

$x$ ,  $z$  ( $x < z$ ) in least-squares refinement. The positions  $x$ ,  $x$ ,  $z$  and  $x$ ,  $z$ ,  $z$  were refined together, each with an occupancy of 4.5 carbon atoms; this solution corresponds to three molecular sites, each centered about the threefold axis, but with nonequivalent carbon atoms in each molecule. Successful refinement yielded thermal parameters of 3 (3) Å<sup>2</sup> and 10 (4) Å<sup>2</sup>, respectively, indicating again, although weakly, that the position  $x$ ,  $x$ ,  $z$  is a favored one.

Refinement with nine carbons at  $x$ ,  $x$ ,  $z$  converged with a thermal parameter of 10 (3) Å<sup>2</sup>. The final  $R$  is equal to that of the structure described in the preceding paragraph. This solution corresponds to three molecular sites with equivalent carbon atoms; the molecular centers lie off the threefold axes and the C–C bonds are 0.7 (3) Å in length, too short to be correct but understandable as an aberration attributable to thermal motion foreshortening and the ancillary effects of generating three diatomic molecular sites from three atomic sites. The acetylene bond length in the gas is 1.201 (5) Å,<sup>10</sup> and in the C<sub>2</sub>H<sub>2</sub> complex of zeolite 4A, the bonds are imprecisely determined (for the same reasons as discussed here): 1.03 (15) and 0.92 (10) Å.<sup>11</sup>

A final difference Fourier function indicated very broad peaks of height 0.8 (1) e Å<sup>-3</sup> in the vicinity of the acetylene molecules; this is taken to indicate that the model of thermally isotropic carbon atoms on mirror planes is too simple, but that within that constraint this structure is correct. There is no crystallographic indication of the presence of additional acetylene molecules.

With nine carbon atoms at  $x$ ,  $x$ ,  $z$ , each carbon atom is 2.61 (10) Å from Mn(II). This distance is approximately independent of the choice of model. The interaction is therefore weak and apparently due to an electrostatic interaction between the dipositive Mn(II) ions and the polarizable  $\pi$ -electron density of the acetylene molecules. Since the manganese ions are dipositive, their  $d$  orbitals are contracted, and the synergistic bonding<sup>12</sup> between the metal and a weak  $\sigma$ -donor-strong  $\pi$ -acceptor such as acetylene is appreciably inhibited.

Although the uncertainty in the C–C bond is great, apparently no significant nonbonded approaches are made by acetylene to the zeolite framework. The closest such approach is 3.5 Å to an O(3) oxygen atom; the acetylenic hydrogens are therefore far from framework atoms as well.

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**Supplementary Material Available.** A listing of positional, thermal, and occupancy parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or micro-

(10) L. E. Sutton, "Interatomic Distances and Configuration in Molecules and Ions," Supplement, The Chemical Society, London, 1965, p S16s.

(11) A. A. Amaro and K. Seff, *J. Phys. Chem.*, **77**, 906 (1973).

(12) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 749.

fiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-8180.

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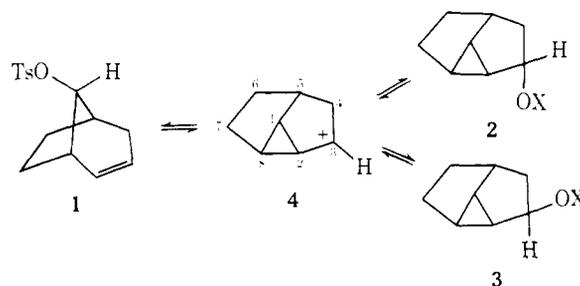
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## Experimental and Theoretical Evidence for Nonplanar Carbonium Ions. The Secondary Cyclopropylcarbiny System

Sir:

Our studies of the solvolysis of *anti*-8-bicyclo[3.2.1]oct-2-enyl *p*-toluenesulfonate (**1**)<sup>1</sup> and the epimeric *endo*- and *exo*-tricyclo[3.3.0.0.2,8]octan-3-yl derivatives (**2** and **3**) have strongly implicated the tricyclic cyclopropylcarbiny cation **4** as the common product de-



termining intermediate in these reactions. Controlled acetolysis and hydrolysis of **1**, **2**, and **3** give products having the bicyclo[3.3.0]oct-7-en-2-yl and bicyclo[3.2.1]oct-2-en-8-yl (**1**) carbon skeletons in essentially constant proportions ( $\sim 1.5$ – $1.8$ ), as well as acetates and alcohols having the tricyclic carbon skeleton of **2** and **3**. However, in each case the *endo*/*exo* product ratio of **2**/**3** was much greater than unity under kinetic control. For example, acetolysis of **1** (partial), **2**-OPNB, and **3**-OPNB at 76.1° showed values for **2**-OAc/**3**-OAc of >33, 14, and 3.3, respectively, whereas hydrolysis results (aqueous acetone or dioxane buffer) showed **2**-OH/**3**-OH ratios of 58, 48, and 40, respectively.<sup>2</sup> The relative rate of hydrolysis,  $k_{2\text{-ODNB}}/k_{3\text{-ODNB}}$ , was found to be about 29.<sup>2</sup>

The observed preference for *endo* tricyclic product **2** is surprising since examinations of molecular models indicate that steric control of attack at C-3 in **4** will favor *exo* approach. Furthermore, modified Westheimer calculations<sup>3</sup> of the atomic coordinates and torsional angles of planar **4** (with tricyclo[3.3.0.0.2,8]octan-3-one as a model) show that the *endo* lobe of the empty  $p_z$  orbital at C-3 is oriented for maximum overlap *only* with the C-2–C-8 bent cyclopropyl bond again suggesting that *exo* nucleophilic attack should predominate.

(1) N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964).

(2) N. A. LeBel, R. G. Isakson, and R. A. Greengard, manuscript to be published. The minor variations in product ratios from the various precursors can be accounted for by ion-pair effects, product instability, and experimental error or a combination thereof. Solvolysis of the bicyclo[3.3.0]oct-7-en-2-yl substrates has also been examined.

(3) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wirtz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971); N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972). We are indebted to Professor Allinger for calculations on this structure and for stimulating discussions.

The literature describes several other polycyclic cyclopropylcarbinyl epimers which give similar product distributions when solvolyzed and which possess relatively small solvolytic rate ratios. Typical of this set are those which involve cations **5**,<sup>4</sup> **6**,<sup>5</sup> **7**,<sup>6</sup> and **8**. Importantly, cyclopropylcarbinyl-cyclopropylcarbinyl rearrangements have not been observed during solvolytic generation and capture of these intermediates, most probably because the favored two-step mechanism<sup>7</sup> *via* a bicyclobutonium species would introduce prohibitive strain energy into the system.

Existing theory accommodates these stereochemical observations as resulting from a blend of steric and (undefined) stereoelectronic factors. We now can report theoretical evidence that cation **4** is deformed from the expected planar,  $sp^2$ -hybridized geometry at C-3, and the accumulated experimental and theoretical results further suggest that nonplanarity may be a general phenomenon with geometrically constrained cyclopropylcarbinyl cations in the ground state and in the transition state for solvent capture.

Extended Hückel<sup>8</sup> and INDO<sup>9</sup> MO calculations of cation **4** suggest a bending of the C-3-H bond of 13 and 8.5°, respectively, toward the exo side of the molecule.<sup>10</sup> Similarly, INDO calculations were carried out as described above with cations **5**-**8**. Our results from these studies are summarized in Chart I.

Although simple symmetrically substituted carbonium ions appear to have a planar geometry, molecular orbital calculations suggest that the ethyl cation and the propyl cation have cationic centers that deviate from planarity by 2.9 and 5.4°, respectively.<sup>12</sup> Since the cations in the present study are geometrically restricted, we sought to determine the underlying reasons for their deviation from planarity. Numerous theoretical calculations have established that "bisected" cyclopropylcarbinyl cations are more stable than the conformationally isomeric "perpendicular" forms.<sup>12</sup> In order for cations **4**-**7** to deviate substantially from planarity, the stabilization provided by cyclopropylcarbinyl delocalization must be comparable to or greater than the out-of-plane deformation energy

(4) Psinortricyclyl; R. K. Lustgarten, *J. Amer. Chem. Soc.*, **93**, 1275 (1971).

(5) Bicyclo[3.1.0]hexan-3-yl; G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); P. R. Brook, R. Mellam, and A. H. Bloss, *Chem. Commun.*, 425 (1968); E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971); R. N. McDonald and G. E. David, *J. Amer. Chem. Soc.*, **94**, 5079 (1972); E. C. Friedrich and M. A. Saleh, *ibid.*, **95**, 2617 (1973); E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973). 1,5-Tri- and tetramethylene bridged analogs were reported by P. G. Gassman, R. N. Steppel, and E. A. Armour, *Tetrahedron Lett.*, 3287 (1973).

(6) Bicyclo[3.2.1]octan-6-yl; N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, **85**, 3193 (1963).

(7) K. B. Wiberg and G. Szeimes, *ibid.*, **92**, 571 (1970).

(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

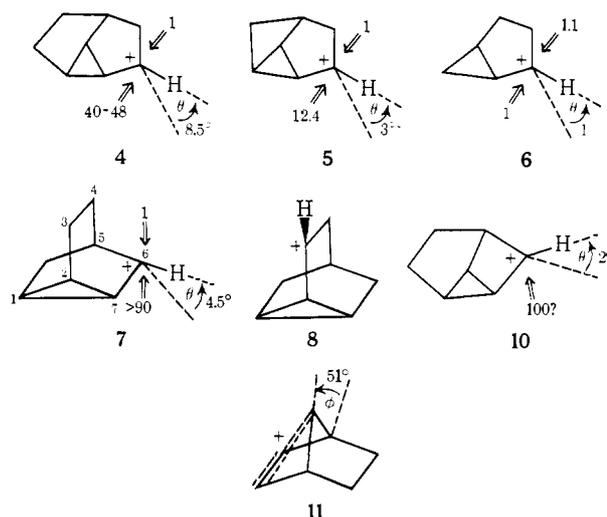
(9) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967). A copy of this program was obtained from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., No. 141.

(10) The parameters for the EH calculations have been given elsewhere.<sup>11</sup> The atomic coordinates of the cation were obtained by energy minimization of the corresponding ketone by the modified Westheimer method.<sup>3</sup> The  $sp^2$  carbon atom of the carbonyl group was taken as an approximation of the planar cationic center at C-3 in **4**. A C-3-H bond distance of 1.08 Å was used. Carbon atoms 2, 3, and 4 were held in the  $x, y$  plane at a fixed C-2-C-3-C-4 bond angle until an energy minimum was achieved using the INDO and EH formations.

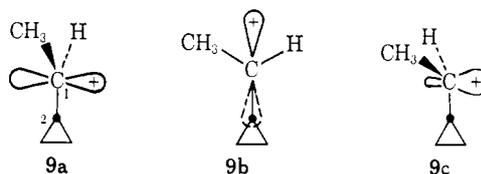
(11) R. D. Bach and H. F. Henneke, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

(12) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, **7**, 253 (1973).

Chart I. C-H Bond Out-of-Plane Bending Angles ( $\theta$ ) from INDO Calculations, and Experimental Stereochemical Hydrolysis Results ( $\Rightarrow$ ) for Some Polycyclic Cyclopropylcarbinyl Cations



associated with  $sp^2$ - $sp^{>2}$  rehybridization (*i.e.*, rotation about C-1-C-2 in a cyclopropylcarbinyl cation should be competitive with rehybridization as a means of stabilization). Our INDO calculations of bisected planar cation **9a** suggest that the rotational barrier for interconversion to the perpendicular form **9b** is 22.2 kcal/mol. Rotation to a conformation midway between **9a** and **9b** (*i.e.*, 45°) requires 10.6 kcal/mol. However, the rehybridization energy for the process **9a**  $\rightarrow$  **9c** is a function of the cosine of the angle sub-



tended by two bonding atomic orbitals,<sup>13</sup> and partial rehybridization of **9a** to  $sp^{2.16}$  at C-1 requires only 9.3 kcal/mol. This corresponds to an out-of-plane bend ( $\theta$ ) of 26.5°. On the other hand, complete rehybridization of **9a** to the  $sp^3$  cation **9c** ( $\theta = 54.7^\circ$ ) would demand 45.6 kcal/mol.<sup>14</sup> The carbonium ion centers in cations **4**, **5**, **6**, and **7** all have the C-H bond bent 1-8.5° in a direction that approaches a more nearly bisected cyclopropylcarbinyl geometry. Thus, because rotation is inhibited for these systems, rehybridization occurs until the best balance between the increase in energy accompanying out-of-plane deformation and the decrease in energy associated with cyclopropylcarbinyl stabilization is attained.

The above calculations, however, apply only to isolated molecules in the gas phase. Interaction of the cationic center with solvent molecules would be expected

(13) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965, p 17.

(14) In general,  $sp^2 \rightarrow sp^3$  rehybridization energies are greater than rotational barriers with simple cyclopropylcarbinyl cations. According to INDO calculations the rehybridization energies for the cyclopropylcarbinyl and dimethylcyclopropylcarbinyl cations are 36.7 and 64.0 kcal/mol, respectively, whereas the rotational barriers (bisected  $\rightarrow$  perpendicular) are 29.0 and 17.5 kcal/mol (C-1-C-2 bond length 1.536 Å), respectively. The latter value is in good agreement with experimental data.<sup>18</sup>

(15) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970).

on the basis of stereoelectronic considerations to occur preferentially from the endo side of the molecule, *i.e.*, the more directed lobe of the vacant p orbital. Indeed, endo solvation of the partially rehybridized cationic center at C-3 of **4** may result in further deviation from planarity due to the fact that an increase in  $\theta$  is accompanied by enhanced cyclopropylcarbinyl stabilization.

The results, shown in Chart I together with reported hydrolysis capture ratios, are in excellent accord with the concept of stereoelectronic control in which extensive rehybridization of the carbonium ion center in the transition state for solvent capture has occurred. For example, cation **5**, which is rehybridized in the ground state to a smaller degree than **4**, affords an endo/exo ratio of only 12.4:1 again with preference for the *most hindered side*. Cation **6**, which is only deformed slightly, exhibits a shallow energy minimum and solvolytic generation of **6** affords a product distribution which is easily accounted for on the basis of steric approach control. Cation **7**, which exhibits an unusually high endo/exo ratio, reflects the cyclopropylcarbinyl stabilization in the transition state in addition to steric inhibition to exo attack. Cation **8** has a symmetrical, bisected arrangement, and calculations, as well as experiment, indicate that it is essentially planar at C-2.

A rather dramatic example of the rehybridization phenomenon is given by the tricyclo[2.2.1.0<sup>2,7</sup>]hepten-3-yl cation **10** which is estimated to be bent 29° and which, if it had a discrete lifetime, would give exclusively the endo product. Our INDO calculations suggest that **10** is lower in energy than an undistorted *anti*-7-norbornenyl cation (**11**,  $\phi = 0^\circ$ ). However, the true cation **11**, in which the cation-containing bridge is bent toward the double bond ( $\phi = 51^\circ$ , calculated), acquires bishomocyclopropenyl stabilization. Our results now provide a unique explanation for the very high solvolytic rate of *endo*-**10**-OPNB.<sup>16</sup> Further, the increase in the C-2:C-7 product ratio from **11** in the presence of powerful nucleophiles has been suggested to result from a product-like transition state for the formation of an endo tricyclic product,<sup>16</sup> and we describe the transition state as resembling nonplanar cation **10**.

Two final points can be made. The rehybridization phenomenon postulated in this work is completely consistent with the recent observations of Rhodes and DiFate.<sup>17</sup> These workers have demonstrated that cyclopropyl stabilization of an adjacent nonplanar cationic center is quite effective even in the 30° geometry which is closely approached by cations **4** and **5**. Furthermore, it is becoming increasingly obvious that most carbocations that are not symmetrically substituted will exist in a nonplanar form.

(16) See, for example, S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967); J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).

(17) Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972).

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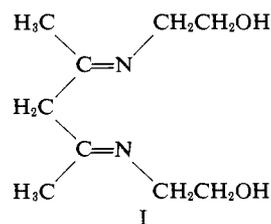
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## Magnetic Exchange in Binuclear Copper(II) Complexes. Antiferromagnetic Coupling through Hydrogen-Bonded Oxygen-Hydrogen-Oxygen Bridges

Sir:

There have been numerous studies<sup>1-4</sup> of binuclear copper(II) compounds; most of these compounds have copper-copper distances of 3.10 Å or less and their magnetic moments show temperature-dependent behavior that is indicative of exchange coupling. Although the coupling observed for such compounds could be due to direct metal-metal interaction, there is evidence that the coupling results from indirect exchange (superexchange) through the bridging groups.<sup>4</sup> For virtually all of the compounds that show antiferromagnetic coupling, the superexchange could, however, occur by either a  $\sigma$  or a  $\pi$  pathway. We have prepared and studied a binuclear copper(II) complex in which the copper ions are bridged by hydrogen bonded O-H-O bridges with a copper-copper distance of 5.0 Å; although the copper-copper distance rules out direct exchange and the hydrogen bridged arrangement makes a  $\pi$  pathway unlikely, the magnetic properties of the compound indicate antiferromagnetic coupling. This example, thus, provides evidence for indirect exchange *via* a  $\sigma$  pathway.

The compound is the neutral copper(II) complex of the dianion of the tetradentate ligand, I, formed by



the condensation of 2,4-pentanedione and 2-aminoethanol. The compound was prepared by the reaction of stoichiometric amounts of copper(II) acetate and potassium hydroxide with an excess of 2,4-pentanedione in 2-aminoethanol as solvent. Although the ligand contains three ionizable protons, only two of the protons (one from the methylene group between the two C=N groups and one from an alcohol OH group) are lost in forming the neutral copper(II) complex; the green needles of empirical formula CuC<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> could be recrystallized from toluene and the molecular weight, using a vapor pressure osmometer, corresponded to a dimer (498 obsd *vs.* 495 calcd) in chloroform. Precession photographs (Zr-filtered Mo K $\alpha$  radiation) indicated that the crystals were triclinic and the refinement has confirmed the space group as *PT*. The crystal was transferred to a Picker four-circle automated diffractometer and the angle settings for 22 reflections were used to obtain reduced cell parameters of  $a = 9.554(2)$  Å,  $b = 13.023(3)$  Å,  $c = 11.656(2)$  Å,  $\alpha = 131.36(1)^\circ$ ,  $\beta = 97.96(2)^\circ$ , and  $\gamma = 94.41(1)^\circ$ ;

(1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(2) J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **6**, 248 (1972).

(3) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 2216 (1972).

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