

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).

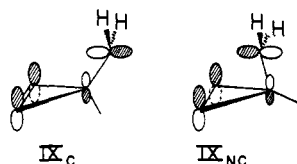
(13) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(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).

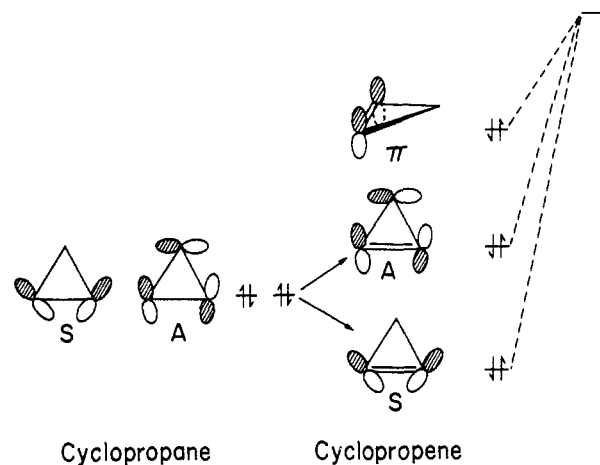


Figure 1. Possible interactions between the cyclopropene valence manifold and the empty orbital on the migrating center. Depicted also is the relationship of the cyclopropene Walsh orbitals to those of cyclopropane.

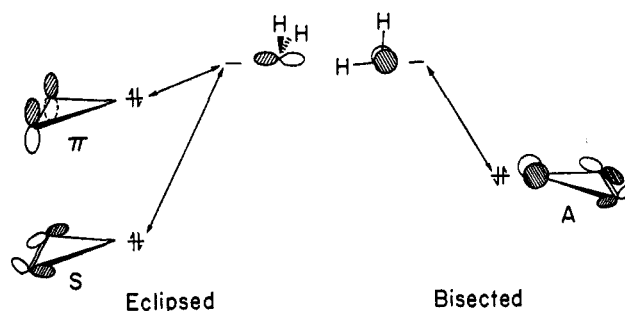


Figure 2. *Left-hand side.* Symmetry allowed interactions between the occupied cyclopropane  $\pi$  system and symmetric Walsh ring component and the vacant orbital on an eclipsed methylene group. Woodward-Hoffmann control. *Right-hand side.* Interaction between asymmetric Walsh component and p orbital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

**Acknowledgment.** Stimulating correspondence with Professor Roald Hoffmann (Cornell) is gratefully acknowledged.

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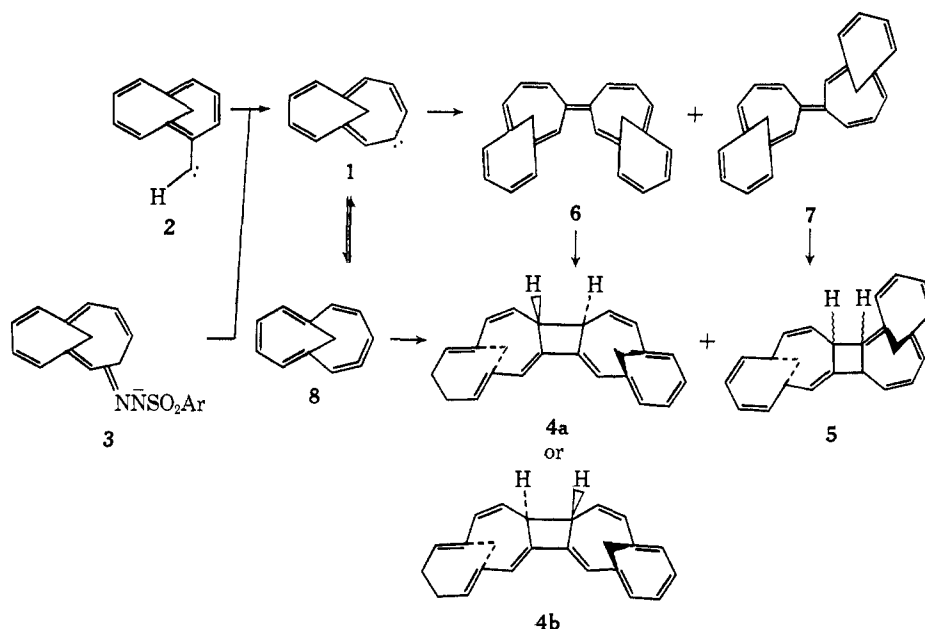
Received January 25, 1974

## 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).



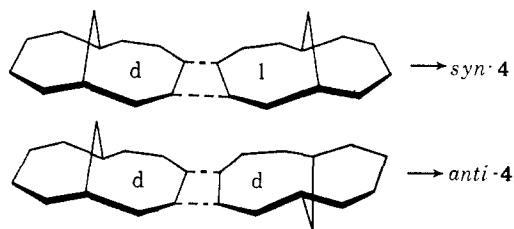
arrangement of 2-methano[10]annulenyliene (2) and from the direct thermolysis of the sodium salt of 3,8-methano[11]annulene tosylhydrazone (3) to give hydrocarbons 4 and 5. The gross structural assignment of 4 and 5 was determined by pmr spectra but the stereochemical relationship of the methylene bridges and of the cyclobutyl hydrogens could not be determined. We now wish to report these stereochemical relationships in 4 and the stereochemical relationship of the methylene bridges in 5.

Chiral 1,6-methano[10]annulene-2-carboxaldehyde ( $[\alpha]_{\text{D}}^{25} 65.4^\circ$ )<sup>2</sup> was prepared by the method of Schlögl.<sup>3</sup> The tosylhydrazone ( $[\alpha]_{\text{D}}^{25} 207.4^\circ$ ) and its sodium salt were prepared in the conventional manner.

Generation of carbene 1 involved addition of 5.79 mg of the chiral salt in 1 ml of dry diglyme to 2.5 ml of dry diglyme saturated with  $\text{N}_2$  which was maintained at reflux. The entire addition of the salt required  $\sim 1$  minute after which the reaction was immediately quenched in an ice bath, poured into water, and extracted with pentane. Chromatography of a portion of the reaction mixture on an analytical tlc plate showed *only* the formation of 4 (23.7% yield by uv spectrum). Product identification was confirmed by comparative tlc and uv with an authentic sample.<sup>1</sup> The generation of 1 from racemic sodium salt of the tosylhydrazone under identical conditions resulted in formation of 4 (7.6%) and 5 (12.1%) as the only isolable products.

Scheme I shows that the formation of 4 from dimer-

Scheme I



ization of two molecules of opposite chirality can only give an isomer of 4 with syn-methylene bridges whereas

(2) Greater than 99% optically pure.<sup>3</sup>

(3) U. Kuffner and K. Schlögl, *Monatsh. Chem.*, **103**, 1320 (1972).

dimerization of two molecules of the same chirality can only occur if the methylene bridges assume an anti relationship—regardless of the mechanism of dimerization. Thus, the sole formation of 4 from the chiral sodium salt establishes an anti relationship between the methylene bridges. By the same arguments, the absence of 5 demonstrates that it must arise from the dimerization of two molecules of *different* chirality which, in turn, once again requires the methylene bridges to be anti.

With the anti relationship of the methylene bridges in 4 established by this experiment and the symmetry (axis or plane) that is required by its pmr spectrum,<sup>4</sup> it is possible to also assign a trans configuration to the cyclobutane hydrogens. Thus, the symmetrical hydrocarbon must have either structure 4a or 4b and its isomer which lacks the necessary symmetry element to establish the stereochemistry of the cyclobutyl hydrogens may be assigned partial structure 5.

Since both cycloheptatrienyliene<sup>5</sup> and 4,9-methano[11]annulenyliene<sup>6</sup> exhibit a marked propensity to dimerize, in an earlier communication<sup>1</sup> we suggested that the two isolated hydrocarbons could arise from initial dimerization of 1 to give fulvalenes 6 and 7 which could then undergo electrocyclic ring closures. It was further pointed out that formation of 6 with methylene bridges syn followed by a symmetry allowed<sup>7</sup> disrotatory  $22 \pi$  electron ring closure would give a hydrocarbon with cis cyclobutane hydrogens, a product that would have the symmetry required by the nmr. From this work, however, it is clear that the product is not that predicted by a symmetry controlled ring closure of 6 and an alternate explanation for its formation must therefore be sought.

It has been reported by Gajewski and Shis<sup>8</sup> as well as

(4) The pmr spectrum of 4 is published and discussed in ref 1.

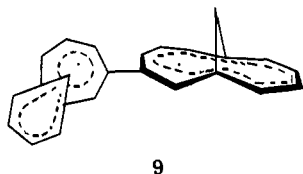
(5) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

(6) R. A. LaBar and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 2359 (1973).

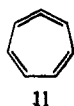
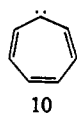
(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 45.

(8) J. J. Gajewski and G. N. Shis, *J. Amer. Chem. Soc.*, **91**, 5900 (1969).

Jacobs, McLennon, and Muscio<sup>9</sup> that perpendicular diallyl diradicals close to dimethylenecyclobutanes in a symmetry allowed conrotatory sense. Analogously, if it is assumed that orbital symmetry dictates the stereochemistry of the cyclobutane hydrogens in the reactions under discussion, diradicals **9** and its 180° rotomer be-



come viable precursors to **4a** and **4b**, respectively.<sup>10</sup> Reasonable progenitors of **9** and its rotomer are the two diastereomeric allenes, **8**. Dimerization of either (allowed conrotatory) or both (allowed disrotatory) would give diradical(s) **9**, which, as mentioned above, could close in an allowed conrotatory sense to give the observed product.<sup>10</sup> In support of **8** as a reasonable intermediate, recent INDO calculations<sup>11</sup> on cycloheptatrienyldiene (**10**) and cycloheptatetraene<sup>12</sup> (**11**)



place the bent, twisted allene at lower energy than the carbene. Since the chemistry of the seven-membered system<sup>5,13</sup> is more consistent with a carbene as the reactive intermediate, this surprising result suggests the possibility of equilibria between aromatic carbenes and their allene forms. Furthermore, such equilibria would be sensitive to ring size. Thus, whereas cyclopropylidene (**12**) would exist only as the carbene, in the



larger rings it is quite possible that such equilibria would not only exist but would be shifted far enough to the allene side to show some or exclusive allene chemistry.<sup>14</sup>

(9) T. L. Jacobs, J. R. McLennon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); see also J. E. Baldwin and R. A. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

(10) The obvious drawback to this suggestion is that only one of the two possible products (**4a** or **4b**) is actually observed. This could be due either to interconversion of the diradicals to give one thermodynamically favored product or instability of one product to reaction or work-up conditions or, possibly, both. Perhaps it is worth noting that substantial amounts of intractable tars are invariably noted in these reactions and, in fact, even the isolated products are rather unstable. With regard to possible interconversion of the two radicals, it should be noted that, in order for them to interconvert, they must pass through **6** (anti) or **7** (syn). Thus, such an isomerization would require breaking the central fulvalene double bond under the reaction conditions. This of course, also introduces the possibility that **4** and **5** arise from sequences such as **1** → **6** → **9** → **4**. As a sole source of **4**, this appears unlikely since at low temperature (-35°) photolysis of **3** also gives **4**.

(11) R. L. Tyner, W. M. Jones, N. Y. Ohrn, and J. R. Sabin, *J. Amer. Chem. Soc.*, submitted for publication.

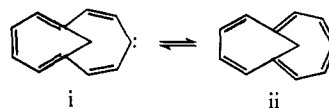
(12) This form was first suggested by K. Untch of Syntex Corporation, at the International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan, Aug 1970.

(13) Cf. E. E. Waali and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 8114 (1973), and references cited.

(14) Although such an equilibrium between **1** and **8** may well be expected to lie further toward the allene structure than in the smaller seven-membered ring, ring size alone cannot be the whole picture since

**Acknowledgment.** The authors gratefully acknowledge the support of this work received from the National Science Foundation. Helpful discussions with Professor John Baldwin are also acknowledged.

the chemistry of **i** ⇌ **ii** is that expected of an aromatic carbene.<sup>6</sup> If such



equilibria exist, the differences in the chemistry of **1** ⇌ **8** and **i** ⇌ **ii** may be due to a trivial but difficult to discern (from models) difference in steric requirements of the two allenes or perhaps differences in the π-electron systems. In both cases, **i** ⇌ **ii** and **1** ⇌ **8**, the chemistry observed is best explained in terms of the intermediate (**i** and **8**) which contains a homobenzenoid component in the π-electron system.

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### Structural Characterization of Tris(pyrrolyldithiocarbamato)iron(IV) Perchlorate. An FeS<sub>6</sub> Complex of Unusually High Oxidation State

Sir:

Electrochemical and synthetic studies by ourselves<sup>1,2</sup> and others<sup>3-13</sup> have established that the dithiocarbamate ligand is extremely effective in stabilizing unusually high oxidation states of the first-row transition metals. X-Ray structural confirmation is now available for the two compounds Cu(R<sub>2</sub>dtc)Br<sub>2</sub><sup>5</sup> and [Ni(R<sub>2</sub>dtc)<sub>3</sub>]Br<sup>14,15</sup> where the high oxidation states Cu(III) and Ni(IV) have been stabilized by the R<sub>2</sub>dtc = *N,N*-di-*n*-butyldithiocarbamate ligand. The crystal structure of the Ni(IV) selenium analog [Ni(Se<sub>2</sub>CN(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>)<sub>3</sub>]Br has also been determined.<sup>7</sup>

Iron(IV) complexes are rare.<sup>10</sup> Despite the fact that [Fe(R<sub>2</sub>dtc)<sub>3</sub>]BF<sub>4</sub> with R<sub>2</sub> = Me<sub>2</sub>, Et<sub>2</sub>, *i*-Pr<sub>2</sub>, pyr, and *c*-Hex<sub>2</sub> were synthesized more than 2 years ago,<sup>10</sup> no structural confirmation of stereochemistry and oxidation state has been reported. We have therefore undertaken a single-crystal structure analysis of [Fe(R<sub>2</sub>dtc)<sub>3</sub>]ClO<sub>4</sub> with a view to elucidating the detailed coordination geometry of the FeS<sub>6</sub>-core and comparing it with that of other metals in high oxidation states.

(1) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973).

(2) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, in press.

(3) H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemsse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969).

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(6) J. Willemsse, P. H. F. M. Rouwette, and J. A. Cras, *Inorg. Nucl. Chem. Lett.*, **8**, 389 (1972).

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(10) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(11) H. C. Brinkhoff, A. M. Grotens, and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, **89**, 11 (1970).

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(13) J. Willemsse and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, **91**, 1309 (1972).

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(15) J. P. Fackler, A. Avdeef, and R. G. Fischer, *J. Amer. Chem. Soc.*, **95**, 774 (1973).