Table IV. Calculation of Fluorescence Rate Constants

Compound	ϵ_{max}	$\bar{\nu}_m$, cm^{-1}	$\Delta\bar{\nu}_{1/2}$, cm^{-1}	k_f, sec^{-1}
1,1-Diphenylethylene	1.19×10^4	4.0×10^4	4.8×10^3	2.6×10^8
Triphenyldiene	1.63×10^4	4.0×10^4	5.90×10^3	4.4×10^8
Tetraphenyldiene	2.34×10^4	3.95×10^4	7.0×10^3	7.3×10^8

was approximated as the band height at the maximum, ϵ_{max}, multiplied by the width of the band at half-height. The pertinent values are listed in Table IV.

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Competitive Photochemical Pathways in the Di-π-methane Rearrangement. Exploratory and Mechanistic Organic Photochemistry. LXIII[1,2]

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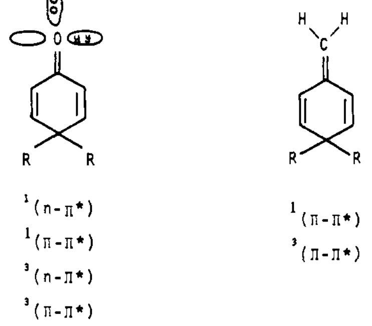
Abstract: The photochemistry of the methylene analogs of the 4,4-diphenyl- and 4,4-dimethylcyclohexadienones was investigated. Direct irradiation of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene afforded 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene in superficial analogy to the dienone type A process. However, in contrast to the dienone situation, the reaction was shown to proceed *via* the singlet, and the triplet was found to give no unimolecular rearrangement. Additionally, the 0.0029 quantum yield suggested a mechanism different than the nearly unit efficiency dienone process. 1-Methylene-4,4-diphenyl-2,5-cyclohexadiene differed in that phenyl migration interceded, affording the cis and trans stereoisomers of 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene. The reaction was highly stereoselective with the trans product predominating 36:1. This reaction, too, was found to utilize the singlet excited state and the triplet was unreactive. The singlet reaction efficiency was enhanced by the availability of the phenyl migration process which had a quantum yield of 0.135 (*vs.* Φ = 0.0029 for the dimethyltriene). The bicyclic dienes from these rearrangements were found to be primary photoproducts which gave rise to further photochemistry. Mechanistic aspects of the reactions are discussed including: the relation to ketone photochemistry, comparison with acyclic di-π-methane rearrangements, and the efficiencies of different available competitive processes.

A number of complex photochemical rearrangements of carbonyl compounds have been given mechanistic explanation using the electronics of the n–π* excited state as a basis.[3,4] The availability of this n–π* excited state derives from the presence of the p_y (nonbonding) orbital at the carbonyl oxygen.

The intriguing possibility of studying molecules lacking this p_y orbital and therefore lacking an n–π* excited state suggested itself. Such a molecule would have available only π–π* excited states and its photochemistry would define the behavior of these states.

Since 4,4-disubstituted cyclohexadienones have been the subject of intensive study in these laboratories,[4] the methylene analogs were selected for the present study.[5] Specifically, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) and 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**1**) were selected. Note Chart I.

Chart I. Excited States Available to Dienones and Methylene Analogs



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[1] For paper LXII of the series, see H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

[2] For a preliminary communication describing a portion of the present work, note H. E. Zimmerman, P. Hackett, D. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

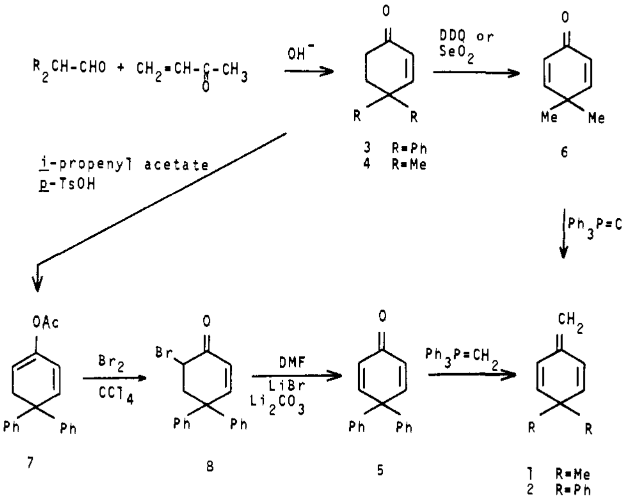
[3] (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (c) H. E. Zimmerman, *Science*, **153**, 837 (1966).

[4] (a) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962); (b) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); **89**, 906 (1967); (c) H. E. Zimmerman and G. Jones, II, *ibid.*, **92**, 2753 (1970); **91**, 5678 (1969).

[5] Very recently we have reported on the photochemistry of the methylene analog of 4,4-diphenylcyclohexenone; see H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969).

Synthesis of Methylene Analogs. These compounds were most conveniently prepared by the Wittig reaction of the corresponding 4,4-disubstituted cyclohexadienones. In the case of 4,4-diphenylcyclohexadienone (**5**), an improved procedure involving bromination of the enone enol acetate and subsequent dehydrobromination was developed. The approaches used are outlined in Chart II and detailed in the Experimental Section.

Chart II. Syntheses of 1-Methylene-4,4-dimethyl-2,5-cyclohexadienone (**1**) and 1-Methylene-4,4-diphenyl-2,5-cyclohexadienone (**2**)



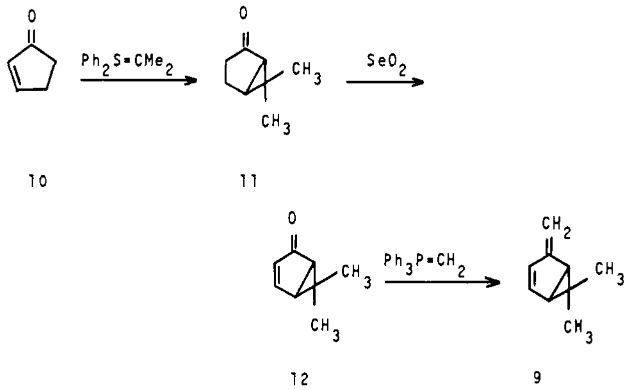
Results

Exploratory Photolyses. Irradiation of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**1**) in exploratory runs using a Vycor filter ($\lambda > 220$ nm) gave two photoproducts. These were separated best on a Carbowax vpc column. The faster moving component proved to be a primary photoproduct and was formed exclusively at low conversions (*vide infra*). In contrast, the slower moving component proved to be a secondary photoproduct and is the subject of a subsequent publication.[6]

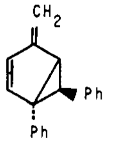
Parallel exploratory photolyses of 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) at low conversion using a 250–305-nm filter afforded two primary photoproducts. These were separated using a reverse-phase liquid–liquid partition polystyrene bead column. The major product, melting at 60–61°, predominated over the minor product, melting at 79–81°, by a ratio of 36:1.

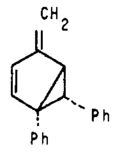
Structure Elucidation of the Primary Photoproduct of 1-Methylene-4,4-dimethylcyclohexadiene (1). The structure of the primary photoproduct of dimethyltriene **1** was suggested by nmr and ir data to be 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**9**); thus, there were observed unsplit but nonequivalent methyls at τ 8.88 and 9.15 and an exocyclic methylene at τ 5.03 with ir absorption at 11.50 μ. This structure was confirmed by independent synthesis. Reaction of diphenylsulfonium isopropylide[7] and cyclopentenone gave 6,6-dimethylbicyclo[3.1.0]-2-hexanone (**11**) which on selenium dioxide oxidation afforded 6,6-dimethylbicyclo[3.1.0]-3-hexen-2-one (**12**). This with methylenetriphenylphosphorane led to **9** (see Chart III).

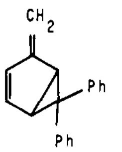
Chart III. Synthesis of 2-Methylene-6,6-dimethylbicyclo[3.1.0]3-hexene (**9**)



Structure Elucidation of Primary Photoproducts from 1-Methylene-4,4-diphenylcyclohexadiene (2). Both products from the photolysis of diphenyltriene **2** proved to be isomeric with starting material. The infrared and nmr spectra of the two suggested a methylenebicyclo[3.1.0]hexene structure in that each compound showed the characteristic 1,1-disubstituted vinyl 11.4-μ infrared band and two singlets in the exocyclic methylene region of the nmr. Thus, structures **13** and **14** were *a priori* possibilities. A type A[3c] rearrangement analogous to that of the dienones would give **14** while phenyl migration, similar to that observed for 4,4-diphenylcyclohexenone,[8] would lead to **13**.


13a


13b


14

The structure of the major photoproduct was deduced by the degradative scheme outlined in Chart IV. The degradation began by hydroxylation of the major photoproduct with osmium tetroxide. Of the two glycols (**15** and **16**) which were obtained, one, **16**, was cleaved with lead tetraacetate to an unsaturated ketone, **17**, which could be hydrogenated to the known *trans*-5,-6-diphenylbicyclo[3.1.0]-2-hexanone (**18**).[8] This evidence established the structure of the major photoproduct of diphenyltriene **2** to be 2-methylene-*trans*-5,-6-diphenylbicyclo[3.1.0]-3-hexene (**13a**).

As further proof, **13a** was independently synthesized from *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one[9] (**17**) *via* Wittig reaction with methylenetriphenylphosphorane as shown in Chart IV.

The structure of the minor photoproduct was determined to be 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13b**). This assignment was based on the facile triplet-sensitized formation of **13b** from 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13a**), consideration of the compound's nmr spectrum, and the identity, except for stereochemistry, of its photochemical reaction with that of its stereoisomer **13a**.[6] The nmr displayed not only the typical exocyclic methylene absorptions at τ 4.90 and 5.01 but also two AB quartets showing further interaction between 1,3-related hy-

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[6] H. E. Zimmerman, D. Juers, J. M. McCall and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3662 (1971).

[7] E. J. Corey and G. H. Posner, *ibid.*, **89**, 3912 (1967).

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

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

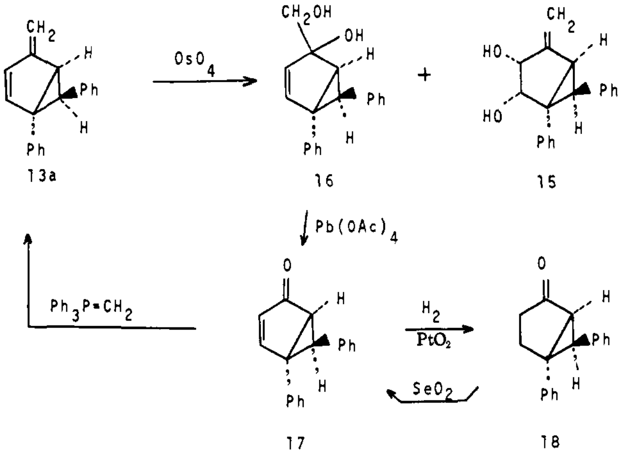
Table I. Quantum Yields for Photolyses of **1** and **2**

Run	Starting material	Added reagent[g]	Light input, mEinstein/mmol	Conv, %	Quantum yield
I-01[a,c]	Dimethyltriene **1**	None	0.130	0.4	0.00308[e]
I-02[a,c]	Dimethyltriene **1**	None	2.180	0.6	0.00286[e]
I-03[a,c]	Dimethyltriene **1**	None	3.880	1.0	0.00316[e]
I-04[a,c]	Dimethyltriene **1**	None	3.481	0.9	0.00266[e]
I-05[b,h]	Dimethyltriene **1**	Benzophenone	11.54	26	<0.00005[e]
I-06[b,b]	Dimethyltriene **1**	Benzophenone	15.57	41	<0.00005[e]
II-01[b,c]	Diphenyltriene **2**	None	1.510	32.0	0.102[f]
II-02[a,c]	Diphenyltriene **2**	None	0.852	9.8	0.116[f]
II-03[b,c]	Diphenyltriene **2**	None	0.806	10.1	0.125[f]
II-04[b,d]	Diphenyltriene **2**	Benzophenone	1.470	4.0	<0.0003[f]
II-05[b,d]	Diphenyltriene **2**	Benzophenone	4.500	11.0	<0.0005[f]

[a] Photolysis in pentane. [b] Photolysis in *tert*-butyl alcohol. [c] Filter transmission 250–305 nm. [d] Filter transmission 315–385 nm [e] In millimoles of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**9**) per millieinstein of light captured. [f] In millimoles of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13a**) per millieinstein of light captured. [g] In sensitized runs, benzophenone absorbed over 99% of the light. [h] Irradiation at 350 nm on micro apparatus.

drogens and also allylic coupling with the *exo*-methylene hydrogens atoms.

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



Determination of Reaction Quantum Efficiency. The quantum yields were determined using the "black box" apparatus described by us earlier[10] and a 250–305-solution filter (note Experimental Section for details). Products were assayed by vpc in the case of the 4,4-dimethyltriene **1** photolysis and by reverse-phase liquid–liquid partition chromatography or nmr for the 4,4-diphenyltriene **2**. Errors due to secondary photolysis were minimized by low-conversion runs and by extrapolation to 0% conversion. The quantum yields were 0.0029 ± 0.0003 for photorearrangement of 1-methylene-4,4-dimethylcyclohexadiene (**1**) to 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**9**) and 0.135, as extrapolated, for the conversion of 1-methylene-4,4-diphenylcyclohexadiene (**2**) to 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13a**). The efficiencies were found to be relatively independent of solvent as might be expected from our results in the irradiation of 1-methylene-4,4-diphenyl-2-cyclohexene.[5] The individual runs are summarized in Table I and detailed in the Experimental Section.

Determination of Reaction Multiplicity. The trienes **1** and **2** were photolyzed using a Bausch and Lomb monochromator (330–370 nm) and the black box[10] apparatus. Benzophenone was used as a sensitizer, and the concentrations of the trienes were adjusted to allow triplet but not singlet energy transfer from benzophenone. In the case of the diphenyltriene **2**, quenching of the formation of benzpinacol from benzophenone and benzhydrol at typical concentrations was utilized. This showed 95% quenching of benzpinacol formation by **2** under reaction conditions, thus demonstrating that efficient energy transfer from benzophenone triplet to **2** was indeed occurring. Although both trienes **1** and **2** were observed to disappear under sensitized conditions with low quantum yields and despite the fact that efficient energy transfer occurred upon triplet sensitization, no bicyclic dienes were formed. By exclusion, this means that the electronic species responsible for the formation of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**9**) from 1-methylene-4,4-dimethylcyclohexadiene (**1**) and 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13**) from 1-methylene-4,4-diphenylcyclohexadiene (**2**) must be the excited singlet. Table I summarizes these sensitization experiments.

Interpretative Discussion

Structural Features of the Rearrangements. In looking at the course of the photochemical rearrangements of 1-methylene-4,4-dimethylcyclohexadiene (**1**) and 1-methylene-4,4-diphenylcyclohexadiene (**2**), we encounter the striking result that, despite similarity of structure of the reactants and also despite formation of a bicyclo[3.1.0]hexene system in the two reactions, there is a basic difference in the reaction course. The two mechanisms are now considered in turn. In the case of the dimethyltriene **1**, the rearrangement is structurally of the di-π-methane type.[11] Thus, the reaction begins with bridging between C-3 and C-5 in the excited state as shown in Chart V to give excited diradical **19**. It is particularly interesting to inspect the further transformation of the resulting di-π-methane species **19** into the bicyclic diene product **9**. This could simply involve ring opening to give **20** followed by reclosure with loss of electronic excitation to give 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**9**). However, since a di-π-methane rearrangement is involved, it seems likely

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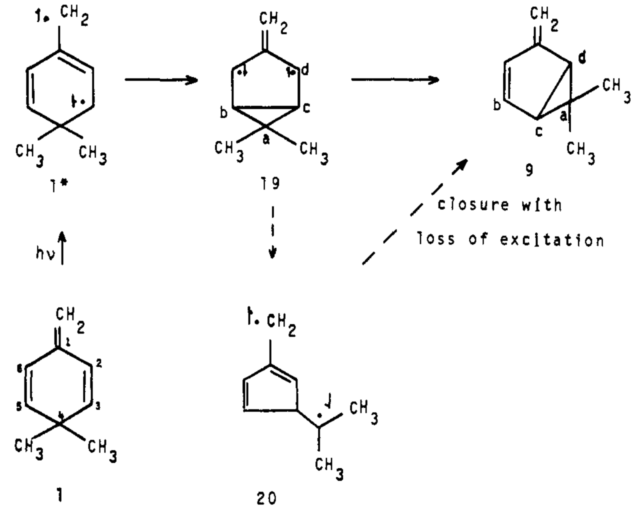
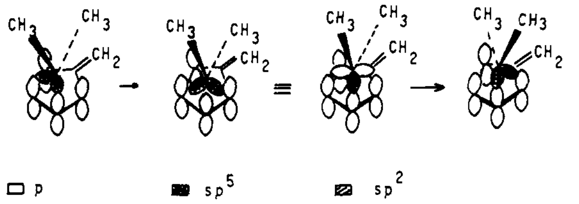
(10) H. E. Zimmerman, R. Keese, J. Nasielski, and J. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

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

Chart V. Mechanism of Rearrangement of 1-Methylene-4,4-dimethylcyclohexadiene (**1**)



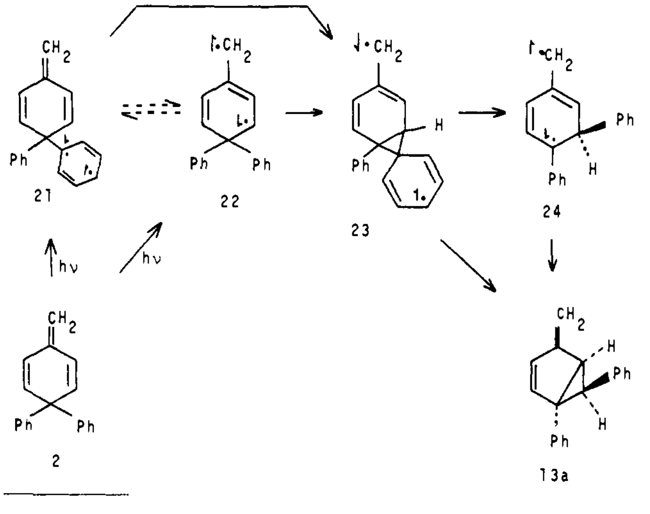
that the slither process postulated earlier[12] is involved. The formation of product **9** from the bridged species **19** then arises directly in one step by a slither of the dimethyl divalent carbon a from carbons b and c of the original skeleton to carbons c and d (note Chart V and eq 1).



(1)

In the case of 1-methylene-4,4-diphenylcyclohexadiene (**2**), a new reaction is seen to intrude with phenyl migration taking precedence over the vinyl–vinyl bonding discussed. Nevertheless, the reaction which does take place is seen to be a di-π-methane rearrangement, except that here the excited state transformation involves phenyl–vinyl bonding rather than vinyl–vinyl bonding. This rearrangement is summarized in qualitative valence bond terms in Chart VI. In this chart the excited state is depicted as having the electronic excitation partitioned between the triene and phenyl moieties, since these are of very similar excitation energy. This partitioning seems most likely to be a dynamic equilibration (note dotted arrows between **21** and **22** in Chart VI) rather than a result of excited state overlap since the ultraviolet spectrum suggests lack of interaction on Franck–Condon excitation (*i.e.*, excitation without change of molecular geometry).[13]

Chart VI. Mechanism of Rearrangement of 1-Methylene-4,4-diphenylcyclohexadiene (**2**)



Another aspect which is of interest is the observation of a marked stereoselectivity in which the trans stereoisomer of 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene (**13a**) predominates at least 36:1 over the cis isomer (**13b**). However, this is not surprising since the same stereochemical preference was observed in the photochemical rearrangements of 4,4-diphenylcyclohexenone[8,14] and 1-methylene-4,4-diphenylcyclohexene[5] to give bicyclic products. The present stereochemistry then provides further support for the generality of inversion of configuration at the methane carbon in the di-π-methane rearrangement as proposed in these earlier examples.

Reaction Multiplicity. The observations that the two rearrangements each take place *via* the singlet excited state and that the triplet excited state, when independently generated, does not react unimolecularly with any appreciable efficiency are consonant with the suggestion we advanced recently regarding the relation between structure and multiplicity in the di-π-methane rearrangement.[11,15] It was noted[15,16] that the presence of a potential free rotor, such as an *exo*-methylene moiety, provided a mechanism for excited state energy dissipation. Since the triplet rearrangements tend to be slower than singlet excited state transformations, this energy dissipation mechanism is more likely to be effective in stopping a triplet transformation than a singlet one, and, in general, the free rotor seems capable of rendering the di-π-methane triplet incapable of reaction.

Regarding the mechanism of this mode of triplet energy dissipation, one can conclude that at some extent of methylene twisting the triplet excited state and the ground state become electronically degenerate, thus allowing more facile intersystem crossing to the ground-state potential energy surface. Additionally, with vibrational modes available to the molecule, it becomes possible for the molecule to convert its electronic excitation temporarily to vibrational excitation as energy dissipation to solvent begins.

Another factor controlling the reaction multiplicity is the vinyl–vinyl excited state bond order for the singlet compared to the triplet. This aspect seems better discussed in the following section concerning reaction efficiency (note below).

Reaction Efficiency. A striking aspect deriving from comparison of the two trienes presently studied is

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(12) (a) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **92**, 3474 (1970); (b) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(13) The similarity of the absorption spectrum of an equimolar mixture of diphenylmethane and 1-methylene-4,4-dimethylcyclohexadiene (**1**) to the spectrum of 1-methylene-4,4-diphenylcyclohexadiene (**2**) suggests little initial interaction between chromophores. Thus, diphenyltriene **2** shows absorption maxima at 247 and 253 nm while the mixture of diphenylmethane and dimethyltriene **1** has maxima at 242 and 249 nm.

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

(15) H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

(16) J. S. Swenton, A. L. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

the different skeletal change in the two systems. The occurrence of phenyl migration in the photolysis of 1-methylene-4,4-diphenylcyclohexadiene (**2**) rather than the vinyl–vinyl bridging observed in the case of 1-methylene-4,4-dimethylcyclohexadiene (**1**) can be interpreted as an inherent preference for the phenyl participation process with intervention of phenyl migration whenever possible.

Actually, comparison of the two quantum efficiencies ($\Phi = 0.135$ for the diphenyltriene **2** *vs.* $\Phi = 0.0029$ for the dimethyltriene **1**) reveals that the reaction of the diphenyltriene is indeed more efficient. It is, of course, conceivable that this efficiency difference derives from a greater rate of excited state decay in the case of the dimethyltriene **1** compared to the diphenyltriene **2**. However, it is difficult to envision extra modes of excited state decay possible for the dimethyl species not available to the diphenyl analog. One might expect the converse. Furthermore, the difference in decay rates would have to be very large to reverse the reactivity order.

The preference of phenyl migration over vinyl–vinyl interaction seems not to derive from an abnormally facile phenyl migration but rather from an abnormally inefficient vinyl–vinyl di-π-methane process. Thus, the quantum efficiency of 0.135 observed for phenyl migration is comparable to the 0.0797 quantum yield found for vinyl–vinyl di-π-methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethylpenta-1,4-diene[11] and the 0.112 efficiency in the case of the phenyl migration reaction of 1-methylene-4,4-diphenylcyclohexadiene.[5] However, the 0.0029 efficiency for the 4,4-dimethyltriene **1** is low compared to all of these processes.

Two possibilities present themselves as explanations for the low quantum yield. First, it is conceivable that incorporation of the cross-conjugated *exo*-methylene group between the termini of the two vinyl groups of the di-π-methane system might serve to decrease the bond order between the vinyl groups in the singlet excited state. However, configuration interaction calculations (note Table II) of the two systems show that the vinyl–vinyl bond order in both the first and second excited states of the simple di-π-methane system (*i.e.*, the "diene" in Table II) is quite similar to that in the dimethyltriene **1** (listed as "triene" in Table II).[17] Hence the reactivity difference does not seem to derive from a basic difference due to cross-conjugation.[18]

A second possibility, which seems reasonable and which can be tentatively accepted as a hypothesis for further study, is that the di-π-methane transformation proceeds more efficiently from the transoid conformation **25** than from the cisoid conformation **26** (note Figure 1).

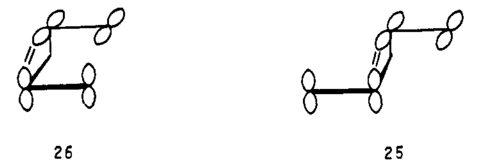

Figure 1. Cisoid *vs.* transoid conformations in di-π-methane processes.

It is noted, however, that cisoid conformations are quite capable of rearranging efficiently in such bicyclic systems as barrelene.[19] However, here the species rearranging is the triplet and the extent to which the reaction efficiency is enhanced by lack of free rotor effects[15,16] is uncertain.

A final point with respect to reaction efficiency which merits attention is the singlet reactivity of these species relative to the unreactive triplet. Interestingly, configuration interaction calculations (Table II) reveal a dramatic enhancement of the vinyl–vinyl bond order of the singlet as the overlap increases and a contrastingly minor change in the case of triplet bonding. This bond order enhancement derives from a change in configuration of the lowest excited singlet resulting from energy crossing in the excited state. This effect seems likely to contribute to triplet inefficiency along with the dissipation of triplet excitation by free rotation (*i.e.*, free rotor effects) about nonendocyclic π bonds.

Table II. Configuration Interaction Calculations

π system	Config and eV[a]	Geometry[b]	Predominant Hückel transitons	Resonance integral between bridging carbons[b]	Bond order between bridging carbons[b]
Triene[c]	S_1 6.7526	Unbridged	$\Psi_2 \rightarrow \Psi_4$ $\Psi_3 \rightarrow \Psi_5$	−0.0048	0.0020
Triene[c]	S_2 6.9978	Unbridged	$\Psi_3 \rightarrow \Psi_4$	−0.0048	0.0004
Triene[c]	T_1 0.6409	Unbridged	$\Psi_3 \rightarrow \Psi_4$	−0.0048	0.0005
Triene[c]	T_2 1.2296	Unbridged	$\Psi_2 \rightarrow \Psi_4$[e] $\Psi_3 \rightarrow \Psi_5$[e]	−0.0048	0.0011
Triene[c]	S_1 5.5913	Partially bridged	$\Psi_3 \rightarrow \Psi_4$	−1.2200	0.5506
Triene[c]	S_2 6.8763	Partially bridged	$\Psi_2 \rightarrow \Psi_4$[e] $\Psi_3 \rightarrow \Psi_5$[e]	−1.2200	0.1742
Triene[c]	T_1 0.8374	Partially bridged	$\Psi_2 \rightarrow \Psi_4$	−1.2200	0.1668
Triene[c]	T_2 1.1192	Partially bridged	$\Psi_3 \rightarrow \Psi_4$ $\Psi_2 \rightarrow \Psi_5$	−1.2200	0.3038
Diene[d]	S_1 8.2199	Unbridged	$\Psi_2 \rightarrow \Psi_3$ $\Psi_1 \rightarrow \Psi_4$	−0.0048	0.0000
Diene[d]	T_1 1.1205	Unbridged	$\Psi_2 \rightarrow \Psi_3$ $\Psi_1 \rightarrow \Psi_4$	−0.0048	0.0000
Diene[d]	S_1 7.6150	Partially bridged	$\Psi_2 \rightarrow \Psi_3$	−1.2200	0.5535
Diene[d]	T_1 0.9749	Partially bridged	$\Psi_2 \rightarrow \Psi_3$	−1.2200	0.2828

[a] Above ground-state configuration. [b] Bridging between carbons b and c in Chart V. [c] *E.g.*, 1-methylene-2,5-cyclohexadiene which has a π system characteristic of the systems studied in this paper. [d] *E.g.*, 1,4-cyclohexadiene which has an unconjugated π system as in the case of divinylmethanes. [e] These configurations are degenerate. [f] Comparison of effect of bridging on lowest singlets and triplets.

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[17] Interestingly, the lowest excited state is not the one involving excitation from the highest bonding MO to the lowest antibonding MO, but rather a linear combination of the configuration in which an electron has been promoted from the highest occupied MO to the second lowest antibonding MO and the one in which an electron has been promoted from the next to highest bonding MO to the lowest antibonding MO. The second excited state is the one envisaged in the simple Hückel picture.

[18] This contrasts with the suggestion made by us earlier.[12a]

[19] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

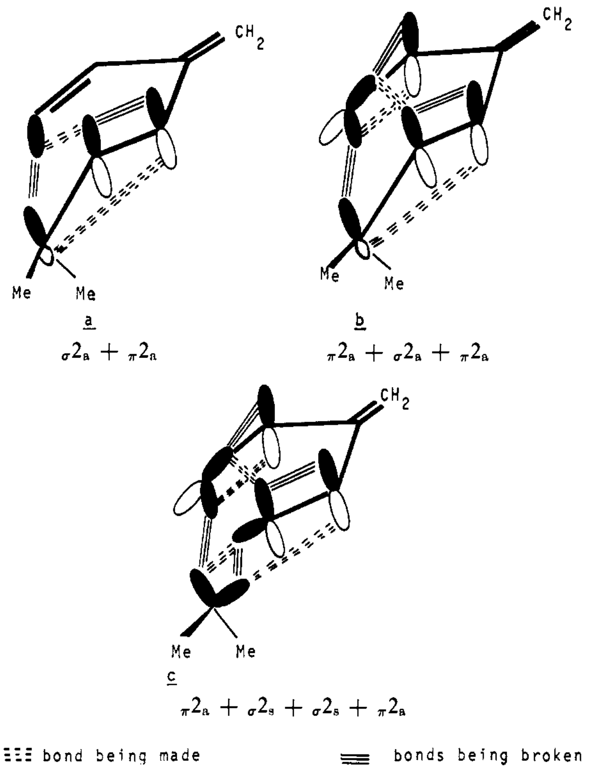

Figure 2. Orbital symmetry considerations for di-π-methane rearrangemement of dimethyltriene **1**.

Another superficially discordant fact is the high quantum yield and very rapid excited state reaction rate for the triplets of 4,4-disubstituted cyclohexadienones in contrast to the methylene analogs **1** and **2**. However, it has been noted earlier[4a,4b,10] that these reactions proceed *via* n–π^* triplets and that these n–π^* triplets have very high vinyl–vinyl (*i.e.*, β–β in the dienones) bond orders. Hence, the difference between the di-π-methane rearrangements discussed presently and the type A rearrangements of dienones can be ascribed to the role of the nonbonding electron promoted to the π system in the excited state.

Di-π- *vs.* σ–π-methane Rearrangements. The present results bear on the question of whether the rearrangements observed are really ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ or more complex. In looking at only the structural change in the 1-methylene-4,4-diphenylcyclohexadiene (**2**) rearrangement, one might conclude that only the C-4 to phenyl bond was involved in adding across a π bond. Similarly, in the case of the 1-methylene-4,4-dimethylcyclohexadiene (**1**) rearrangement, this could be formally construed to involve only the addition of the 4,5 σ bond across the 2,3 π bond with ${}_{\pi}2_{a} + {}_{\sigma}2_{a}$ stereochemistry (note Figure 2a).

Actually, the evidence is that the di-π-methane rearrangement really does require more than a σ and a π bond. Thus, the present evidence clarifies, by lack of methyl migration in the 1-methylene-4,4-dimethylcyclohexadiene, that σ plus π interaction is inefficient.[20] An argument that somehow the presence of the π bond enhances a σ plus π addition is not realistic when one considers that the bond energy of such an sp^2–sp^3 σ bond is greater than an ordinary sp^3–sp^3 σ bond. Consequently, such a vinyl single bond should be less reactive than the comparably located single bond in a molecule having just one double bond.

A more realistic picture of the reaction has been given earlier[11,21] and is shown in Figure 2b to involve a ${}_{\pi}2_{a} + {}_{\sigma}2_{a} + {}_{\pi}2_{a}$ interaction. One can see that such a description is identical with the specification that the array is Möbius, since an odd number of overlaps is involved in an array containing six electrons. With either terminology,[22,23] the reaction is excited state allowed.

One might now inquire how this is related to the slither description given above (see eq 1). The slither description and that of Figure 2b differ only in the consideration of two extra orbitals in the former. Figure 2c shows this expanded set of orbitals consisting of eight basis orbitals instead of the six in Figure 2b. This can be seen to be a ${}_{\pi}2_{a} + {}_{\sigma}2_{s} + {}_{\sigma}2_{s} + {}_{\pi}2_{a}$. Since each "a" corresponds to an inversion, the system of two inversions is Hückel-like and therefore excited state allowed with eight electrons.

Conclusion

It is thus seen that the di-π-methane rearrangement occurs in a variety of different systems and with efficiencies dependent on several structural factors. One structural variation, inclusion of a di-π-methane grouping in a monocyclic ring, is presently seen to strongly diminish the efficiency of the rearrangement and, contrastingly, aryl–vinyl interaction is found to be much more efficient than vinyl–vinyl interaction.

Experimental Section[24]

4,4-Dimethylcyclohexenone. The condensation of 140.0 g (2.00 mol) of methyl vinyl ketone and 140.0 g (1.95 mol) of isobutyraldehyde as described by Eliel and Lukach[25] yielded 111.3 g (47.3%) of 4,4-dimethylcyclohexenone.

4,4-Dimethylcyclohexadienone. 4,4-Dimethylcyclohexenone (11.51 g, 0.093 mol), dichlorodicyanoquinone (23.80 g, 1.105 mol), and purified dioxane (300 ml) were heated under nitrogen at 95–100° for 22 hr. After addition to 50% ether in pentane and washing with 5% aqueous sodium hydroxide and water, the organic phase was dried and concentrated. Distillation afforded 7.305 g (64.5%) of 4,4-dimethylcyclohexadienone, bp 41° (0.15 mm).

The spectral properties agreed with those reported by Zimmerman, *et al.*[26]

1-Methylene-4,4-dimethylcyclohexadiene. Triphenylmethylphosphonium bromide (71.7 g, 201 mmol) was suspended in 2800 ml of ether under nitrogen. A solution of *n*-butyllithium in hexane[27] (95 ml, 219 mmol) was injected, and the reaction mixture was stirred at room temperature for 30 min. 4,4-Dimethylcyclohexadienone (21.39 g, 174 mmol) was injected and the reaction mixture was refluxed for 14 hr. After filtration and washing with water, the solution was dried and concentrated. Fractional distillation yielded 14.50 g (69.5%) of 1-methylene-4,4-dimethylcyclohexadiene, bp 40° (15 mm). Further purification for analysis or photolysis was accomplished by preparative vpc (15% Carbowax on Chromosorb W, 90°).

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(20) Such σ plus π reactions are known but seem from the qualitative details available to be inefficient; note (a) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966); H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); E. C. Sanford and G. S. Hammond, *ibid.*, **92**, 3497 (1970).

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

(22) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966).

(23) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, pp 65–73.

(24) All melting points were taken on a hot-stage apparatus checked with known compounds.

(25) E. L. Eliel and C. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).

(26) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).

(27) *n*-Butyllithium was standardized according to H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

The spectral data were: ir ($CHCl_3$) 3.38, 3.98, 6.03, 6.34, 7.39, 9.0, 10.85, and 11.51 μ; nmr ($CDCl_3$) τ 3.6–4.5 (q, 4 H, J = 10 Hz, –CH=CH–), 5.2 (s, 2 H, =CH_2), 8.85 (s, 6 H, methyls); $\lambda_{\max}^{95\%\ \text{ethanol}}$ 243 (ϵ 23,000), 250 nm (ϵ 20,000).

Anal. Calcd for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.88; H, 10.05.

4,4-Diphenylcyclohexenone. The condensation of 107 g (0.546 mol) of diphenylacetaldehyde and 38.3 g (0.547 mol) of methyl vinyl ketone according to the procedure of Zimmerman, Hancock, and Licke[28] afforded 101.8 g (75.1%) of 4,4-diphenyl-2-cyclohexenone.

5,5-Diphenyl-2-acetoxy-1,3-cyclohexadiene. Following the procedure of Plieninger, *et al.*,[29] 50.0 g (0.202 mol) of 4,4-diphenyl-2-cyclohexenone and 2.0 g (0.012 mol) of *p*-toluenesulfonic acid were heated at 125–130° for 11 hr with 150 ml (1.50 mol) of isopropenyl acetate under a 2.0 × 24 cm column packed with glass beads. A dark colored liquid (36 ml) distilled. The reaction mixture was concentrated, and the residue was triturated with anhydrous ether and filtered. The filtrate precipitated more of this material which was combined with the first crop to give a total of 53.1 g (90.6%) of 5,5-diphenyl-2-acetoxy-1,3-cyclohexadiene, mp 104–106°.

The spectral data were: ir ($CHCl_3$) 3.21, 3.24, 3.28, 3.30, 5.73, 6.00, 6.24, 6.69, 6.92, 7.15, 7.29, 8.22 (broad), 8.52, 8.76, 9.66, 9.88, 10.43, 10.68, 10.93, 11.10, 11.39, 12.01, 14.30, 15.31, and 15.85 μ; nmr (CCl_4) τ 2.90 (s, 10 H, arom), 3.86 (d of d, 1 H, vinyl, J = 10, 0.6 Hz), 4.26 (d of d, 1 H, vinyl, J = 10, 1.0 Hz), 4.65 (t of d of d, 1 H, vinyl, J = 4.5, 1.0, 0.6 Hz), 7.07 (d, 2 H, allylic, J = 4.5 Hz), and 8.03 (s, 3 H, acetyl).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.74; H, 6.25. Found: C, 83.07; H, 6.36.

6-Bromo-4,4-diphenylcyclohex-2-enone. Bromine (7.50 ml, 0.150 mol) was added dropwise to a stirred suspension of 43.1 g (0.149 mol) of 5,5-diphenyl-2-acetoxy-1,3-cyclohexadiene in 150 ml of carbon tetrachloride in an ice bath over 1 hr. After addition was complete all of the material had dissolved, and the reaction mixture was cooled to 10° for 17 hr. The solvent was removed, and the yellow residue was dissolved in chloroform. The solution was washed with saturated sodium bicarbonate and with water, dried, and concentrated. The remaining orange-brown oil was crystallized from ether. The resultant precipitate was filtered and recrystallized from 95% ethanol to yield 41.4 g (85.9%) of 6-bromo-4,4-diphenylcyclohexenone, mp 101.5–104°.

The spectral data were: ir ($CHCl_3$) 3.24, 3.3, 5.92, 6.26, 6.68, 6.90, 7.26, 7.57, 8.24, 8.44, 8.69, 9.36, 9.50, 9.68, 9.81, 9.98, 10.79, 11.97, 14.28, and 15.88 μ; nmr (CCl_4) τ 2.6–3.0 (m, 11 H, arom and –C=CHCO), 3.83 (d, 1 H, vinyl, J = 11 Hz), 5.45 (d of d, 1 H, CHBrCO, J = 12, 6 Hz), and 6.92 (m, 2 H, cyclohexyl).

4,4-Diphenyl-2,5-cyclohexadienone. Following the general procedure of Plieninger, *et al.*,[29] 36.4 g (0.111 mol) of 6-bromo-4,4-diphenylcyclohexenone, 28.0 g (0.38 mol) of lithium carbonate, 32.0 g (0.37 mol) of lithium bromide, and 250 ml of dimethylformamide were stirred at reflux for 11 hr, in the dark, under nitrogen. The reaction mixture was filtered to remove the inorganic salts and concentrated *in vacuo* on the steam bath. The residue was taken up in ether and washed with water. Then the organic layer was dried and concentrated. The residue was taken up in methanol, treated with decolorizing charcoal, and crystallized to yield 18.0 g (65%) of 4,4-diphenylcyclohexadienone, mp 122–123° (lit.[4a] 124–125°).

1-Methylene-4,4-diphenylcyclohexadiene. To a suspension of 16.00 g (45 mmol) of triphenylmethylphosphonium bromide in 750 ml of anhydrous ether was added 25 ml of a 2.0 *M* solution of *n*-butyllithium (50 mmol) in hexane. Addition was dropwise with stirring over 0.5 hr to give a clear yellow solution. A solution of 10.00 g (40.6 mmol) of 4,4-diphenylcyclohexadienone in 750 ml of anhydrous ether was added with stirring over 0.5 hr, and the resultant white suspension was refluxed for 3 hr to give a purple-brown mixture. The mixture was then filtered and the residue thoroughly washed with ether. The filtrate was concentrated and crystallized from methanol to yield 8.10 g (82%) of 1-methylene-4,4-diphenylcyclohexadiene as white needles, mp 89–90.5°.

The spectral data were: ir ($CHCl_3$) 3.24, 3.30, 6.02, 6.27, 6.30, 6.72, 6.92, 8.47, 9.36, 9.68, 10.79, 11.04, 11.37, and 14.31 μ; nmr (CCl_4) τ 2.9–3.0 (m, 10 H, arom), 5.83 (d, 2 H, vinyl, J = 10 Hz), 4.03 (d, 2 H, vinyl, J = 10 Hz), and 5.17 (s, 2 H, =CH_2); $\lambda_{\max}^{t\text{-butyl alcohol}}$ 247 (ϵ 12,300) and 253 nm (sh) (ϵ 11,000).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.24; H, 6.62.

Exploratory Photolysis of 1-Methylene-4,4-dimethylcyclohexadiene. A solution of 724.6 mg (5.93 mmol) of 1-methylene-4,4-dimethylcyclohexadiene in 500 ml of anhydrous ether was photolyzed with a Hanovia 450-W medium-pressure mercury lamp through a Vycor filter for 5 hr. Before and during photolysis, the solution was stirred and swept with vanadous purified nitrogen.[30] Careful distillation of solvent yielded 316.0 mg (2.63 mmol) of volatile photoproduct. Nonvolatile residues (382.4 mg) were obtained (mass loss 7.5%). The volatiles were analyzed by vpc (15% Carbowax on 60–80 Chromosorb W, 24 ft × 0.25 in., 85°) and contained 2.9% 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene, 34.7% secondary photoproduct 1,1-dimethylspiro[2.4]-4,6-heptadiene,[6] and 62.4% starting material. 2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene, whose spectral properties were identical with those of synthetic bicyclic diene, was isolated by preparative vpc (15% Carbowax on 60–80 Chromosorb W, 18 ft × 0.38 in., 80°).

6,6-Dimethylbicyclo[3.1.0]-2-hexanone. Diphenylsulfonium isopropylide was prepared by the method of Corey.[7] A solution of 276.0 g (0.915 mol) of diphenylethylsulfonium fluoroborate and 77.7 g (0.915 mol) of dichloromethane in 1500 ml of dry dimethoxyethane (distilled from sodium–potassium alloy) was cooled under nitrogen to –70°. To this solution was added 1.05 mol of a cold (–70°) solution of lithium diisopropylamide which had been prepared by the addition of 467 ml of a 2.25 *M* solution of *n*-butyllithium in hexane to a solution of 106.0 g (1.05 mol) of diisopropylamine in 150 ml of dry dimethoxyethane. After 30 min, 142 g (1.00 mol) of methyl iodide was added and the reaction mixture was stirred at –70° for 2 hr. Then 1.05 mol of lithium diisopropylamide was added and the reaction was stirred at –70° for 1 hr longer. 2-Cyclopentenone[31] (50.0 g, 0.61 mol) was introduced to the reaction mixture which was then warmed to –20° and maintained at that temperature overnight. After addition of pentane, the mixture was washed repeatedly with 5% hydrochloric acid until the washes remained acidic. After washing with sodium bicarbonate solution and with water, the pentane layer was dried, concentrated, and distilled to give 36.00 g (47.5%) of pure 6,6-dimethylbicyclo[3.1.0]-2-hexanone, bp 46° (0.5 mm). The spectral properties of this compound were identical with those of 6,6-dimethylbicyclo[3.1.0]hexan-2-one prepared by the method of Chapman.[32]

6,6-Dimethylbicyclo[3.1.0]hex-3-en-2-one. A solution of 14.00 g (0.113 mol) of 6,6-dimethylbicyclo[3.1.0]hexan-2-one in 50 ml of water and 150 ml of purified dioxane was stirred under nitrogen at 45°. Portions of selenium dioxide[33] totalling 16.04 g (0.145 mol) were added over 72 hr. After 120 hr, the reaction mixture was poured into 50% ether in pentane and washed with saturated sodium bicarbonate. After drying and concentrating, distillation through a 6 in. Vigreux column yielded 4.80 g (35%) of pure 6,6-dimethylbicyclo[3.1.0]-3-hexen-2-one, bp 50° (0.75 mm).

The spectral data were: (100 MHz, $CDCl_3$) τ 2.60–2.68 (q, 1 H, J = 2, 6 Hz, –CH=), 4.09–4.14 (d, 1 H, J = 6 Hz, –CH=), 7.54–7.62 (d of d, 1 H, J = 4, 2 Hz, cyclopropyl), 8.03–8.08 (d, 1 H, J = 4 Hz, cyclopropyl), 8.78 (s, 3 H, –CH_3), 8.85 (s, 3 H, –CH_3); ir ($CDCl_3$) 5.95, 6.3, 6.9, 7.26, 7.4–7.26, 7.5, 7.8, 8.22, 8.42, 9.0–9.15, 9.96, and 11.92 μ.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.31; H, 8.55.

2-Methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene. Methylenetriphenylphosphorane was prepared by the addition of 14.3 ml of a 2.25 *M* solution of *n*-butyllithium in hexane to 17.3 g (48.1 mmol) of triphenylmethylphosphonium bromide in 450 ml of dry hexane under nitrogen.[34] After stirring 30 min at 45°, 0.884 g (7.25 mmol) of 6,6-dimethylbicyclo[3.1.0]-3-hexen-2-one was added. After heating for 20 hr at 38°, 3.0 g of magnesium sulfate was added, and the reaction mixture was filtered. The filtrate was water washed, dried, concentrated, and bulb-to-bulb distilled. The dis-

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

(29) H. Plieninger, G. Ege, H. J. Grashoff, G. Keilich, and W. Hoffman, *Chem. Ber.*, 94, 2115 (1961).

(30) L. Meites, *Anal. Chem.*, 20, 984 (1948).

(31) E. Garbish, *J. Org. Chem.*, 30, 2109 (1965).

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

(33) Selenium dioxide was purified by sublimation from nitric acid followed by resublimation.

(34) Simultaneous, slow addition of reactants improved both homogeneity and yield of the reaction.

tillate was purified by preparative vpc (15% Carboxwax on Chromosorb W, 80°) to yield 0.1402 g (16.1%) of pure 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene.

The spectral data were: nmr ($CDCl_3$, 100 MHz) τ 4.05 (broad s, 2 H, –CH═CH–), 5.04 (s, 1 H, exocyclic methylene), 5.09 (s, 1 H, exocyclic methylene), 8.02 (m, 2 H, –HCCH–), 8.88 (s, 3 H, $-CH_3$), 9.15 (s, 3 H, $-CH_3$); ir ($CHCl_3$) 3.32, 3.38, 6.14, 6.42, 7.28, 7.40, 7.74, 8.30, 9.00, 10.25, 10.60, 11.50, and 12.05 μ; $\lambda_{\max}^{\text{ether}}$ 253 nm (ϵ 11,400).

Anal. Calcd for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 90.14; H, 10.10.

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[30] 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[30] 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 band width 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.[35]

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%.

Exploratory Photolysis of 1-Methylene-4,4-diphenylcyclohexadiene. 1-Methylene-4,4-diphenylcyclohexadiene (11.335 g, 45.7 mmol) was photolyzed in three approximately equal quantities on the macro photolysis apparatus through filter C using a semiquantitative technique.[36]

In a typical run, 4.002 g (16.4 mmol) of the starting material in 750 ml of *tert*-butyl alcohol was irradiated with 22.2 mEinstein of light. The photolysate was concentrated and crystallized 2.749 g of starting material from methanol. The mother liquor 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). Then they were 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 effluent was scanned at 254 nm. Elution in 40-ml fractions gave: fractions 72–88, 429 mg, crude 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]3-hexene; fractions 89–102, 202 mg, starting material.

This procedure on the other two batches gave an additional 1001 mg of crude bicyclic diene and a recovery of 5.690 g of starting material when a total of 39.7 mEinstein of light was used for both photolyses. The crude bicyclic diene from all three runs was crystallized from methanol to yield 930 mg of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene. The mother liquor from this crystallization was concentrated and submitted to the polystyrene bead chromatography described above. Fractions 69–75 gave 49 mg of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene. Fractions 76–86 afforded 328 mg of additional *trans*-bicyclic diene.

In summary, photolysis of 11.335 g (45.7 mmol) of 1-methylene-4,4-diphenylcyclohexadiene with 61.9 mEinstein afforded a total of 1.258 g of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene (approximate $\Phi = 0.082$) and 0.049 g of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (approximate $\Phi = 0.0032$).

The spectral data for the *trans*-bicyclic diene were: ir ($CHCl_3$) 3.22, 3.25, 3.31, 6.12, 6.24, 6.68, 6.91, 9.33, 9.75, 11.42 (br), and 14.46 μ; nmr (CCl_4) τ 2.6–3.1 (m, 10 H, arom), 4.0 (broad d, 1 H, $J = 5.5$ Hz, –HC═). 4.41 (broad d, 1 H, $J = 5.5$ Hz, –HC═), 4.87 (broad s, 1 H, exocyclic methylene), 5.02 (s, 1 H, exocyclic methylene), 7.01 (d, 1 H, $J = 8.5$ Hz, cyclopropyl), 7.30 (broad d, 1 H, $J = 8.5$ Hz, cyclopropyl); $\lambda_{\max}^{t\text{-butyl alcohol}}$ 247 nm shoulder (ϵ 10,700).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.23; H, 6.76.

The spectral data for the *cis*-bicyclic diene were: ir ($CHCl_3$) 3.22, 3.24, 3.31, 6.13, 6.25, 6.69, 6.92, 7.53, 9.19, 9.32, 9.75, 11.46 (br), 12.02, and 14.38 (broad) μ; nmr (CCl_4) τ 2.7–3.45 (m, 10 H, arom), 3.66 (broad d, 1 H, $J = 5.0$ Hz, –HC═), 4.13 (d, 1 H, $J = 5.0$ Hz, –HC═), 4.90 (broad s, 1 H, H_2C═), 5.01 (s, 1 H, H_2C═), 7.10 (m, 1 H, cyclopropyl), 7.75 (d, 1 H, $J = 4.0$ Hz, cyclopropyl); $\lambda_{\max}^{t\text{-butyl alcohol}}$ 268 (ϵ 13,400), 222 nm (shoulder, ϵ 20,400).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.41; H, 6.76.

Hydroxylation of 2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene. A solution of 135 mg (0.53 mmol) of osmium tetroxide in 3.0 ml of ether was added to a solution of 122 mg (0.50 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene in 2.0 ml of ether. This mixture, which immediately began to turn black, was allowed to stand for 15 hr. After the solution had been concentrated, the residue was refluxed for 3 hr with 800 mg of sodium bisulfite in 57% ethanol. Then the reaction mixture was diluted with water and was chloroform extracted. The organic extracts were dried and concentrated to yield 128 mg of crude hydroxylated material.

This was combined with two more batches prepared similarly from 100-mg portions of *trans*-bicyclic diene. The total yield of crude material was 320 mg which was chromatographed on a 2 × 80 cm deactivated (Mallinkrodt 100–200 mesh, silicAR cc-107 slurried with water and dried 15 hr at room temperture) silicic acid column slurry packed in 10% methanol–chloroform. After the column was eluted with 500 ml of chloroform, the hydroxylation product was applied, and fractions 1–19 were eluted with chloroform; fractions 20–34 were eluted with 2% methanol–chloroform. Elution in 25-ml fractions gave: fractions 9–12, 39 mg, unidentified material; fractions 13–19, 79 mg (22%), 2-methylene-

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

[36] These 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.

3,4-dihydroxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexane, mp 136–137° (recrystallized from chloroform in hexane); fractions 20–34, 94 mg (26%), 2-hydroxy-2-hydroxymethylene-*trans*-5,6-diphenylbicyclo-[3.1.0]-3-hexene, mp 117–118° (recrystallized from chloroform in hexane).

Spectral data of 2-methylene-3,4-dihydroxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexane were: ir ($CHCl_3$) 2.75–3.05, 6.01, 6.24, and 6.69 μ; nmr ($CDCl_3$) τ 2.48–2.85 (m, 10 H, arom), 4.72 (broad s, 1 H, exocyclic methylene), 4.88 (broad s, 1 H, exocyclic methylene), 5.87 (d, 1 H, J = 5 Hz, –CHO–), 6.88 (broad s, 1 H, hydroxyl), 7.21 (d, 1 H, J = 8.5 Hz, cyclopropyl), 7.41 (d, 1 H, J = 8.5 Hz, cyclopropyl), and 7.69 (broad s, 2 H, –CHOH).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.00; H, 6.52. Found: C, 81.81; H, 6.70.

The spectral properties of 2-hydroxy-2-hydroxymethylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene were: ir ($CHCl_3$) 2.75–3.10, 6.23, and 6.70 μ; nmr ($CDCl_3$) τ 2.50–2.95 (m, 10 H, arom), 3.79 (d, 1 H, J = 5.5 Hz, vinyl), 4.59 (broad d, 1 H, J = 5.5 Hz, vinyl), 6.60–7.08 (m, 5 H, –CH_2OH, –OH, and cyclopropyl), and 7.79 (d, 1 H, J = 9.0 Hz, cyclopropyl).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.00; H, 6.52. Found: C, 81.81; H, 6.31.

Oxidation of *trans*-5,6-Diphenyl-2-hydroxymethylene-2-hydroxybicyclo[3.1.0]-3-hexene. A solution of 50 mg (0.18 mmol) of *trans*-5,6-diphenyl-2-hydroxymethylene-2-hydroxybicyclo[3.1.0]-3-hexene in 3.0 ml of dry acetone was added to 270 mg (0.61 mmol) of lead tetraacetate in 3.0 ml of dry acetone and the mixture was stirred for 0.5 hr. Then, 40 ml of ether and 40 ml of hexane was added and the solution was washed with 5% aqueous potassium hydroxide and water, dried, and concentrated *in vacuo* to yield 41 mg (93%) of *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 71–90° (remelt 71–72°) when crystallized from methanol. This was identical with that previously reported.[9]

Catalytic Hydrogenation of *trans*-5,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one. A suspension of 50 mg of platinum oxide in 2.0 ml of ethyl acetate and 30 μl of triethylamine was equilibrated with hydrogen at atmospheric pressure. Then a solution of 53 mg (0.22 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 2.0 ml of ethyl acetate was added and the mixture was stirred under hydrogen. The calculated amount of hydrogen for the reduction of the olefinic double bond (5.1 ml, 0.22 mmol) was absorbed in 30 min and no more hydrogen was absorbed during the next 15 min. The reaction was filtered and concentrated *in vacuo* to give 48 mg (91%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexen-2-one, mp 74–76°, after crystallization from ethanol. This material was identical (ir, nmr, mixture melting point) with an authentic sample[8] of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

***trans*-5,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one.** This material was prepared by selenium dioxide oxidation of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexanone as previously described by Zimmerman and Morse.[9]

2-Methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene. *n*-Butyllithium (1.15 ml of a 2 *M* hexane solution, 2.30 mmol) was added to a stirred suspension of 785 mg (2.20 mmol) of triphenylmethylphosphonium bromide in 25 ml of ether under nitrogen. After stirring for 20 min, a dark yellow solution had formed. Then, 500 mg (2.03 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 20 ml of ether was added over 5 min, and the mixture was stirred at reflux for 3.5 hr. The reaction mixture was filtered, and the precipitate was washed. Then the filtrate was concentrated to yield 255 mg (51%) of 2-methylene-*trans*-5,6-diphenylbicyclo-[3.1.0]-3-hexene. The spectral properties of this material were identical with material obtained from the photolysis of 1-methylene-4,4-diphenylcyclohexadiene.

Photolysis Solvents, Sensitizers. *n*-Pentane was stirred with fuming sulfuric acid, stirred with basic permanganate, distilled from KOH, and passed through an alumina–silver nitrate column.[37] Ethyl ether (Mallinckrodt anhydrous) was used without further purification. *tert*-Butyl alcohol was distilled from calcium hydride. Benzophenone was recrystallized five times from ethanol with decolorizing carbon to mp 47.5–48°.

Quantum Yields for 1-Methylene-4,4-dimethylcyclohexadiene. Dilute solutions of 0.001–0.01 *M* 1-methylene-4,4-dimethylcyclohexadiene in purified pentane or *tert*-butyl alcohol were irradiated on the macro or micro photolysis apparatus to low conversion. No filter decay or change in optical density of photolysate was observed after photolysis. Mass analysis for starting material, 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene, and secondary photolysis product, 1,1-dimethylspiro[2.4]-4,6-heptadiene, was by Carbowax analytical vpc columns. *p*-Xylene and mesitylene were used as internal standards.

For runs I-02, I-03, and I-04, calculated quantum yields are corrected for the efficient secondary photolysis of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene using the known[6] quantum yields for conversion of the bicyclic diene to 1-methylene-4,4-dimethylcyclohexadiene (Φ = 0.039) and 1,1-dimethylspiro[2.4]-4,6-heptadiene (Φ = 0.041). Thus, the total mass of bicyclic diene formed photochemically is equal to the sum of the observed mass of bicyclic diene and 1.95 times the mass of spiroheptadiene observed. Data for individual quantum yields are listed as follows: mass starting material, added reagent if any, solvent, apparatus, filter or wavelength, temperature, light input, mass of photoproducts, mass of unreacted triene, conversion, and quantum yield of formation of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene.

Run I-01. Starting triene (745.8 mg, 6.215 mmol); 775 ml of pentane; macro; filter D; 25°; 0.81 mEinstein; 0.300 mg (0.0024 mmol) of bicyclic photoproduct; no spiro photoproduct; 754.6 mg (6.213 mmol) of unreacted triene; conversion, 0.39%; Φ = 0.00308.

Run I-02. Starting triene (285.0 mg, 2.380 mmol); 740 ml of pentane; macro; filter C; 25°; 5.19 mEinsteins; 0.834 mg (0.00694 mmol) of bicyclic photoproduct; 0.486 mg (0.00406 mmol) of spiro photoproduct; 284.0 (2.370 mmol) of unreacted triene; conversion, 0.60%; Φ = 0.00286.

Run I-03. Starting triene (97.1 mg, 0.810 mmol); 740 ml of pentane; macro; filter C; 25°; 3.14 mEinsteins; 0.284 mg (0.00236 mmol) of bicyclic photoproduct; 0.467 mg (0.00389 mmol) of spiro photoproduct; 95.5 mg (0.795 mmol) of unreacted triene; conversion, 1%; Φ = 0.00316.

Run I-04. Starting triene (213.3 mg, 1.775 mmol); 740 ml of pentane; macro; filter C; 25°; 6.19 mEinsteins; 0.650 mg (0.00542 mmol) of bicyclic photoproduct; 0.680 mg (0.00566 mmol) of spiro photoproduct; 212.2 mg (1.768 mmol) of unreacted triene; conversion, 0.93%; Φ = 0.00266.

Run I-05. Starting triene (10.7 mg, 0.0890 mmol); 49.0 mg (0.269 mmol) of benzophenone; 39.6 ml of *tert*-butyl alcohol; micro; 350 nm; 28°; 1.026 mEinsteins; no photoproducts; 7.9 mg (0.0659 mmol) of unreacted triene; conversion, 26%; $\Phi_{\text{disappearance}}$ = 0.0023

Run I-06. Starting triene (10.7 mg, 0.0890 mmol); 49.0 mg (0.269 mmol) of benzophenone; 39.6 ml of *tert*-butyl alcohol; micro; 350 nm; 28°; 1.384 mEinsteins; no photoproducts; 5.6 mg (0.0525 mmol) of unreacted triene; conversion, 41%; $\Phi_{\text{disappearance}}$ = 0.0026.

Quantum Yields. 1-Methylene-4,4-diphenylcyclohexadiene. Dilute solutions of 0.001–0.005 *M* 1-methylene-4,4-diphenylcyclohexadiene in *tert*-butyl alcohol or *n*-pentane were irradiated on the macro apparatus. No filter decay was observed after photolysis. A small (<10%) change in optical density is not corrected for. However, these quantum yields, which were run to different conversions, may be extrapolated, and the quantum yield at 0% conversion may be obtained. Photolyzed solutions were concentrated *in vacuo*. In runs II-02 and II-03, the residue was analyzed by nmr using 4-methoxybenzophenone as an internal standard. In the other runs, the residue was subjected to reverse-phase liquid–liquid chromatography on polystyrene beads as described above. In this case, quantum yields were determined gravimetrically by weighing appropriate fractions from the chromatogram. Data for individual quantum yields are listed as follows: mass starting material, added reagent if any, solvent, temperature, light input, mass of bicyclic photoproduct, mass of unreacted triene, conversion, and quantum yield of formation of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene.

Run II-01. Starting triene (1.100 g, 4.51 mmol); 740 ml of *tert*-butyl alcohol; filter C; 27°; 6.81 mEinsteins; 170 mg (0.696 mmol) of bicyclic photoproduct; 29 mg (0.119 mmol) of a mixture of bicyclic photoproduct and starting triene; 81 mg of unidentified material; 748 mg (3.07 mmol) of unreacted triene; conversion, 32%; Φ = 0.102.

Run II-02. Starting triene (381.7 mg, 1.565 mmol); 740 ml of pentane; filter D; 1.331 mEinsteins; 37.8 mg (0.153 mmol) of bicyclic photoproduct; 374.0 mg (1.53 mmol) of unreacted triene: conversion, 9.8%; Φ = 0.116.

Run II-03. Starting triene (406.6 mg, 1.670 mmol); 740 ml of *tert*-butyl alcohol; filter D; 1.346 mEinsteins; 41.3 mg (0.169 mmol) of bicyclic photoproducts; 362.0 mg (1.482 mmol) of unreacted triene; conversion, 10.1%; Φ = 0.125.

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(37) E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

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.

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[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]

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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

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[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).