Although this research opens the way to the chemical determination of the hydrophobic binding sites of proteins, some caution in interpretation is required. The yield of radioactive glutamic acid is small (1–3%) and although the identification of the glutamic acid is reasonably secure, its detailed mode of formation must still be proved. At most, the equations shown in this communication must be read as diagrams pertaining only to that portion of the photolyzed product that yields glutamic acid.

[17] National Science Foundation Fellow, 1965–1969.

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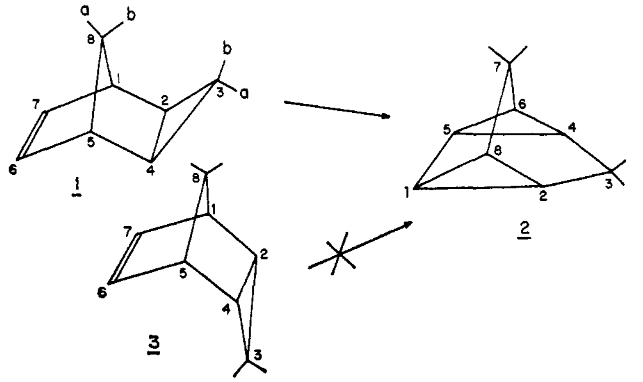
Rhodium(I)-Catalyzed Valence Isomerization of *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene

Sir:

Valence isomerizations are receiving continuing interest. Recently several examples have been reported of these reactions in the presence of catalytic amounts of transition metal complexes.[1,2] It was concluded that reactions which are "forbidden" (energetically unfavorable) according to the Woodward–Hoffmann postulate under thermal conditions may occur under mild conditions in the presence of a suitable transition metal complex.[2,3]

In this communication we report on an example of a transition metal complex catalyzed valence isomerization in which a cyclopropane ring and a double bond are involved. *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**),[4,5] either pure or dissolved in $CDCl_3$, was converted quantitatively into tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**2**) in the presence of 10 mole % of $Rh_2(CO)_4Cl_2$ at room temperature.

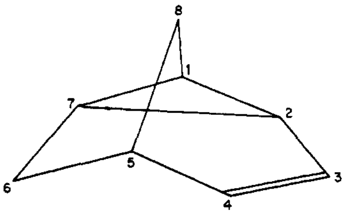


Product **2** had been reported earlier by Freeman[6] and LeBel.[7] Our spectral data (complex peaks centered at 1.61 and 1.26 ppm in the ratio 6:4; parent peak at *m/e* 106 and C–H stretching frequency at 3020 cm^{-1}, characteristic of cyclopropane rings) are about identical with those reported by Freeman and LeBel.

During the reaction, the red catalyst $Rh_2(CO)_4Cl_2$ was converted into a yellow, catalytically less active, complex. The elemental analysis and the infrared data (a terminal carbonyl group (2040 cm^{-1}), an acyl group (1700 cm^{-1}), and a bridged chloride (283 cm^{-1})) suggest a structure similar to that reported for the complex obtained from cyclopropane and $Rh_2(CO)_4Cl_2$, which contains a 1-rhodiacylopent-2-one ring.[8]

The *exo* arrangement of the fused cyclopropane ring in **1** is required for the occurrence of valence isomerization. This is demonstrated by the failure of the *endo* isomer **3**[9] to undergo a similar reaction. Even at 100° **3** did not react. The results can be explained in terms of the geometry of the tricyclic systems. In the *exo* isomer **1**, the π orbitals of the double bond, together with the orbitals forming the cyclopropyl bent bond between C_2 and C_4, are ideally situated for interaction with the orbitals of the rhodium atom, considering the reported edgewise coordination of cyclopropane toward tetravalent platinum.[10]

It is of interest to note that valence isomerization of **1** under thermal (200°) and photochemical conditions has been reported to yield tricyclo[3.2.1.0^{2,7}]oct-3-ene (**4**)[11] and **2** (20%)[6], respectively. Irradiation of the endo isomer **3** leads also to **2** (19%).[6] Apparently, the spatial arrangement of the fused cyclopropane is not critical under these conditions. The reaction pathways of the conversion of **1** into **2** under catalyzed as well as under photochemical conditions have in common that occupied antibonding orbitals—either by back-bonding from the metal or by excitation—are involved



4

The conversion of **1** into **2** suggests a possible route for the preparation of tetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonane (**6**) (triasterane) from *exo,exo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]-nonane (**5**).[12]

All attempts to effect the conversion failed; the starting material was quantitatively recovered. Only the complex $Rh_2(CO)_4Cl_2$ was converted into a yellow complex, with presumably a structure similar to that of the complex obtained from **1**.

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[1] H. C. Volger and H. Hogeveen, *J. Am. Chem. Soc.*, **89**, 2486 (1967); *Rec. Trav. Chim.*, **86**, 830 (1967); *Chem. Commun.* 1133 (1967).

[2] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4788 (1967).

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[4] S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, *J. Org. Chem.*, **26**, 3122 (1961); H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

[5] Nmr data of **1**: δ (ppm from TMS) H(1,5) 2.71, H(2,4) 1.03, H(3a) 0.79, H(3b) 1.45, H(6,7) 6.35, H(8a) 1.06, H(8b) 0.96; $J(1,5\text{–}6,7)$ 1.72 cps (triplet), $J(3a, 3b)$ = 6.3 cps; $J(2,3b)$ = 3.0 cps $J(2,3a)$ = 7.5 cps, $J(8a,8b) \approx$ 8 cps (AB pattern).

[6] P. K. Freeman, D. G. Kuper, and V. N. Mallikarjuna Rao, *Tetrahedron Letters*, 3303 (1965).

[7] N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, **87**, 4301 (1965).

[8] R. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc.*, *A*, 845 (1968).

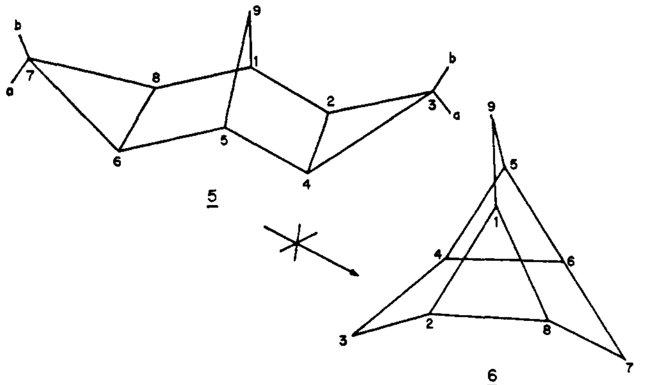
[9] K. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); K. Tori and M. Ohtsuru, *Chem. Commun.* 886 (1966).

[10] N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *ibid.*, 396 (1966).

[11] H. E. Simmons quoted in H. Prinzbach, W. Eberbach, M. Klaus, G. v. Veh, and U. Scheidegger, *Tetrahedron Letters*, 1681 (1966).

[12] Nmr data of **5′** (for preparation see ref 4): δ (ppm from TMS) H(1,5) 2.35, H(2,4,6,8) 1.07, H(3a,7a) 0.31, H(3b,7b) 0.82, H(9) 0.51, $J(1,9)$ = 1.70 cps, $J(1,2)$ < 0.30 cps, $J(2,3a)$ = 7.0 cps, $J(2,3b)$ = 3.20 cps, and $J(3a,3b)$ = 6.40 cps. The assignment of the *exo,exo* configuration was based on comparison of the nmr data with those of cyclopropane derivatives with established *exo* and *endo* configurations.[9,13]

[13] R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Letters*, 4759 (1967).



5

6

The absence of *exo–endo* isomerization of **5** in the presence of $Rh_2(CO)_4Cl_2$ makes the occurrence of an equilibration between **5** and **6** unlikely. The failure of the valence isomerization of **5** may be due to greater changes in geometry necessary to effect the conversion.

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Bond Index Description of Delocalization

Sir:

A study of nonclassical behavior in carbonium ions[1] and strained ring systems[2] made apparent the desirability of a simple method for determining whether a localized description of a molecule is feasible, given approximate molecular orbital coefficients.[3,4] Extant methods are not suitable; in nonplanar systems, the definition of "delocalization energy" loses its simplicity. The bond order also becomes difficult to interpret for these systems. In this report we describe an interpretation of Wiberg's bond index,[5] which makes possible a detailed description of delocalization, by partitioning the charge into various valence-bond (VB) structures.

The bond index is simply the square of the bond order: $W_{ab} = (P_{ab})^2 = 4\Sigma(i,j \text{ occupied})C_{ia}C_{ib}C_{ja}C_{jb}$; i and j label the doubly occupied molecular orbitals of a closed-shell molecule, and a and b label atomic orbitals in the LCAO expansion. The sum of W_{ab} over all atomic orbitals b, since we assume $\Sigma(b)C_{ib}C_{jb} = \delta_{ij}$, is a dimensionless quantity proportional to the charge in orbital a: $\Sigma(\text{b})W_{ab} = 4\Sigma(i)C_{ia}{}^2 = 2q_a$. The sum may be partitioned into terms as follows.

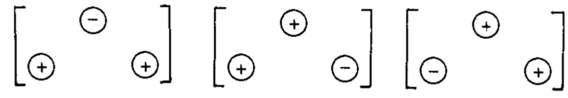
$$q_a = \frac{1}{2}W_{aa} + \frac{1}{2}\sum(K)\sum(b \text{ in } B_K)W_{ab}$$

The first term on the right may be considered the charge in orbital a which is not involved in bonding to other orbitals. The difference $[q_a - (W_{aa}/2)]$ will be referred to as the "active charge" in orbital a and is separated into charges participating in covalent valence bond structures B_K. These statements will be given some clarity by the examples below.

Consider the (definitely delocalized) π system in allyl cation: the doubly occupied Hückel π orbital is

$$\Phi = \frac{1}{2}[\phi_1 + \sqrt{2}\phi_2 + \phi_3]$$

The active charges are $(A_1, A_2, A_3) = (0.375, 0.500, 0.375)$. Note that the total active charge, 1.250 electrons, falls short of the total charge of 2.000 electrons. The remaining charge is involved in ionic structures shown below.

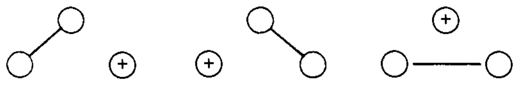


(q_2 = 0.500) (q_3 = 0.125) (q_1 = 0.125)

I_1 I_2 I_3

The overemphasis of ionic structures is a property of the simplest molecular orbital theory, which takes no account of electron interaction. A direct valence-bond calculation would have assigned smaller weight to the ionic forms above.

Of more interest is the relative weights of the valence-bond structures of greater covalency. Consider the structure B_1 in which C_1 is bound to C_2.



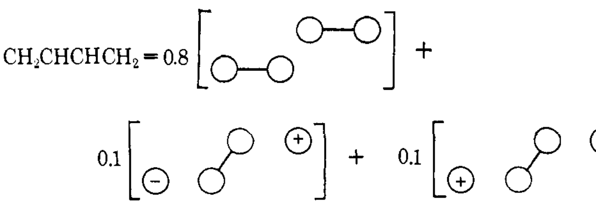
B_1 B_2 B_3

The bond indices predict that the charges involved in B_1 are $(^1/_2W_{12}, {}^1/_2W_{21}, 0.00)$, which equals (0.25, 0.25, 0.00). The mirror valence-bond structure accounts for (0.00, 0.25, 0.25) electrons. Finally, the valence-bond structure B_3 in which C_1 is bound to C_3 comprises the remaining active charge, (0.125, 0.000, 0.125). Therefore, the π charge in allyl cation can be viewed as consisting of the three covalent structures and the three ionic structures, in this way

$$q^{\pi}(CH_2CHCH_2{}^+) = {}^1/_4(B_1 + B_2) + {}^1/_8(B_3) + {}^1/_4(I_1) + {}^1/_{16}(I_2 + I_3)$$

This partitioning of charge into VB structures is unambiguous only if the wave functions corresponding to the structures are orthonormal. The structures are not orthogonal in general, but the assumption of an orthogonalized atomic orbital basis set as in most simple π-electron theories and the CNDO method[4] assures the essential orthogonality.

In the following examples we discuss only the distribution of the active charge in various molecules, since the ionic structures are not of immense importance. The active charge in butadiene is composed of three structures



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(2) C. Trindle and O. Sinanoğlu, *ibid.*, in press.

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(5) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968); "Bond Order and Bond Indices," private communication. In the latter note, Wiberg points out the similarity between the MO π bond indices (W_{12} = 0.444; W_{14} = 0.111) and the VB π bond order (0.46 and 0.07) in benzene.