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]

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

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(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.

(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

(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).