether-hexane gave pure enone, mp 96–97° (lit.⁴ mp 94–95°), mixture melting point undepressed, ir identical with known material.

Sodium Metaperiodate Cleavage of 1-Hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene.⁴⁰ A solution of 0.575 g (2.05 mmol) of 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene in 80 ml of 75% ethanol was stirred 24 hr with 1.105 g (5.1 mmol) of sodium metaperiodate at room temperature under nitrogen. Tlc of the mixture showed no diol present after this time. The solution was diluted with ether, washed with water, dried, and concentrated. The residue was crystallized from methylene chloride-hexane giving 413 mg (81%) of 4,4-diphenylcyclohex-2-en-1-one, mp 90.5–92°, mixture melting point with authentic material undepressed.

Sodium Metaperiodate Cleavage of 2-Hydroxy-2-hydroxymethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. A solution of 925 mg (3.3 mmol) of 2-hydroxy-2-hydroxymethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 70 ml of 80% ethanol was stirred 36 hr at room temperature with 1.76 g (8.25 mmol) of sodium metaperiodate. The solution was diluted with ether, washed four times with water, dried, and concentrated *in vacuo*. The residue was chromatographed on a 2.0×45 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 10% ether in hexane. Elution in 100-ml fractions gave: fractions 1–5, 10% ether in hexane, nil; 6–13, 15%, 491 mg (60%) of crystalline *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, melting point after recrystallization from benzene-hexane 75–76°.

Sodium Metaperiodate Cleavage of 2-Hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. A solution of 1.055 g (3.77 mmol) of 2-hydroxy-2-hydroxymethyl-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 50 ml of 80% ethanol was stirred 25 hr at room temperature with 2.01 g (9.4 mmole) of sodium metaperiodate. The solution was diluted with ether, extracted three times with saturated sodium chloride solution, dried, and concentrated *in vacuo*. The residue was crystallized from hexane-benzene giving 0.7064 g (76%) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, melting point after recrystallization from benzene-hexane 113.5–115.5°.

Osmium Tetroxide Catalyzed Oxidation of 1-Methylene-4,4-diphenyl-2-cyclohexene. Method B. A modification of the method of Zelikoff and Taylor⁴¹ was used. To a solution of 334 mg (1.35 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene and 500 mg (4.70 mmol) of sodium chlorate in 15 ml of 80% dioxane-water was added 9.3 mg (1.0 ml of a solution of 0.93 g in 100 ml of water) of osmium tetroxide. The brown solution was stirred at room temperature for 24 hr, after which tlc showed absence of diene. The mixture was poured into water and extracted with ether, and the ether layer was dried and concentrated *in vacuo* to give 45 mg of crystalline diol. The remaining oil was chromatographed on a 1.5×55 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 10% methanol in chloroform. Elution in 100-ml fractions gave: fractions 1–4, chloroform, 110 mg of dark oil shown to contain some 4,4-diphenylcyclohexenone by ir; 5–9, 2% methanol in chloroform, 198 mg (52%) of 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene. The diol isolated from the column was combined with that crystallized previously to give 243 mg (64%), mp 107–108° after recrystallization from benzene-hexane.

1-Methylene-4,4-diphenyl-2-cyclohexene-6-³H. Tritium oxide (7.5 μ l, 0.83 mCi, Volk Radiochemicals) was injected into a mixture of 2.502 g (1.01 mmol) of 4,4-diphenylcyclohexenone and 1.00 g of basic alumina (Fisher chromatographic grade) in 50 ml of dioxane (spectroquality) under nitrogen. After stirring for 72 hr at 90°, the solution was filtered to remove alumina, taken up with ether, extracted ten times with water, dried, and concentrated *in vacuo*. The residue was recrystallized from dichloromethane-hexane to give 2.163 g (86.5%) of 4,4-diphenylcyclohexenone, mp 96.5–98°, activity 24.0 μ Ci/mmol.

To a stirred suspension of 3.900 g (9.6 mmole) of methyltriphenylphosphonium iodide in 75 ml of ether under nitrogen was added 4.07 ml (2.36 M, 9.6 mmol) of *n*-butyllithium solution. The solution was stirred for 15 min and a solution of 2.163 g of radioenone (8.7 mmol, 24.0 μ Ci/mmol) in 75 ml of ether was added dropwise over 30 min. The mixture was refluxed 2 hr, filtered, washed with water, dried, and concentrated *in vacuo*. The residue was chromatographed on a 4.5×28 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 250-ml fractions gave: fractions 1–3, 2% ether in hexane, nil; 4–8, 2%, 1.108 g of 1-methylene-4,4-diphenyl-2-cyclohexene-6-³H₂; 9–14, 15%, 0.572 g of recovered 4,4-diphenylcyclohexenone; yield based on reacted ketone 70.5%, activity 23.9 μ Ci/mmol.

Effect of Oxidation Scheme on Tritium Label 4,4-Diphenylcyclohexenone-6-³H₂ (2.590 g, 10.5 mmol, 17.4 μ Ci/mmol) was treated with methylenetriphenylphosphorane (from methyltriphenylphosphonium iodide and *n*-butyllithium) as before to give 1.950 g of 1-methylene-4,4-diphenyl-2-cyclohexene-6-³H₂ (76%). The hydrocarbon was oxidized by stirring 7 hr at room temperature with 2.0 g (7.9 mmol) of osmium tetroxide in 50 ml of ether. After removal of solvent, the residue was refluxed with 5.0 g of sodium bisulfite in 50% ethanol for 1.5 hr. The mixture was diluted with

(40) E. L. Jackson, *Org. Reactions*, 2, 341 (1944).

(41) M. Zelkoff and H. A. Taylor, *J. Amer. Chem. Soc.*, 72, 5039 (1950).

ether, filtered, washed with water, dried, concentrated, and crystallized from carbon tetrachloride to give 1.682 g (76%) of 1-hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene, mp 107.5–108°.

1-Hydroxy-1-hydroxymethyl-4,4-diphenyl-2-cyclohexene-6-³H_x (0.5752 g, 2.06 mmol) from the previous reaction was treated with 1.105 g (2.5 equiv) of sodium metaperiodate in 80 ml of 75% ethanol for 24 hr. The solution was diluted with ether–benzene, washed with water, dried, and concentrated *in vacuo*, yielding 0.494 g of 4,4-diphenylcyclohexenone-6-³H_x (97%). Recrystallization from methylene chloride–hexane gave pure material, mp 92.0–92.5°, activity 17.4 μCi/mmol (*i.e.*, no isotopic exchange occurred at any stage of the oxidation scheme).

Exploratory Photolysis of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. A solution of 0.135 g (0.55 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 90 ml of cyclohexane was irradiated 15 min through a Vycor filter in the previously described immersion apparatus. Removal of the solvent *in vacuo* and analysis by nmr (CCl₄) showed the presence of 1-methylene-4,4-diphenyl-2-cyclohexene by the aromatic absorption at τ 2.85, the vinyl AB quartet at *ca.* 3.83, and the singlet for the ring methylenes at 7.70. The formation of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane was indicated by the characteristic aromatic multiplet near τ 3.0 and the central doublet of the cyclopropyl AB quartet at τ 7.55. The approximate diene:*cis* ratio was 2.5:1.

Exploratory Photolysis of 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. A solution of 0.1195 g (0.49 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane in 90 ml of cyclohexane (5.4 × 10⁻³ M) was irradiated 30 min through a Vycor filter in the previously described quartz immersion apparatus. Removal of solvent *in vacuo* and analysis by nmr (CCl₄) showed the absence of any detectable amount of 1-methylene-4,4-diphenyl-2-cyclohexene. The formation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane was indicated by aromatic absorption at τ 2.80, broadening of the exocyclic methylene absorptions, and the characteristic absorptions at τ 7.42 and 7.90. Additional absorptions at τ 2.88 and 5.82 were identified as those of 1-methylene-3,4-diphenyl-2-cyclohexene (*vide infra*). An additional singlet at 6.77 has not been assigned to any known product.

3,4-Diphenylcyclohex-2-en-1-one was prepared according to the method of Zimmerman and Hancock,⁴ melting point after recrystallization from methanol, 100.5–102° (lit.⁴² mp 99–99.5°).

1-Methylene-3,4-diphenyl-2-cyclohexene. To a stirred suspension of 10.800 g (30.2 mmol) of methyltriphenylphosphonium bromide in 250 ml of dry ether was added under nitrogen 12.6 ml (2.30 M, 29.0 mmol) of a hexane solution of *n*-butyllithium. The yellow solution was stirred under nitrogen for 15 min followed by dropwise addition over 30 min of a solution of 5.000 g (20.2 mmol) of 3,4-diphenylcyclohex-2-en-1-one in 80 ml of benzene–ether. The white suspension was refluxed 3 hr, cooled, diluted with hexane, filtered, and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 25 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 3% ether in hexane. Elution in 200-ml fractions gave: fractions 1–3, 3% ether in hexane, nil; 4–7, 3%, 4.478 g (90%) of 1-methylene-3,4-diphenyl-2-cyclohexene. Sublimation of the hydrocarbon at 80° (0.005 mm) gave pure 1-methylene-3,4-diphenyl-2-cyclohexene: mp 81–82°; nmr (CDCl₃) τ 2.50–2.95 (m, with singlet at 2.80, 10 H, aromatic), 3.11 (s, 1 H, =CH–), 4.93 and 5.05 (br s, 2 H, =CH₂), 5.92 (t, 1 H, benzylic methine at C-4), 7.60–8.20 (m, 4 H, ring CH₂); ir (CHCl₃) 3.23, 3.25, 3.32, 3.40, 3.49, 6.16, 6.25, 6.70, 6.93, 9.30, 9.68, 9.80, 11.14, 11.40, and 14.30 μ .

Anal. Calcd for C₁₅H₁₈: C, 92.63; H, 7.37. Found: C, 92.37; H, 7.55.

Osmium Tetroxide Catalyzed Oxidation of 1-Methylene-3,4-diphenyl-2-cyclohexene. Method B. A solution of 394 mg (1.6 mmol) of 1-methylene-3,4-diphenyl-2-cyclohexene and 513 mg (4.8 mmol) of sodium chlorate in 25 ml of 80% dioxane–water was treated with 18.6 mg of osmium tetroxide at 75° for 45 min. The mixture was cooled, diluted with ether, washed three times with water, dried, and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 25 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 10% methanol in chloroform. Elution in 100-ml fractions gave: fractions 1–4, chloroform, 98 mg of black oil; 5–14, 4% methanol in chloroform, 356 mg (80%) of 1-hydroxy-1-hydroxymethyl-3,4-diphenyl-2-cyclohexene. The pres-

ence of two stereoisomers was indicated by the broad melting range, 52–104°, and the nmr spectrum: τ 2.88 (br, s, 10 H, aromatic), 3.65 and 3.80 (s, vinyl H on different isomers, *ca.* 3:1), 6.0 (br m, 1 H, methine at C-4), 6.36 (two overlapping singlets, 2 H, –CH₂O–, *ca.* 3:1), 6.85 (br s, 2 H, OH), 7.5–9.15 (m, 4 H, ring CH₂). The mixture of isomers was deemed suitable for cleavage to the ketone.

Sodium Metaperiodate Cleavage of 1-Hydroxy-1-hydroxymethyl-3,4-diphenyl-2-cyclohexene. A solution of 356 mg (1.27 mmol) of 1-hydroxy-1-hydroxymethyl-3,4-diphenyl-2-cyclohexene from the previous reaction in 15 ml of 95% ethanol was stirred 2.25 hr at room temperature with 680 mg (3.2 mmol) of sodium metaperiodate. The reaction mixture was diluted with ether, washed with water, dried, and concentrated *in vacuo*. The residue was triturated with ether to give 260 mg (82.5%) of crystalline 3,4-diphenylcyclohex-2-en-1-one, which upon recrystallization from benzene–hexane was identical with authentic material by ir, mp 99.5–101°, and mmp 100–101.5°.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane-3-³H_x. Tritium oxide (6.75 μl, 0.75 mCi, Volk Radiochemicals) was injected into a stirred mixture of 1.500 g (6.04 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 0.50 g of basic alumina (Fisher chromatographic grade) in 50 ml of spectroquality dioxane under nitrogen. After heating the mixture at 95° for 48 hr, it was cooled, diluted with ether, filtered, and washed six times with water. The ether extract was dried, concentrated *in vacuo*, and decolorized by passing through a 4.4 × 10 cm column of 5% Norit–silica gel slurry packed in 20% ether in hexane. Elution with 1500 ml of 20% ether in hexane gave 1.439 g (95.9%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-3-³H_x which was recrystallized from benzene–hexane (mp 74–75°) and used in the next step.

To a stirred suspension of 2.192 g (6.14 mmol) of methyltriphenylphosphonium bromide in 125 ml of dry ether under nitrogen was added 2.80 ml (2.19 M, 6.14 mmol) of *n*-butyllithium solution. The yellow solution was stirred for 15 min followed by dropwise addition of a solution of 1.260 g (5.07 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-3-³H_x in 50 ml of dry ether. The mixture was refluxed under nitrogen for 5.5 hr, cooled, diluted with hexane, filtered, and concentrated *in vacuo*. The residue was chromatographed on a 4.0 × 16.0 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 500-ml fractions gave: fractions 1–4, 2% ether in hexane, 0.8812 g of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane-3-³H_x; 5–8, 15%, 0.2075 g of recovered *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-3-³H_x; yield based on reacted ketone 84.5%; specific activity 35.25 μCi/mmol.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane-3-³H_x. Tritium oxide (4.5 μl, 1.0 mCi, Volk Radiochemicals) was injected into a stirred mixture of 1.200 g (4.83 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 0.50 g of basic alumina (Fisher chromatographic grade) in 50 ml of spectroquality dioxane under nitrogen. The mixture was stirred at 95° for 30 hr, cooled, diluted with ether–benzene, washed several times with water, dried, and concentrated *in vacuo*. The yellowish residue was purified by passing through a 4.4 × 12 cm column of 5% Norit on silica gel slurry packed in 10% ether in hexane. Elution with 3000 ml of 18% ether in hexane gave 1.157 g (96.4%) of pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-³H_x, mp 113–115° after recrystallization from benzene–hexane.

To a stirred suspension of 2.180 g (6.10 mmol) of methyltriphenylphosphonium bromide in 100 ml of dry ether under nitrogen was added 2.5 ml (2.19 M, 5.5 mmol) of *n*-butyllithium solution. The yellow solution was stirred for 30 min, followed by dropwise addition of a solution of 1.062 g (4.28 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-3-³H_x (from the preceding reaction) in 75 ml of benzene–ether over 30 min. The mixture was refluxed for 3 hr, cooled, filtered, and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 20 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 2% ether in hexane. Elution in 500-ml fractions gave: fractions 1–4, 2% ether in hexane, 0.842 g of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane-3-³H_x; 5–8, 18%, 0.158 g of recovered *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-3-³H_x; yield based on reacted ketone 94.0%; specific activity 10.39 μCi/mmol.

Irradiation of 1-Methylene-4,4-diphenyl-2-cyclohexene in Methanol. A solution of 0.587 g (2.4 mmol) of 1-methylene-4,4-diphenyl-2-cyclohexene in 725 ml of anhydrous methanol was irradiated using a General Electric AH6 high-pressure mercury arc centered at the focus of a parabolic reflector. Light was filtered through three 2.4-cm path length water-cooled compartments containing the following filter solutions: cell 1, 2.0 M nickel sulfate in

(42) E. C. Dodds, R. L. Huang, W. Lawson, and R. Robinson, *Proc. Roy. Soc. (London)*, B140, 470 (1953).

5% sulfuric acid; cell 2, 0.8 M cobalt sulfate in 5% sulfuric acid; cell 3, 4.4×10^{-4} M bismuth trichloride in 1.2 M hydrochloric acid; transmission 0% below 250 nm, 16% at 273 nm, 0% above 300 nm; incident light was measured by ferrioxalate actinometry before and after the sample run and was monitored with a backup cell for transmission through the diene solution. Irradiation for 6.0 hr resulted in absorption of 3.18 mEinstein (corrected for transmission). The solvent was removed *in vacuo* and the residue analyzed by nmr spectroscopy. In addition to starting diene, signals were present for 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane and a trace of the *cis* isomer (*vide supra*). Comparative integration of the exocyclic methylene signals at τ 4.95 and 5.20 indicated a diene:bicyclic ratio of 72:28 corresponding to 163 mg of product formed. The quantum yield is thus 0.21 ± 0.02 mmol/mEinstein (error estimated from error of nmr measurement and actinometry).

Acetone Sensitization of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane. The light source was a General Electric AH-6 high-pressure mercury arc centered at the focus of a parabolic reflector 13.7 cm long and 14.0 cm in diameter. Light was filtered through three 2.4-cm water-cooled compartments containing the following filter solutions: cell 1, 2.0 M nickel sulfate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate in 5% sulfuric acid; cell 3, 1.0×10^{-3} M bismuth trichloride in 6 M hydrochloric acid; transmission 0% below 260 nm, 20% at 283 nm, 0% above 306 nm. Incident light was measured by ferrioxalate actinometry before and after the sample run and was monitored for transmission through the sample by an actinometer cell behind the sample cell during the sample run.

A solution of 478 mg (1.95 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane in 730 ml of reagent grade acetone was irradiated using the above system with the acetone calculated to absorb *ca.* 99% of the incident light. After photolysis for 6.0 hr during which the solution absorbed 2.93 mEinstein of light, the solvent was removed and the residue analyzed by nmr spectroscopy. No 1-methylene-4,4-diphenyl-2-cyclohexene was indicated by the spectrum, which analyzed for *ca.* 88% 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane and 12% 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane. The quantum yield based on 12% (0.23 mmol) of *cis* isomer produced is 0.078 ± 0.008 mmol/mEinstein.

Low-Temperature Irradiation of 1-Methylene-4,4-diphenyl-2-cyclohexene. A 0.17 M solution of 1-methylene-4,4-diphenyl-2-cyclohexene in methylcyclohexane was irradiated for 7.5 hr at $-105 \pm 5^\circ$ in a Beckman Model VLT-2 variable-temperature infrared cell (path length 0.1 mm). The light source was an Osram HBO 200-W super-pressure mercury arc in conjunction with a Bausch and Lomb high-intensity monochromator set at 242 nm (band width 37 nm). The reaction course was followed by spectral analysis using a Perkin-Elmer Infracord Model 137 spectrophotometer. After irradiation, the spectrum at -105° showed the disappearance of diene by the decrease in intensity of the methylene absorption at 11.30μ and the appearance of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane by the development of absorptions at 11.48, 11.55, 13.20, and 13.52 μ . Comparison was made with the spectrum of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane taken at -105° . No additional absorptions appeared and the spectrum did not change upon warming to room temperature overnight and recooling to -105° .

Quantum Yield Equipment. Quantum yield irradiations were carried out on an L-shaped optical bench in quartz-faced⁴³ thermostated cells 26 mm i.d. \times 10 cm optical path, under deoxygenated nitrogen with stirring. One actinometer cell was situated perpendicularly to the main optical path to receive the light from a beam splitter consisting of a $2 \times 2 \times \frac{1}{16}$ in. quartz plate mounted at 45° to the light path. The light source used was an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator.

Quantum Yield Irradiations. The basic procedure for each run involved run 1 with actinometer solution in two consecutive, identical cells and the side cell, run 2 with reactant solution in the first cell and actinometer solution in the second and side cells, and run 3, identical with run 1. The transmission to reflection ratio of the quartz beam splitter (*ca.* 9:1) was calculated during runs 1 and 3. Available light was calculated from runs 1 and 3, and from the light deflected by the beam splitter to the side cell during run 2. The available light was corrected for light transmitted by the sample to the second cell (less than 5%).

Potassium ferrioxalate actinometry⁴⁴ was used. After irradiation of 0.006 M ferrioxalate in 0.1 N sulfuric acid, 2.00- or 5.00-ml aliquots were withdrawn, treated with 3.0 ml of 0.1% 1,10-phenanthroline monohydrochloride in water and 2.0 ml of buffer (49.3 g of sodium acetate and 10.0 ml of concentrated sulfuric acid diluted to 1 l. with water), and diluted to 25.0 ml with water. Absorbance of the ferrous phenanthroline complex was measured at 510 nm on a Beckman Model DU spectrometer and ferrous ion production read from a graph of ferrous ion concentration vs. absorbance after correction for blank readings. The quantum efficiency for ferrioxalate reduction at 242 nm was taken as 1.25.

Ca. 0.01 M solutions of radioactive substrates in cyclohexane were irradiated at constant temperature. Ultraviolet spectra taken after photolysis agreed with calculated spectra assuming Beer's law behavior. The ^3H organic solution was diluted accurately to 100 ml and aliquots were withdrawn volumetrically for isotopic dilution with accurately weighed excesses of pure ^1H photoproducts and starting material. The isotopically diluted mixtures were then oxidized to their corresponding ketones and the specific activities determined. Control reactions showed the absence of any photoproducts in the radioactive starting materials used.

Specific Activity of ^3H Compounds. Specific activities were determined by counting 1–20-mg samples in 15 ml of a scintillator solution of 4.0 g of PPO (2,5-diphenyloxazole, Nuclear-Chicago) and 0.05 g of POPOP (1,4-bis[2-(5-phenyloxazolyl)]benzene, Nuclear-Chicago) in 1 l. of toluene (Matheson Coleman and Bell, scintillation grade) in a Nuclear-Chicago Mark I scintillation system. Quench correction was done by channels ratio on a ^{133}Ba external standard.

Quantum Yields. Specific data for individual determinations are listed beginning with conditions for the irradiation of ^3H -labeled reactant (weight, solvent, temperature, wavelength, and amount of light) and followed by isotope dilution data. The weight of each ^1H compound used to dilute an aliquot of the labeled reaction mixture is followed by the method of osmium tetroxide oxidation used, the weight of ketone realized, the number of recrystallizations (from benzene-hexane), recovered weight, melting point, asymptotic specific activity (nanocuries per millimole) with standard error, calculated amount of starting material recovered or product produced; and quantum yield. The quantum yield for disappearance of reactant has been obtained only as the sum of quantum yields for appearance of products, since the low conversions made the absolute errors in amounts of reactant used and recovered comparable in magnitude to their difference.

Run I-01. 1-Methylene-4,4-diphenyl-2-cyclohexene- ^3H (104.0 mg, 422.2 μmol), specific activity 36.08 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 24.0° , irradiated at 242 nm (band width 22 nm), 0.0382 mEinstein.

1-Methylene-4,4-diphenyl-2-cyclohexene (919.7 mg, 3734 μmol) added to ^3H -photolysate (10.4 mg, 42.2 μmol): method A, 713.5 mg, 4, 436 mg, 94–95°, 407.2 \pm 2.7, 426.0 μmol recovered.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (966.4 mg, 3924 μmol) added to ^3H -photolysate (93.6 mg, 380.0 μmol): method A, 748 mg, 6, 107 mg, 74–75°, 34.59 \pm 0.34, 4.18 μmol produced; $\phi = 0.109 \pm 0.004$.

Run I-02. 1-Methylene-4,4-diphenyl-2-cyclohexene- ^3H (134.0 mg, 544.0 μmol), specific activity 36.08 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 24.0° , irradiated at 242 nm (band width 37 nm), 0.232 mEinstein.

1-Methylene-4,4-diphenyl-2-cyclohexene (886.0 mg, 3597 μmol) added to ^3H -photolysate (13.4 mg, 54.4 μmol): method A, 678 mg, 5, 454 mg, 94.5–95.5°, 536.3 \pm 3.5, 542.7 μmol recovered.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (1167 mg, 4738 μmol) added to ^3H -photolysate (100.5 mg, 408.0 μmol): method A, 636 mg, 14, 98 mg, 113.2–115°, 1.24 \pm 0.015, 0.217 μmol produced; $\phi = 0.00093 \pm 0.00007$.

Run I-03. 1-Methylene-4,4-diphenyl-2-cyclohexene- ^3H (106.8 mg, 433.6 μmol), specific activity 36.08 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 24.0° , irradiated at 242 nm (band width 37 nm), 0.0905 mEinstein.

1-Methylene-4,4-diphenyl-2-cyclohexene (641.8 mg, 2606 μmol) added to ^3H -photolysate (10.7 mg, 43.4 μmol): method A, 614 mg, 4, 292 mg, 94–95°, 588.5 \pm 3.8, 432.1 μmol recovered.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (877.3 mg, 3562 μmol) added to photolysate (10.7 mg, 43.4 μmol): method A, 118 mg, insufficient material for necessary purification.

(43) An epoxy adhesive not containing aromatic or other low-energy chromophores was used to cement quartz faces to Pyrex cells.

(44) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (922.2 mg, 3744 μmol) added to ^3H -photolysate (85.5 mg, 347.1 μmol): method A, 696 mg, 15, 69.7 mg, 113–115°, 0.581 \pm 0.009, 0.0753 μmol produced; ϕ = 0.00083 \pm 0.00007.

Run I-04-S. 1-Methylene-4,4-diphenyl-2-cyclohexene-6- ^3H (95.1 mg, 386.1 μmol), specific activity 36.08 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of distilled chlorobenzene⁴⁵ at 24.5°, irradiated at 264 nm (band width 22 nm), 0.0432 mEinstein.

1-Methylene-4,4-diphenyl-2-cyclohexene (918.3 mg, 3728 μmol) added to the ^3H -photolysate (9.5 mg, 38.6 μmol): method A, 837 mg, 4, 284 mg, 92–93°, 360.9 \pm 2.6, 386.2 μmol recovered.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (1580 mg, 6415 μmol) added to ^3H -photolysate (85.6 mg, 347.5 μmol): method A, 647 mg, 9, 101 mg, 75–76°, 1.33 \pm 0.02, 0.262 μmol produced; ϕ = 0.0061 \pm 0.0004.

Run II-01. 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane-3- ^3H (89.6 mg, 363.8 μmol), specific activity 35.25 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 25.0° irradiated at 242 nm (band width 22 nm), 0.0950 mEinstein.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (1358 mg, 5513 μmol) added to ^3H -photolysate (8.96 mg, 36.4 μmol): method B, 390 mg, 3, 102 mg, 74.5–76°, 233.4 \pm 2.1, 367.0 μmol recovered.

1-Methylene-4,4-diphenyl-2-cyclohexene (793.9 mg, 3223 μmol) added to ^3H -photolysate (44.8 mg, 181.9 μmol): method B, 363 mg, 7, 164 mg, 94.5–96°, 48.9 \pm 0.4, 8.95 μmol produced; ϕ = 0.0943 \pm 0.0039.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (1318 mg, 5351 μmol) added to ^3H -photolysate (35.8 mg, 145.5 μmol): method B, 859 mg, 9, 186 mg, 113.5–115°, 8.27 \pm 0.07, 3.14 μmol produced; ϕ = 0.0311 \pm 0.0020.

Run II-02. 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane-3- ^3H (96.8 mg, 393.0 μmol), specific activity 35.25 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 25.0°, irradiated at 242 nm (band width 22 nm), 0.0683 mEinstein.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (1508 mg, 6124 μmol) added to ^3H -photolysate (9.68 mg, 39.3 μmol): method B, 740 mg, 3, 322 mg, 75–76°, 230.1 \pm 1.6, 399.6 μmol recovered.

1-Methylene-4,4-diphenyl-2-cyclohexene (934.2 mg, 3793 μmol) added to the ^3H -photolysate (38.7 mg, 157.2 μmol): method B, 376 mg, 4, 101 mg, 93–94°, 24.0 \pm 0.2, 6.46 μmol produced; ϕ = 0.0946 \pm 0.0039.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (1174 mg, 4767 μmol) added to ^3H -photolysate (48.4 mg, 196.5 μmol): method B, 922 mg, 8, 156 mg, 112.5–113.5°, 9.16 \pm 0.08, 2.47 μmol produced; ϕ = 0.0361 \pm 0.0022.

(45) Neat chlorobenzene (9.82 *M*) was calculated to absorb 96.5 \pm 2.0% of the available light by the method of integrated extinction coefficients.⁴

Run III-01. 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane-3- ^3H (95.4 mg, 387.3 μmol), specific activity 10.39 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 25.0°, irradiated at 242 nm (band width 22 nm), 0.176 mEinstein.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (1272 mg, 5164 μmol) added to ^3H -photolysate (9.59 mg, 38.9 μmol): method B, 706 mg, 3, 545 mg, 113.5–115.5°, 75.7 \pm 0.5, 377.3 μmol recovered.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (1411 mg, 5729 μmol) added to ^3H -photolysate (47.7 mg, 193.8 μmol): method B, 832 mg, 7, 170 mg, 75.5–76.5°, 2.48 \pm 0.02, 2.85 μmol produced; ϕ = 0.0162 \pm 0.0010.

1-Methylene-4,4-diphenyl-2-cyclohexene (1565 mg, 6354 μmol) added to ^3H -photolysate (38.1 mg, 154.7 μmol): method B, 807 mg, 9, 116 mg, 93–94°, 0.261 \pm 0.005, 0.400 μmol produced; ϕ = 0.0023 \pm 0.0002.

Run III-02. 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane-3- ^3H (96.0 mg, 389.8 μmol), specific activity 10.39 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 25.0°, irradiated at 242 nm (band width 22 nm), 0.121 mEinstein.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (902.5 mg, 3664 μmol) added to ^3H -photolysate (9.66 mg, 39.2 μmol): method B, 595 mg, 3, 442 mg, 115.5–117°, 105.5 \pm 0.8, 373.6 μmol recovered.

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (1567 mg, 6360 μmol) added to ^3H -photolysate (48.1 mg, 195.3 μmol): method B, 824 mg, 8, 136 mg, 74–75°, 1.66 \pm 0.02, 2.02 μmol produced; 0.0167 \pm 0.0010.

1-Methylene-3,4-diphenyl-2-cyclohexene (1191 mg, 4836 μmol) added to ^3H -photolysate (38.2 mg, 155.2 μmol): method B, 663 mg, 9, 149 mg, 99.5–101°, 1.11 \pm 0.02, 1.29 μmol produced; ϕ = 0.0107 \pm 0.0008.

Run III-03. 2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane-3- ^3H (99.3 mg, 403.2 μmol), specific activity 10.39 $\mu\text{Ci}/\text{mmol}$, in 39.0 ml of cyclohexane at 25.0°, irradiated at 242 nm (band width 22 nm), 0.106 mEinstein.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]hexane (1130 mg, 4587 μmol) added to ^3H -photolysate (10.0 mg, 40.6 μmol): method B, 789 mg, 2, 404 mg, 115–115.5°, 88.9 \pm 0.6, 392.7 μmol recovered.

1-Methylene-3,4-diphenyl-2-cyclohexene (1070 mg, 4344 μmol) added to ^3H -photolysate (49.8 mg, 202.1 μmol): method B, 549 mg, 9, 77 mg, 99–100.5°, 1.49 \pm 0.02, 1.23 μmol produced; ϕ = 0.0117 \pm 0.0009.

1-Methylene-4,4-diphenyl-2-cyclohexene (1247 mg, 5063 μmol) added to ^3H -photolysate (39.5 mg, 160.3 μmol): method B, 726 mg, 9, 142 mg, 93–94°, 0.223 \pm 0.006, 0.273 μmol produced; ϕ = 0.0026 \pm 0.0003.

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