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The Photochemistry of Acyclic Acetylenic Di-π-methane Systems. Syntheses of Substituted Isomeric Acetylenic Cyclopropanes[1a-c]

G. W. Griffin,* D. M. Chihal,[1d] J. Perreten, and N. S. Bhacca

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122

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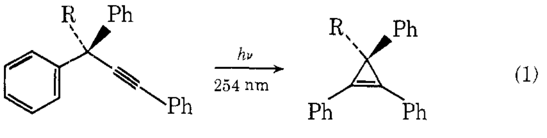
In this paper we describe the synthesis and photochemistry of *cis*- and *trans*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne which were studied in order to assess and extend the synthetic utility and mechanistic understanding of the di-π-methane reaction. It is clear from this study that the traditional di-π-methane rearrangement involving migration of an sp^2 center to an sp^2 site may be extended to include migration of an sp bonded carbon atom to an sp^2 terminus. An intriguing aspect of the di-π-methane conversions observed is the efficiency with which the phenylacetylenic function participates as the migrating function even when a styryl moiety is available for interaction. This photoreaction provides a convenient synthesis for phenylacetylenic cyclopropanes capable of incorporating a diverse group of additional substituents. Triplet sensitized irradiation of the trans enyne substrate was utilized to obtain sufficient quantities of the cis isomer for study and is a process which competes with di-π-methane photocyclization at least in benzene. In no case where sensitizers were employed was cyclopropane formation observed which indicates that the chemically significant excited state in the formation of these di-π-methane photoproducts is singlet in character.

The di-π-methane rearrangement constitutes a basic class of photochemical transformations and extensive effort has been expended to define the scope, limitations, and synthetic utility of this interesting reaction.[2] Of late we have focused our attention on the effect of altering hybridization at various centers in both the migrating and stationary π moieties on the photochemical behavior of several di-π-methane substrates. To date examples incorporating an acetylenic sp atom at the terminus of the stationary moiety,[3] as well as an allenic group as the migrating component in the reactant,[4a-c] have been investigated in our laboratories.

Not unexpectedly, if one of the requisite pair of π bonds is incorporated in an aromatic nucleus, the di-π-methane rearrangement is restricted to migration of the aromatic ring from the sp^3 center to an acetylenic sp terminus with concomitant cyclopropene formation. For example, it was found that the direct photorearrangements of **1a** and **1b** afford the cyclopropenes **2a** and **2b** as primary photoproducts (eq 1).[3]

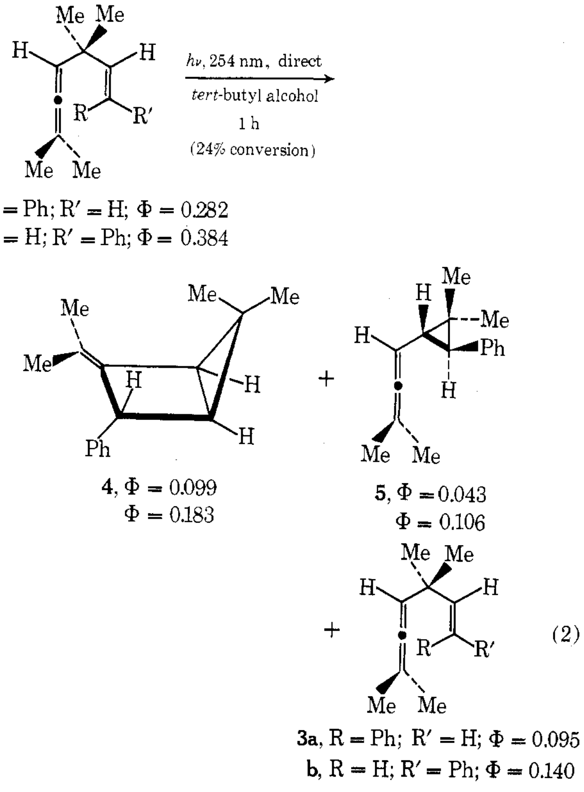


(1)

1a, R = Ph
b, R = OMe

2a, R = Ph
b, R = OMe

In parallel studies conducted concurrently with the present work we have observed that introduction of an sp hybrid center at a site within the potential migrating group may exert a pronounced effect upon the di-π-methane rearrangement. For example, with the isomeric allenes **3a** and **3b** as substrates it was possible to demonstrate that an allenic group is capable of altering the course of the reaction such that typical di-π-methane products are the minor photoproducts observed and [2 + 2] intramolecular cycloadditions dominate the reaction course.[4a-c] In this case the major photoproduct observed upon direct irradiation of the trans allene **3b** in *tert*-



3a, R = Ph; R′ = H; Φ = 0.282
b, R = H; R′ = Ph; Φ = 0.384

4, Φ = 0.099
Φ = 0.183

5, Φ = 0.043
Φ = 0.106

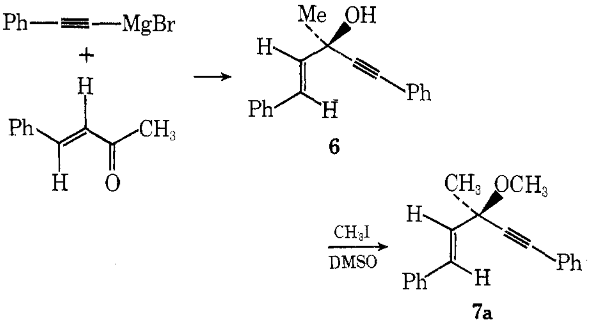
(2)

3a, R = Ph; R′ = H; Φ = 0.095
b, R = H; R′ = Ph; Φ = 0.140

butyl alcohol is the bicyclo[2.1.0]pentane **4**. The anticipated trans allenic cyclopropane **5** as well as the alternate geometric isomer **3a** are formed as minor products through competing processes. The allenic cis di-π-methane substrate **3a** was found to undergo facile cis–trans isomerization with subsequent rearrangement of the trans isomer **3b** to **4** and **5** (eq 2). The bicyclo[2.1.0]pentane was shown to be formed in a triplet photochemical process while the cyclopropane **5** is generated in a singlet excited state reaction.[4]

In the present study we wish to describe the effect of introducing a phenylethynyl group which interposes sp hybrid centers at each terminus of the potential migrating group while maintaining an sp^2 hybrid center at the probable migratory receptor site. To our knowledge the isomeric alkynes employed, *trans*- and *cis*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**7a, 7b**), represent the first such substrates incorporating sp hybrid carbon atoms in which the anticipated cyclopropane is formed efficiently upon direct irradiation.[1a–c,2] We also desired to assess and/or reaffirm certain stereochemical aspects of the potential di-π-methane rearrangements and the isomeric acetylenes **7a** and **7b** embody the prerequisite structural features. Although it may not be possible to rely upon quantum yield data obtained for these and other substrates employed in our laboratories and by other investigators to evaluate *true* migratory aptitudes of π-substituent groups from such quantum yield data due to variations in photophysical behavior which generally accompany structural modification, the information may provide "relative migratory efficiencies" which are sufficiently invariant to provide synthetically useful yardsticks.

Synthesis and Structure of the Isomeric Allylic Acetylenes 7. The synthesis of *trans*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**7a**) was achieved in 60% overall yield by addition of phenylethynylmagnesium bromide to benzalacetone.[5] The resulting alcohol, *trans*-1,5-diphenyl-3-methyl-1-penten-4-yn-3-ol (**6**),[6] was subsequently O-methylated with methyl iodide in dimethyl sulfoxide to give the trans enyne **7a** in high purity. The overall reaction scheme is delineated in eq 3.



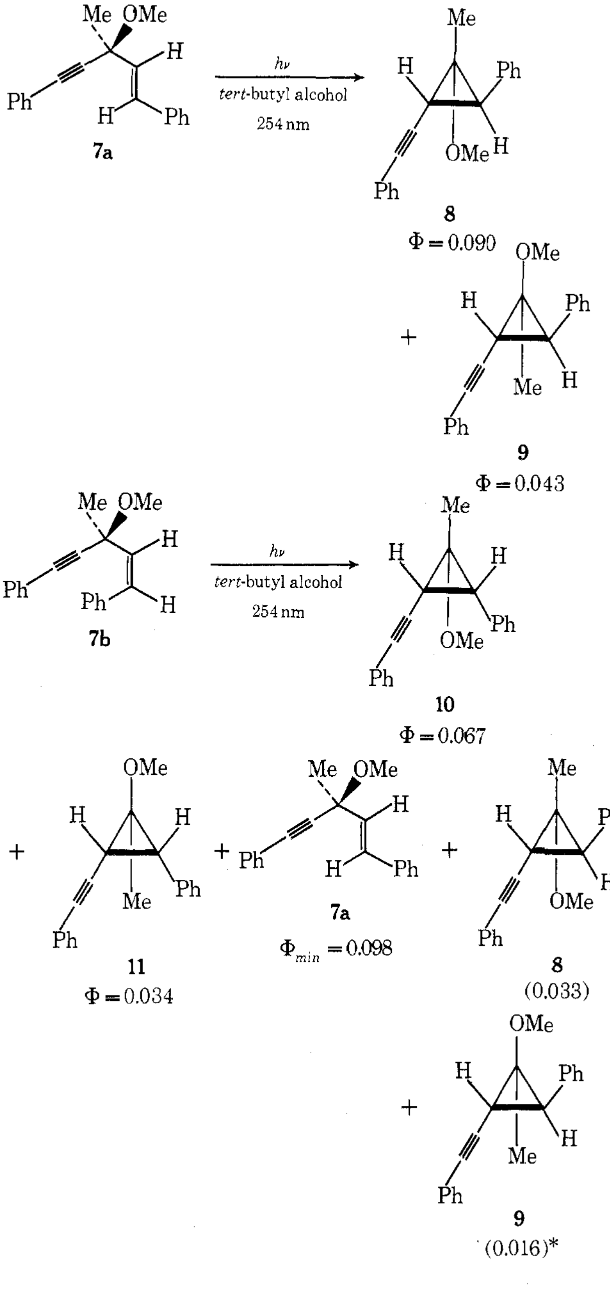
(3)

The cis isomer, *cis*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**7b**), is obtained conveniently by acetophenone sensitized photoisomerization of the trans isomer **7a**. The photoequilibrated mixture consists of approximately equimolar amounts of **7a** and **7b**.[7] Isolation of pure samples of **7b** proved a complicated and tedious task since both enynes are relatively unstable to heat, acidic conditions, and oxygen, and tend to decompose upon elution during chromatographic separations unless the special precautions outlined in the Experimental Section are exercised during the chromatographic separation and subsequent purification by bulb-to-bulb distillation.

The gross skeletal structures of **7a** and **7b** were confirmed by combustion analysis, mass spectrometry, ^{1}H NMR, and infrared spectroscopy. The stereochemistry of the acetylenic ethers was deduced from observed spectral properties and mode of formation. A band appearing at 970 cm^{-1} characteristic of trans 1,2-disubstituted alkenes[8] is observed in the infrared spectrum of **7a** and is absent in the spectrum of **7b**. Furthermore, trans vicinal NMR coupling constants for vinyl protons in isomeric 1,2-disubstituted alkenes are generally larger than their cis counterparts.[9] Such is the case with **7a** and **7b** where coupling constants of 15.5 and 12.0 Hz, respectively, are observed. In addition, five of the ten aromatic protons of each isomer are deshielded as would be anticipated in view of the presence of an adjacent ethynyl substituent on the ring.[10] In contrast, the signals assigned to the corresponding aromatic protons of the olefinic counterparts are found at higher field, which provides additional evidence that **7a** and **7b** are in fact enynes. Characteristic signals for the vinyl and aromatic protons are also present.

Photochemical Investigations. Direct irradiation of *trans*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**7a**) in *tert*-butyl alcohol at 254 nm for 30 min affords two main photoproducts, *r*-1-methoxy-1-methyl-*t*-2-phenyl-*c*-3-phenylethynylcyclopropane (**8**) and *r*-1-methoxy-1-methyl-*c*-2-phenyl-*t*-3-phenylethynylcyclopropane (**9**), in a 2:1 ratio, respectively (eq 4).[11] Quantum yield experiments employing potassium ferrioxalate actinometry were performed on **7a** in *tert*-butyl alcohol at 254 nm and gave quantum yields (average

Scheme I



(4)

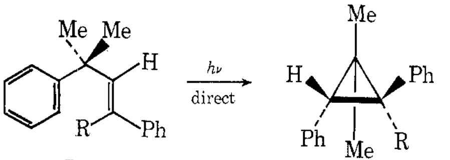
(5)

Table I. Results of Direct Irradiations of 7a and 7b[a,b]

Compd irradiated	Solvent	Concn, mol/l.	Time, h	% conversion	% composition					
					7a	7b	8	9	10	11
7a	*tert*-Butyl alcohol	0.045	0.5	9.0	91.0	0.0	6.1	2.9	0.0	0.0
7a	Benzene	0.038	0.5	35.6	64.4	3.5	18.8	9.6	3.8	Trace
7b	*tert*-Butyl alcohol	0.041	0.5	18.5	6.9	81.5	2.6	1.2	5.2	2.6
7b	Benzene	0.040	0.5	32.7	21.6	67.3	3.4	1.6	3.6	2.4
7b	Acetonitrile	0.037	0.5	41.3	20.6	58.7	5.8	2.6	6.9	5.4

[a] Direct irradiations were conducted at 254 nm. [b] Product ratios were determined by NMR.

of four runs) for **8** and **9** of 0.090 and 0.043, respectively.[12] The quantum yield values determined for the photoproducts obtained from **7a** upon direct irradiation in *tert*-butyl alcohol are tabulated in Scheme I. The quantum yield for the rearrangement of an external reference, namely 1,1,3-triphenyl-3,3-dimethyl-1-propene (**12b**),[13a] was determined under conditions identical with those employed with **3a, 3b, 7a,** and **7b** in order to ensure that the quantum yield measurements on **8, 9, 10,** and **11** are consistent with those values reported by Zimmerman and co-workers for other di-π-methane systems. Our values determined for 1,1,3-triphenyl-3,3-dimethyl-1-propene (**12b**) compare favorably with that obtained by Zimmerman (Φ = 0.036) (eq 6).[13b]



(6)

12a, R = H
b, R = Ph

13a, $\Phi = 0.42^{13b}$
b, $\Phi = 0.0356^{13a}$

Direct irradiation of the alternate geometric isomer **7b**, namely *cis*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne, under essentially identical conditions gives *r*-1-methoxy-1-methyl-*c*-2-phenyl-*c*-3-phenylethynylcyclopropane (**10**) and *r*-1-methoxy-1-methyl-*t*-2-phenyl-*t*-3-phenylethynylcyclopropane (**11**) in a 2:1 ratio, respectively; however, in contrast to the irradiation of the trans enyne **7a**, lesser amounts of **7a, 8,** and **9** are observed as photoproducts of **7b** (eq 5). That photoisomerization of **7b** to **7a** is a competing process in this case is evident from the product distribution as well as quantum yield data. Subsequent rearrangement of the trans isomer **7a** accounts for the presence of the trans cyclopropanes **8** and **9** among the photoproducts obtained from **7b**. No corresponding photoisomerization of **7a** to **7b** in *tert*-butyl alcohol is detectable, although such is not the case in benzene where competing cis–trans photoequilibration is observed. Quantum yield measurements performed by methods identical with those used with **7a** were conducted on **7b**.[12] The averages of four repetitive quantum yield determinations for the formation of **10, 11,** and **7a** are 0.067, 0.034, and 0.098, respectively. Reliable quantum yield data were not obtained on **8** and **9** since these are secondary photoproducts. The value cited for **7a** represents a minimum value since it is undoubtedly depleted as formed to give **8** and **9**. The values based on direct formation from **7b** were monitored and are cited for reference purposes only to provide some idea of the magnitude of partitioning between **7b** and **7a** in the event that the photoreaction is perhaps used synthetically and a knowledge of by-product formation becomes significant. For convenience a complete summary of the photoproducts obtained from **7b** in *tert*-butyl alcohol in addition to the photochemistry described for this isomer are depicted in Scheme I (eq 4 and 5) along with the aforementioned quantum yield data. The product distribution results obtained on direct photolyses of **7a** and **7b** in *tert*-butyl alcohol and other solvents are summarized in Table I.

Only trans–cis photoisomerization was found to occur upon irradiation of **7a** at 350 nm for 12 h in the presence of the sensitizer acetophenone. This photoequilibration leads to an essentially equimolar mixture of **7a** and **7b**. The equilibrium mixture may be approached by irradiating **7b** under similar conditions. Although the triplet energy of acetone is substantially higher than that of acetophenone and that photoisomerization occurs with the latter sensitizer, the equilibration is incomplete even after 20 h at which time **7a** predominates by a factor of 3:1. This difference in sensitizer efficiency is reasonably attributed to the differential absorption coefficients of the two ketones at 350 nm. Of primary significance is the fact that in no case where sensitizers were employed was cyclopropane formation observed from either **7a** or **7b** which indicates that the chemically significant excited state in the formation of these di-π-methane photoproducts, namely **8, 9, 10,** and **11**, is singlet in character.

Structure of the Photoproducts. The set of acetylenic methoxycyclopropanes **8, 9, 10,** and **11**, which like their precursor pair **7a** and **7b** are highly unstable, were isolated using procedures similar to those employed in the isolation of the latter. The structures of **8, 9, 10,** and **11** were established using 100-MHz NMR, ir, and appropriate NOE spectral data. Combustion analytical and mass spectrometric data confirm that the cyclopropanes are isomeric with the precursor acetylenes **7a** and **7b**. An infrared absorption band in the region of 2250 cm^{-1} in each product attests to the fact that the acetylenic moiety is retained. Additional support for the retention of the acetylenic group is apparent from the NMR spectrum of the cyclopropanes. The chemical shift observed for five aromatic protons in each of the isomeric cyclopropanes provides additional evidence that the phenylethynyl moiety is preserved.[10] In addition, the chemical shift for the remaining five aromatic protons is normal. Furthermore, it is evident from the disappearance of the two olefinic proton doublets and the emergence of the AB doublet of doublets in the NMR spectra of the photoproducts that the photoreaction involves conversion of **7a** and **7b** to isomeric cyclopropanes at the expense of the styryl group rather than the phenylethynyl group. Differentation of the cis and trans isomeric cyclopropanes was achieved on the basis of the magnitude of vicinal spin-spin interactions of the cyclopropyl protons. Since J_{cis}(6.5–12.0 Hz) is larger than J_{trans}(3.5–8.5 Hz) in such systems the magnitude of the vicinal proton coupling in **10** (11.0 Hz) and **11** (9.5 Hz) attests to their cis geometry.[14,15] Correspondingly, trans configurations were assigned to **8** and **9** on the basis of the vicinal coupling observed for both isomers (6.5 Hz).

Our conclusions regarding the stereochemistry of **8, 9, 10,** and **11** are based on the long-range anisotropic shielding and deshielding effects induced by the phenyl ring, the acetylenic bond, the oxygen of the methoxy group, and the methyl substituent. The results of this self-consistent correlation are depicted graphically in Figure 1 with the relevant peaks

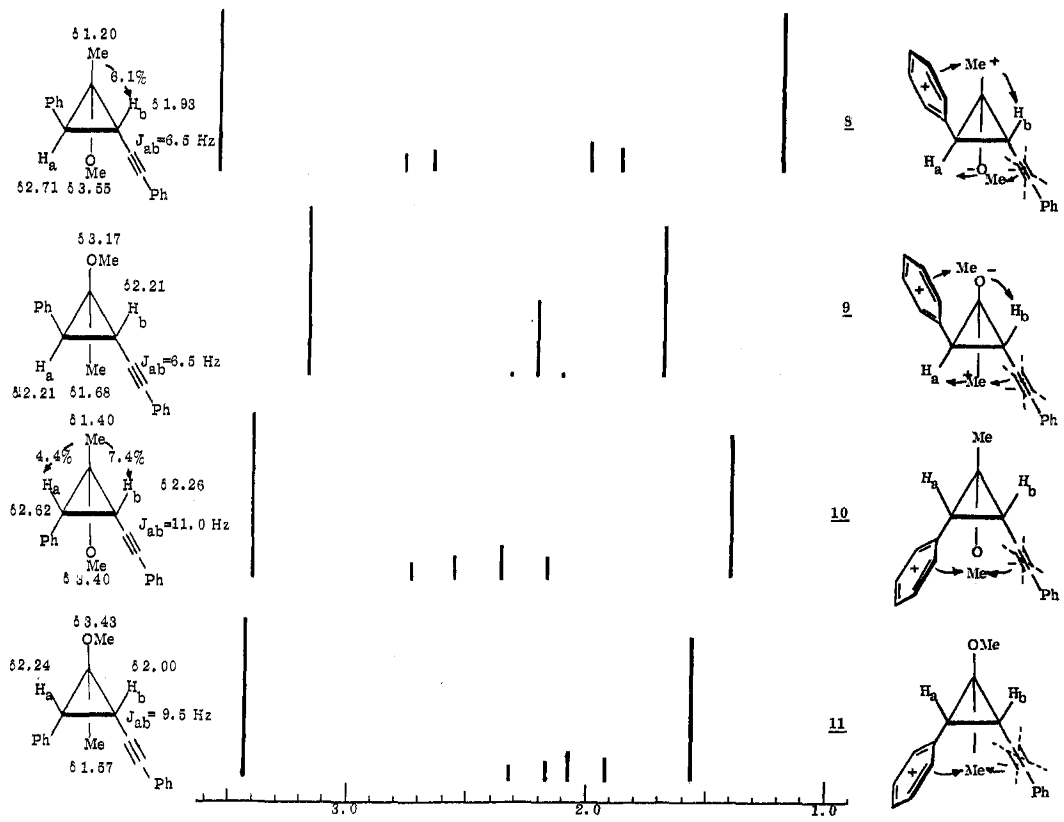


Figure 1.

plotted to assist the reader in analyzing those spectra where minor impurities are present since they were obtained at a time when we had not achieved sample purification levels ultimately required and reached for combustion analysis on these highly unstable compounds. The respective structures presented alongside the NMR traces are labeled to indicate the significant interaction responsible for the anisotropic shifts employed in the analysis as well as NOE results to be discussed later. The NMR signals for the corresponding protons of the four cyclopropanes may be compared readily by reference to Figure 1. The methoxy signal in **8** is deshielded (δ 3.55) by the acetylenic bond. The shifts observed for the methoxy signals of **10** and **11** do not vary greatly from the values observed for those groups in the precursor substrates. In **10** the deshielding effect of the acetylenic bond on the methoxy protons is compensated by the shielding experienced due to the phenyl ring giving rise to a signal at δ 3.40. The methoxy group in the cyclopropane **11** is trans to both the acetylenic bond and phenyl ring and thus is not significantly affected by either and the NMR signal appears at δ 3.43. The methyl groups of the cyclopropanes **8**, **9**, **10**, and **11** are affected in a manner corresponding to that observed for the methoxy substituents. A shielding effect is exerted on the methyl group of **8** by the aryl substituent and the NMR signal appears at δ 1.20; however, the opposite is true in the case of the methyl substituent of **9** which is deshielded (δ 1.68) by the acetylenic bond. The NMR signals of the methyl groups of **10** and **11** as might be expected, are found within these two extremes at δ 1.40 and 1.57, respectively. In the di-π-methane product, **10**, the methyl group is relatively unaffected by the substituents on the cyclopropane ring since it too is trans to these substituents. It is interesting that these anisotropic effects tend to cancel each other in the case of the cyclopropane **11**. The effect of the methyl and methoxy groups on the cyclopropyl protons H_a and H_b can be seen in the trans di-π-methane products, **8** and **9**. Here it is found that H_a of the cyclopropane **8** is shifted to lower field by the methoxy group, while H_b is displaced to higher field by the methyl group which results in a differential shift of the cyclopropyl proton signals of 0.78 ppm. Interestingly H_a of the other trans di-π-methane product, **9**, is shifted to higher field by the methyl group while H_b is shifted to lower field by the methoxy group creating a near superposition of the two NMR signals at δ 2.21. The anistropic solvent effect of benzene-d_6 was required to resolve these peaks.

The appropriate nuclear Overhauser experiments were performed on the cyclopropanes to verify the NMR spectral assignments. Upon radio-frequency irradiation of the methyl group of **8** there is an NOE of 6.1% observed for H_b, while no such effect is apparent for H_a, which confirms the proposed stereochemistry of the trans cyclopropanes, **8** and **9**. Similarly, radio-frequency irradiation of the methyl group of **10** gives an NOE of 4.4% on H_a and 7.4% on H_b, as expected if the proposed stereochemistry of the cis cyclopropanes, **10** and **11**, is correct.[15]

Results and Discussion

The acetylenic di-π-methane substrates *trans*- and *cis*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**7a** and **7b**, respectively) incorporate both styryl and phenylethynyl groups. The primary objective in this study was to assess the migratory potential of a phenylethynyl moiety in the di-π-methane rearrangement and the possible utility of such a process for the synthesis of substituted acetylenic cyclopropanes. In addition we wished to evaluate the effect of C-1 olefinic stereochemistry on the reaction course; however, during the preparation of our initial publication in this area,[1a,b] the results of an independent investigation of the stereochemical consequences which occur at C-1 in the di-π-methane rearrangement of a diene were reported.[16]

An intriguing aspect of the di-π-methane conversions observed for **7a** and **7b** is the efficiency with which the phenylacetylenic function participates as the migrating moiety in the rearrangement even when a styryl group is available for interaction. Although phenylethynyl migration occurs to the exclusion of detectable styryl migration, no reliable general relative migratory aptitude data for sp and sp^2 centers can be inferred from the results since other factors may play a role in determining the reaction selectivity (vide infra).

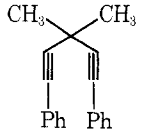
A useful qualitative valence bond representation for conventional concerted di-π-methane rearrangements, first recognized by Zimmerman and co-workers[17a,b] (Scheme II), is commonly invoked to characterize points along the potential energy hypersurface leading from the excited state reactant to ground state product. The fact that the di-π-methane photorearrangement of **7a** (and perhaps **7b**) occurs stereospecifically to produce the respective trans and cis cyclopropanes with retention of configuration at C-1[16] is assumed to be associated with a high degree of concertedness in the bond cleavage and bond formation processes required for atom reorganization of the di-π-methane type. Although the reaction stereospecificity is inconsistent with a sequential process, insufficient data are available to define the "degree of concertedness" (i.e., the reaction is concerted, but not synchronous). It should not be misconstrued that such formulations in Scheme II necessarily represent intermediates since it is not known that they correspond to energy minima. At most, they may represent shallow depressions in the energy surface. To the extent, however, that these species are useful in defining odd-electron disposition as the reaction course is traversed one should expect predictions based on this scheme to correlate with experiment. This approach has indeed stimulated extensive research and provides a qualitative model which allows one to visualize the overall gross molecular transformation along the reaction coordinate with extraordinary predictive success.

Application of this analysis to the concerted reorganization of **7a** and **7b** proves instructive. Initial π,π-bridging between C-2 and C-4 results in formation of **14** which incorporates a center with sp^2 character in the cyclopropyl ring and concomitant development of incipient arylcyclopropylcarbinyl and vinylphenyl radical sites, C-1 and C-5, respectively.

In pertinent cases previously studied[17b,c] the sole photoproducts isolated result from those pathways which involve migration of the less conjugated π moiety to the more conjugated one. Zimmerman and Pratt[17b] propose that the controlling feature in determining the overall regioselectivity is maintenance of odd-electron stabilization during the second step, i.e., cyclopropyl ring-opening process. In the case at hand (**14**) collapse of the cyclopropane ring by path a in which benzyl radical delocalization is maintained is apparently favored over cleavage by path b in which the corresponding residual radical is phenylvinyl in character; i.e., **15** is probably of lower energy than **16.** Cyclization of the diradical **15** with incorporation of the vinyl rather than ethynyl moiety into the cyclopropane ring of the product is not only consistent with Zimmerman's mechanistic representation of the process, but clearly in accord with our experimental results.

The effect of strain on the observed regioselectivity cannot be discounted and the preference for formation of cyclopropanes **8, 9, 10,** and **11** rather than cyclopropenes such as **17** from **7a** and **7b** may be attributed in whole or in part to unfavorable strain factors. As the reaction proceeds from the π–π bridged species **14** incorporating a single sp^2 center by path b to **16** the vinyl radical interacts and a cyclopropenyl photoproduct **17** must be generated possessing two such sp^2 centers. Path a may be operative and path b apparently circumvented simply because of the lower strain energy reflected in the transition state of the former. It is also possible that products formed through path b may escape detection as a result of the inherent photolability and higher absorptivity characteristic of such arylcyclopropenes (particularly those bearing conjugated styryl substituents including **17**) and the possible intervention of facile secondary photoreactions.[3,18]

In this connection it is noteworthy that atypical photobehavior was observed by Zimmerman and Pincock[1c] with a 1,4-pentadiyne (**17a**) which formally constitutes a di-π-methane system. For reasons of the type described above perhaps no di-π-methane rearrangement is observed upon irradiation of the diyne **17a.** When analyzed in the light of our



17a

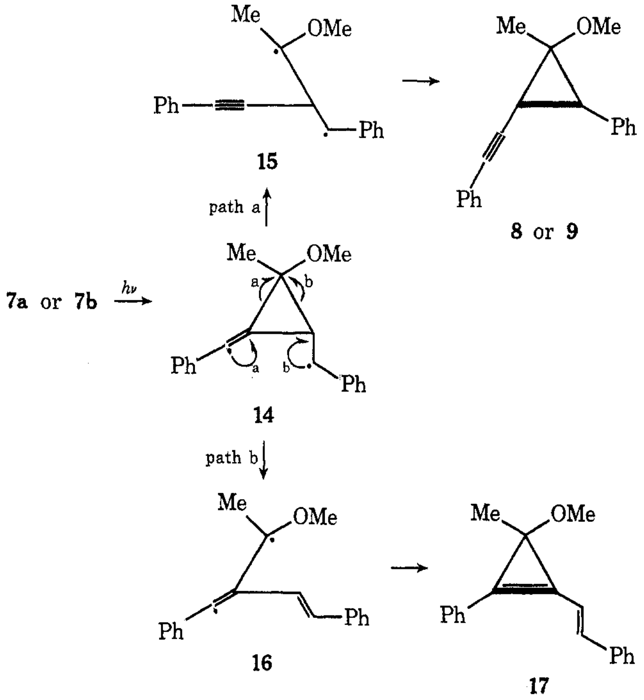
data conceivable 1,3 bridging in the Zimmerman and Pincock compound is reversible and/or insufficient driving force arising from adverse strain factors may exist which preclude the subsequent ring cleavage process. It is proposed that photoinduced 1,5 ethynyl–ethynyl bridging occurs to produce a diradical which acts as an energetic hydrogen abstractor to give as the ultimate product a 1,3-cyclopentadiene. It is significant that the dialkyne **17a** fails to undergo the di-π-methane rearrangement although arylacetylenic systems including **1a** (and **1b**) and acetylenic substrates such as **7a** (and **7b**) photorearrange.

Our data confirm that formation of the di-π-methane products **8, 9, 10,** and **11** from **7a** and **7b** occurs exclusively from the singlet excited state. This result is consistent with results obtained previously for other acyclic di-π-methane systems.[2,17a–e] Furthermore, the observation that cis–trans equilibration is a reaction which may occur from the triplet manifold also parallels the observations made by other investigators on related acyclic di-π-methane systems.

The stereochemical consequences observed for the di-π-methane rearrangement of the substrates **7a** and **7b** also constitute salient features of the photorearrangement process which occurs with these acetylenic systems. To reiterate, the trans isomer **7a** when irradiated at 254 nm yields the related trans cyclopropanes **8** and **9** exclusively. On the other hand the cis enyne **7b** yields the expected cis cyclopropanes **10** and **11** as well as the trans isomer **7a.** Isomerization of **7b** to **7a** competes efficiently with rearrangement. Thus from the results obtained to date reliable quantum yield data can only be extracted for the formation of **10** and **11** since **7a** is known to photorearrange to **8** and **9** under identical conditions and should begin to photoreact to some extent immediately upon production of **7b.** Therefore the value cited for **7a** must represent a minimum quantum yield because of the secondary photoreactions which must occur. The values presented in parentheses for **8** and **9** are not true quantum yields either since **8** and **9** undoubtedly do not arise directly and solely from **7b.** The possibility exists that **8** and **9** (Scheme I) are produced in part as a result of a single step rearrangement of **7b.** A third source for the photoproducts **8** and **9** obtained from **7b** may be the secondary photoisomerization of **10** and **11.** Such a process is not without precedent.[18] Owing to the complexity of the photoreactions of **7b** and the thermo- and photolability of the products and reactants, we have not been able to exclude conclusively the partial formation of **8** and **9** either directly from **7b** or from a secondary photoreaction of **10** and **11** formed initially. While the trans enyne **7a** unquestionably undergoes the di-π-methane rearrangement stereoselectively to produce trans cyclopropanes via the singlet state with retention of stereochemistry at C-5,[16] the question of whether the cis enyne **7b** behaves similarly is clouded by the efficient competing photoisomerization of **7b** to **7a** which provides the trans enyne **7a,** a known precursor for the corresponding trans cyclopropanes.

An equivalent representation to that depicted in Scheme II for the reactions under consideration is given in Scheme III

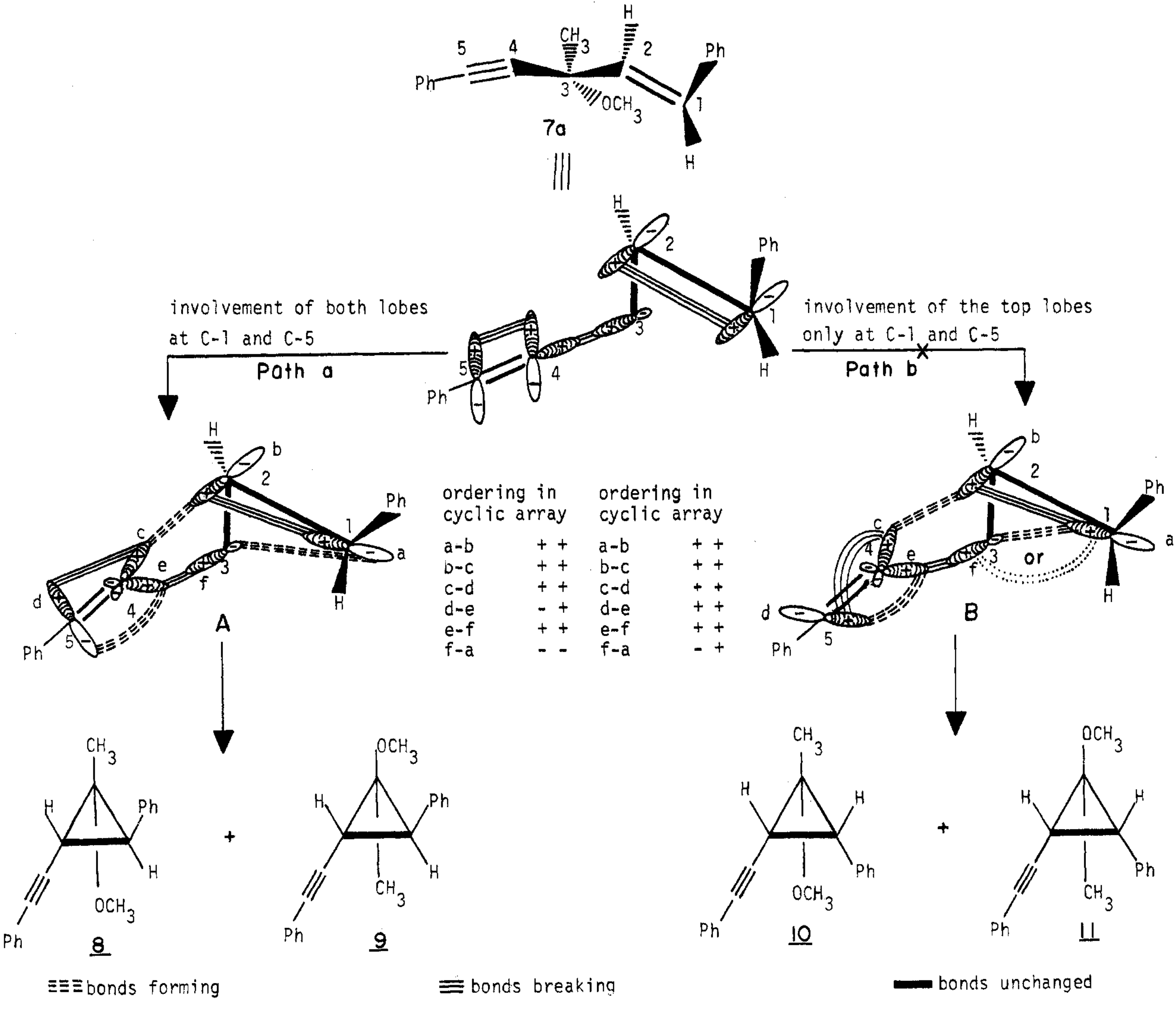
Scheme II



and depicts the change in basis orbitals as the reaction proceeds. It should be noted that the descriptions presented in the latter scheme represent cyclic arrays of six local orbitals containing $(4n + 2)$ π electrons. The basis orbital sets designated are of the form used for mixing through a secular determinant to give the final molecular orbitals and the selection of lobe orientation (i.e., + and − assignments) is arbitrary. Thus no overlap of a bonding or antibonding nature is implied by the interactions embodied in these formulations; the number of odd (plus-minus or minus-plus) interactions may be correlated with the final results of molecular orbital mixing.[17b] Moreover, this more sophisticated representation provides a different perspective from the valence bond approach of Scheme II and offers the added advantage of furnishing a theoretical interpretation for the observed stereochemistry and a more graphic rationale for the regioselectivity.

The significant orbitals involved (Scheme III) at the onset of the reaction are orbitals a and b (i.e., the original olefinic bond linking atoms 1 and 2), between orbitals e and f (the initial sp–sp^3 σ bond C_3–C_4) as well as that between c and d (the preexisting π-acetylenic C_4–C_5 bond). As the reaction ensues interactions may be written between orbitals b and c (constituting the π–π bridging between C_2 and C_4), between orbitals d and e (regenerating the acetylenic C_4–C_5 linkage), as well as between orbitals a and f (the formation of the C_1–C_3

Scheme III. Allowed Basis Orbital Arrays for the Di-π-methane Rearrangement for the Trans Enyne 7a



ordering in cyclic array		ordering in cyclic array	
a-b	+ +	a-b	+ +
b-c	+ +	b-c	+ +
c-d	+ +	c-d	+ +
d-e	− +	d-e	+ +
e-f	+ +	e-f	+ +
f-a	− −	f-a	− +

bond with emergence of the cyclopropyl ring). From available evidence Zimmerman proposes that the last interaction designated probably lags behind the other processes.[2a] This is not unreasonable since prior intervention of other steps in the reorganization should precede bonding to the saturated sp^3 hybridized C-3 atom of the reactant. The relative significance of this time lag may be magnified substantially by the increase in stability which should accrue as a result of the replacement of one methyl substituent of the geminal pair (normally present in conventional di-π-methane substrates) by a methoxy group such as found in **7**; i.e., an alkoxy substituent is more effective in stabilizing a free-radical center than a methyl group.

For purposes of illustration we have followed the precedent established by Zimmerman and Pratt[17b] in Scheme III, of (1) arbitrarily considering the syn rather than anti conformations of a given isomer in this case trans **7a** and (2) in utilizing one of two configurations at C-3 in depicting the basis orbital arrays; however, the overall stereochemical reasoning is independent of what conformation or even configuration is assumed with these racemic systems (vide infra). Two differing 6 π Möbius-like arrays with the requisite odd number of syn discontinuities (one in each case) may be generated depending on whether the same lobes or alternate lobes of the terminal π orbitals are utilized. The pair of six local orbital Möbius arrays a–b–c–d–e–f are categorized as antiaromatic in the ground state, but are aromatic and stable in the excited state, and thus the reorganizations depicted in Scheme III (≡≡≡ and ═════) are both allowed photochemical processes.

The question now arises as to which of the two alternative cyclic arrays (A or B) most accurately represents the preferred reaction course. In a series of previous papers Zimmerman and co-workers, and we independently, have established that the di-π-methane rearrangement proceeds with retention of configuration at carbons 1 and 5 of the 1,4-pentadienyl system.[2a,16,17b] For example, at carbon atom 5 (incorporated in the migrating moiety) it was confirmed that cis substitution remains cis on the π bond of the vinylcyclopropane product while the converse is true for the trans isomer; i.e., *at least superficially*[2a] the π bond of the reactant simply survives the reorganization (vide infra).[17b] Since the acetylenic bond of **7a** and **7b** is linear and radially symmetrical, the problem of stereochemistry at this center is meaningless in this context despite the participation invoked in the valence bond approach delineated in Scheme II.

In the case of the other terminal center 1 of the di-π-methane substrate the evidence compiled by Zimmerman and co-workers[16] and independently accumulated in our laboratory[1a,b,4a] using different substrates shows that cis reactant gives cis product while trans gives trans product in a stereospecific process. Thus the stereochemistry of a double bond of the reactant determines the configuration of the relevant cyclopropyl substituent of the product. That electronic factors rather than least motion considerations are responsible for this phenomenon has been demonstrated in an elegant and convincing manner by Zimmerman et al.[16]

Information which resolves the remaining question of stereochemical uncertainty, namely the configurational fate at C-3, has recently been assembled by Zimmerman and collaborators.[17d] The results verify the tentative conclusions drawn from data obtained earlier with cyclic substrates[17e] that inversion occurs at this insulating sp^3 center in the acyclic di-π-methane systems as well.[17a]

In light of these stereochemical data it is possible to deduce which array (A or B) displayed in Scheme III most accurately depicts the overall molecular reorganization in the case of **7a** and to validate the conclusions on the basis of the new experimental results obtained. It is apparent that the primary arrays of six local orbitals depicted in Scheme III at half-reaction are of Möbius character [one sign inversion between adjacent orbitals, e and d in the case of A, and a and f in B (≡≡≡)] and thus are allowed in the excited state. The torsional motion(s) at C-1 and 3 required by the interactions depicted in array A convert the trans enyne **7a** by path a into the cyclopropanes **8** and **9** bearing trans aryl and phenylethynyl groups which is the course anticipated on the basis of data cited and constitutes the results observed experimentally for **7a**. Moreover, since bond making and bond breaking occur at alternate lobes of orbital e on C-3 (≡≡≡) inversion of the type documented in a 1,4-pentadienyl system[17d] is incorporated in the display A. In contrast the angular rotation necessitated at C-1 and C-3 in B in order to achieve a–f orbital overlap of the type designated (≡≡≡) while ensuring the requisite sign discontinuity and inversion at C-3 does not accommodate the observed data and reveals the preferred route; i.e., path b is unacceptable since the net result is formation of "cis" cyclopropanes. This is contrary to precedent documented experimentally for a variety of systems including those described herein.

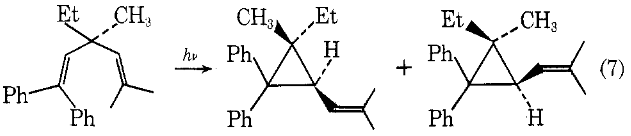
On the other hand, if the angular motions necessary to preserve trans stereochemistry in the product are imposed at C-1 and C-3 (:::::) the e–f orbital overlap becomes ++ (or −−) and the sign discontinuity is dissipated. This operation precludes inversion at C-3, since only one lobe of orbital f is implicated and furthermore, the electronic character of the entire array is altered; i.e., the system is rendered aromatic and of lowest energy in the ground state (Hückel in character with no sign discontinuities present in a six π electron system) and the reaction becomes excited state forbidden. Hence the preferred reaction stereochemistry would appear to involve disrotatory twisting of C-1 with respect to C-3 of the type shown in array A rather than B.

It is interesting to speculate on the possible effects of introducing the acetylenic π system into di-π-methane substrates. In considering 1,5-pentadienyl analogues, in order to accommodate all stereochemical data, it is convenient to select and compare basis orbital arrays for these $4n + 2$ π-electron systems in which the sign discontinuity is reserved for the migrating alkenyl moiety.[6,17b,d] In fact the resulting enforced rotation has led Hixson, Mariano, and Zimmerman[2a] to advance the esoteric proposal that the migrating double bond of the reactant merely appears to survive the rearrangement when indeed orbital reorganization with rotation has occurred in the process.

In cases such as **7a** and **7b**, however, where the presence of the radially symmetrical C_4–C_5 acetylenic bond may no longer impose such restrictions, additional sign discontinuities may be assimilated into this moiety. Perhaps then alternate allowed arrays may exist since no stereochemical repercussions are detectable. If in fact both C_4–C_5 π orbitals of the acetylenic bond are considered explicitly in **7a** and **7b** these systems then become $4n$ in character. Furthermore, regardless of any rehybridization which is invoked at the C_4 reaction center (sp and p, "sp^3 and sp^3" and "sp^5 and sp^5"),[16] it may be shown that introduction of an additional sign discontinuity into the reaction wave function is unavoidable and consequently the initial conclusions remain unchanged. Thus, while an additional sign disparity is introduced the array becomes $4n$ in character and remains aromatic and allowed (of lowest energy) in the excited state.

Perhaps the most intriguing stereochemical feature of the work described relates to the relative ratio of epimers formed as products in the rearrangement of **7a** and **7b**. The epimer which is formed in higher yield in the case of the isomeric pairs **8** and **9** as well as **10** and **11** is that bearing the methoxy and phenylethynyl groups affixed to the same side of the ring (**8** and **10**, respectively). It is interesting to speculate on the origin of this selectivity factor (~2.1 for **8**:**9** and **10**:**11**). Reference to

A values (conformational free-energy differences)[19] shows that a methyl group is much larger than a methoxy group and thus the intervention of adverse steric factors cannot be invoked to explain the results since the larger methyl group would be expected to encounter less interaction during cyclization with the collinear phenylacetylenic group than with the phenyl substituent. It is interesting in this regard that in the conversion of **18** to **19** and **20,** Zimmerman found that the more stable isomer with the ethyl trans to isopropylidene is favored albeit only slightly (4:5) (eq 7).[17d] That a more pronounced effect on the product ratio is not apparent with **18** in the di-π-methane reorganization could be due to the fact that an ethyl substituent is only slightly larger than a methyl group.[19] In summary, since the epimer selectivity favoring the photoproducts **8** and **10** obtained from **7a** and **7b**, respectively, manifest in these cases (2:1) is contrathermodynamic, we cannot ascribe the effect to steric factors and feel justified in invoking secondary electronic effects between the methoxy group and the incipient acetylenic bond to explain the magnitude of the observed specificity.



18 **19** **20**

It should be noted that the syn-syn conformer of **7a** depicted in Scheme III is simply one of two such possible U-shaped geometries. An alternative one exists in which the pendant π moieties are rotated about the C$_3$–C$_4$ and C$_2$–C$_3$ bonds on the sp^3 hybrid center into the plane of the page. This simply has the effect of exchanging the methyl and methoxy substituents (i.e., methoxy becomes cis to phenyl), but the same epimer pairs (**8** and **9** and **10** and **11**) are generated from the corresponding enynes by the operations depicted (Scheme III). Additionally s-transoid conformations of **7a** leading to vinylalkynyl bridging may be written, but again this does not affect the configurational conclusions and the stereochemical predictions are invariant to the choice of conformer selected.

It should be noted that the photoreactions of **7a** and **7b** may also be designated as $4n + 2$ electron $[_\sigma 2_a + {}_\pi 2_a + {}_\pi 2_a]$ electrocyclic processes using the Woodward–Hoffmann analysis and are of lowest energy (allowed) in the excited state. This is a more favorable "cycloaddition" than the alternative $[_\sigma 2_s + {}_\pi 2_a + {}_\pi 2_a]$ interaction. The overall treatment in this manner represents an alternative, but equivalent approach to that formulated in valence bond (Scheme II) or MO terms (Scheme III) devised by Zimmerman.[2a,17a,b] Clearly a system with an odd number of sign inversions will also generate an odd number of antarafacial components and is Möbius while the converse holds true and a Hückel system is defined if an even number of (or zero) sign inversions is present.

In summary it is clear from the results obtained in this study that the traditional di-π-methane rearrangement incorporating only sp^2 hybrid di-π centers may be extended to include systems which also contain sp centers in which the acetylenic moiety migrates efficiently and cyclopropanes are produced. We had previously established[3] that an aryl.π system also cyclizes albeit less efficiently to the terminus of an acetylenic bond to give a cyclopropene. The present study in addition to providing new synthetic routes to acetylenic cyclopropanes also is of mechanistic significance and provides additional information with respect to the concerted character of di-π-methane reactions. The regioselectivity and stereospecificity of the photorearrangements of **7a** and **7b** reinforce the mechanistic proposals made by other workers in the field while our work in this area was in progress. For example, we have confirmed that the stereochemistry at the α position in the styryl chromophore (carbon atom 5 of the di-π-methane system) is maintained during the course of the reaction; i.e., the trans acetylenic alkene gives trans cyclopropanes while the alternate cis substrate gives the cis analogues. Furthermore, as others have found,[2] one may interpret the selectivity exhibited in the photoreactions of **7a** and **7b,** i.e., the migration of phenylethynyl to the exclusion of styryl, in terms of formation of the more stable of the two possible "diradical-like" transition states; however, this may be fortuitous and other factors such as steric effects or strain inherent in a potential cyclopropene nucleus may in fact be responsible for the specificity of the process. It is also of interest that the multiplicity dependent behavior of acyclic di-π-methane systems containing sp hybrid centers parallels that found for those containing only sp^2 hybrid unsaturated groups. It should be noted, however, that in the case of the allenes **3a** and **3b** an alternate reaction competes efficiently with the di-π-methane rearrangement.[4] Our efforts in this area continue with our eventual goal that of obtaining additional information on the migratory aptitudes of various groups in the di-π-methane rearrangement which in turn may shed additional light on the degree of concerted or sequential character of the reaction and extend its synthetic utility.

Experimental Section

General. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 337 and 257 spectrophotometers and were calibrated against polystyrene. The ultraviolet spectra and absorbance values were determined on a Cary Model 17 spectrophotometer. The proton magnetic resonance spectra were obtained on Varian A-60, HA-100, and Hitachi Perkin-Elmer R-20B instruments using deuteriochloroform as the solvent with tetramethylsilane (1%) as the internal standard unless otherwise specified. The mass spectral studies were conducted using a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Woelm neutral alumina and added phosphor was used for column chromatographic separations which were conducted in Vycor columns to facilitate visualization with a hand-held ultraviolet scanning lamp. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Direct irradiations were conducted in serum-capped 15 cm × 12.5 mm i.d. fused quartz tubes. Sensitized irradiations were carried out in serum-capped Pyrex round-bottom flasks or Pyrex test tubes. A Rayonet photochemical reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-W low-pressure lamps was used as a light source unless otherwise specified. The lamps were of the type G8 T5 (254 nm) or F8 T5 (broad emission at 350 nm). A Rayonet MGR-100 Merry-Go-Round or MGR-200 Mini-Go-Round apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.) was utilized in all kinetic and quantum yield studies to ensure uniform exposure of individual samples, which were rotated at 5 rpm. The solutions to be irradiated were degassed either by nitrogen sparging for 25 min or by the multiple freeze–thaw technique.

***trans*-1,5-Diphenyl-3-methyl-1-penten-4-yn-3-ol (6).**[6] A solution of ethylmagnesium bromide was prepared under nitrogen by placing 2.2 g (0.09 mol) of magnesium turnings in 50 ml of anhydrous diethyl ether and slowly adding 10 g (0.09 mol) of ethyl bromide. The mixture was stirred for 2 h prior to careful addition of 8.4 g (0.08 mol) of phenylacetylene in 15 ml of anhydrous diethyl ether. This solution was stirred for 20 h before adding 8.4 g (0.05 mol) of benzalacetone[5] in 30 ml of anhydrous diethyl ether dropwise. The resulting reaction mixture was then stirred for 3 h and 100 ml of a 10% ammonium chloride solution was slowly added. The two phases were separated and the aqueous layer extracted with a 1:1 ether–pentane solution. The combined organic phases were washed with water and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the excess phenylacetylene was removed by heating to 50–60 °C at 0.5 Torr for 1 h. The product **6** which solidified was recrystallized from hexane and 12.5 g (90%) was obtained: ir (KBr) 971 cm^{-1} (trans 1,2-disubstituted alkene); NMR (CCl$_4$) δ 7.45–6.95 (broad s, 10 H, aromatic), 6.76 (d, 1 H, J = 15.0 Hz, olefinic), 6.18 (d, 1 H, J = 15.0 Hz, olefinic), 2.35 (broad s, 1 H, hydroxyl), 1.69 (s, 3 H, methyl); mass spectrum m/e M$^+$ 248.

***trans*-1,5-Diphenyl-3-methyl-3-methoxy-1-penten-4-yne (7a).**

To a stirred solution of 12.6 g (0.05 mol) of the alcohol **6** in 100 ml of dimethyl sulfoxide was slowly added 8.2 g (0.05 mol) of iodomethane. This was followed by the addition of 1.8 g (0.04 mol) of solid sodium hydroxide. The flask was stoppered and stirred for 60–72 h at ambient temperature. The reaction mixture was then poured into 1 l. of water and extracted three times with 250-ml portions of a 1:1 ether–pentane solution. The organic extracts were combined and washed twice with water and then dried over anhydrous sodium sulfate. The residual yellow oil remaining after removal of the volatile solvents under reduced pressure crystallized upon trituration or standing. The product was recrystallized from a 1:1 ether–pentane solution to give 12.7 g (0.05 mol, 96%) of the white crystalline ether **7a:** mp 77–78 °C; ir (KBr) 970 cm^{-1} (trans 1,2-disubstituted alkene[8]); uv λ_{max} (EtOH) 252 nm (ϵ 30 000); NMR ($CDCl_3$) δ 7.60–7.18 (m, 10 H, aromatic), 6.93 (d, 1 H, J = 15.5 Hz, olefinic), 6.14 (d, 1 H, J = 15.5 Hz, olefinic), 3.40 (s, 3 H, methoxy), 1.72 (s, 3 H, methyl); mass spectrum *m/e* M^+ 262.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.07; H, 6.83.

***cis*-1,5-Diphenyl-3-methyl-3-methoxy-1-penten-4-yne (7b).** The cis acetylenic alkene **7b** was readily prepared by photoisomerization of the trans isomer **7a.** A solution of 2.5 g (0.01 mol) of **7a** in 1 l. of dry hexane and 125 ml of acetophenone was sealed in a 2-l. Pyrex round-bottom flask. The solution was purged with nitrogen for 0.5 h prior to irradiation, with stirring, at 350 nm for 12 h. The hexane and acetophenone were removed under reduced pressure and the pale yellow residual oil was found to consist of an equimolar mixture of **7a** and **7b.**[7] This mixture was then chromatographed on a 2.5 cm i.d. Vycor column packed to a height of 60 cm with Woelm grade III neutral alumina with added phosphor. The sample was eluted with hexane and the elution progress was followed by visualization with a 254-nm hand lamp. Only partial separation could be obtained and once elution of the sample began to occur from the column, 30-ml fractions were collected. The first one or two fractions contained pure **7b;** later fractions contained **7a** contaminated with **7b** with the concentration of **7a** constantly increasing as later fractions emerged. The last fractions consisted of pure **7a.** The hexane was allowed to evaporate at ambient temperature in a current of air in a hood. The chromatographic separation was repeated with samples enriched in **7b** in order to obtain greater amounts of pure **7b.** Finally **7b** was distilled at 100 °C and 5–10 μm in a bulb-to-bulb Kugelrohr apparatus to obtain pure **7b,** a colorless oil; bp 100 °C (5–10 μm); ir (KBr) absence of 970 cm^{-1} absorption (excludes trans-disubstituted alkene);[8] NMR ($CDCl_3$) δ 7.52–6.98 (m, 10 H, aromatic), 6.57 (d, 1 H, J = 12.0 Hz, olefinic), 5.72 (d, 1 H, J = 12.0 Hz, olefinic), 3.38 (s, 3 H, methoxy), 1.72 (s, 3 H, methyl); mass spectrum *m/e* M^+ 262.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.80; H, 7.01.

Direct Irradiations of *trans*- and *cis*-1,5-Diphenyl-3-methoxy-1-penten-4-yne (7a and 7b, Respectively). Procedure A. Solutions of **7a** and **7b** (0.037–0.045 M) dissolved in *tert*-butyl alcohol, benzene, and acetonitrile were irradiated at 254 nm for varying periods of time. A pale yellow semisolid oil was obtained upon removal of the volatile solvents in the case of **7a** and **7b,** respectively. The composition of each sample was established by NMR analysis. The data are summarized in Table I.

Procedure B. In a typical preparative irradiation, a solution of 3.5 g (7.6 mmol) of **7a** in 1320 ml of benzene was irradiated at 254 nm for 40 min. After removal of the solvent, the resulting mixture was chromatographed on a 2.5-cm i.d. Vycor column packed to a height of 60 cm with Woelm grade III neutral alumina with added phosphor. The progress of the separation of the sample on the column was followed with a 254-nm hand lamp during elution with hexane. Only partial separation could be achieved and 30-ml fractions were collected once the sample began to elute from the column. The early fractions contained **7b** followed by mixtures of **7b** and **7a.** Later samples contained **7a** while the final samples contained a mixture of *r*-1-methoxy-1-methyl-*t*-2-phenyl-*c*-3-phenylethynylcyclopropane (**8**) and *r*-1-methoxy-1-methyl-*c*-2-phenyl-*t*-3-phenylethynylcyclopropane (**9**). The last fractions were then rechromatographed on a 9-mm o.d. Vycor column packed with Woelm grade III neutral alumina to a height of 50 cm. The chromatography was performed as previously described. In each case bulb-to-bulb distillation of the cyclopropane fractions in a Kugelrohr apparatus at 100 °C and 5–10 μm was required before adequate purity could be achieved. The first compound to be eluted was shown to be **9**, a white, crystalline solid: mp 68–69 °C; ir (KBr) 2220 cm^{-1} (acetylene); uv λ_{max} (EtOH) 252 nm (ϵ 21 300); NMR ($CDCl_3$) δ 7.53–7.02 (m, 10 H, aromatic), 3.17 (s, 3 H, methoxy syn to phenyl), 2.21 (2 overlapping doublets discernible in benzene-d_6, J = 6.5 Hz, 2 H, cyclopropyl), 1.68 (s, 3 H, methyl, anti to phenyl); mass spectrum *m/e* M^+ 262.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.87; H, 7.16.

The second compound to be eluted was shown to be **8**, a white, crystalline solid: mp 36.5–37 °C; ir (KBr) 2225 cm^{-1} (acetylene); uv λ_{max} (hexane) 252 nm (ϵ 20 400); NMR ($CDCl_3$) δ 7.50–7.02 (m, 10 H, aromatic), 3.55 (s, 3 H, methoxy anti to phenyl), 2.71 (d, 1 H, J = 6.5 Hz, benzylic cyclopropyl H), 1.93 (d, 1 H, J = 6.5 Hz, phenylethynylcarbinyl H), 1.20 (s, 3 H, methyl syn to phenyl); mass spectrum *m/e* M^+ 262.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.92. Found: C, 86.71; H, 7.10.

Procedure C. In a typical preparative irradiation of **7b,** 1.0 g (3.8 mmol) in 90 ml of benzene was irradiated at 254 nm for 1 h. The resulting mixture was processed as described in B. The chromatographic fraction containing **8,** *r*-1-methoxy-1-methyl-*c*-2-phenyl-*c*-3-phenylethynylcyclopropane (**10**), and *r*-1-methoxy-1-methyl-*t*-2-phenyl-*t*-3-phenylethynylcyclopropane (**11**) was then rechromatographed as outlined in procedure B. The first compound to emerge was **10,** a white, crystalline solid: mp 48–49 °C; NMR ($CDCl_3$) δ 7.48–7.08 (m, 10 H, aromatic), 3.40 (s, 3 H, methoxy syn to phenyl), 2.62 (d, 1 H, J = 11.0 Hz, cyclopropyl benzilic H), 2.26 (d, 1 H, J = 11.0 Hz phenylethynylcarbinyl H), 1.40 (s, 3 H, methyl anti to phenyl); mass spectrum *m/e* M^+ 262.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.84; H, 7.09.

The second compound eluted, namely **11,** was obtained as a colorless liquid: ^1H NMR ($CDCl_3$) δ 7.58–7.09 (m, 10 H, aromatic), 3.43 (s, 3 H, methoxy anti to phenyl), 2.24 (d, 1 H, J = 9.5 Hz, benzylic cyclopropyl H), 2.00 (d, 1 H, J = 9.5 Hz, phenylethynylcarbinyl H), 1.57 (s, 3 H, methyl syn to phenyl); mass spectrum *m/e* M^+ 262. The third compound to elute was assigned structure **8.**

Sensitized Irradiations of *trans*- and *cis*-1,5-Diphenyl-3-methyl-3-methoxy-1-penten-4-yne (7a, 7b). The procedure followed and data obtained upon sensitized irradiation of **7a** and **7b** in hexane using acetophenone as a sensitizer are described in the procedure for the preparation of **7b.** Acetone also functions as a convenient sensitizer for **7a,** but affords a smaller percentage of **7b** even when irradiations were carried out for longer time periods.

Quantum Yield Determinations for the Rearrangement of *cis*- and *trans*-1,5-Diphenyl-3-methyl-3-methoxy-1-penten-4-yne (7a and 7b Respectively). 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[12] was employed. 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 100-MHz NMR. Quantum yields which are quoted in Scheme II represent an average of four determinations.

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Registry No.—**6**, 60184-29-4; **7a**, 42053-37-2; **7b**, 42053-36-1; **8**, 42053-40-7; **9**, 42053-41-8; **10**, 42053-38-3; **11**, 42053-39-4; ethyl bromide, 74-96-4; phenylacetylene, 536-74-3; benzalacetone, 122-57-6.

References and Notes

(1) (a) Presented in part at the 27th Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, Dec 1–3, 1971, Abstract No. 238, p 81. (b) A preliminary account of this work has appeared: J. Perreten, D. M. Chihal, G. W. Griffin, and N. S. Bhacca, *J. Am. Chem. Soc.*, **95**, 3427 (1973). (c) While this work was in progress, the photochemistry of a diphenylethynylmethane was reported [H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **95**, 3246 (1973)]. An unusual mechanistic departure (see ref 16) from the anticipated course of reaction was observed in which reductive cyclization to give a cyclopentadiene occurs with

obligatory initial 1,5 bonding at the acetylenic termini. (d) Taken in part from the Dissertation submitted in partial fulfillment for the requirements of the Ph.D. degree of D. M. Chihal, University of New Orleans, 1975.

(2) (a) For a comprehensive review of the di-π-methane rearrangement see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973). (b) For a classic early example of the di-π-methane reaction see H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).

(3) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Am. Chem. Soc.*, **93**, 2327 (1971).

(4) (a) Presented in part at the 28th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 6–8, 1972, Abstract No. 222, p 76. (b) D. C. Lankin, D. M. Chihal, G. W. Griffin, and N. S. Bhacca, *Tetrahedron Lett.*, 4009 (1973); D. C. Lankin, D. M. Chihal, N. S. Bhacca, and G. W. Griffin, *J. Am. Chem. Soc.*, **97**, 7133 (1975).

(5) H. Gilman, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1961, p 77.

(6) *Caution:* It has been noted in one case that the alcohol **6** induces an allergic reaction upon contact even with the vapors with the response becoming increasingly severe upon repeated exposure. Symptoms include periorbital edema, erythema, and nausea.

(7) Irradiation of **7b** under the same conditions likewise gives a mixture of **7a** and **7b** of similar composition.

(8) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962, p 25.

(9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Oxford, 1969, p 301.

(10) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 251.

(11) The nomenclature for the acetylenic cyclopropanes **8, 9, 10,** and **11** is in accord with "IUPAC Tentative Rules for the Nomenclature of Organic Chemistry, Section E. Fundamental Stereochemistry, Rule E-3.3", *J. Org. Chem.*, **35**, 2849 (1970). The designations *r, c,* and *t* refer to the reference center and cis and trans substituents, respectively.

(12) (a) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956). (b) It has been shown experimentally, ref 12c, and theoretically, ref 12d, 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 actinometer cell and similar criticisms might be advanced concerning our determinations with **7a** and **7b** despite the fact that the Mini-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 nearly monochromatic light source used and the flat cell surfaces exposed. (c) G. F. Vesley, *Mol. Photochem.*, **3**, 193 (1971). (d) M. D. Shetlar, *ibid.*, **5**, 287 (1973).

(13) (a) A sample of this compound was generously supplied by Professor H. E. Zimmerman, Department of Chemistry, University of Wisconsin, Madison, Wis. (b) We wish to thank Professors Zimmerman and Hixson for communication of data regarding the compounds **12a** and **12b** prior to publication and for fruitful correspondence and discussions during the preparation of this manuscript.

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(15) The risks inherent in relying solely on physical methods for structure elucidation have been detailed recently [H. E. Zimmerman and L. M. Tolbert, *J. Am. Chem. Soc.*, **97**, 5497 (1975), ref 12]. We feel, however, that our cyclopropane stereochemical assignments are secure in view of the availability of all isomers, the reliability of NOE experiments, the validity of coupling constant data, and the total self-consistency of the interpretation in the case of these unstable, compounds which are otherwise difficultly accessible by alternate synthetic means.

(16) During the preparation of our initial publication (see Acknowledgment and p 542, ref 2a) the results of an independent investigation of the stereochemistry of the di-π-methane rearrangement at carbon atom 1 of a diene were reported. See H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Am. Chem. Soc.* **94**, 5504 (1972); **96**, 1459 (1974).

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Formation of an Unusual Steroidal Oxetane and Its Transformation Products

Elliot L. Shapiro,* Lois Weber, Stuart Polovsky,[19] and James Morton

Natural Products Research Department, Schering Corporation, Bloomfield, New Jersey 07003

Andrew T. McPhail* and Kay D. Onan

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Derek H. R. Barton

Chemistry Department, Imperial College, London SW 7 2AY, England

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Chlorination of 6-chloro-16-methylene-17α-hydroxy-4,6-pregnadiene-3,20-dione (**1b**) gave unexpectedly 12% of an oxetane **3a**. Treatment of **3a** with base gave a D-homo seven-membered ring system **7** which with acid afforded the 15-acetyl androstadiene **9a**. The elucidation of these structures, and related transformations, are discussed, together with the application of single-crystal x-ray analyses for unequivocal structural determination.

In connection with studies of structural and pharmacological modifications of the progestogen, 6-chloro-16-methylene-17α-hydroxy-4,6-pregnadiene-3,20-dione acetate (**1a**),[1] two of us[2] sought to prepare 6-chloro-16β-chloromethyl-16α,17α-oxido-4,6-pregnadiene-3,20-dione (**2**).[3] Generation of the 16β-chloromethyl-16α,17α-oxido moiety from the 16-methylene-17-hydroxy unit has been accomplished previously by use of *N*-chlorosuccinimide[4] or chlorine.[3,5] With the 17-hydroxy **1b** available, it appeared that conversion to **2** might be effected, even though it was recognized that chlorination of the 4,6-dien-3-one system might also occur.[6] Using chlorine, the required compound **2** was obtained in moderate yield, but a significant amount of an unexpected oxetane, **3a**, was also produced. It is the formation of **3a**, its structural characterization, and subsequent transformation products (particularly **7** and **9**) which are the subject of this report. Elucidation of the constitution of **3a** was attempted initially by chemical transformations and interpretation of the various physical data presented in Tables I–III and Table X (elementary analyses, included in supplementary material), but this approach led to conflicting conclusions. Its structure, as well as structure **9a**, were finally established unequivocally by single-crystal x-ray analysis.

Treatment of **1b** with 1.1 equiv of chlorine (in the presence of 1.1 equiv of pyridine) for 5 min gave the 16β-chloromethyl 16α,17α-oxide (**2**) in 54% yield and another product in approximately 12% yield, as well as unreacted **1b**. Efforts to increase the yield of this minor product relative to the oxide **2**