

- Trifunac, *ibid.*, **92**, 2183 (1970).
- (5) J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, **58**, 2746 (1973); **59**, 2869 (1973); G. T. Evans, P. D. Fleming, and R. G. Lawler, *ibid.*, **58**, 2071 (1973); F. J. Adrian, *ibid.*, **54**, 3918 (1971).
- (6) H. Paul and H. Fischer, *Z. Naturforsch. A*, **25**, 443 (1970); *Helv. Chim. Acta*, **56**, 1575 (1973); R. Livingston and H. Zeldes, *J. Chem. Phys.*, **53**, 1406 (1970).
- (7) B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968); R. W. Fessenden, *ibid.*, **58**, 2489 (1973); A. D. Trifunac and E. C. Avery, *Chem. Phys. Lett.*, **27**, 141 (1974); **28**, 294 (1974).
- (8) P. W. Atkins, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Commun.*, 513 (1970).
- (9) P. W. Atkins, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Phys. Lett.*, **8**, 55 (1971).
- (10) R. Kaptein and J. A. den Hollander, *J. Am. Chem. Soc.*, **94**, 6269 (1972); J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *ibid.*, **92**, 5761 (1970); J. F. Garst and R. H. Cox, *ibid.*, **92**, 6389 (1970); J. I. Morris, R. C. Morrison, D. W. Smith, and J. F. Garst, *ibid.*, **94**, 2406 (1972).
- (11) F. J. Adrian, *J. Chem. Phys.*, **57**, 5107 (1972); H. Fischer, *Chem. Phys. Lett.*, **4**, 611 (1969).
- (12) S. K. Wong and J. K. S. Wan, *J. Am. Chem. Soc.*, **94**, 7197 (1972).
- (13) S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *J. Am. Chem. Soc.*, **95**, 622 (1973); *J. Chem. Phys.*, **58**, 985 (1973); *Can. J. Chem.*, **52**, 251 (1974).
- (14) P. W. Atkins and G. T. Evans, *Mol. Phys.*, **27**, 1633 (1974).
- (15) J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, **62**, 1706 (1975).
- (16) F. J. Adrian, *J. Chem. Phys.*, **61**, 4875 (1974).
- (17) A. J. Dobbs and K. A. McLauchlan, *Chem. Phys. Lett.*, **30**, 257 (1975).
- (18) B. B. Adeleke, K. Y. Choo, and J. K. S. Wan, *J. Chem. Phys.*, **62**, 3822 (1975).
- (19) M. Leung and M. A. El-Sayed, *J. Am. Chem. Soc.*, **97**, 669 (1975).
- (20) H. M. Vyas, S. K. Wong, B. B. Adeleke, and J. K. S. Wan, *J. Am. Chem. Soc.*, **97**, 1385 (1975).
- (21) (a) J. Bargon and K. G. Seifert, *Ber. der Bunsenges. Phys. Chem.*, **78**, 1180 (1974); (b) H. M. Vyas and J. K. S. Wan, *Chem. Phys. Lett.*, **34**, 470 (1975).
- (22) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395 (1961); B. M. Monroe and S. A. Welner, *ibid.*, **91**, 450 (1969); J. F. Arnett and S. P. McGlynn, *ibid.*, **95**, 7599 (1973); B. M. Monroe, *Adv. Photochem.*, **8**, 77 (1971).
- (23) R. G. Lawler, *Prog. Nucl. Magn. Reson. Spectrosc.*, **9**, 147 (1973).
- (24) P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963); D. S. Kendall and P. A. Leermakers, *ibid.*, **88**, 2766 (1966).
- (25) A. Samuni, D. Behar, and R. W. Fessenden, *J. Phys. Chem.*, **77**, 777 (1973).
- (26) R. Kaptein, *J. Am. Chem. Soc.*, **94**, 6251 (1972).
- (27) D. A. Hutchinson, H. M. Vyas, S. K. Wong, and J. K. S. Wan, *Mol. Phys.*, **29**, 1767 (1975).
- (28) F. J. Adrian, *Chem. Phys. Lett.*, **26**, 437 (1974). Note: G. L. Closs [*Chem. Phys. Lett.*, **32**, 277 (1975)] has pointed out that the experimental data could also be explained by the radical-pair mechanism.

The Photochemistry of Phenylpropenyl Allenes. Suppression of the Di- π -methane Rearrangement in an Acyclic Allenic System through Involvement of the Triplet Excited State^{1a,b}

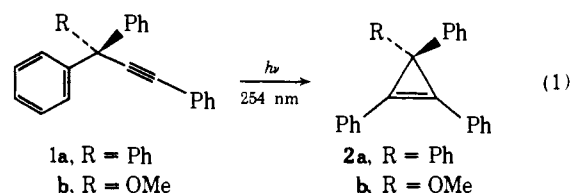
D. C. Lankin, D. M. Chihal, N. S. Bhacca,^{1c} and G. W. Griffin*

Contribution from the Department of Chemistry, University of New Orleans,
New Orleans, Louisiana 70122. Received October 15, 1974

Abstract: The photochemistry of *cis*- and *trans*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene was studied in order to extend the synthetic utility and mechanistic understanding of the di- π -methane reaction. A systematic variation of the hybridization at various reactive centers in the migrating π -moiety is in progress. In this paper we describe the effect of introducing an sp hybrid center one carbon removed from the migrating terminus. The requisite *cis* and *trans* allenic di- π -methane substrates were synthesized and subjected to direct and sensitized irradiations. It has been observed, upon *direct* irradiation of the *trans* isomer, that 2-isopropylidene-*anti*-3-phenyl-5,5-dimethylbicyclo[2.1.0]pentane is the major photoproduct. The anticipated *trans* vinylcyclopropane, namely *trans*-3,3-dimethyl-2-(3',3'-dimethylallenyl)-1-phenylcyclopropane, as well as the noncyclic alternate *cis* geometric isomer is observed as minor photoproducts formed by way of competing processes. The allenic *cis* di- π -methane substrate was observed to undergo primarily *cis*-*trans* isomerization with subsequent rearrangement of the *trans* isomer to a bicyclo[2.1.0]pentane and *trans* cyclopropane. *Sensitized* irradiations of both isomeric allenic substrates give bicyclo[2.1.0]pentane formation as well as *cis*-*trans* isomerization. No di- π -methane rearrangement to cyclopropanes is observed. Quenching studies indicate that the triplet state of *cis*- and *trans*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene is the chemically significant excited state in the formation of the bicyclo[2.1.0]pentane. The suppression of the di- π -methane rearrangement is discussed.

It is now recognized that di- π -methane rearrangements constitute a basic class of photochemical transformations and considerable effort has been devoted to defining the scope and limitations of this intriguing reaction.² An area of considerable interest to us relates to the effect induced on the photochemical behavior of di- π -methane substrates by altering hybridization at various centers of the migrating group. Of initial concern has been the photochemistry of di- π -methane systems in which at least one of the π -moieties is a substituted acetylene.³ For example, we have found that the photorearrangements of **1a** and **1b**, where one π -moiety is acetylenic in character and the other is incorporated within an aromatic ring afford the cyclopropenes **2a** and **2b**, respectively, as the *primary* photoproducts^{3c} (eq 1).

More recently, our studies^{3a-c} of the photochemistry of the isomeric acetylenes **3a** and **3b** have revealed that the

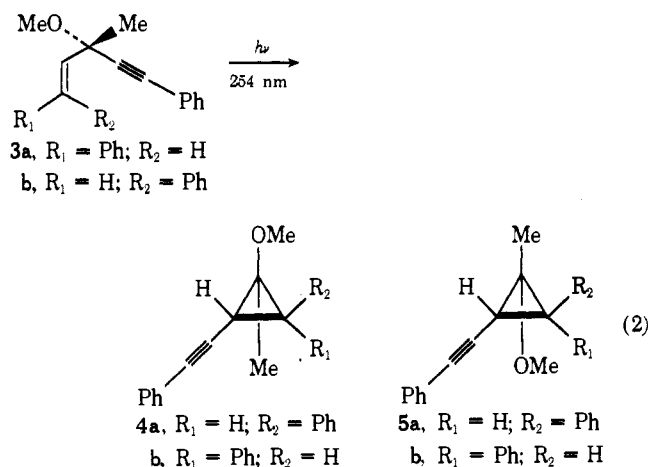


acetylenic cyclopropanes **4a** and **5a** as well as **4b** and **5b**, respectively, are the major photoproducts detected. Interestingly *no* cyclopropenes were observed although they constitute potential rearrangement products of **3a** and **3b** (eq 2). This work confirms that the formation of the cyclopropanes is highly stereospecific; i.e., **3a** affords **4a** and **5a**, while **3b** gives **4b** and **5b**. In this respect, the stereochemical course of the reaction of **3a** and **3b**, determined at low con-

Table I. Results of Direct Irradiations of Allenes **7a** and **7b**^{a,b}

Compd irradiad	Solvent	Concn, mol/l.	Time, hr	% conversion	% composition			
					7a	7b	8	9
7a	Benzene	0.047	0.5	48.1	51.9	7.1	26.1	14.9
7a	<i>tert</i> -Butyl alcohol	0.047	0.5	39.9	60.0	3.4	23.6	12.9
7b	Benzene	0.028	0.5	51.6	18.0	48.4	21.3	12.3
7b	<i>tert</i> -Butyl alcohol	0.028	0.5	66.8	7.0	33.2	38.1	21.7
7b	<i>tert</i> -Butyl alcohol	0.028	3.0	100.0	0.0	0.0	58.5	41.5

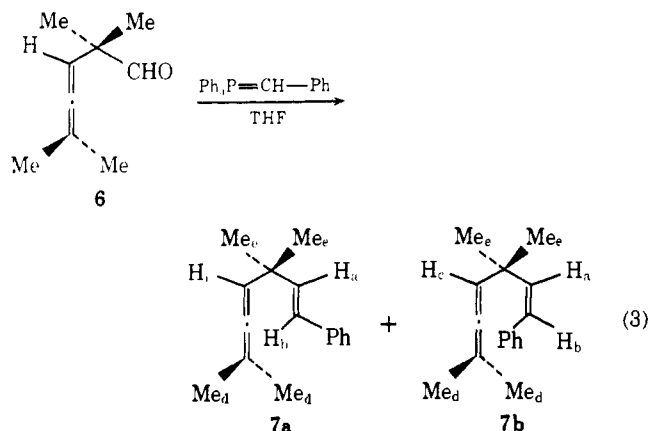
^a Direct irradiations were conducted at 254 nm. ^b Product ratios were determined by ¹H NMR on a Varian HA-100 spectrometer.



version, parallels the stereochemical results reported for less complex 1,4-pentadienyl systems.⁴

As a logical extension of our studies concerning the introduction of sp-hybrid centers at sites within a possible migratory group, we elected to study the photochemistry of an allenic system, which incorporates the sp center, one carbon removed from the potential migratory terminus. Surprisingly little attention has been devoted to the photochemistry of allenens.⁵ To our knowledge no examples of allenic di- π -methane rearrangements are known.² Since we also desired to assess the possible stereochemical consequences in such a reaction, the isomeric allenens **7a** and **7b** were selected for study. An unexpected, primary photoproduct obtained from **7a** and **7b** in addition to the anticipated allenic cyclopropane also permitted us to compare intramolecular cycloaddition reactions in an allenic di- π -methane system with that in a similarly substituted 1,4-pentadiene analog.^{4a} The allenic aldehyde **6**, a readily available substrate,⁶ provided an ideal precursor for the desired di- π -methane substrates.

Syntheses and Structures of the Propenyl Allenens. The isomeric allenens **7a** and **7b**, are obtained in approximately equimolar amounts from the known 2,2,5-trimethyl-3,4-hexadien-1-al (**6**)⁶ by treatment with benzylidenetriphenyl-

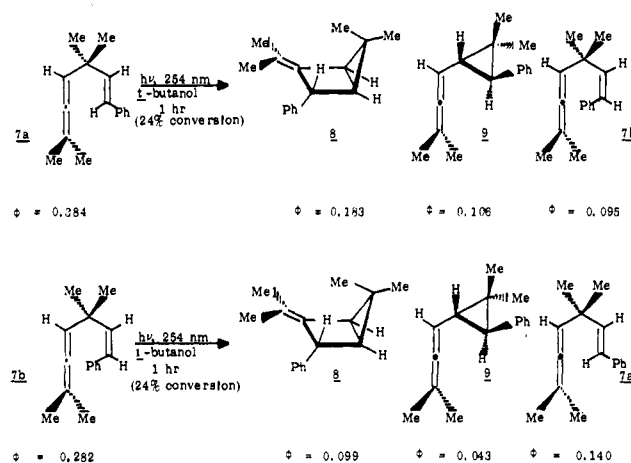


phosphorane in tetrahydrofuran (eq 3). The gross structures of **7a** and **7b**, separated by preparative GLC, were confirmed by mass spectrometry and combustion as well as infrared analyses. The stereochemistry of the allenic hydrocarbons, in turn, was deduced from observed spectral properties and mode of formation. Both **7a** and **7b** exhibit a band in their infrared spectra at 1950 cm⁻¹, which confirms the presence of an allenic group. A band at 965 cm⁻¹ appears in the infrared absorption spectrum of **7a** which is absent in that of **7b** and is characteristic of *trans*-1,2-disubstituted alkenes.⁷

In addition, a comparison of the magnitude of the ¹H NMR olefinic coupling constants of **7a** and **7b** serves to confirm the infrared assignment. Coupling constants for *trans* vicinal vinyl protons in isomeric 1,2-disubstituted alkenes are generally larger than their *cis* counterparts⁸ and such is the case for **7a** and **7b** where coupling constants of 15.5 and 12.5 Hz were observed for the *trans* and *cis* isomers, respectively.

Photochemical Investigations. Direct irradiation of **7a** in *tert*-butyl alcohol and in benzene at 254 nm leads to the formation of three photoproducts, the methylene bicyclo[2.1.0]pentane (**8**) (a "housane"), the allenic cyclopropane **9**, as well as **7b**, the alternate geometric isomer. In a like manner, direct irradiation of the *cis* isomer **7b** under the same conditions affords the housane **8**, the cyclopropane **9**, and the geometric isomer **7a**. The gross photochemical results together with the quantum yields^{9a} obtained upon irradiation of **7a** and **7b** in *tert*-butyl alcohol are tabulated in Scheme I. The results of additional photolyses in which the effects of irradiation time and solvent were studied are de-

Scheme I



icted in Table I. As an external reference for comparing our quantum yields directly with those observed by Zimmerman for other di- π -methane systems, the quantum yield of the rearrangement of a sample of 1,1,3-triphenyl-3,3-dimethyl-1-propene^{9b} was determined in our laboratories under conditions identical with those employed with **7a** and **7b**. The value obtained for the quantum yields is within ex-

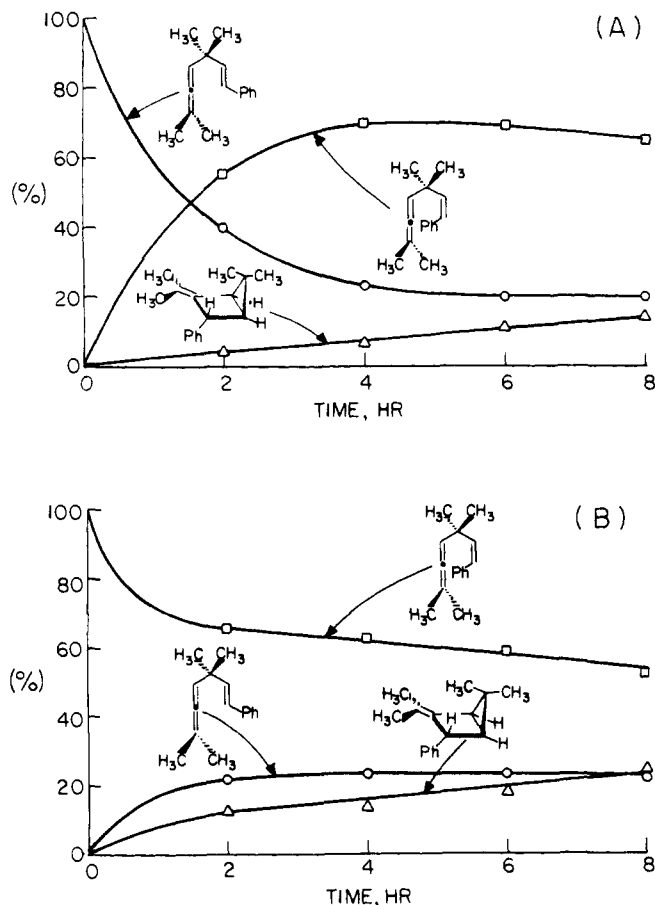


Figure 1.

perimental error of that obtained previously by Zimmerman.^{9c}

In contrast, sensitized irradiation of **7a** and **7b** in acetone ($E_t = 80$ kcal) as a solvent sensitizer induces cis-trans equilibration.^{9d} Surprisingly the housane **8** is the major photoproduct which is significant from a mechanistic standpoint. This represents the first example reported of bicyclo-[2.1.0]pentane formation in the condensed phase upon photolysis of a simple acyclic di- π -methane substrate in which a triplet excited state is an obligatory intermediate. Other di- π -methane systems are reported to afford housane products^{4a,10} but, in these cases, the excited singlet states have been implicated. The results of acetone sensitized irradiations of **7a** and **7b** conducted at low conversion levels are shown in Figure 1. It is significant that, even after prolonged irradiation (>50% conversion), the cyclopropane **9** could not be detected among the photoproducts of **7a** and **7b**. It is also of interest that the relative concentrations of the isomers become approximately equal and the slopes equivalent after 8 hr (A) and 2 hr (B). Furthermore housane formation is found to occur more rapidly from **7b** than **7a**. It is noteworthy that the ratios of both **7a** and **8** to **9** decrease upon irradiation of the trans allene **7a** in the presence of a triplet quencher solvent. Thus the rates of reaction by two pathways, which sensitization experiments indicate are triplet in character, namely, trans to cis photoisomerization and -cyclization to housane, diminish relative to cyclopropane formation. The results of similar experiments obtained with the cis allene **7b** are more complex. In this case, the ratios of both **7a** and **8** to **9** increase. Although these data upon cursory analysis appear to indicate that formation of **9** has been quenched upon irradiation of **7a** in a triplet solvent quencher, closer examination of the data in con-

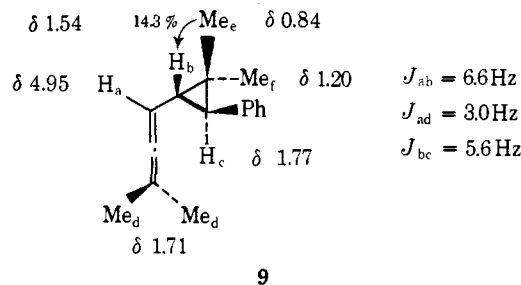
Table II. Results of Direct Irradiation in Piperylene^a

Allene	Concn, mol/l.	Time, hr	% conversion	% composition ^b			
				7a	7b	8	9
7a	0.032	0.5	26.8	73.1	6.1	10.9	9.8
7b	0.032	4.5	34.2	21.8	65.8	9.4	3.0

^a Irradiations were conducted at 254 nm. ^b Product ratios were determined by ¹H NMR.

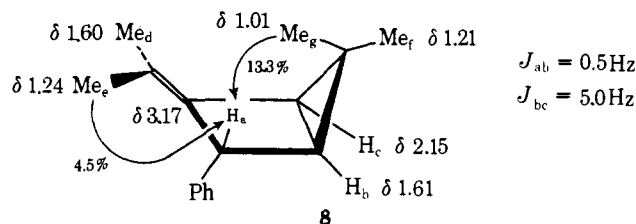
junction with other results clearly shows that this is not the case. This problem will be discussed at length in the Interpretive Discussion section and a self-consistent mechanism proposed which accommodates the relevant data. The results of the quenching experiments are summarized in Table II.

Structure of the Photoproducts. The structures of the photoproducts **8** and **9** were established from ¹H NMR and ir spectral data. Combustion analytical results and mass spectrometric data confirm that **8** and **9** are isomeric with the precursor allenes **7a** and **7b**. Retention of the allenic moiety and loss of the styryl chromophore in **9** was confirmed from the infrared spectrum, which exhibits a band at 1950 cm⁻¹ characteristic of allenes. Through ¹H NMR analysis, it was shown that long range coupling exists between Me_d and H_a ($J_{ad} = 3.0$ Hz). Such long range coupling is observed in the ¹H NMR spectra of **7a** and **7b** ($J_{cd} = 3.0$ Hz) and is typical for structurally related allenic systems.⁶ The trans stereochemistry assigned to **9** is apparent from the magnitude of the observed vicinal cyclopropyl hydrogen coupling constant ($J_{bc} = 5.6$ Hz) and from the nuclear Overhauser effects found for cyclopropane **9**. Upon radio frequency irradiation of the methyl group of **9** labeled e, there is an NOE of 14.3% observed for H_b, while no such

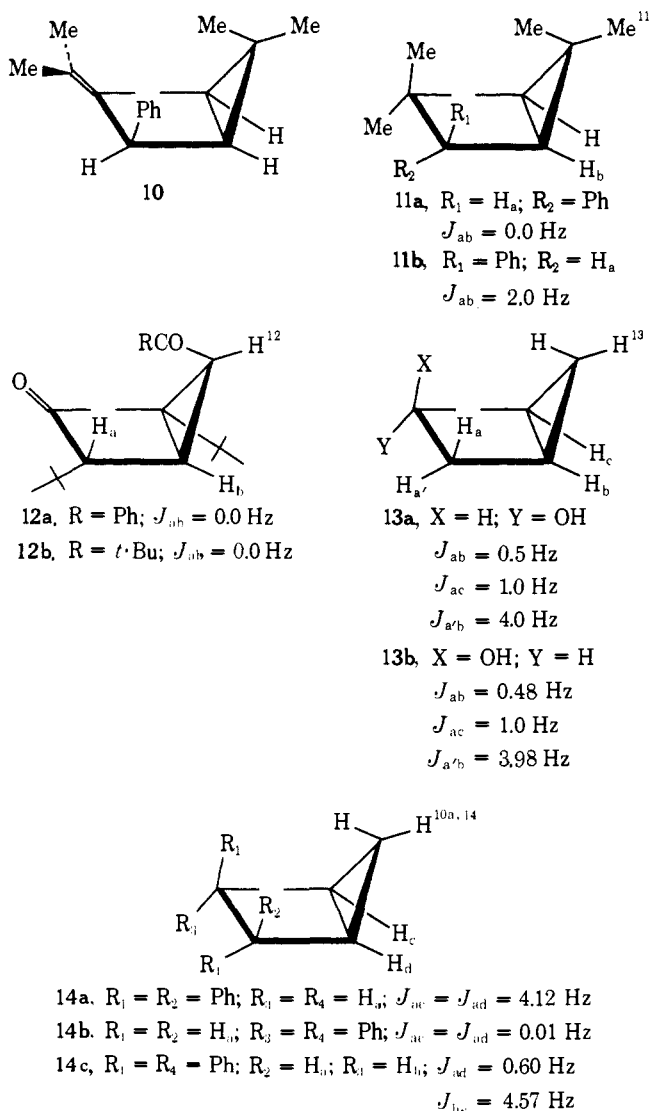


effect is apparent for H_c, which confirms the proposed trans stereochemistry. An examination of the cyclopropyl hydrogen coupling constants for **4a** and **5a** ($J_{trans} = 6.3$ Hz, for both)^{3a,b} and **4b** and **5b** ($J_{cis} = 9.5$ and 11.5 Hz, respectively)^{3a} provides additional support for the assigned structure.

The structure of the housane **8** was deduced from its spectral properties, mode of formation, and its subsequent thermal conversion to the allene **7a**. An examination of the ¹H NMR spectrum of **8** shows, in addition to the signal envelope for the aromatic protons, the presence of four distinct methyl groups and three unique saturated protons. The chemical shifts, proton assignments, and observed nuclear Overhauser effects are indicated on structure **8** below. The broadened singlet at δ 3.17 for H_a and the sharp doublet, centered at δ 1.61 and obscured by the singlet at δ



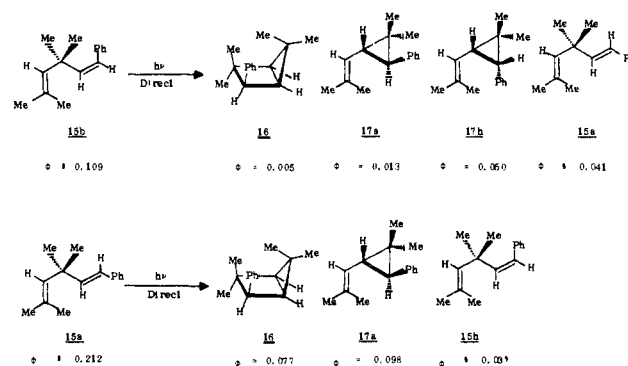
1.60, for H_b ($J_{ab} < 0.5$ Hz) provide confirmatory evidence for the indicated anti stereochemistry of the phenyl ring. The two lower field signals assigned to the protons of Me_d and Me_e are broadened and are of lesser intensity relative to the two higher field signals for Me_f and Me_g . This is attributed to long range homoallylic coupling to H_a and this interpretation has been confirmed by double resonance experiments. Additional support for the stereochemistry assigned to **8** was obtained from the nuclear Overhauser effects observed. The indicated NOE's of 13.3 and 4.5% were observed between the signals assigned to Me_g and H_a as well as Me_e and H_a , respectively. Furthermore, if the bicyclo[2.1.0]pentane photoproduct possessed the alternate epimeric structure **10**, a coupling constant (J_{ab}) of 2–4 Hz would be expected on the basis of published data.^{10a,11–14} An examination of the appropriate vicinal coupling constants designated on the structurally related model com-



pounds **11–14** provides confirmatory evidence that the magnitude of such constants may be used reliably in structural assignments of this type.

Furthermore, the housane **8** when thermolyzed at 100° for 3 hr or upon thermolysis during gas chromatography (injector port > 220°) reverts to the allenes **7a** and **7b** in the former case and only **7a** in the latter case, further substantiating the isomeric nature of **7a**, **7b**, and **8**. Such a reaction is not without precedent in bicyclo[2.1.0]pentane chemistry.¹⁵

Scheme II



Interpretive Discussion

The results of the photochemical investigations of **7a** and **7b**, which are described herein, contrast in a striking manner to those results obtained for the olefinic analogs **15a** and **15b** (Scheme II). Pertinent points related to the photochemical reactions of **7a** and **7b**, such as excited state multiplicity and stereochemistry, will be considered and the influence of an allene moiety on the di- π -methane rearrangement discussed. A self-consistent mechanism for the photoreactions of both **7a** and **7b** which accounts for the observed data will also be proposed and discussed.

The formation of the di- π -methane rearrangement product, cyclopropane **9**, occurs exclusively from the singlet excited state. This observation parallels the results which have been obtained with other acyclic di- π -methane substrates. This result is also in accord with the trend that has emerged in the case of acyclic di- π -methane systems that the di- π -methane rearrangements proceed via the singlet excited state.^{3,4,10,11} Furthermore, the stereochemical results of allenic cyclopropane formation described in this paper, upon initial examination, appear to contrast with the results obtained for **15a** and **15b**^{4a} and other related olefinic^{4b} and acetylenic^{3a,b} systems. Only one cyclopropane **9** is obtained from the photolysis of **7a** or **7b**,¹⁶ and thus it would appear that, in the case of these allenes, the di- π -methane rearrangement is a nonstereospecific process; however, this is not the case. The quantum yields tabulated in Scheme I indicate that, in fact, the cis isomer **7b** is undergoing rapid cis-trans equilibration to the trans isomer **7a** and this in turn is converted to the allenic trans cyclopropane **9** in a secondary photochemical reaction. Surprisingly, the processes which compete with the di- π -methane rearrangement, namely formation of the housane **8** and geometric isomerization, appear more efficient than the di- π -methane rearrangement. Thus, while the di- π -methane rearrangement is the minor pathway observed in the case of **7a**, it is completely suppressed in the case of **7b**. The fact that **9** is formed at all in the photolysis of **7b** is attributed to the fact that **7a** has an absorbance which is almost tenfold that of **7b** at 254 nm. Therefore, as the concentration of **7a** increases upon irradiation of **7b**, **7a** preferentially absorbs the light and is transformed into both **8** and **9**. The formation of **9** exclusively from **7a** implies that the highly regioselective^{3a,b,4} and stereospecific^{2,4} nature of the di- π -methane rearrangement remains operative; however, the stereospecificity in the allenic system under study is masked by more efficient competing processes which dominate the excited state behavior of **7a**.

On the basis of the quantum yields obtained for the di- π -methane rearrangement of the allenic systems **7a** and **7b** with those of other substrates such as the dienes **15a** and **15b** (Scheme II) it might appear that allenic migration is slightly more favorable than that of a vinyl or for that mat-

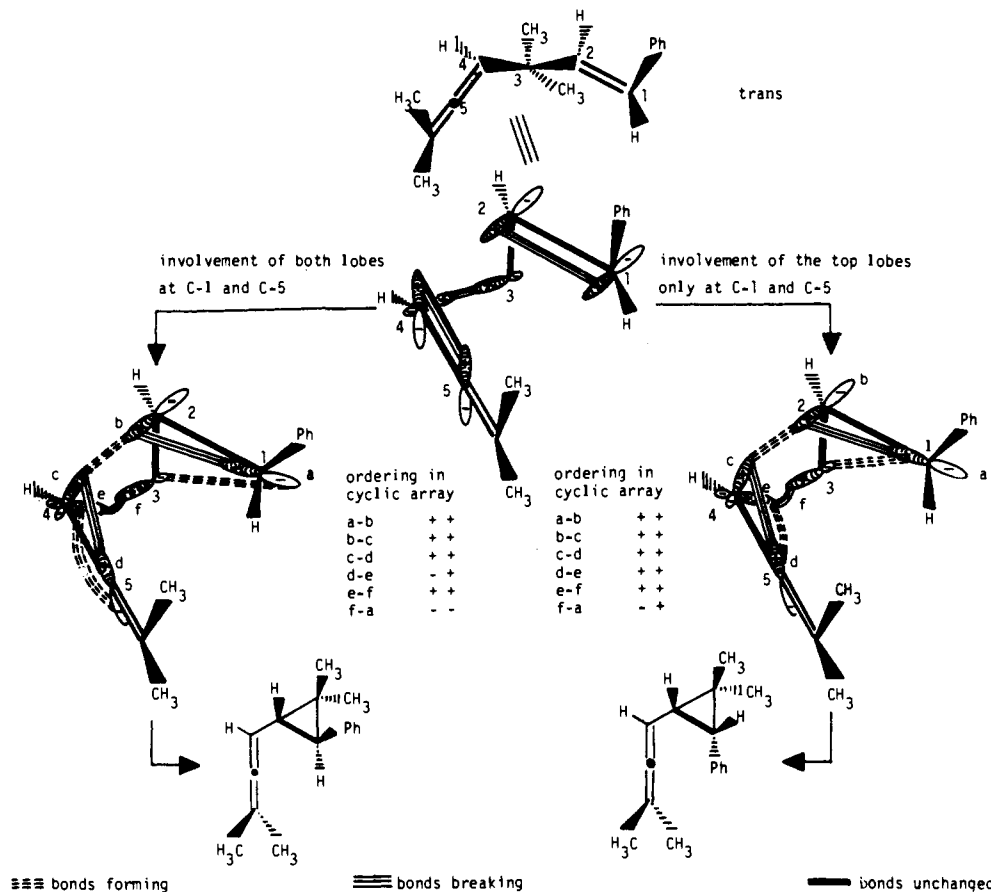


Figure 2.

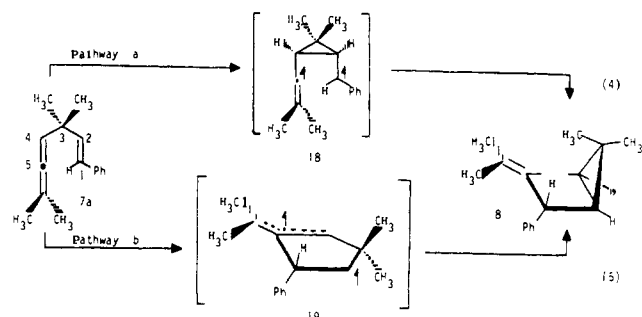
ter phenyl group^{9c} although less favorable than phenylethynyl migration.^{3c} This presupposes, however, that the quantum yields for all partitioning, photophysical processes which compete with the singlet photorearrangements are similar in magnitude which is improbable. In fact in the case of **7a** and **7b** intersystem crossing from the singlet state competes to such an extent with rearrangement that housane **8** formation exceeds that of allenic cyclopropane production.

The orbital array for the conversion of **7a** to **9** is depicted in Figure 2 using the Möbius-Hückel approach. It is apparent that the process may be described as a $4n + 2$ ($\pi 2_a + \sigma 2_a + \pi 2_a$) electrocyclic process which is of lowest energy ("allowed") in the first excited state.¹⁷

In the formation of the methylenehousane **8**, we again see a departure from the results reported for the photochemistry of the alkenes **15a** and **15b**, related to the allenes **7a** and **7b**.^{4a} Sensitization and quenching studies confirm that the housane **8** arises primarily from the excited triplet state of **7a** and **7b**. This suggests that a facile mode exists for intersystem crossing of the singlet states of **7a** and **7b** to the triplet manifold which apparently is not accessible in the case of **15a** and **15b** and is probably due to the influence of the allene moiety.¹⁸ In contrast, the housane **16** derived from **15a** and **15b** is formed exclusively from the singlet excited state. The fact that an efficient mode of intersystem crossing manifests itself in the allenic system is probably the major reason why the di- π -methane rearrangement is suppressed. This efficient mode for intersystem crossing reduces the lifetime of the excited singlet state to the point that efficient di- π -methane rearrangement does not take place. Another unusual aspect of the reactions of **7a** and **7b** became evident during the quenching studies, the results of which are presented in Table II. It may be seen that the for-

mation of **8** is incompletely quenched in neat piperylene. This result may be rationalized in at least two ways: (a) **8** is formed from **7a** and **7b** at least partially by way of the singlet excited state; and/or (b) the intramolecular cycloaddition of **7a** and **7b** to give **8** competes favorably with the rate of diffusion-controlled quenching ($\sim 10^{10} \text{ sec}^{-1}$). Precedent exists for the latter process in other systems and, for example, is documented in the literature of 2,5-cyclohexadienone photochemistry.¹⁹

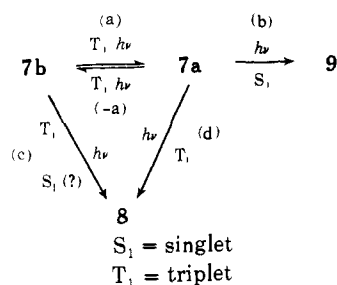
Two routes may be envisioned for formation of the housane **8** from the triplet excited state, and these are depicted in eq 4 and 5: pathway a in which the intermediacy of a benzyl and vinyl diradical **18** is proposed (2,4-bonding) and pathway b, which involves the intermediacy of an allylic and a tertiary diradical **19** (1,5-bonding).²⁰ Either pathway



should give rise to the more thermodynamically stable housane **8**, i.e., since a triplet mechanism involving spin inversion prior to cyclization precludes a concerted closure and formation of the more stable epimer is not unexpected.

In Scheme III, a self-consistent mechanism is presented which accounts for the observed photoreactions of **7a** and **7b**. Upon direct irradiation of **7a** in *tert*-butyl alcohol, three

Scheme III



photoproducts are observed, **7b**, **8**, and **9**. As indicated in Table III, the ratio of housane **8** to cyclopropane **9** remains relatively constant as the reaction progresses which supports the contention that **8** and **9** are primary photoproducts since no additional products are observed. The absorbance of **7a** is approximately tenfold that of **7b** at 254 nm, and therefore small amounts of **7b** produced as a minor photoproduct from **7a** will absorb an insignificant amount of the incident radiation. Thus photoreactions of **7b** are assumed to be negligible when compared with those of **7a**. As previously noted, triplet sensitized reactions of **7a** give rise to **7b** and **8**, while the cyclopropane **9** is conspicuously absent as a photoproduct. Clearly **9** must be formed in a singlet process while **7b** and **8** must arise predominantly from the triplet manifold. The results of supporting quenching studies using piperylene as a solvent quencher are more complex to interpret. The quencher has an absorption maximum in the neighborhood of 220 nm with a high extinction coefficient and therefore absorbs *most* of the incident radiation. The substrate **7a** will absorb less radiation and, as expected, a decrease in absolute yield of product per unit time is observed. Since we are interested solely in relative changes in the ratio of photoproduct concentrations in the presence and absence of the quencher, the reduced conversion level is not crucial. Furthermore, we cannot conclude that all processes are quenched since studies with triplet sensitizers show that the cyclopropane **9** is not formed from the populated triplet state and thus must be formed in a singlet process. From the quantum yield data and the data found in Tables I, II, and III, it is apparent that the quencher reduces the ratio of **8:9** from approximately 2:1 to 1:1 for the photoreactions of **7a**, and thus the conversion of **7a** to **8** is partially, but not completely, quenched. The reason for incomplete quenching as discussed previously relates to the fact that intramolecular cycloaddition to give **8** not unexpectedly can compete effectively with the diffusion-controlled quenching process. Thus the quenching studies support the conclusions based on sensitization experiments relative to the multiplicities of the photoprocesses which are operative in the case of **7a**, namely, that **7b** and **8** are excited triplet state products while **9** is formed from the excited singlet manifold (Scheme III).

The results of the irradiation of **7b** where isomerization to the trans isomer **7a** is the dominant process are more difficult to rationalize. Our proposed mechanism is nevertheless straightforward and also consistent with the observed facts. Direct irradiation of **7b** in *tert*-butyl alcohol gives three photoproducts, **7a**, **8**, and **9**; however, as seen in Table IV, the ratio of housane to cyclopropane **9** decreases as the conversion level increases, in contrast to the results observed for **7a**. This suggests that one or more of these products is formed at least in part in a secondary photoprocess. Since cis to trans isomerization is known to be the dominant photoprocess which occurs upon *direct* irradiation of **7b**, the concentration of **7a** increases rapidly with time. In view of the fact that the absorbance of **7a** is tenfold that of **7b** at

Table III. Ratios of **8:9** with Respect to Percent Conversion on Direct Irradiation^{a,b}

Compd irradiated	% conversion	Relative concentration			Ratio 8:9
		7b	8	9	
7a	24	1.0	1.9	1.1	1.7:1.0
7a	40	1.0	6.9	3.8	1.8:1.0

^a Direct irradiations were conducted at 254 nm. ^b Product ratios were determined by ¹H NMR on a Varian HA-100 spectrometer.

Table IV. Ratios of **8:9** with Respect of Percent Conversion on Direct Irradiation^{a,b}

Compd irradiated	% conversion	Relative concentration			Ratio 8:9
		7a	8	9	
7b	24	1.0	0.7	0.3	2.3:1.0
7b	67	1.0	5.4	3.1	1.8:1.0

^a Direct irradiations were conducted at 254 nm. ^b Product ratios were determined by ¹H NMR on a Varian HA-100 spectrometer.

254 nm, it is evident that, as the concentration of **7a** increases and **7b** decreases, a larger percentage of the incident radiation will be absorbed by the former. Obviously once the concentration of **7a** has reached only one-tenth that of **7b**, it will absorb as much radiation as **7b**. Thus photoproducts derived from **7a** soon begin to predominate as the conversion level increases; i.e., significant quantities of **8** and **9** are formed from **7a** in secondary photochemical processes.

Sensitized photolysis of **7b** produces two photoproducts, the trans allene **7a** and the housane **8**. No cyclopropane **9** is formed from the populated triplet state, indicating that **9** is formed in a singlet photochemical process while the other photoproducts are formed primarily through the triplet manifold. It is also significant in light of the results of quenching studies with **7b** that the housane **8** is formed more rapidly from the cis allene **7b** than from the trans allene **7a** in triplet sensitized reactions (Figure 1). Upon irradiation of **7b** in the presence of piperylene as a solvent triplet quencher, the ratio of **8:9** is increased, as indicated from the quantum yield data and the data in Tables I, II, and IV, from approximately 2:1 to 3:1. Based on these data and corresponding data for **7a**, it might be argued that formation of **8** from **7a** and **9** from **7b** is quenched; however, when the other data previously discussed are considered in conjunction with these facts, this interpretation may be excluded. As previously stated, the cyclopropane **9** has been shown to be produced exclusively from the singlet excited state while **8** at least primarily arises from the triplet state in the case of both **7a** and **7b**. Furthermore, as we have noted **7a** and **7b** rapidly equilibrate via the triplet state, and this fact in conjunction with the difference in extinction coefficients for these two compounds supports our contention that **9** arises solely from **7a**. The proposed explanation for the increase in the ratio of **8:9** is consistent with the mechanism advanced in Scheme III. In the presence of a triplet quencher, it is apparent that the rate of reaction by triplet paths a and c should be decreased while that through b should be essentially unaffected; however, reaction by path b is dependent upon the previous step a, which is reduced, and thus step b should also be diminished. Furthermore, it should be reiterated that the rate of formation of **8** from **7a** through triplet path d is lowered in the presence of the triplet quencher to the extent that the photoconversions d and b are equally efficient. In addition, those data from sensitized irradiation studies conducted on **7a** and **7b** in acetone which are tabulated in Figure 1 indicate that reaction by path c is more facile than by path d. Even those molecules of **7b** which undergo conversion through path a to **7a** and subsequently ab-

sorb another quantum of light can partition by any or all of three separate paths, -a, b, or d. Thus the probability of a molecule reacting by path a followed by path b or d, two-photon processes, is less than that of a molecule undergoing reaction through path c, a one-photon process, particularly since paths b and d are less efficient than path c. It is not unreasonable then to find that the ratio of **8** to **9** is increased from 2:1 to 3:1 for **7b**, in a solvent quencher. In summary the probability of formation of **8** by a partially quenched, one-photon, triplet reaction or alternatively in part via a singlet mechanism as previously discussed is more probable than formation of **9** by a two-photon process in which the first step is a partially quenched, triplet reaction, where three nearly equally efficient subsequent photoprocesses compete for consumption of the product **7a** upon absorption of the second photon of light. The increase in the relative quantity of **8** vs. **9** produced in the quenching experiments with **7b** is quite plausible and, in the absence of additional data, the self-consistent mechanism for the photo-reactions of both **7a** and **7b** outlined in Scheme III represents a viable mechanistic proposal.

In addition, several points regarding the observations presented here deserve further comment and emphasis. The unusual feature of the photochemistry observed for **7a** and **7b** is that cycloaddition leading to **8** represents the major reaction pathway and that the di- π -methane process, affording **9**, constitutes the minor reaction mode. These results are to be contrasted with those obtained for the structurally related acyclic 1,4-dienic systems,^{4a} where vinylcyclopropane rather than bicyclo[2.1.0]pentane formation is the major reaction pathway.^{10a} Recently, it has been asserted^{10a} that, in the absence of *gem*-dimethyl substitution at the insulating C-atom flanked by the π -moieties, bicyclo[2.1.0]pentane formation should dominate in 1,4-pentadienyl systems at least in the singlet manifold. In the present case, the housane **8** is the major photoproduct formed upon direct irradiation despite the fact that such substitution is present. Furthermore, in the case of **7a**, the fact that **9** is the sole di- π -methane product formed at low conversion parallels previous observations in related systems that di- π -methane rearrangement proceeds in a highly stereospecific manner and suggests that the reaction is largely concerted in character.^{3b,4} In addition the formation of the bicyclo[2.1.0]pentane **8** having the anti configuration from **7a** and **7b** is primarily triplet in character although a singlet component has not been excluded. Thus sequential bond formation involving diradical intermediate(s) with overall stereochemistry being controlled by thermodynamic factors provides a plausible mechanistic explanation for formation of the more stable epimer **8**. It should be noted that formation of **8** in part through a concerted pathway from **7a** and **7b** is consistent with the principles of orbital symmetry conservation.²¹ Two possible modes of disrotatory cyclization are available for **7a** and **7b** and thermodynamic arguments may again be invoked to rationalize the preferential formation of epimer **8**. Finally, the formation of **8**, having the anti configuration, as the sole bicyclic photoproduct from **7a** and **7b**, is in contrast to the formation of the single epimer **16** having the syn configuration from the related diolefinic system.^{4a} Possibly this apparent inconsistency may reflect subtle electronic and/or steric differences between the olefinic and allenic moieties.^{4a}

The pronounced influence of the allene moiety on the course of the di- π -methane rearrangement of **7a** and **7b** constitutes a radical departure from the photochemistry which is observed for the acetylenes **3a** and **3b**, both of which contain sp hybrid centers (albeit located at both termini of the migrating center rather than one as in the case of **7a** and **7b**), and for the olefinic analogs of **7a** and **7b**,

namely **15a** and **15b**. The major difference in the photochemistry of the allenes **7a** and **7b** and the olefins **15a** and **15b** appears to be related to the efficiency with which **7a** and **7b** undergo intersystem crossing to the triplet manifold, thus causing a decrease in the efficiency with which the singlet state may undergo reaction. Our efforts in this area are continuing with the ultimate hope of obtaining information on the migratory aptitudes of various groups in the di- π -methane reaction.

Experimental Section

General. Infrared spectra were recorded on Perkin-Elmer 337 and 257 spectrophotometers and were calibrated against polystyrene. The ultraviolet spectra and extinction coefficients were determined on a Cary Model 15 spectrophotometer. The proton magnetic resonance spectra were obtained on Varian A-60, HA-100, and Hitachi Perkin-Elmer R-20B spectrometers using deuteriochloroform as the solvent with 1% tetramethylsilane as the internal standard unless otherwise specified. The mass spectral studies were conducted using a Hitachi Perkin-Elmer RMU-6E spectrometer.

Analytical gas chromatograms were obtained on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector using Perkin-Elmer support coated open-tubular (SCOT) capillary columns. Integration of peak areas was achieved either by multiplication of peak height by peak width at half-height or with a Hewlett-Packard Model 3370A electronic digital integrator. Preparative gas chromatographic separations were achieved on an Aerograph Model A-90P gas chromatograph equipped with a 7 ft \times 0.25 in. in DC-550 (30% on Chromosorb P) column, operated isothermally at a column temperature of 125°, injector temperature of 175°, detector temperature of 243°, and a helium flow rate of 160 ml/min. Woelm neutral alumina with added phosphor was used for column chromatographic separations in which quartz columns were used. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Direct irradiations were conducted in serum capped 15 cm \times 12.5 mm i.d. fused quartz tubes. Sensitized irradiations were run in serum capped Pyrex round-bottomed flasks or Pyrex test tubes. A Rayonet RPR-100 reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-W low-pressure lamps was employed as a light source unless otherwise specified. The lamps utilized were either G8T5 (254 nm) or F8T5 (broad emission at 350 nm) types. A Rayonet MGR-100 merry-go-round or MGR-200 mini-go-round apparatus rotated at 5 rpm²² (The Southern New England Ultraviolet Co., Middletown, Conn.) was utilized in all kinetic and quantum yield studies to ensure uniform exposure of individual samples. The photoreactions were run at conversion levels as low as possible to allow detection of the primary photoproducts and to reduce errors in observed quantum yields obtained as a result of the occurrence of secondary photochemical processes. The solutions to be irradiated were degassed either by nitrogen sparging for 25 min or by the multiple freeze-thaw cycle technique.

cis- and *trans*-7-Phenyl-2,5,5-trimethylhepta-2,3,6-triene. A solution of 20.4 g (0.15 mol) of 2,5,5-trimethylhexa-2,3-dien-6-ol (**6**)⁶ was slowly added to a stirred solution of benzylidetriphenylphosphorane, which had previously been generated by heating benzyltriphenylphosphonium chloride (58.2 g, 0.15 mol) under reflux with 10 g of sodium hydride in 500 ml of tetrahydrofuran for 1 hr. The temperature was maintained at 40° during the addition and, after 24 hr, the initially reddish-orange solution had acquired a brown color. Solid ammonium chloride (1-2 g) was then added, with stirring, until the gas evolution had subsided. The solvent was evaporated under reduced pressure, and the resulting dark brown mass was subjected to vacuum distillation [82-100° (0.15 Torr)]. A colorless liquid was obtained (12.7 g) which was then chromatographed (3 \times 20 cm column) in hexane on Woelm neutral alumina, grade III, with phosphor added, in order to remove the last traces of triphenylphosphine oxide. The mixture of products obtained by chromatography, after evaporation of the hexane, was shown by GLC and ¹H NMR to consist of an equimolar mixture of *trans*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene (**7a**) and *cis*-7-phenyl-2,5,5-trimethylhepta-2,3,6-triene (**7b**). The second isomer to emerge having a GLC retention time of 51.3 min was identified

as **7a**: ir (CHCl₃) 1950 (C=C=C), 1600 (phenyl), 1250, 965 (trans-1,2-disubstituted alkene),⁷ 860, 690 cm⁻¹; uv λ_{max} (MeOH) 252 (ε 19300); ¹H NMR (CDCl₃) δ 7.19 (m, 5 H, aromatic), 6.35 (d, 1 H, *J* = 15.5 Hz, olefinic), 6.05 (d, 1 H, *J* = 15.5 Hz, olefinic), 4.94 (septet, 1 H, *J* = 3.0 Hz, allenic), 1.70 (d, 6 H, *J* = 3.0 Hz, allenic methyls), 1.19 (s, 6 H, *gem*-dimethyls); mass spectrum *m/e* M⁺ 212.

Anal. Calcd for C₁₆H₂₀: C, 90.51; H, 9.49. Found: C, 90.22; H, 9.73.

The alternate isomer **7b** has a GLC retention time of 30.0 min which permits baseline separation: ir (CHCl₃), 1950 (C=C=C), 1600 (phenyl), 700 cm⁻¹; uv λ_{max} (MeOH) 228 (ε 17500); ¹H NMR (CDCl₃) δ 7.15 (m, 5 H, aromatic), 6.37 (d, 1 H, *J* = 12.5 Hz, olefinic), 5.55 (d, 1 H, *J* = 12.5 Hz, olefinic), 4.94 (septet, 1 H, *J* = 3.0 Hz, allenic), 1.62 (d, 6 H, *J* = 3.0 Hz, allenic methyls), 1.08 (s, 6 H, *gem*-dimethyls); mass spectrum *m/e* M⁺ 212.

Anal. Calcd for C₁₆H₂₀: C, 90.51; H, 9.49. Found: C, 90.68; H, 9.30.

Direct Irradiations. Procedure A. The data summarized in Table 1 were obtained by subjecting weighed samples of both **7a** and **7b** to irradiation in both benzene and *tert*-butyl alcohol solutions at 254 nm for varying periods of time. In each case, after removal of solvent, a pale-yellow oil was obtained whose composition was determined quantitatively by ¹H NMR analysis.

Procedure B. In a typical preparative irradiation, a solution of a mixture of **7a** and **7b** (1:1), 2.0 g (9.4 mmol), in 60 ml of *tert*-butyl alcohol was irradiated at 254 nm for 15 hr until the starting material was nearly consumed (>95% conversion). After removal of the solvent, the resulting product mixture was subjected to preparative GLC. The first product to emerge (27.1 min) was trapped in a "U" tube at -78° and crystallized to a solid melting at ambient temperature. This product was shown to be 2-isopropylidene-*anti*-3-phenyl-5,5-dimethylbicyclo[2.1.0]pentane (**8**): ir (liquid film) 3010, 2950, 2910, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 7.18 (s, 5 H, aromatic), 3.17 (br s, 1 H, benzylic proton), 2.15 (br d, 1 H, *J* = 5.0 Hz, allylic bridgehead proton), 1.61 (d, 1 H, *J* = 5.0 Hz, bridgehead proton), 1.60 (s, 3 H, isopropylidene methyl *anti* to phenyl), 1.24 (s, 3 H, isopropylidene methyl *syn* to phenyl), 1.21 (s, 3 H, *exo*-cyclopropyl methyl), 1.01 (s, 3 H, *endo*-cyclopropyl methyl); mass spectrum *m/e* M⁺ 212.

Anal. Calcd for C₁₆H₂₀: C, 90.51; H, 9.49. Found: C, 90.60; H, 9.39.

The second product, an oil which could not be crystallized, with retention time of 36.6 min was shown to be *trans*-3,3-dimethyl-2-(3',3'-dimethylallyl)-1-phenylcyclopropane (**9**): ir (liquid film) 3070, 3050, 3010, 2960, 2910, 2860, 1950 (C=C=C), 1600 (C=C), 1360 (split, *gem*-dimethyls), 745, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.14 (m, 5 H, aromatic), 4.95 (m, 1 H, allenic), 1.77 (d, 1 H, *J* = 5.6 Hz, benzylic cyclopropyl), 1.54 (dd, 1 H, *J* = 5.6, *J* = 6.6 Hz, allenic cyclopropyl), 1.71 (d, 6 H, *J* = 3.0 Hz, allenic methyls), 1.20 (s, 3 H, cyclopropyl methyl *syn* to phenyl), 0.84 (s, 3 H, cyclopropyl methyl *anti* to phenyl); mass spectrum *m/e* M⁺ 212.

Anal. Calcd for C₁₆H₂₀: C, 90.51; H, 9.49. Found: C, 90.45; H, 9.54.

Sensitized Irradiations. The data tabulated in Figure 1 were obtained by irradiating identical weighed samples of **7a** and **7b** independently in 10 ml of acetone at 350 nm for varying periods of time. A merry-go-round apparatus was employed. The solvent was removed in vacuo, and the composition of the photoreaction mixture was determined quantitatively by ¹H NMR.

Quenching Studies. Weighed samples of **7a** and **7b** were irradiated in neat piperylene at 254 nm. In each case, removal of the solvent in vacuo provided a pale-yellow oil. Here again the composition of the photoreaction mixture was determined by ¹H NMR. These results are summarized in Table II.

Quantum Yield Measurements. Quantum yields were determined in *tert*-butyl alcohol solutions (0.11–0.15 *M*), contained in matched quartz cuvettes, at 254 nm. Potassium ferrioxalate actinometry was employed.^{9a} A mini-go-round was used to ensure uniform irradiation of actinometer and sample solutions. The quantitative determination of the composition of the irradiated solutions was achieved by ¹H NMR. Quantum yields which are quoted represent an average of four determinations.

Thermolysis of the Methylene Bicyclo[2.1.0]pentane **8.** A solution of **7a** in 400 ml of dry, distilled reagent-grade acetone was ir-

radiated at 350 nm for 12 hr. After removal of the solvent, the composition of the reaction mixture was found, by ¹H NMR, to be **7a** (10%), **7b** (41%), and **8** (49%). The reaction mixture was then flushed with nitrogen (3 hr) and heated at 100° for 3 hr, while maintaining a positive pressure of nitrogen in the vessel. The cooled reaction mixture was dissolved in diethyl ether and eluted on a column (3 × 2.5 cm) of Woelm neutral alumina grade III, to remove traces of yellow polymeric material. After removal of the solvent from the eluate, the composition of the mixture was determined as previously described and found to be **7a** (22%), **7b** (73%), and **8** (5%). In a control experiment, it was demonstrated that **8** was stable under the chromatographic conditions which were employed in this experiment.

In an additional experiment, a pure sample of **8** was injected into the gas chromatograph, where the injector port was maintained at 220°. This resulted in nearly quantitative isomerization of **8** to **7a**.

Acknowledgment. We acknowledge the Army Research Office, Durham (Grant ARO-D-31-124-73-G4), the National Science Foundation (Grant GP28171), and particularly the donors of the Petroleum Research Fund (Grant PRF 5471-AC1), administered by the American Chemical Society, for support of this research. The authors also thank Dr. K. Ehrlich, Mr. E. Burgue, Miss D. Natal, and Miss G. Caldwell for valuable technical assistance rendered in connection with work, as well as Professor R. C. Pettersson for his assistance in obtaining several microscale infrared spectra on the photoproducts **8** and **9** described in this work. In addition, we are indebted to Professor H. E. Zimmerman for the sample of 1,1,3-triphenyl-3,3-dimethyl-1-propene which allowed us to confirm the accuracy of our quantum yield determinations and thus to permit cross comparison of a wider variety of di- π -methane systems. We also acknowledge the assistance of Dr. E. Elder and Mrs. J. Thompson for aid in the preparation of the manuscript.

References and Notes

- (1) (a) Presented in part at the 28th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 6–8, 1972; Abstr. 222, p 76. (b) A preliminary account of this work has appeared: D. C. Lankin, D. M. Chihal, G. W. Griffin, and N. S. Bhacca, *Tetrahedron Lett.*, 4009 (1973); (c) Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803.
- (2) For a comprehensive review of the di- π -methane reaction, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
- (3) (a) Presented in part at the 27th ACS Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, Dec 1–3, 1971; Abstr. 238; (b) J. Perreten, D. M. Chihal, G. W. Griffin, and N. S. Bhacca, *J. Am. Chem. Soc.*, **95**, 3427 (1973); (c) B. Hailton, M. Kullig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *ibid.*, **93**, 2327 (1971). (d) While our work was in progress,^{3a} an unusual mechanistic departure from the anticipated course of rearrangement was reported by Zimmerman [H. E. Zimmerman and J. A. Pincock, *ibid.*, **95**, 3246 (1973)] in which reductive cyclization to give a cyclopentadiene occurs with mandatory 1,5 bonding at the termini when both π moieties are substituted acetylenes. (e) D. M. Chihal, J. Perreten, D. C. Lankin, N. S. Bhacca, and G. W. Griffin, unpublished results.
- (4) (a) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Am. Chem. Soc.*, **96**, 1459 (1974); *ibid.*, **94**, 5504 (1972); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); *ibid.*, **92**, 1409 (1970); (c) P. S. Mariano and J. K. Ko, *ibid.*, **94**, 1766 (1972).
- (5) For examples of other photochemical reactions exhibited by allenic systems, see (a) H. R. Ward and E. Karafiath, *J. Am. Chem. Soc.*, **90**, 2193 (1968); H. R. Ward and E. Karafiath, *ibid.*, **91**, 522 (1969); (c) H. R. Ward and E. Karafiath, *ibid.*, **91**, 7475 (1969); (d) J. A. Deyrup and M. Betkouski, *Tetrahedron Lett.*, 1131 (1973); (e) R. C. Cookson and P. Singh, *J. Chem. Soc. C*, 1477 (1971).
- (6) R. S. Bly and S. U. Koock, *J. Am. Chem. Soc.*, **91**, 3292 (1969).
- (7) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962, p 25.
- (8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, England, 1969, p 301.
- (9) (a) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956). (b) A sample of this propene was generously supplied by Professor H. E. Zimmerman, Department of Chemistry, University of Wisconsin, Madison, Wis. (c) H. E. Zimmerman, private communication. (d) Both benzophenone (*E*₁ = 68 kcal) and acetophenone (*E*₁ = 73 kcal) function as sensitizers; however, the results were complicated by the fact that these sensitizers undergo competing reactions, presumably of the Paterno-Büchi type, probably with the allenic portion of **7a** and/or **7b**.
- (10) (a) E. Block and H. W. Orf, *J. Am. Chem. Soc.*, **94**, 8438 (1972); (b) H.

- E. Zimmerman and J. A. Pincock, *ibid.*, **95**, 2957 (1973); (c) *ibid.*, **94**, 6208 (1972). Several examples of mercury sensitized gas-phase photo-reactions of 1,4-pentadienes, which afford [2.1.0]bicyclopentanes are known. See J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967).
- (11) H. Kristinsson and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 5970 (1967).
- (12) (a) D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971); (b) T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **89**, 3846, 3850 (1967).
- (13) K. B. Wiberg and D. E. Barth, *J. Am. Chem. Soc.*, **91**, 5124 (1969).
- (14) E. Block, H. W. Orf, and R. E. K. Winter, *Tetrahedron*, **28**, 4483 (1972).
- (15) J. A. Berson, W. Bauer, and M. M. Campbell, *J. Am. Chem. Soc.*, **92**, 7515 (1970).
- (16) The fact that a single cyclopropane is formed from **7a** and **7b** contrasts with our earlier report that *cis*-cyclopropane formation may occur to a minor extent.¹⁰ It may now be stated with certainty that the *cis* epimer of **9** is not detectable among the reaction products, at least within the limits of our ¹H NMR analytical methods (0.5%).
- (17) (a) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 5143 (1974); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966).
- (18) The triplet nature of the housane formation was not observed prior to our initial report of this work.¹⁰ Undoubtedly rearrangement of **8** to **7** during isolation occurred, and thus the former went undetected in our preliminary experiments (see Experimental Section).
- (19) (a) H. E. Zimmerman and H. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967); (b) *ibid.*, **86**, 1436 (1964); (c) M. H. Fisch and J. H. Richards, *ibid.*, **85**, 3029 (1963); (d) *ibid.*, **90**, 1547 (1968).
- (20) 1,5-Bonding of the type proposed in path b is not without precedent. It has been established by labeling experiments that a 1,4-diacetylene studied by Zimmerman and Pincock [H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **95**, 3246 (1973)] reacts by a mechanism involving this type of initial bonding. Of course, conversely 2,4-bonding of the type proposed in path a is commonly advanced as the initial step in the *dl*- π -methane rearrangement.²
- (21) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1970.
- (22) It has been shown experimentally (ref 23a) and theoretically (ref 23b) that irradiation of samples in cylindrical cells in a merry-go-round apparatus may seriously affect the observed quantum yield when the sample cell contains a solvent of different refractive index from that employed in the actinometry cell, and similar criticisms might be advanced concerning our determinations with **7a** and **7b** despite the fact that the merry-go-round was employed with flat quartz cuvettes. In view of our ability to reproduce the reported quantum yield data for the photoisomerization of 1,1,3-triphenyl-3,3-dimethyl-1-propene, it appears that such arguments are invalid here, perhaps because of the essentially monochromatic light source used and the flat surfaces.
- (23) (a) G. F. Vesley, *Mol. Photochem.*, **3**, 193 (1971); (b) M. D. Shetlar, *ibid.*, **5**, 287 (1973).

Reactions of Oxophlorines and Their π Radicals¹

J.-H. Fuhrhop,^{*2a} S. Besecke,^{2a} J. Subramanian,^{2a} Chr. Mengersen,^{2a} and D. Riesner^{2b}

Contribution from the Gesellschaft für Molekularbiologische Forschung, 3301 Stöckheim über Braunschweig, West Germany, and the Institut für Organische Chemie der Technischen Universität Braunschweig, 3300 Braunschweig, West Germany. Received September 24, 1974

Abstract: A detailed investigation of the reactivities of octaethylloxophlorine (**1**), its tautomer *meso*-oxyoctaethylporphyrin (**2**), and its metal complexes is presented. These compounds can be reversibly oxidized in a one-electron step. The oxidation potentials in neutral solutions are about 300 mV lower than those observed for related porphyrins. In alkaline solutions, an anion is formed by deprotonation, and these potentials are further lowered by 300 mV. Irradiation of the zinc complex with visible light first leads to a π radical. In the absence of oxygen, the π radical forms an ether linkage between the bridge oxygen and the methylene carbon of an ethyl group whereas, in the presence of oxygen, the radical is oxidized and decarbonylated, leading to the formation of an oxaporphyrin and carbon monoxide. A simple semiquantitative estimation of carbon monoxide using Dräger tubes is described. The macrocycle of the oxaporphyrin was converted by base to a biliverdin derivative. This reaction was fully reversed by acetic anhydride. The π radicals of oxophlorines dimerize in some organic solvents ($\Delta H_{293^\circ} = -14$ kcal mol⁻¹), and the rate constant obtained by temperature-jump methods ($k_R = 2 \times 10^6$ M⁻¹ sec⁻¹) is considerably smaller than that observed for unsubstituted porphyrin radicals. Further oxidation of **1** with Tl(III) salts leads to α, γ -dioxoporphodimethenes. Electrophilic substitutions in α -oxyporphyrins occur in the γ position. Some redox potential measurements on the amino and thio analogs of **1** are also presented, and a rationalization of the experimental data on the *meso*-substituted and unsubstituted porphyrin ligands aided by MO calculations is offered. The central conclusion drawn from experimental and model calculation is that *meso* hydroxylation of a porphyrin changes its benzene-type reactivity to that of a polyene.

Oxophlorines **1** and **3** and oxyporphyrins **2** and **4** constitute pairs of tautomers³ which play an important part in the catabolism of heme⁴ and are chemically different from unsubstituted porphyrins. Except for the formation of derivatives of the hydroxy group of **2** and the oxidative cleavage of iron complexes of **2**,^{3,5-7} no further reactions of these systems have been investigated. We have found that oxophlorines and their metal complexes are oxidized at low potentials to π radicals which undergo a variety of interesting secondary reactions in high yields.

Results and Structural Assignments

π Radicals and Their Diamagnetic Dimers. Octaethylloxophlorine **1a** was oxidized by air, Fe(III) salts, and a variety of other agents to the π radical **6**. The magnetic susceptibility in chloroform was 1.6 μ_B . The neutrality of the radical follows from elemental analysis (no counterion) and chromatographic behavior. The electronic spectrum of **6a** con-

sists of one band covering the whole visible range with a broad peak around 620 nm extending into the near infrared and a weak Soret band at 400 nm (Figure 1). Addition of acids to a chloroform solution of this radical leads to a diamagnetic cation of the nonoxidized oxophlorine **1a**, which shows a strong visible absorption at 680 nm.³ In the infrared, both **1a** and **6a** produce strong bands around 1600 cm⁻¹, which indicates some double-bond character of the C=O bonds. The reaction **1a** \rightarrow **6a** is fully reversible with reductants.

The radical **6a** seems to be always present in small amounts, even in spectroscopically pure preparations of **1a**, and hence one always finds an ESR signal⁸⁻¹⁰ and no ¹H NMR^{6,8-10} spectra. At low temperatures, however, the ESR signal disappears,⁹ the electronic spectrum changes considerably, and well-defined, although broad, proton resonance signals are found.⁹ A similar behavior has been observed for unsubstituted metalloporphyrin cation radicals¹¹