

sensitivities suggest that the chromophores of these two pigments have similar conformations when bound to opsin. Since steric hindrance prohibits the 11-*cis* isomer of 14-methylretinal from assuming the crystal conformation of 11-*cis*-retinal, it is clear that this conformation of 11-*cis*-retinal is not the only one that can fit into the binding site. The 12-*s-trans* conformation **2** is a possibility but determination of the exact conformation requires further studies.

In line with a general phenomenon seen for other natural and artificial pigments,<sup>14</sup> 14-*m*-isorhodopsin I absorbs at shorter wavelength (494 nm) than the 11-*cis* pigment (508 nm). Of the three geometric isomers of 13-desmethyl-14-methylretinal tested for their reactivity with opsin, only the 11-*cis* isomer (*cf.* **12**)<sup>17</sup> formed a pigment, but in low yield and unstable:  $\lambda_{\text{uv}}$  492 nm, CD 487 and 300 nm (positive signs) (both measured in 2% Triton X-100).

**Acknowledgments.** We thank Sally Chambers for technical assistance.<sup>18</sup>

(17) *Cf.* footnote *b* in Table I.

(18) This work was supported by NIH Grants EY-00433 and EY-60000 and by the Hoffmann-La Roche Foundation.

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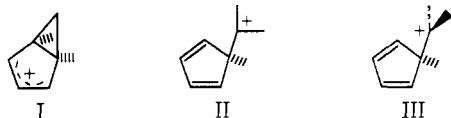
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### Degenerate Rearrangement in Homocyclopropenyl Cation. Violation of Orbital Symmetry Control for a Sigmatropic Migration<sup>1</sup>

Sir:

The stereospecific circumambulation of cyclopropane about the cyclopentadienyl ring in bicyclo[3.1.0]hexenyl cation (**I**) provided one of the earliest examples of or-



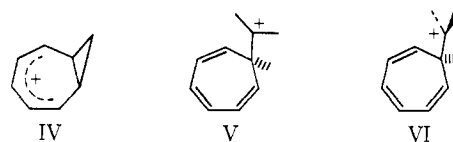
bital symmetry control over a sigmatropic migration process.<sup>2,3</sup> The maintenance of positive orbital overlap during these suprafacial [1,4] shifts necessitates passing through a bisected as opposed to an eclipsed cyclopentadienylcarbinyl transition state (**II** and **III**, respectively) at each step of the way. Although experimental data are presently unavailable on the stereochemistry of the [1,6] rearrangement in the next higher cationic analog, homotropylium<sup>4</sup> (**IV**), theoretical molecular orbital calculations indicate that it too falls

(1) Presented as part of the Symposium on Theoretical Organic Chemistry, American Chemical Society 29th Southwest Regional Meeting, El Paso, Texas, Dec 6-7, 1973.

(2) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971), and references therein.

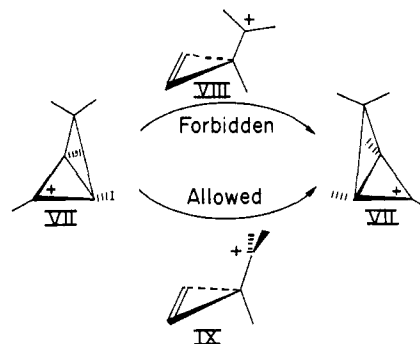
(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) For a discussion of the difficulties involved see J. A. Berson and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 8907 (1972).



under orbital control, this time the eclipsed cycloheptatrienylcarbinyl cation (**VI**) being the preferred intermediate structure.<sup>5</sup> In each of these examples the best available level of theory indicates the symmetry forbidden transition state (**III** and **V** respectively for rearrangement in the bicyclo[3.1.0]hexenyl and homotropylium cations) to lie approximately 10 kcal/mol higher in energy.<sup>5a,c,6</sup>

Our attention in this communication focuses on the circumambulation process in the lower homolog of bicyclo[3.1.0]hexenyl cation, the homocyclopropenyl system (**VII**). Here again two transition state pathways



are conceivable, and, as before, orbital symmetry arguments (this time for a [1,2] migration) should enable us to choose between them. Thus on this basis alone, we would anticipate an eclipsed cyclopropenylcarbinyl type structure (**IX**) to be preferred over a bisected one (**VIII**). Realize, however, that the manifold of high-lying occupied molecular orbitals on cyclopropane contains not only a  $\pi$  component but also a pair of in-plane orbitals analogous to the Walsh functions of cyclopropane<sup>7</sup> (Figure 1). It has already been noted that interaction between the asymmetric Walsh cyclopropane orbital and the carbonium center in cyclopropylcarbinyl results in far greater net stabilization than the corresponding interaction involving the symmetric component.<sup>8-10</sup> As the magnitude of this differential stabilization is fairly large (theoretical molecular orbital calculations

(5) (a) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8908 (1972); (b) *ibid.*, **95**, 5807 (1973); (c) *ibid.*, submitted for publication.

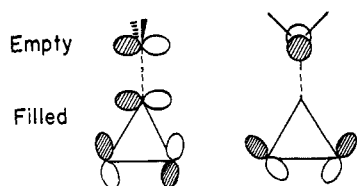
(6) Experimentally, the symmetry forbidden transition state for circumambulatory rearrangement in heptamethyl bicyclo[3.1.0]hexenyl cation lies at least 5.7 kcal/mol above the allowed structure: R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).

(7) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); for a discussion see R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

(8) For reviews of the experimental literature see H. G. Richey, Jr., in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, p 1201; K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, *ibid.*, p 1295.

(9) Theoretical molecular orbital calculations: (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970), and references therein to earlier work; (b) W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972); (c) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972); (d) W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 302 (1974).

(10) The conjugative interaction present in bisected cyclopropylcarbinyl displays itself in terms of an extremely short ring-carbonium center bond length (1.384 vs.  $\sim$ 1.52 Å in methylcyclopropane). The corresponding linkage in eclipsed cyclopropylcarbinyl (1.480 Å) is indicative of a much diminished interaction. Theoretical ring-carbonium center bond lengths for bisected and eclipsed cyclopropenylcarbinyl (1.384 and 1.524 Å, respectively) show similar effects.



suggest that bisected cyclopropylcarbinyl is some 31 kcal/mol more stable than the eclipsed form<sup>9d</sup>), one might expect this effect to totally outweigh the 10 kcal/mol (estimated from calculations on related systems<sup>5a,c</sup>) gained by maintenance of orbital symmetry during the sigmatropic rearrangement process. Lacking experimental data, it is of interest to probe the matter further theoretically.<sup>11</sup>

4-31G level calculations<sup>16</sup> (at optimum STO-3G molecular geometries) indicate circumambulation *via* the Woodward-Hoffmann allowed eclipsed cyclopropenylcarbinyl transition state to require 64.6 kcal/mol, far higher than theoretical estimates for the corresponding symmetry allowed processes in bicyclo[3.1.0]hexenyl (20 kcal/mol<sup>5a,c</sup>) and homotropylium (43 kcal/mol<sup>5a,c</sup>) carbocations.<sup>17</sup> Some 38 kcal/mol less are required for passage through the alternative (and Woodward-Hoffmann forbidden) bisected cyclopropenylcarbinyl cation. We have thus uncovered an extreme case of a symmetry controlled process in which the orbital manifold beneath the highest occupied function plays the dominant role.<sup>18</sup> It can be seen that stabilizing (but distant) interactions involving the ring  $\pi$  system and the symmetric Walsh cyclopropene component as well

(11) We have used single determinant molecular orbital theory throughout. Following past practices, the minimal STO-3G basis functions<sup>12</sup> are employed to calculate equilibrium and transition state geometries alike, the detailed procedures for which have already been discussed.<sup>13</sup> Computations at interesting points are then performed using the 4-31G extended basis set<sup>14</sup> in order to more accurately assess relative molecular energetics. All calculations have been carried out using the GAUSSIAN 70 series of computer programs.<sup>15</sup> Complete structural and energetic details will be presented in an upcoming full report.

(12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

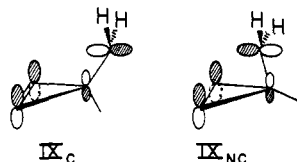
(13) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(14) R. Ditchfield, W. J. Hehre, and R. F. Stewart, *J. Chem. Phys.*, **54**, 724 (1971).

(15) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

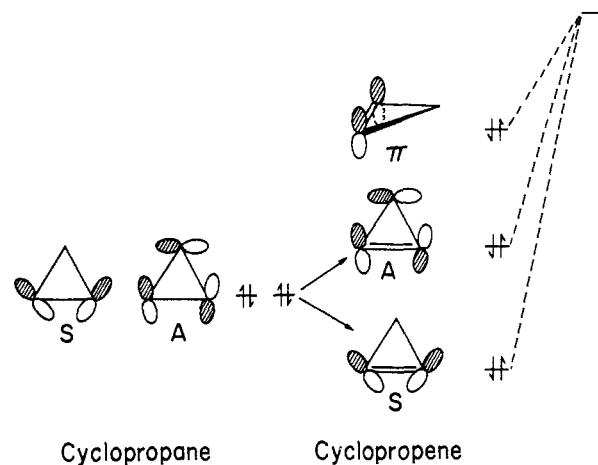
(16) Theoretical (4-31G) energies (au): homocyclopropenyl (VII), -153.79574; bisected cyclopropenylcarbinyl (VIII), -153.75315; eclipsed cyclopropenylcarbinyl (IX<sub>c</sub>), -153.70063; eclipsed cyclopropenylcarbinyl (IX<sub>nc</sub>), -153.69285.

(17) We find two local minima on the C<sub>3</sub>H<sub>5</sub><sup>+</sup> potential surface corresponding to eclipsed cyclopropenylcarbinyl. In terms of the highest occupied molecular orbital these may be depicted as follows

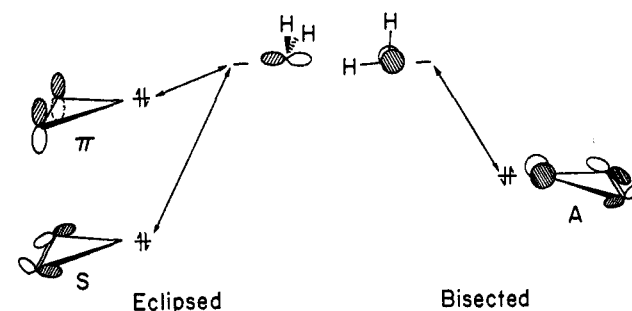


Although the open "classical" structure (IX<sub>c</sub>) is some 4.9 kcal/mol more stable, the tighter "nonclassical" form (IX<sub>nc</sub>) might more properly be termed the Woodward-Hoffmann allowed transition state for degenerate rearrangement, and we have used its energy relative to homocyclopropenyl cation for the purpose of discussion. We thank Professor Hoffmann for suggesting to us the probable existence of two forms of eclipsed cyclopropenylcarbinyl.

(18) Such a phenomenon has been termed *subadjacent orbital control* by its original discoverers: J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972). Other recent examples include: J. A. Berson and R. W. Holder, *J. Amer. Chem. Soc.*, **95**, 2037 (1973); S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *ibid.*, **95**, 3806 (1973).



**Figure 1.** Possible interactions between the cyclopropene valence manifold and the empty orbital on the migrating center. Depicted also is the relationship of the cyclopropene Walsh orbitals to those of cyclopropane.



**Figure 2.** *Left-hand side.* Symmetry allowed interactions between the occupied cyclopropane  $\pi$  system and symmetric Walsh ring component and the vacant orbital on an eclipsed methylene group. Woodward-Hoffmann control. *Right-hand side.* Interaction between asymmetric Walsh component and p orbital on a bisected methylene. Subadjacent control.

(left-hand side of Figure 2) are sacrificed in order to allow for interaction between the empty orbital on the migrating (bisected) methylene group and the asymmetric Walsh (right-hand side of Figure 2). It is apparent in this instance that the importance of overlap of the interacting orbitals outweighs their desire to be close in energy.

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## Generation of Chiral 3,8-Methano[11]annulenylidene. Stereochemical and Mechanistic Implications

Sir:

We recently reported the generation of 3,8-methano-[11]annulenylidene (1)<sup>1</sup> from the carbene-carbene re-

(1) P. H. Gebert, R. W. King, R. A. LaBar, and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 2357 (1973).