other compounds with retention times comparable to the alkene were detected.

The structure of the alkene **2** rests on its spectra and chemical reactivity. The nmr spectrum shows a triplet at δ 5.68 (area 0.97) and a complex absorption at δ 0.8–2.8 (area 13.0), the infrared spectrum (CCl_4) shows significant peaks at 3050 and 1620 cm^{-1}, and the mass spectrum shows the molecular ion at m/e 122. The intensities of the isotopic peaks at m/e 123 and 124 (10.1 and 0.7%, respectively) correspond to those calculated for the formula C_9H_{14}. On standing in air **2** reacts with oxygen and polymerizes. Treatment of a solution of **2** in 80% aqueous acetone (6 ml) with one drop of 70% perchloric acid at room temperature produces a high yield of bicyclo[3.3.1]nonan-1-ol, identical with an authentic sample.[17] No other volatile products of this reaction could be detected by glpc. We are currently investigating the chemistry of this and other highly strained alkenes in our efforts to delineate the limits of Bredt's rule.[18,19]

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(17) Kindly supplied by Professor William G. Dauben.

(18) This work was generously supported by grants from the Petroleum Research Fund and from the Faculty Research Fund of the Horace H. Rackham School of Graduate Studies of the University of Michigan.

(19) NOTE ADDED IN PROOF. Since submission of this paper Professor James A. Marshall has informed us that his research group has independently prepared bicyclo[3.3.1]non-1-ene (**2**) using a completely different synthetic approach. We thank Professor Marshall for his cooperation in communicating his results to us prior to publication.

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Electron Transfer between Anion and Molecule of Hexahelicene

Sir:

Earlier measurements of electron-transfer rates between anions and neutral molecules of an optically active substance have revealed only a small difference in the transfer rates between like optical configurations and between enantiomers.[1] The optical activity in the case first reported, 1-(α-naphthyl)-1-phenylethane, originates in an asymmetric center at which the density of the transferring electron is small.

We now report measurements with hexahelicene, a molecule in which a large asymmetry exists in the π-electron system.[2,3] The measurements have been carried out in the fast exchange limit[4] for the potassium salt in tetrahydrofuran. At 23° the results are $k_{DD} = [(6.9 \pm 0.2) \times 10^8]\nabla\ M^{-1}\ sec^{-6}$ and $k_{DL} = [(1.7 \pm 0.2) \times 10^8]\nabla\ M^{-1}\ sec^{-1}$, where ∇ is the second moment. The ratio of rates obtained from the above data does not require measurement of the second moment. The measured second moment is 17.6 gauss^2. The absolute rates are then $k_{DD} = (1.2 \pm 0.3) \times 10^{10}\ M^{-1}\ sec^{-1}$ and $k_{DL} = (3.0 \pm 0.3) \times 10^9\ M^{-1}\ sec^{-1}$, where the errors include the uncertainties in the second moment.

It is possible that the difference is directly related to the asymmetry in the π-electron distribution. If the wave function for the transferring electron in the enantiomers is represented by

$$\psi^{\pm} = a\psi_S \pm b\psi_A$$

where ψ_S and ψ_A are the symmetric and antisymmetric parts with respect to inversion, the interactions between like and unlike enantiomers are given by

$$V_{++} = V_{--} = a^2V_{SS} + b^2V_{AA}$$

$$V_{+-} = V_{-+} = a^2V_{SS} - b^2V_{AA}$$

$V_{++} = V_{--}$ is the interaction energy between a radical ion and neutral molecule of the same optical configuration; V_{+-} is the corresponding quantity for an enantiomeric pair. V_{SS} is the interaction term between the symmetric parts of the functions in the two reacting molecules, and V_{AA} is the interaction between their antisymmetric parts.

The next step in our work is a search for the connection between the electronic behavior as revealed by optical rotations of the anions and the rate measurements.

Acknowledgment. We wish to thank Professor M. S. Newman, who generously supplied both the racemic and the optically active hexahelicene used in the experiments. The preparation of the hexahelicene was supported by the Petroleum Research Fund of the American Chemical Society. This work has been supported by the National Institutes of Health under Grant GM 13205 and by the National Science Foundation.

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(1) W. Bruning and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 373 (1966).

(2) (a) M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956); (b) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(3) The anions exhibit large rotations and Cotton effects in the visible region. The observation will be reported in another communication.

(4) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **46**, 2314 (1967).

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Mechanisms of Photochemical Reactions in Solution. XLVII.[1] Cyclization of Compounds Containing Phenyl and Conjugated Dienyl Chromophores

Sir:

Molecules containing two unconjugated chromophoric units have been of considerable interest to spectroscopists.[2,3] Coupling between the groups leads to perturbation of both the energies and intensities of spectroscopic transitions compared to those of model systems in which the chromophores are isolated. Such coupling should also have significant implications for photochemistry. For example, cases are known in which the lowest lying excited singlet state is mainly localized in one part of a molecule and the lowest triplet in another, with weak coupling between the units providing an efficient path for energy transfer between the chromophores.[4] Internal energy transfer as a precursor to occurrence of photoreactions characteristic

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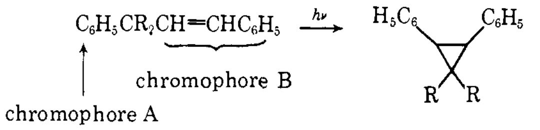
(1) Part XLVI: H. Gotthardt, R. Steinmetz, and G. S. Hammond, *Chem. Commun.*, 480 (1967).

(2) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 437–449.

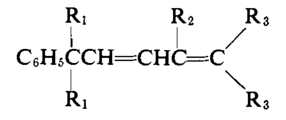
(3) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 7.

(4) P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963).

of one of the units has also been observed.[5] We are interested in cases in which a chemical change involves both chromophoric groups. Photocyclization of derivatives of propene-bearing phenyl substituents on the terminal carbon atoms[6,7] is an example.



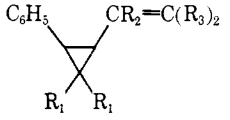
In the excited states the excitation is probably largely localized in chromophore B, and coupling with the phenyl group, chromophore A, is not readily detectable by any means other than the chemical transformation. However, in molecules such as **1** the situation is more interesting. The excitation energy of the lowest excited singlet state should be largely localized in the phenyl group, but in the triplets the excitation locus should move to the diene unit.[8]



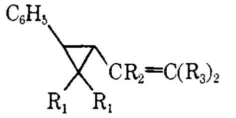
$C_6H_5C(R_1)_2CH{=}CHC(R_2){=}C(R_3)_2$

1a, $R_1 = R_3 = CH_3$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = H$

The dienes have been prepared by addition of appropriate Wittig reagents to phenyldimethylacetaldehyde.[9] Irradiation of the hydrocarbons with a mercury resonance lamp leads to smooth cyclization to mixtures of stereoisomeric phenylvinylcyclopropanes (**2**) in which compounds believed to be the *trans* isomers predominate.



cis-**2a–c**



trans-**2a–c**

cis and *trans* isomers of **1a** have been separated by vapor chromatography. However, irradiation of either the *trans* isomer or a mixture leads to production of the same mixture containing 10% *cis*-**2a** and 90% *trans*-**2a**. Interruption of the reaction at low conversion shows that *cis–trans* photoisomerization occurs so rapidly that most of the **2** is produced while the diene system is close to a photostationary state. The structures of the cyclopropanes are clearly indicated by their spectra. The compounds all contain vinyl groups (nmr) that are unconjugated with the benzene ring (ultraviolet). Resonances due to the two methyl groups attached to the rings are separated by τ 0.3–0.4 indicating that one is *cis* and one *trans* to the phenyl group. Resolution of the high-field nmr signals due to the ring protons in **2a** and **2c** is incomplete because they are overlapped by allylic methyl protons. Integration shows that the total areas of the unresolved portion of the spectra are appropriate relative to the sharp signals due to the methyl groups attached to the ring and unresolved signal assigned to the aromatic protons. The stereochemistry of **2a** and **2b** was indicated by catalytic hydrogenation over platinum[10] to produce the 1-phenyl-2,2-dimethyl-3-isobutylcyclopropanes followed by base-catalyzed equilibration of the latter by the method of Closs and Moss.[11] In the equilibrated mixture the cyclopropane derived from the predominant photoproduct (*trans*-**2a**) predominated by a wide margin and was, therefore, presumed to have the *trans* configuration. There is no evidence for photochemical interconversion of the stereoisomeric alkenylcyclopropanes,[12] so predominant formation of the *trans* isomer in photocyclization is the result of kinetic control. It is interesting that the same steric preference was observed in photocyclization of the phenylpropenes.[6,7]

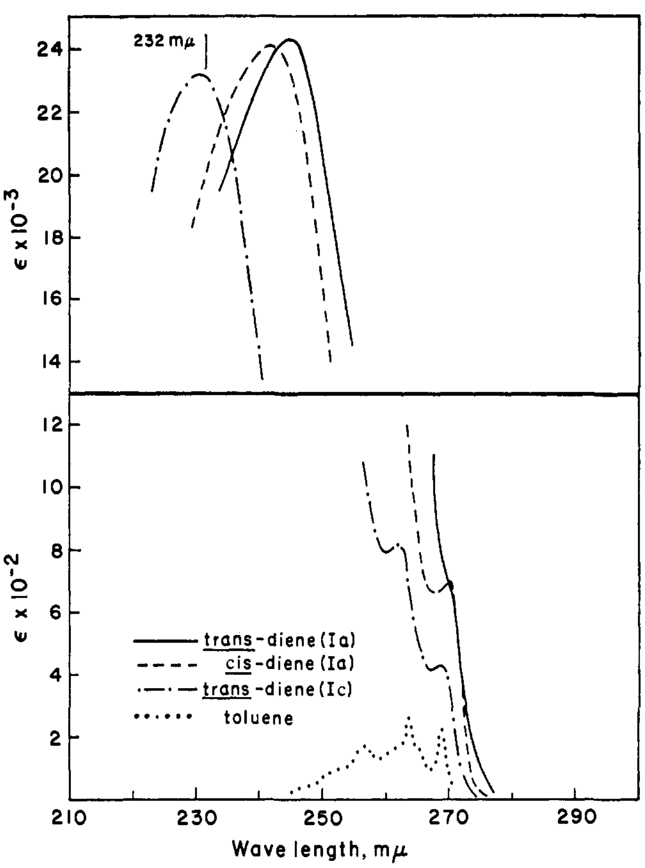


Figure 1. Spectral maxima for three 5-phenyl-1,3-butadienes.

Figure 1 shows the absorption spectra of compounds *cis*-**1a**, *trans*-**1a**, and *trans*-**1c** along with the spectrum of toluene and λ_{max} for a trisubstituted alkylbutadiene. There seem to be inflections on the long-wavelength side of the broad, almost featureless spectra of the

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(5) See, for example, H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965); or G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, **87**, 4959 (1965).

(6) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Hodson, and G. Klose, *ibid.*, **87**, 1410 (1965).

(7) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

(8) For a discussion of conjugated dienes as acceptors of triplet excitation, see R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(9) The aldehyde was prepared in 90% yield by treatment of β,β-dimethylstyrene oxide with formic acid.

(10) J. A. D'yakonov and V. F. Myznikov, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, 1, 489 (1953); through *Chem. Abstr.*, **49**, 883 (1955).

(11) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(12) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5970 (7967).

arenedienes. This may correspond to the $^{1}L_b$ band of benzene;[13] if so, it is apparently slightly red shifted. The intense maxima which occur variously from 2310 to 2450 A are probably related to the first π,π^* transition of butadiene,[14] with a large red shift and an increase in oscillator strength. Since both features fall at long wavelength relative to the transitions in the reference compounds, more than two excited states must be interacting. If the intense maximum is related to the butadiene transition, it must be mixed with other benzene-like transitions in addition to the $^{1}L_b$ band. This is in no way surprising but indicates that definitive analysis of the spectra will require data from the vacuum ultraviolet. Key features of the spectra of three of the compounds are shown in Figure 1.

Even though chromophoric groups are directly coupled, the cooperative chemical reaction is not rapid enough to become the dominant mode of decay. We have not determined quantum yields for the cyclization, but they must be rather low, since *cis–trans* isomerization is more rapid. The mechanism of isomerization is in itself interesting and may be related to either or both of two other phenomena: (1) quening of excited singlet states of aromatic hydrocarbons by conjugated dienes[16] and (2) the fact that all attempts to effect ring closure of compounds **1** using photosensitizers as the primary light absorbers have been totally unsuccessful. Energy is, however, transferred to the substrates because *cis–trans* isomerization occurs. Apparently, as was the case with the phenylpropenes,[6,7] ring closure occurs only in the excited singlet states, not in the triplets formed by energy transfer.

Acknowledgment. This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, under Contract No. AF 49(638)-1479.

(13) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

(14) According to Woodward's rules[15] the 2100-A maximum of butadiene is shifted 50 A to the red for each alkyl substituent on the diene unit. Thus the predicted maxima for the compounds whose spectra are shown in Figure 1 are: **1a**, 2250 A, and **1c**, 2200 A.

(15) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).

(16) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

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Mechanisms of Photochemical Reactions in Solution. XLVIII.[1] Rearrangement of Phenylvinylcyclopropanes

Sir:

In the accompanying communication we have described the preparation of *cis*- and *trans*-3,3-dimethyl-2-(2′,2′-dimethylvinyl)-1-phenylcyclopropane (**2a** and **2b**, respectively, 90% yield). The compounds are themselves photolabile when irradiated with a mercury resonance lamp. This reactivity is not a complication in the preparation of **2a** and **2b** since the acyclic precursors (compounds **1** in ref 1) absorb more strongly[2] than the cyclopropane derivatives.

As is shown in Chart I, irradiation of **2a** and **2b** gives the same set of products which include neither the dienes from which the cyclopropanes were prepared nor the cyclopentene that would have been expected from thermal rearrangement of a vinylcyclopropane.[3] The photoproducts **3**, **4**, and **5** are produced in the ratio 1:6:2. The principal product formed by path B was isolated in 50% yield by vapor chromatography and shown to consist of two constituents, **4a** and **4b**, in the ratio 1:2.2. The structure of **5** was assigned on spectral evidence.[4] Infrared and nmr spectra of both **5** and the compound to which it was converted on hydrogenation showed that the substances contained disubstituted benzene nuclei. All nmr resonances of both compounds were compatible with the structure shown.

The assignment of structures to **4a** and **4b** is based on both chemical and spectral evidence. The nmr spectra show the absence of vinyl protons, the presence of four methyl groups, signals at relatively high field due to the bridgehead protons, and signals at lower field for the benzylic protons. The *syn* structure is assigned to **4a** because the resonance from the benzylic proton is split into a doublet, with $J = 2$ cps, centered at τ 7.10. The corresponding signal in **4b** occurs as a singlet at τ 7.12. Vicinal protons attached to cyclobutanes have generally been found to be more strongly coupled in the *cis* than in the *trans* configuration. A confirmatory indication is provided by the occurrence of the signal due to bridgehead protons in **4b** at relatively high field (τ 9.02 and 8.91) compared to **4a** (τ 8.43 and 8.34), probably because of the diamagnetic anisotropy of the adjacent phenyl group. The ultraviolet spectra of both compounds resemble those of alkylbenzenes.

Assignment of the more strained *syn* structure to **4a** is consistent with its chemical reactivity. On being heated to 250° the compound undergoes smooth conversion to a single product. The isomer **4b** is stable at 250° but at 290° is converted to four products, none of which has vapor chromatographic retention times equal to the product from **4a**. One of the products from **4b** does have the same retention time as **7**, a compound formed more conveniently by acid-catalyzed rearrangement of the bicyclopentanes. No attempt has been made to isolate and characterize the pyrolysis products. No interconversion of **4a** and **4b** was observed in the pyrolytic experiments.

Compound **4a** is hydrogenated smoothly to **9** at atmospheric pressure and room temperature in the presence of palladium on charcoal; **4b**, on the other hand, resisted most attempted hydrogenations in the presence of the same catalyst as well as metallic platinum and Raney nickel. In a single experiment hydrogen was taken up and **6**, identical with material produced by hydrogenation of **7**, was formed. We believe that rearrangement to **7**, catalyzed by adventitious acid, preceded hydrogenation.

Acid-catalyzed isomerization of the bicyclopentanes is almost completely stereospecific. On treatment with

(1) Part XLVII: H. Kristinsson and G. S. Hammond, *J. Am. Chem Soc.*, **89**, 5968 (1967).

(2) The values of ϵ_{max} at 2537 A are about 16.200 for the acyclic compounds and about 1000 for the cyclopropane.

(3) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4896 (1960).

(4) Satisfactory elementary analyses were obtained for all new compounds.