(>80%) were acetic acid, unreacted acetate, and 1,2-dibromo-2-methylbutane by comparison (glpc retention time, ir, and ^{1}H nmr) with authentic samples. The unreacted acetate and 1,2-dibromide were isolated by distillation. The rotation of the acetate is recorded in Table III. The isolated dibromide was racemic.

Bromination of 1-Bromo-2-methylbutane with Bromine-81. 1-Bromo-2-methylbutane (0.11 g) and bromine-81 (60 mg) were degassed in a Pyrex ampoule and irradiated at 30° with two 200-W bulbs until the solution was colorless (0.5 hr). The unreacted 1-bromo-2-methylbutane and the 1,2-dibromo-2-methylbutane were isolated by glpc on the 20 ft × 0.25 in. glpc column packed with 15% diethylene glycol succinate at a temperature of 110°. The mass spectra of the compounds were recorded on an A.E.I. MS9 instrument. The 1-bromo-2-methylbutane had incorporated no additional bromine-81 and the dibromide had been formed by the incorporation of one atom of bromine-81 into each molecule of the bromobutane. The ratios of the parent peaks and M − 29 peaks averaged for three sets of spectra are given in Table IV.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

The Influence of Rotational Freedom on Excited Diene Reactivity. The Direct and Photosensitized Reactions of 5,5-Diphenyl-1,3-cyclohexadiene[1]

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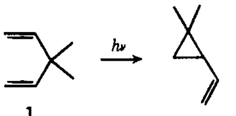
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received December 22, 1970*

Abstract: The direct and sensitized photochemistry of 5,5-diphenyl-1,3-cyclohexadiene (**7**) has been studied in detail. Direct excitation of **7** at 2537 Å afforded 1,1-diphenyl-1,3,5-hexatriene (**8**) in 80% yield; the structure of the triene was established by hydrogenation to 1,1-diphenylhexane. Sensitized photolysis of **7** with Michler's ketone (E_t = 61 kcal/mol), 2-acetonaphthone (E_t = 59.5 kcal/mol), or fluorenone (E_t = 53.3 kcal/mol) afforded two products in a ratio of 91:9 (80–90% yield). The major product was identified as *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**10**) and the minor product as *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (**12**) by comparison with synthesized authentic samples. In contrast, preparative irradiations using the high-energy sensitizers acetone (E_t > 75 kcal/mol), *m*-methoxyacetophenone (E_t = 72.4 kcal/mol), and benzophenone (E_t = 68.5 kcal/mol) yielded in addition to **10** and **12** moderate amounts of *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**11**). Quantum yield studies indicated that both the singlet- and triplet-excited states of the diene have reactive processes of moderate efficiency, $\Phi_{\text{dir}} = 0.35$ and $\Phi_{\text{sens}} = 0.26$. The results reported here are discussed in relation to the triplet reactivity of the diene chromophore in the di-π-methane rearrangement.

The recognition of the di-π-methane to vinylcyclopropane transformation (eq 1) as a general photochemical transformation by Zimmerman[3] has been followed by intense interest in this area. While numerous examples of this process now abound in the literature establishing its generality and synthetic usefulness, several mechanistic aspects of the reaction remain of general interest. One of these is the dependence of the multiplicity of the rearranging state on the structural character of the substrate.[4] Thus, molecules having the possibility of rotational freedom in the excited state (*i.e.*, acyclic olefins and dienes having exocyclic methylene groups) undergo rearrangement most efficiently in the excited singlet state.[5] The largest class of such compounds has conjugated diene and phenyl moieties as typified by **3**.[6,7] In contrast, rigid systems as exemplified by benzonorbornene (**5**) undergo rearrangement most efficiently in the triplet state (eq 3).[8,9]



(1)

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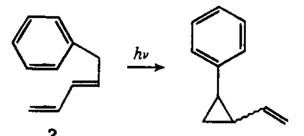

(2)

3 4

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[1] (a) For a preliminary report see J. S. Swenton, A. L. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970); (b) for a parallel study see H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

[2] (a) Ohio State University Fellow, 1970; (b) undergraduate research participant, 1969; (c) National Science Foundation undergraduate research participant, 1969.

[3] H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967).

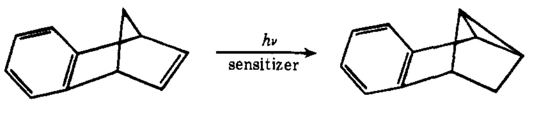
[4] H. E. Zimmerman and R. S. Mariano, *ibid.*, **91**, 1718 (1969).

[5] (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (b) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); (d) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967); (e) E. C. Sanford and G. S. Hammond, Paper 63, Western Regional American Chemical Society Meeting, Anaheim, Calif., Oct 6, 1969.

[6] Recently, examples of diphenylethylenes and styrenes as partners in the reaction have been reported. These species also react most efficiently in the singlet state: (a) ref 4; (b) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970); (c) *ibid.*, **92**, 6267 (1970). See also (d) M. Comtet, *ibid.*, **91**, 7761 (1969); (e) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

[7] The multiplicity of the rearranging state has not been completely established in several cases: R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, **91**, 2409 (1969); S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, 34, 2363 (1969); W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 5817 (1970). For these molecules either singlet and triplet give the same product, or intersystem crossing is facilitated by the aromatic ring, and both direct and sensitized reaction yield the triplet reactant.

[8] (a) E. Ciganek, *ibid.*, **88**, 2882 (1966); (b) J. R. Edman, *ibid.*, **88**, 3454 (1966); (c) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and

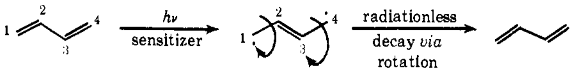


(3)

5 6

At the time this work was begun, we considered two plausible explanations for the lack of triplet reactivity for compounds such as **3** in the di-π-methane process. First, such systems possess formally nonconjugated phenyl and diene moieties. While this is certainly an oversimplification since some interaction between the chromophores is inevitable, the suggestion does lead to an interesting postulate. The singlet energies of the separate diene and phenyl species are comparable;[10] however, the diene triplet is much lower in energy than the aromatic triplet. Thus, the inertness of compounds such as **3** in the triplet state could be ascribed to the unreactive character of the low-energy diene triplet.

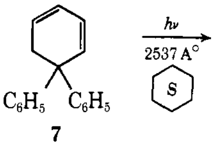
A second explanation was derived from our interest[14] in the importance of geometric change in modifying photochemical reactivity of the excited state. If isomerizations were important in radiationless processes as recently proposed by Noyes, *et al.*,[15] then acyclic diene triplets might have facile deactivation pathways *via* rotation about the 1,2 or 3,4 positions (eq 4).[16] If this proposal were correct, the low triplet reactivity of these phenyl-conjugated diene species would arise from facile deactivation of the triplet *via* rotation.



(4)

To distinguish between these two possibilities, 5,5-diphenyl-1,3-cyclohexadiene (**7**) was chosen for study. While the system possessed the formally nonconjugated phenyl and diene moieties, the incorporation of the diene linkage into a ring removed the possibility of free rotation about the ends of the diene system. Then, if an inert diene triplet were responsible for the low reactivity in these systems, compound **7** would be unreactive. However, if deactivation of the diene triplet resulted from rotation about bonds of low π-bond order in the excited state, the acyclic diene **7** should exhibit reactivity commensurate with other triplet states in this rearrangement.

Direct Irradiation of 5,5-Diphenyl-1,3-cyclohexadiene. While our primary concern was the triplet reactivity of **7**, for completeness we also investigated its direct photolysis. Preparative irradiation of **7** with either a 2537-Å source or Corex-filtered light from a 450-W medium-pressure source resulted in the formation of one major product in 80% yield. The nmr strongly suggested that the photoisomer was the triene (**8**):[17] τ 2.7 (s, 10 H), 2.83–3.33 (multiplet which was partly obscured by aromatic absorption, 2 H), 3.83–4.16 (multiplet, 2 H), and 4.48–5.00 (multiplet, 2 H). Complete confirmation of structure was obtained by hydrogenation of the photoproduct to the known hydrocarbon **9**.



7

$(C_6H_5)_2C{=}CHCH{=}CHCH{=}CH_2 \xrightarrow[H_2]{PtO_2} (C_6H_5)_2CH(CH_2)_4CH_3$ (5)

8 9

To establish the efficiency of the ring-opening reaction relative to other potential photochemical processes, quantum yields were measured for direct excitation. As noted in Table I, the measured quantum efficiencies decreased with per cent conversion of diene. Since the triene also showed strong absorption at 253.7 nm, the limiting quantum yield was calculated from an equation which took into account light absorption by the product triene.[18] The calculated values indicated the limiting efficiency of the process to be about 0.4.[19]

Product Identification from the Sensitized Reactions of 5,5-Diphenyl-1,3-cyclohexadiene. While the direct photolysis of **7** had proceeded *via* the well-known cyclohexadiene–hexatriene process, this reaction was

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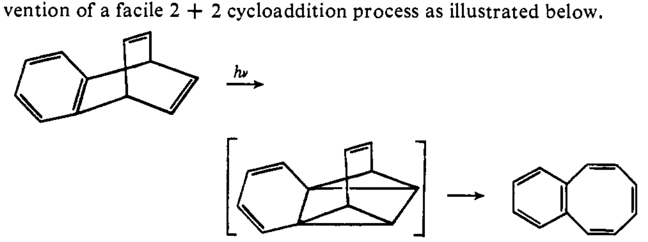
M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967); (d) J. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (e) P. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968); (f) R. S. H. Liu, *ibid.*, **90**, 215 (1968); (g) H. Hart and R. K. Murray, *ibid.*, **91**, 2183 (1969); (h) H. E. Zimmerman and C. O. Bender, *ibid.*, **92**, 4366 (1970).

(9) The low singlet state reactivity of rigid systems such as benzonorbornene[8a,b] and barrelene derivatives[8c–e] is probably due to the intervention of a facile 2 + 2 cycloaddition process as illustrated below.



(10) While it has been assumed that the benzene-like singlet is lowest,[11] this point does not appear firmly established. The benzene singlet is at 109 kcal/mol;[12] however, Srinivasan suggests that the 0–0 band for butadiene could be as low as 107 kcal/mol.[13]

(11) E. C. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 3497 (1970).

(12) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 254.

(13) R. Srinivasan, *Advan. Photochem.*, **4**, 117 (1966).

(14) A discussion on the importance of geometric change in the photochemistry of biaryls has been presented: J. S. Swenton, B. H. Williams, and T. Ikeler, Symposium on Excited State Chemistry, Paper 104, Western Regional American Chemical Society Meeting, Anaheim, Calif., Oct 7, 1969.

(15) D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, *Advan. Photochem.*, **5**, 329 (1968).

(16) In the more rigid systems this mode of energy dissipation would not be available; thus, these molecules would have maximum opportunity for rearrangement.

(17) The initially formed triene is undoubtedly the cis isomer. Even though the ir of the isolated triene showed only weak absorption in the area characteristic of a trans double bond (10.2–10.4 μ), the triene from these preparative irradiations may be a mixture of cis and trans isomers. Furthermore, the triene appeared to be somewhat unstable upon storage at room temperature. The uv spectrum of freshly prepared triene (cyclohexane) showed maxima at 318 (ε 16,100) and 233 nm (ε 14,700). Samples which had remained at room temperature for several days showed a similar wavelength distribution, but reduced extinction coefficients.

(18) The equation for calculating the quantum yield was

$$\frac{-d[\text{diene}]}{dt} = \frac{\epsilon_{\text{diene}}[\text{diene}]I\Phi}{\epsilon_{\text{diene}}[\text{diene}] + \epsilon_{\text{triene}}[\text{triene}]}$$

which upon integration yields

$$\Big[[\text{diene}]_0 - [\text{diene}]_t\Big]\left[1 - \frac{\epsilon_{\text{triene}}}{\epsilon_{\text{diene}}}\right] + \frac{\epsilon_{\text{triene}}}{\epsilon_{\text{diene}}}[\text{diene}]_0 \log_e \frac{[\text{diene}]_0}{[\text{diene}]_t} = I\Phi$$

In the equation $[\text{diene}]_0$ = initial diene concentration, $[\text{diene}]_t$ = diene concentration at time "t", I = light absorbed, ϵ_{triene} at 253.7 nm = 6250, and ϵ_{diene} at 253.7 nm = 2970. For simplification the reverse reaction of triene to cyclohexadiene was neglected in the kinetic scheme as it is of low efficiency relative to the forward reaction.

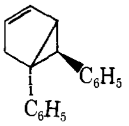
(19) The quantum efficiencies for the ergosterol–precalciferol and the lumisterol–precalciferol reactions are 0.26 and 0.41, respectively (ref 13, p 133).

Table I. Quantum Yields for Direct Irradiation of 5,5-Diphenyl-1,3-cyclohexadiene at 2537 Å

Run	Concn diene $\times 10^{-3}$ *M*	mE absorbed	% conversion of diene	Φ_{prod}	Φ_{diss}	Φ_{calcd}
1	1.67	0.099	18		0.31	0.39
2	1.67	0.132	25		0.32	0.43
3	1.71	0.198	33		0.29	0.42
4	1.71	0.325	44		0.24	0.39
5	1.71	0.650	61		0.17	0.40
6	1.67	0.065	16	0.43		
7	1.48	0.097	24	0.36		

undoubtedly that of a singlet state. To generate the triplet state of the diene we employed the usual triplet sensitization method. Since the expected triplet energy of **7** was low (*i.e.*, cyclohexadiene, E_t = 53.4 kcal/mol),[20] initial preparative studies were done with 2-acetonaphthone (E_t = 59.5 kcal/mol). Acetonaphthone should efficiently populate the diene triplet state yet should minimize complications often found with higher energy ketone sensitizers (hydrogen abstraction, oxetane formation, further sensitized reaction of photochemical products).

The 2-acetonaphthone-sensitized reaction of **7** proceeded cleanly in 80–90% yield to a 91:9 mixture of two products. From mechanistic considerations, we considered four possible structures, **10–13**, for the two observed photoisomers. Since spectroscopic data would at best be only suggestive in distinguishing between these and other possibilities (this is especially true for the cis–trans pairs), the syntheses of these four compounds were undertaken.



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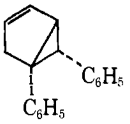
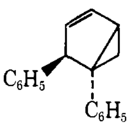
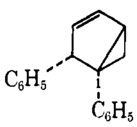


11

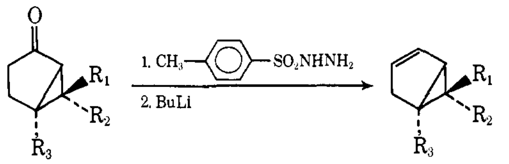


12



13

trans- **and** ***cis*****-5,6-Diphenylbicyclo[3.1.0]hex-3-ene, 10 and 11.** These compounds were readily prepared by conversion of the known ketones[21] **14** and **15** to the corresponding olefins **10** and **11** by the tosylhydrazone–butyllithium procedure.[22] The two olefins were isolated as crystalline solids exhibiting analytical and spectroscopic data consistent with the proposed structures. No evidence for rearranged products was noted under these mild conditions. Comparison of **10** with the major product from sensitized photolysis of **7** showed the two materials to be indistinguishable.



(6)

14, $R_1 = R_3 = C_6H_5$; $R_2 = H$

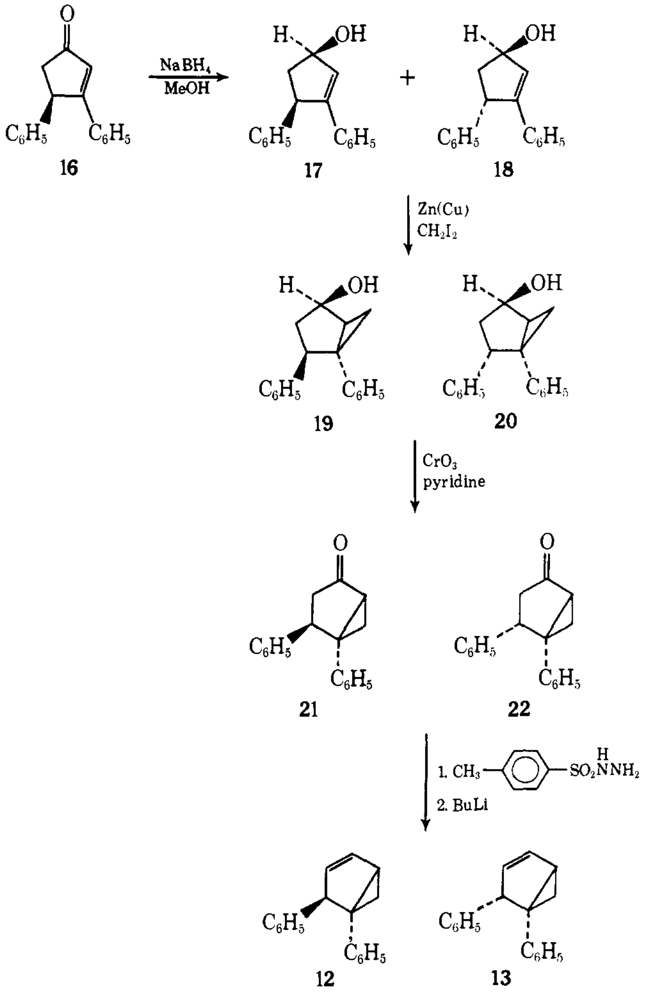
15, $R_1 = H$; $R_2 = R_3 = C_6H_5$

10, $R_1 = R_3 = C_6H_5$; $R_2 = H$

11, $R_1 = H$; $R_2 = R_3 = C_6H_5$

trans- **and** ***cis*****-4,5-Diphenylbicyclo[3.1.0]hex-2-ene, 12 and 13.** Having established the structure of the major photoisomer, there remained only the structure of the minor product. The synthesis of the remaining two isomers proved more formidable. As starting material we chose the readily available cyclopentenone, **16**. Reduction of **16** with sodium borohydride yielded a 75:25 mixture of two alcohols which could be separated by careful silica gel chromatography. The major product was assigned as **17** and the minor product as **18** on the basis of steric-approach control in the hydride reduction. Since the stereochemical assignment of the alcohols was critical to eventual establishment of product stereochemisty, additional support for product structure was sought. Meerwein–Ponndorf–Verley reduction of **16** yielded **17** and **18** as major products in a ratio of 1:2.[23] The reversal of product ratio in the MPV re-

Scheme I. Synthesis of *cis*- and *trans*-4,5-Diphenylbicyclo[3.1.0]hex-2-ene



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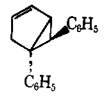
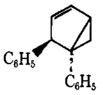
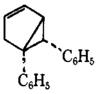
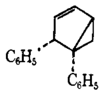
(20) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

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

(22) (a) R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967); (c) W. G. Dauben, M. E. Larber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *ibid.*, **90**, 4762 (1968).

(23) The different result noted in the MPV reduction from that previously reported by other workers [P. Blandon, S. McVey, P. L.

Table II. Preparative Sensitized Irradiation of 5,5-Diphenyl-1,3-cyclohexadiene[a]

Run	Diene, g	Sensitizer (E_t, kcal/mol)	Conditions	Composition, %				Yield,[c,d] %
								
1	0.32	2-Acetonaphthone[b] (59.5)	0.5 hr, benzene	91	9	<1	<1	87
3	0.34	Michler's ketone[b] (61)	0.5 hr, ether	89	11	<1	<1	80
3	0.34	Fluorenone[b] (53.3)	0.5 hr, ether	90	10	<1	<1	81
4	0.30	Acetone (>75)	1 hr, acetone solvent	73	9	18		80
5	0.30	*m*-Methoxyacetophenone[b]	1 hr, benzene	76	15	9	<1	81
6	0.30	Benzophenone[b,e] (68.5)	1 hr, benzene	61	12	27	<1	33

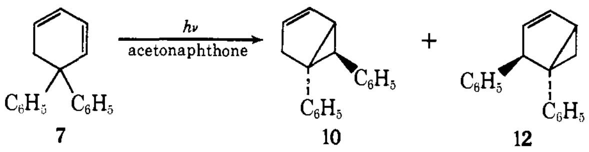
[a] Irradiations performed on 150 ml of solution under purified nitrogen using Pyrex-filtered light from a 450-W Hanovia medium-pressure source. [b] 0.3 g of sensitizer in 150 ml of solvent. [c] Analyses were performed on the crude reaction mixture using 2-acetonaphthone or fluorenone as calibrated standards. [d] Product ratios determined by vpc and nmr integration of the vinyl region were within ±1%. [e] Benzophenone is a particularly poor sensitizer for the production of **10** and **12** from **7**. The other products formed in the benzophenone sensitizations were not investigated further.

Table III. Quantum Yields of Sensitized Photolyses of 5,5-Diphenyl-1,3-cyclohexadiene

Run	Concn diene $\times 10^{-3}$ *M*	Sensitizer	mE absorbed	% conversion of diene	Φ_{diene}	Φ_{prod}
1	9.44	2-Acetonaphthone	0.46	15	0.23	0.26
2	8.53	2-Acetonaphthone	0.31	16	0.25	0.27
3	8.53	2-Acetonaphthone	0.46	19	0.20	0.27
4	8.53	2-Acetonaphthone	0.54	24	0.24	0.25
5	9.89	Benzil	0.29	15	0.32	0.26
6	9.89	Benzil	0.43	21	0.28	0.23

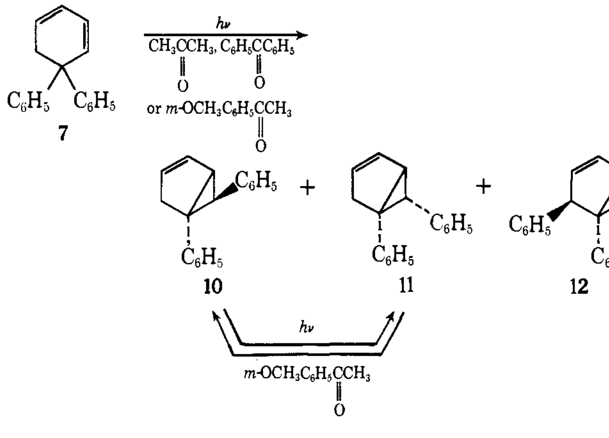
duction *vs.* the sodium borohydride route further supported the stereochemical assignment for **17** and **18**.

Having available the epimeric alcohols **17** and **18** and utilizing the known directive effect of the hydroxyl group in the Simmons–Smith reaction,[24] the essential product stereochemistry was then established. Oxidation of the cyclopropyl alcohols **19** and **20** followed by conversion of the resulting ketones to the olefins **12** and **13** completed the synthetic work (see Scheme I). The trans isomer showed vpc retention times and nmr and ir spectra identical with the minor photoproduct. Thus, the reaction sequence can be written as



(7)

Effect of Sensitizers on Product Yields of 7 and the Efficiency of the Reaction. While the essential qualitative aspects of the sensitized chemistry had been established, we briefly examined the effect of sensitizers on the rearrangement.[25] With sensitizers having triplet energies of 53.3–61 kcal/mol the products were only **10** and **12**, while sensitization with pyrene (E_t = 48.7 kcal/mol) was totally ineffective. Furthermore, it was established that **10** was stable to acetonaphthone sensitization indicating that **12** was not formed by a secondary process from **10**. The results with the high-energy sensitizers, benzophenone (E_t = 68.5 kcal/mol), *m*-methoxyacetophenone (E_t = 72.4 kcal/mol), and acetone (E_t > 75 kcal/mol), were somewhat different. Preparative irradiations of **7** using these sensitizers yielded in addition to **10** and **12** significant amounts of **11**. Since **10** and **11** were interconverted under *m*-methoxyacetophenone sensitization, the formation of **11** (Table II, runs 4–6) was reasonable due to further photolysis of initially formed **10**. To establish this supposition, the time dependence of the ratio of **11**/**12** in the *m*-methoxyacetophenone sensitization was determined.[26] When the reaction was followed by vpc, no **11** could be detected until nearly all the diene **7** was consumed.



(8)

The remaining point to be established was the quantum efficiency of the sensitized reaction. Table III records the quantum yields for the photosensitizer reaction of **7** at 350 nm. The average value for diene disap-

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Pauson, G. D. Broadhead, and W. M. Horspool, *J. Chem. Soc. C*, 306 (1966)] apparently stems from the difficulty in separating the two alcohols **17** and **18** by chromatography and the similarity of their spectroscopic properties (see Experimental Section).

(24) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

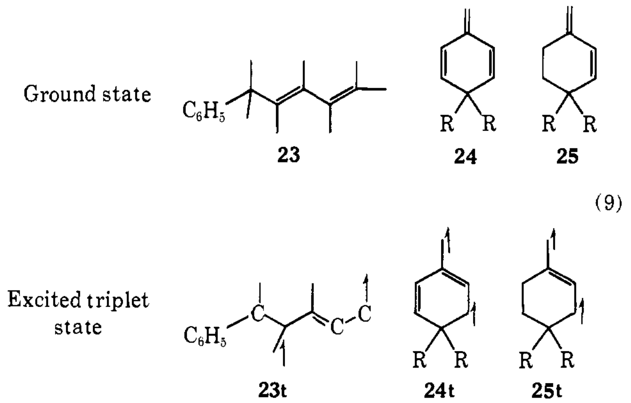
(25) It was previously suggested that the products from sensitized photolysis of **7** were sensitizer dependent.[1b] From the results delineated below, the only reaction which is sensitizer dependent is the photolysis of **10** to give **11**.

(26) Ideally the time dependence of the **10**:**11** ratio should be followed. However, the complete separation of **10** from starting diene was difficult under conditions in which **12** was resolved from **10**.

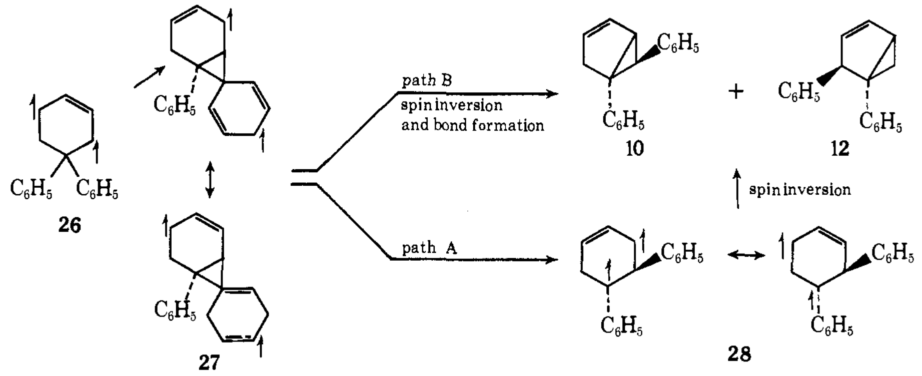
pearance (Φ_{diene}) was 0.24 while the sum of the product appearance yields (Φ_{prod}) was 0.26. These determinations, together with the results from the direct irradiations (*vide supra*), established that both the singlet and triplet excited states of **7** have available photochemical processes of moderate efficiency. Thus, **7** is one of the small number of molecules exhibiting different intramolecular photochemistry of similar efficiency emanating from states of different multiplicity.

Discussion

The work presented here has shown that the cisoid diene moiety of **7** is capable of efficient involvement in the di-π-methane process. These results convincingly demonstrate that the low-triplet reactivity of systems such as **23–25** in this reaction was not due to the inherent lack of reactivity of the low-energy diene triplet. Rather it appears reasonable to attribute the reduced triplet reactivity in these substrates to deactivation mechanisms involving rotation about linkages of low π-bond order in the excited triplet state, **23t–25t**.



(9)



(10)

Since *a priori* the singlet states of these dienes (*i.e.*, **23**, **24**, **25**) are also subject to rotational deactivation, one might inquire why reaction occurs in the excited singlet state. That rotation does occur about the 1,2-(3,4)-diene linkage in the singlet state is known from recent work on the 1,3-pentadienes[27a] and 2,4-hexadienes.[27b,c] Interestingly, however, the mechanism for the singlet-state isomerization differs markedly from the triplet-state process.[28] While the interpretations of the singlet-state reactions are not completely clear, two points are worth noting. First, for some molecules the singlet-state isomerization (*i.e.*, *trans*- to *cis*-1,3-pentadiene) is less facile than the triplet-state reaction. Second, the results indicate that the lifetime of the excited diene singlet is very short. Thus, one rationale for the singlet-state chemistry of **23–25** is that the rate of rearrangement *vs.* the rate of rotational deactivation may be larger in the singlet than in the triplet state. However, in view of the very short lifetime of the diene singlet, the fundamental reason for the singlet reactivity of **23–25** is the extremely rapid rate of the singlet di-π-methane process.

Another interesting point noted here is the large predominance of **10** *vs.* **12** (91:9) from **7** and the exclusive trans stereochemistry of the products. If the reaction of triplet diene **26** is viewed as proceeding by diradical **28** (path A), then the preference of ring closure to give **10** over **12** must be explained. This selectivity does not reflect ground-state thermodynamics, as thermal equilibration of **10** and **12** in the temperature range 130–190° gives an equilibrium mixture of 60% **10** and 40% **12**; thus, the product ratio is determined by some kinetic factor in the excited state. From consideration of models it is tenuous to conclude ring closure is more favorable to give **10** due to steric factors, especially since the geometry of the excited state is unknown. A rationale preferable to us is that the triplet reactivity of **7** is subject in some degree to orbital symmetry control. This mechanism as crudely depicted in eq 10 (path B) shows that spin inversion in the bridged species precedes or is concerted with product formation. As noted by Woodward and Hoffman, orbital symmetry relationships may dictate to an excited molecule one set of motions which is facile and another set which is difficult.[30] The predominance of **10** may then be attributed to an allowed process in the excited state (a ${}_{\sigma}2_{\text{A}} + {}_{\pi}2_{\text{A}}$ interconversion) *vs.* the forbidden reaction to yield **12** (a ${}_{\sigma}2_{\text{A}} + {}_{\pi}4_{\text{A}}$ process). That a triplet state is the reactant does not prevent orbital symmetry control from being

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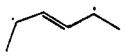
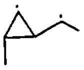
(27) (a) S. Boúe and R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 3226 (1970); (b) R. Srinivasan, *ibid.*, **90**, 4498 (1968); (c) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

(28) Evidence suggests the triplet-sensitized 2,4-hexadiene isomerization proceeds *via* a 1,4-biradical intermediate, *i.e.*,



and has the consequence that one quantum of light isomerizes both ends of the diene system.[29] In contrast, the proposed intermediate for the direct cis–trans isomerization of 1,3-pentadienes and 2,4-hexadienes is the cyclopropylmethylene intermediate[27a,c]



This process involves cis–trans isomerization at only one end of the diene system.

(29) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

(30) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., p 100.

important, as intersystem crossing to the ground state or product may occur readily along the reaction pathway. It is unfortunate that the product ratio from the triplet reaction could not be compared with that from the singlet process. However, the ring opening of diene **7** to the hexatriene **8** apparently is much more facile than the potential but not observed di-π-methane process. Further work is in progress to compare the product ratio for this type of reaction from states of differing multiplicity.

Experimental Section

Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer. Uv spectra were determined with a Cary 14 recording spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. Nmr spectra were measured at 60 MHz using tetramethylsilane as internal standard. All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were carried out in an atmosphere of purified nitrogen.

Preparation of 5,5-Diphenylcyclohexadiene (7). A mixture of 12.40 g (0.05 mol) of 4,4-diphenylcyclohex-2-en-1-one, 9.30 g (0.05 mol) of *p*-toluenesulfonylhydrazine, 0.5 ml of concentrated hydrochloric acid, and 150 ml of tetrahydrofuran was stirred and refluxed for 24 hr. After the addition of 100 ml of anhydrous benzene, the solvent and benzene–water azeotrope were distilled off. The residual oily solid was dried *in vacuo*, dissolved in 250 ml of anhydrous benzene, and cooled in an ice bath. To the stirred cooled solution under a nitrogen atmosphere was added *via* syringe 40 ml of butyllithium (22.7 wt % in hexane) over a period of 1 hr. After addition, the ice bath was removed, and the reaction mixture stirred at room temperature for 2 hr. The reaction mixture was then refluxed for 0.5 hr on the steam bath and finally poured into 250 ml of water. The organic material was extracted with ether (two 250-ml portions) and the ether layer washed with 10% sodium bicarbonate (two 75-ml portions) and water (100 ml). The ether solution was dried over calcium chloride and the solvent removed *in vacuo*. The crude product was purified by chromatography on silica gel (2.3 × 80 cm column). Elution proceeded as follows: 1% ether–hexane, 0.4 l., nil; 1% ether–hexane, 1 l., 4.5 g of the desired 5,5-diphenylcyclohexadiene. Recrystallization of this material from hexane yielded 3.9 g (34%) of pure material:[31] mp 56–58°; ir (KBr) 6.23 (w), 6.72 (m), 6.95 (m), 9.31 (m), 12.50 (m), 13.15 (s), 14.20 (s, broad), 14.55 (s); nmr (CCl_4) τ 2.85 (s, 10 H), 3.83–4.00 (m, 2 H), 4.08–4.30 (m, 2 H), 7.10–7.20 (m, 2 H).

Preparative Irradiation of 5,5-Diphenyl-1,3-cyclohexadiene (7). A mixture of 1.00 g (4.3 mm) of the diene and 0.6439 g of 2-acetonaphthone in 150 ml of benzene was irradiated for 2 hr in a stirred reactor under nitrogen with Pyrex-filtered light from a 450-W Hanovia medium-pressure source. The solvent was removed on the rotary evaporator, and the residual light yellow oil chromatographed on Silica Gel (90 × 2.4 cm column slurry packed in 1% ether–hexane). Elution proceeded as follows: 1 l., 1% ether–hexane, nil; 1.25 l., 2% ether–hexane, nil; 0.45 l., 2% ether–hexane, 0.95 g of light yellow oil analyzing by vpc (5 ft × 1/8 in., 5% SE-30 on Varaport 30, injector temperature 160°, column temperature 145°) as a 90:10 mixture of **10** and **12**. Recrystallization of the oil from 95% ethanol yielded 0.74 g of **10** as white crystals, mp 52–55° (97% pure by vpc). Careful preparative vpc chromatography (5 ft × 1/4 in., 5% SE-30 on 60–80 Chromosorb P, injector 170°, column 146°, and collector 149°) yielded **12** as a colorless oil. Inspection of both the crude reaction mixture and the mixture after chromatography showed none of the corresponding cis isomers to be present. The vpc retention times (0.125 in. × 5 ft 5% SE-30 on 100–120 mesh Varaport 30, injection temperature 150°, column temperature 145°) were as follows: *cis*-4,5-diphenyl-, 8.5 min; *cis*-5,6-diphenyl-, 10.5 min; *trans*-4,5-diphenyl-, 11.5 min; *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene, 12.5 min.

Photochemical Preparation of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one, 14 and 15. A solution of 6.0 g of 4,4-diphenylcyclohex-2-en-1-one in 1 l. of benzene was irradiated under a nitrogen atmosphere with a 450-W Hanovia medium-pressure source (Pyrex filter) for 40 hr.[32] The reaction is conveniently followed by vpc (5% SE-30 on 100–120 mesh Varaport 30, 155°). The retention times were as follows: cis photoketone (26 min), trans photoketone (29 min), and starting enone (32 min). Removal of the solvent *in vacuo* yielded a yellow oil which was chromatographed on silica gel (100 × 2.5 cm). Elution proceeded as follows: 5% ether–hexane, 2 l., nil; 8% ether–hexane, 2 l., nil; 10% ether–hexane, 2 l., 2.9 g (48%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one after one recrystallization from hexane–methylene chloride, mp 74–76° (lit.[21] 73–74°); 10% ether–hexane, 0.5 l., nil; 10% ether–hexane, 4 l., 2.0 g (33%) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one after one recrystallization from hexane–methylene chloride, mp 116–118° (lit.[21] 116–118°).

***cis*-5,6-Diphenylbicyclo[3.1.0]hex-2-ene (11).** A mixture of 1.0 g (4.02 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**15**) and 0.76 g (4.04 mmol) of *p*-toluenesulfonylhydrazine was dissolved in 10 ml of tetrahydrofuran, one drop of hydrochloric acid was added, and the solution was refluxed for 8 hr. After removal of the water formed by azeotropic distillation with benzene (150 ml), concentration *in vacuo* yielded a yellow oil. In a similar manner to that described (*vide supra*) this material was treated with 6.0 ml of 22% butyllithium in hexane. The usual work-up yielded 1.2 g of yellow oil which was chromatographed on silica gel (60 × 2 cm column slurry packed in hexane). Elution proceeded as follows: hexane, 500 ml, nil; 1% ether–hexane, 500 ml, nil; 2% ether–hexane, 500 ml, 0.389 g (432) of light yellow oil homogeneous by vpc. Upon standing in the refrigerator, the oil crystallized. Sublimation, followed by recrystallization from 95% ethanol, yielded the analytical sample, mp 69–70°; the ir (KBr) showed the characteristic absorption of unsaturated and aromatic linkages at 6.23 (m), 13.13 (s), 14.05 (s), and 14.35 μ; the nmr (CCl_4) showed the aromatic protons (10 H) as a complex multiplet τ 3.08–3.50, the two vinyls as multiplets centered at 3.93 (1 H) and 4.50 (1 H), the methylene protons as a broad singlet at 7.14 (2 H), and the cyclopropyl hydrogens at 7.45 (broad singlet, 1 H), 8.20 (broadened doublet, J = 4.5 Hz, 1 H).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.94; H, 6.98.

***trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-ene (10).** In a procedure analogous to that utilized for the cis isomer, 1.0 g (4.02 mmol) of **14** was converted to its tosylhydrazone and this with butyllithium to the *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene. Chromatography of the reaction mixture on silica gel (60 × 2 cm column slurry packed in 1% ether–hexane) proceeded as follows: 1% ether–hexane, 1.2 l., nil; 2% ether–hexane, 500 ml, 0.50 g (53%) of yellow oil which was homogeneous by vpc and crystallized on standing. Sublimation followed by recrystallization from 95% ethanol yielded analytically pure material: 0.38 g; mp 56–57°; the ir (KBr) showed the characteristic absorption of unsaturated and aromatic linkages at 6.23 (m), 13.05 (m), 13.14 (m), 13.56 (s), 13.68 (s), 14.06 (m), and 14.35 (s) μ. The nmr (CCl_4) showed in the aromatic region two partially resolved singlets at τ 2.93 and 3.00 (10 H). The vinyl hydrogens appeared as multiplets centered at τ 4.28 (1 H) and 4.90 (1 H). The high-field absorptions occurred from τ 7.09 to 7.66 (4 H) with the main signal occurring at 7.45.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.19; H, 6.82.

Meerwein–Ponndorf–Verley Reduction of 3,4-Diphenylcyclopent-2-en-1-one (16). A mixture of 2.4 g (14.5 mm) of 3,4-diphenylcyclopent-2-en-1-one, 40 ml of toluene, 40 ml of *N*-methylpyrrolidone, and 80 ml of 2-propanol was stirred and refluxed (bath temperature 100–105°) for 9 hr. During this time 350 ml of distillate was collected, the volume of the solution being maintained approximately constant by the addition of fresh isopropyl alcohol. The reaction mixture was poured onto 50 g of ice, 200 ml of 5% sodium hydroxide was added, and the organic material was extracted with ether (two 100-ml portions). After washing the ether extracts with saturated sodium chloride, drying over calcium sulfate, and removal of the ether *in vacuo*, there was obtained a reddish-yellow oil. Chromatography of this material on silica gel (70 × 2 cm column, 20% ether–hexane) yielded 3.0 g of a mixture of ketone **16** and alcohols **17** and **18**. The nmr analysis of the mixture showed the following composition: 35% starting ketone **16**, 21% **17**, and 44% **18**. Complete separation of the two epimeric alcohols on silica gel or alumina proved difficult. The most successful procedure involved chromatography on Davidson silica gel

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[31] This preparation had been previously reported without details (ref 23c) to yield 7 in 55% yield (no melting point reported).

[32] This procedure was modified to afford appreciable quantities of both **14** and **15** from the published procedure of H. E. Zimmerman and K. G. Hancock, *J.Amer. Chem. Soc.*, **90**, 3749 (1968).

using 15% ether–hexane as eluent. This provided a partial separation of the two alcohols, **18** being obtained pure by careful recrystallization of the latter alcohol fractions. The ir spectrum provided the most facile means of differentiating between **17** and **18**. Whereas **17** shows a strong doublet in the ir (KBr) at 10.18 and 10.32, **18** shows only very weak absorption in this region. Pure **18** obtained from crystallization of the latter chromatographic fractions from hexane–methylene chloride had: mp 98–100°; ir (KBr) 3.09 (s, broad), 6.72 (s), 6.93 (s), 7.53 (s), 7.91 (m), 9.43 (s, broad), 9.73 (s), 9.91 (s), 13.13 (s), 13.29 (s), 14.36 (s), 14.61 (s) μ; nmr ($CDCl_3$) τ 2.76 (structured s, 10 H), 3.55 (broad s, 1 H), 4.84 (broad s, 1 H), 5.47 (broad s, 1 H), 7.42–7.83 (m, 3 H).

Sodium Borohydride Reduction of 3,4-Diphenylcyclopent-2-en-1-one (16). To a stirred solution of the ketone, 10 g (43 mmol), in 200 ml of anhydrous methanol, was added portionwise 3.0 g (79 mmol) of sodium borohydride. After stirring for 0.5 hr, 50 ml of water was added and the solution was heated to reflux for 0.25 hr. Removal of the methanol yielded a solid residue which was transferred with 100 ml of ether to a separatory funnel. The organic phase was washed successively with 100 ml of water and 100 ml of saturated sodium chloride solution and then dried over Drierite. Distillation of the solvent yielded 9.5 g of white solid, mp 98–105°. Analysis of this mixture of alcohols by nmr showed 75% **17** and 25% **18**. Three careful recrystallizations of the alcohol fraction from hexane–chloroform yielded 3.9 g of pure **17**: mp 108.5–110.5° (lit.[23] mp 107–108.5°); ir (KBr) 3.02 (s), 3.30 (m), 3.45 (m), 6.23 (m), 6.73 (m), 6.93 (m), 7.12 (m), 7.49 (s), 7.68 (m), 7.83 (m), 8.08 (m), 9.31 (m), 9.35 (m), 9.57 (s), 9.78 (m), 10.15 (s), 10.30 (s), 11.68 (m), 11.78 (m), 13.10 (s), 14.24 (s), 14.50 (s) μ; nmr ($CDCl_3$) τ 2.83 (s, 10 H), 4.55 (t, 1 H), 5.08 (broad s, 1 H), 5.77 (structured q, 1 H), 7.04 (structured eight-line signal, 1 H), 8.00–8.50 (m, 2 H).

Simmons–Smith Reaction of 18. The Simmons–Smith reagent was formed by gently warming a mixture of 0.7 g of zinc–copper couple, 0.8 g (3 mmol) of methylene iodide, and a crystal of iodine in 20 ml of anhydrous ether until reaction was initiated. To this preformed reagent, a mixture of 1.6 g (6 mmol) of methylene iodide and 0.30 g (1.3 mmol) of **18** in 5 ml of anhydrous tetrahydrofuran was added dropwise, the addition being noticeably exothermic. After 20 min of refluxing and stirring, an additional 3 g of zinc–copper couple was added and the reaction refluxed for an additional 7 hr (bath temperature 40–45°). The reaction mixture was filtered through Celite; the combined filtrate and ether washings were successively extracted with saturated ammonium chloride (three 60-ml portions), 10% sodium bicarbonate (three 60-ml portions), and saturated sodium chloride (three 60-ml portions). Removal of the solvent from the calcium sulfate dried organic phase yielded an oil which was chromatographed on silica gel (15 × 1.5 cm column) slurry packed in 5% ether–hexane. Elution proceeded as follows: 200 ml each of 5, 10, and 20% ether–hexane, nil; 200 ml each of 35 and 50% ether–hexane, 0.29 g of colorless oil. Trituration of the oil with ether–hexane yielded a white solid, mp 86–88°, which was recrystallized from hexane–methylene chloride to yield 0.14 g (47%) of **20** as white needles: mp 90–91°; ir (KBr) 3.05 (s), 3.30 (m), 3.40 (m), 6.72 (m), 6.92 (m), 7.49 (m), 9.52 (s), 9.72 (m), 13.10 (broad, s), 13.30 (s), and 14.30 (broad, s) μ.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.14; H, 7.34.

***cis*-4,5-Diphenylbicyclo[3.1.0]hexan-2-one (22).**[33] To a solution of Sarett reagent formed from 0.8 g of chromium trioxide and 9 ml of pyridine was added 0.10 g (4 mm) of **20** dissolved in 2 ml of pyridine. After the reaction mixture had stirred for 12 hr under a nitrogen atmosphere, 50 ml of ether was added and the inorganic salt filtered off using a Celite pad. The combined filtrate and ether washings were washed with water (50 ml), 5% hydrochloric acid (three 70-ml portions), 10% sodium bicarbonate (two 70-ml portions), and saturated sodium chloride solution (two 70-ml portions). After drying the ether solution over Drierite, removal of solvent yielded a clear oil which crystallized upon trituration with hexane–ether to yield 0.059 g (59%) of **22**. Recrystallization of this material from hexane–methylene chloride yielded the analytical sample: mp 75–76°; the ir (KBr) showed numerous sharp absorptions, the most intense bands being due to the carbonyl (5.79 μ) and the aromatic absorptions (12.80, 13.10, 14.40).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 87.06; H, 6.50. Found: C, 86.91; H, 6.38.

Simmons–Smith Reaction of 17. The Simmons–Smith reagent was formed by gently warming a mixture of 9 g (34 mmol) of methylene iodide, 3.5 g (27 mmol) of zinc–copper couple, and 60 ml of anhydrous ether containing a crystal of iodine until a vigorous exothermic reaction initiated. After the exothermic reaction had subsided, the alcohol, 3.06 g (13 mmol) dissolved in 40 ml of tetrahydrofuran–ether (3:1), was added dropwise to the preformed Simmons–Smith reagent; the addition was noticeably exothermic. The reaction mixture was refluxed (bath temperature 50–55°) and vigorously stirred for 24 hr; then the resulting purple brown solution was filtered through Celite. The filtrate and ether washings (*ca.* 100 ml) were extracted with saturated ammonium chloride (four 60-ml portions), 10% sodium bicarbonate (three 60-ml portions), and saturated sodium chloride (three 60-ml portions). After drying the organic phase over calcium sulfate and removal of solvent *in vacuo*, there was obtained a light yellow oil which crystallized upon trituration with hexane yielding 2.2 g (67%) of **19** as white crystals, mp 104–106°. Recrystallization from hexane–chloroform yielded analytically pure material: mp 105.0–106.5°; ir (KBr) 3.02 (s), 3.30 (m), 3.48 (m), 6.23 (m), 6.75 (s), 6.96 (m), 7.58 (m), 9.13 (m), 9.3–9.7 (s, structured), 10.13 (s), 13.24 (s, structured), and 14.35 (s) μ.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.19; H, 7.27.

***trans*-4,5-Diphenylbicyclo[3.1.0]hexan-2-one (21).** To a solution of Sarett reagent formed from 1.0 g of chromium trioxide and 12 ml of pyridine was added 0.5 g (2 mmol) of **19** dissolved in 3 ml of pyridine. After the reaction mixture had stirred for 24 hr under nitrogen, 50 ml of ether was added and inorganic salts filtered through Celite. The filtrate and benzene washings (75 ml) were extracted successively with 5% hydrochloric acid (five 50-ml portions), 10% sodium bicarbonate (two 50-ml portions), and saturated sodium chloride (two 50-ml portions). After drying the organic phase over calcium sulfate, removal of the solvent *in vacuo* yielded an oily residue which slowly recrystallized. Recrystallization of this material from hexane–methylene chloride yielded 0.34 g (68%) of white crystalline material, mp 92–95°. Further recrystallization yielded the analytical sample, 95–96°. The ir (KBr) showed numerous sharp medium-intensity absorptions; characteristic strong absorptions occurred at 5.77, 13.20, 13.38, 14.30 μ (broad). The 12.80–13.40 region served as a convenient region for differentiating the trans isomer **21** from the cis isomer **22**.

***cis*-4,5-Diphenylbicyclo[3.1.0]hex-3-ene (13).** A mixture of 2.0 g (8 mmol) of **22** and 1.5 g (8 mmol) of *p*-toluenesulfonylhydrazine was dissolved in 50 ml of 95% ethanol, 0.1 mmol of concentrated hydrochloric acid was added, and the mixture was refluxed on the steam bath for 0.5 hr. Removal of the solvent on the rotary evaporator afforded a foamy solid which showed the complete absence of the carbonyl absorption in the ir. After drying overnight *in vacuo*, the crude tosylhydrazone was dissolved in 50 ml of anhydrous benzene and cooled to 0° in the ice bath. To this stirred cooled solution was added 14 ml of butyllithium (1.33 *M* in hexane) over a period of 15 min. The color of the light yellow solution remained unchanged during the addition of the first 6–7 ml, then gradually became redder during addition of the remaining butyllithium, finally affording a dark orange reaction mixture. After refluxing on the steam bath for 15 min, the dark red reaction mixture was quenched with water and worked up in the usual manner. The dark oil after distillation of the ether was chromatographed on silica gel using 2% ether–hexane as eluent to afford 1.1 g of yellow oil homogeneous by vpc. Crystallization proved futile, but sublimation of the oil onto a Dry Ice cooled cold-finger at 0.1 mm yielded 0.65 g (35%) of **24** as a white crystalline solid; mp 52–57°. The analytical sample had mp 58–59°; ir (KBr) 3.29 (m), 6.23 (m), 6.72 (m), 6.95 (m), 9.34 (m), 9.62 (m), 9.79 (m), 10.21 (m), 10.84 (m), 10.02 (m), 12.01 (s), 12.12 (s), 12.72 (s), 13.37 (s), 13.94 (s), and 14.42 (s, and broad) μ; nmr (CCl_4) τ 3.00 (10 H, doublet), 3.66 (1 H, mult), 4.31 (1 H, mult), 5.86 (1 H, mult), 7.69 (1 H, mult), 8.70 (1 H, quartet, J = 3, 8 Hz), 9.32 (1 H, triplet, J = 3 Hz).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.80; H, 7.15.

***trans*-4,5-Diphenylbicyclo[3.1.0]hex-2-ene (12).** In a procedure analogous to that for the cis isomer, 2.0 g (8 mmol) of **21** was converted to the tosylhydrazone and subsequently treated with butyllithium. Preparative thin-layer chromatography (silica gel, hexane eluent) of the resulting yellow oil (1.3 g) yielded 0.8 g of a colorless

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(33) The poor yields obtained in the MPV reduction and the difficulty of separating either **17** from **18** or **19** from **20** do not make this route attractive for the preparation of **22**. It proves much more convenient to carry out the Simmons–Smith reaction and the Sarett oxidation on a mixture of **17** and **18** from the sodium borohydride reduction. The two ketones **21** and **22** can then be separated by elution chromatography on Woelm activity II neutral alumina using benzene–hexane elution.

oil. All attempts at crystallization failed even though the material appeared homogeneous by vpc and showed the expected spectroscopic properties. In contrast to the other olefins synthesized, this material was especially prone to thermal and base-catalyzed rearrangement. The homogeneous clear oil showed: exact mass, 232.1249 observed *vs.* 232.1251 calculated; ir (neat) 3.27 (m), 6.23 (m), 6.69 (m), 6.91 (m), 9.18 (m), 9.28 (m), 9.38 (m), 9.67 (m), 11.80 (m), 12.20 (m), 12.60 (m), 13.20 (s), 13.80 (s), 14.35 (s) μ; nmr (CCl_4) τ 2.82 (10 H, mult), 3.82 (1 H, mult), 4.38 (1 H, quartet), 5.45 (1 H, mult), 8.00 (1 H, mult), 8.92 (1 H, quartet, $J = 4, 8$ Hz), 9.40 (1 H, triplet, $J = 4$ Hz).

Direct Irradiation of 5,5-Diphenylcyclohexadiene (7). A degassed stirred solution of 0.40 g of 5,5-diphenylcyclohexadiene in 75 ml of cyclohexane was irradiated for 9 hr through quartz with a bank of 16 RPR 2537-Å lamps (New England Ultraviolet Co.). The vpc (5 ft × $^1/_8$ in., 5% SE-30 on Aeroport 30) indicated greater than 97% conversion of starting material and the formation of one major product in greater than 80% yield as determined by vpc integration. Isolation of the product by chromatography on neutral alumina yielded a colorless oil which readily polymerized on standing at room temperature. The nmr showed τ 2.77 (s, 10 H), 2.83–3.33 (mult partly obscured by aromatic absorption, 2 H), 3.83–4.16 (mult, 2 H), and 4.48–5.00 (mult, 2 H).[34]

In a second experiment, 0.40 g of 5,5-diphenyl-1,3-cyclohexadiene in 75 ml of cyclohexane was irradiated identically as described above. The crude photolysis mixture was then hydrogenated using 0.10 g of platinum oxide as catalyst (36 psi at room temperature for 21 hr). The yield of 1,1-diphenylhexane by vpc was 82%. The vpc-purified material showed an identical retention time and ir and nmr spectra with authentic material.[35]

Quantum Yield for Disappearance of 7 at 2537 Å. The quantum yield for diene disappearance was measured by irradiating 10 ml of about 1.7 × 10^{-5} *M* **7** in purified cyclohexane in quartz test tubes using four RPR 2537-Å lamps in a merry-go-round apparatus. The solution was purged with purified nitrogen prior to irradiation and the sample was sealed. Potassium ferrioxalate[36] actinometry gave light intensities on the order of 6.5 × 10^{-3} mE/(min)(10 cm^3). The solution was analyzed by flame ionization vpc (12 ft × $^1/_8$ in. column, 5% Carbowax 20M on 60–80 mesh Chromosorb G at 180°) using 2-acetonaphthone as standard. For good precision it was necessary to calibrate the instrument immediately prior to analysis with known mixtures of diene **7** and 2-acetonaphthone. The results of these studies are given in Table I.

Quantum Yields for Sensitized Reactions of 7. The quantum yields for the sensitized reactions of **7** were conducted with 350-nm light from a Bausch and Lomb high intensity grating monochromator (front and back slits at 5.0 mm). The cylindrical photolysis cell contained two identical compartments, each 4.5 cm in diameter with a 5-cm optical path. The cell was constructed from 4.5-cm Pyrex tubing and had optical quartz faces and a quartz spacer which separated the two compartments. In addition, each cell compartments was equipped with a $^{14}/_{20}$ ₮ male joint and a $^6/_{25}$ female joint for a thermometer.

Quantum yield determinations consisted of two irradiations. First, with potassium ferrioxalate in both compartments the material was irradiated and the ferrous ion concentration in the actinometer measured. Typical values of light intensity were on the order of 7.9 × 10^{-3} mE/(min)(65 ml). The second irradiation was carried out with the sample in the first cell and a fresh solution of potassium ferrioxalate in the back cell. Typical concentrations of diene **7** and sensitizer were 9.4 × 10^{-3} and 12.8 × 10^{-3} *M*. With this concentration of sensitizer, less than 1% of the incident irradiation was transmitted to the back cell. After irradiation of the magnetically stirred, nitrogen-purged, photolysis solution, the assay for starting material and product was made by vpc using 2-acetonaphthone as standard. As in the case of the direct excitation, calibration of the vpc using known mixtures of diene and internal standards immediately prior to analysis was necessary to obtain good results. The results of these measurements are given in Table III.

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[34] Our material shows an nmr spectrum identical with the material reported by Zimmerman and Epling.[1b]

[35] The authentic sample was synthesized by the reaction of 2 equiv of phenylmagnesium bromide with methyl hexanoate followed by dehydration of the resulting tertiary alcohol with a trace of *p*-toluenesulfonic acid in benzene. The resulting olefin was then hydrogenated with platinum oxide catalyst to the known 1,1-diphenylhexane.

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Dimerization of Chloroprene and Related Dienes

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Abstract: From the rates and products obtained in thermal dimerizations of chloroprene and other dienes, it is proposed that two mechanisms are operative—one which is probably concerted and electrocyclic in nature, requiring at least one cisoid diene unit, and leading to vinylcyclohexenes, the other diradical in nature, leading largely to divinylcyclobutanes, and appreciable only when favorable substitution is present.

Wheland and Bartlett have recently reported an apparent instance of simultaneous biradical 1,2- and concerted 1,4-cycloadditions to cyclopentadiene.[1] We wish to report some dimerizations of dienes which provide further information about such competition. This investigation was orginally undertaken to resolve apparent conflicts between the results of Robb and coworkers[2,3] and reports by previous workers[4–6] and observations in this laboratory concerning the products of dimerization of chloroprene (2-chloro-1,3-butadiene). Several related dimerizations have been included to verify the apparent significance of the results with chloroprene.

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