1.0[6,12] or 1.10–1.17[16] and the replacement of a solvent molecule from $RhClH_2(PPh_3)_2$(solvent) by an olefin is rate limiting. (2) While the reduction, the isomerization, and the hydrogen–deuterium exchange[17] of olefins under hydrogen take place rapidly at room temperature, the transfer-hydrogenation scarcely proceeded below 100°. Therefore, the steps which can correspond to the steps in the former reactions may not be rate determining in the latter. All the hydrogen transfer steps in the latter other than the oxidative addition step have the corresponding ones in the former which involve the steps $RhClH_2(PPh_3)_2$(olefin) $\rightleftarrows$ $RhClH(alkyl)(PPh_3)_2$ (+ solvent) $\rightarrow$ $RhCl(PPh_3)_2$(solvent). (3) The initial rate seems to be zero order in the concentration of cyclopentene. (4) The possibility of a radical mechanism may be eliminated because the transfer-hydrogenation was not retarded at all by the addition of pyrocatechol (1.0 *M*) which is an inhibitor of radical reactions.[18]

Notwithstanding the report that $RhCl(PPh_3)_3$ gave $RhCl(CO)(PPh_3)_2$ on warming in dioxane with excess triphenylphosphine and $[RhCl(PPh_3)_2]_2$ without the phosphine, we observed neither the formation of the carbonyl complex nor the dimer in the transfer-hydrogenation in dioxane. Moreover, the dimer gave $RhCl(PPh_3)_2(C_4H_8O_2)$ on warming in dioxane. Perhaps this is due to the ability of dioxane to cleave the chloro bridge of the dimer. Another indication of the strong complexing power of dioxane is the fact that the addition of 0.2 *M* triphenylphosphine did not depress the rate of the transfer-hydrogenation in spite of the strong inhibition by added phosphine in the hydrogenation by molecular hydrogen in benzene.[6]

(16) S. Siegel and D. W. Ohrt, *Chem. Commun.*, 1527 (1971).

(17) (a) A. I. Odell, J. B. Richardson, and W. R. Roper, *J. Catal.*, **8**, 393 (1967); (b) A. S. Hussey and Y. Takeuchi, *J. Org. Chem.*, **35**, 643 (1970); (c) G. V. Smith and R. Shuford, *Tetrahedron Lett.*, 525 (1970).

(18) D. C. Dittmer and P. A. Fonty, *J. Amer. Chem. Soc.*, **86**, 91 (1964).

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Subjacent Orbital Control. An Electronic Factor Favoring Concertedness in Woodward–Hoffmann "Forbidden" Reactions[1]

Sir:

The exceptionally fruitful ideas of Woodward and Hoffmann on the electronic control of chemical reactions have been summarized in the statement[2] "orbital symmetry is conserved in concerted reactions." It has been widely assumed that a "forbidden" process, in which orbital symmetry in the Woodward–Hoffmann sense was not conserved, would proceed by a nonconcerted two-step pathway involving discrete diradical or ionic intermediates.[3,4] By implication, the forbidden reaction would have a transition state with net antibonding character. It would be reasonable, therefore, to postulate that if extrasymmetric factors precluded the symmetry-allowed process, the system would shun the forbidden concerted pathway in favor of one in which the reactive sites tended to overlap as little as possible. This would have the important consequence that reactions proceeding by other than allowed pathways would tend to occur in two steps and stereorandomly. We wish to suggest that this conclusion is misleading and that there is a significant electronic factor favoring stereospecific, *concerted, forbidden* reactions.[6]

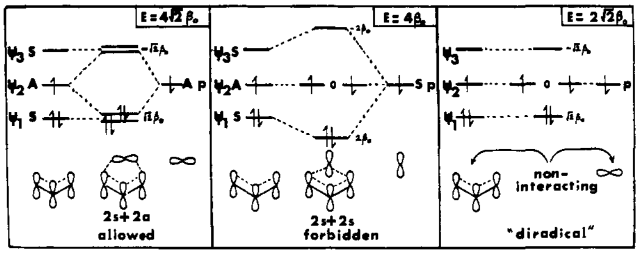

Figure 1. Schematic diagram of orbital energies and topologies of three different suprafacial 1,3-sigmatropic rearrangement transition states derived by interaction of an allyl unit with a carbon p orbital.

Figure 1 shows the essentials of the argument applied to the case of suprafacial 1,3-sigmatropic rearrangement of carbon. There are two idealized transition state geometries for concerted processes, one in which the migrating carbon retains configuration (a forbidden $2_s + 2_s$ reaction), another in which inversion occurs (an allowed $2_s + 2_a$ reaction). The energy level scheme is derived by permitting interaction between the allyl and p orbitals in the two topological combinations corresponding to the transition state geometries. We consider first, for didactic purposes, the case in which the energies themselves are derived from simple Hückel calculation on the assumption of equal nearest-neighbor interactions (all nonzero off-diagonal matrix elements $= \beta_0$).

Consider a hypothetical two-step rearrangement *via* a model diradical in which distance or orbital perpendicularity ensures zero interaction between the allyl and p orbitals and therefore favors stereorandomization of the products. It is clear from Figure 1 that the transition state for the allowed reaction is stabilized relative to that in such a diradical case largely because of the lowering of an antisymmetric nonbonding level, the highest occupied molecular orbital (HOMO) of the allyl unit, to a strongly bonding level.

However, Figure 1 also shows that there can be appreciable stabilization of the forbidden transition state. This results not from an effect on the HOMO but instead from the interaction of the carbon p orbital with a *subjacent*, bonding allyl orbital. Two of the four electrons involved thus can be accommodated in a more stable orbital than is the case in the separated fragments. The energies of the electrons in the allyl HOMO (ψ_2) and

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[1] The support of this work by the National Science Foundation (GP-11017X) and by the Hoffmann-LaRoche Foundation is gratefully acknowledged.

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 1.

[3] Reference 2, p 173.

[4] In some cases,[5] the "diradicals" may not represent true local potential minima.

[5] *Cf.* (a) R. Hoffmann, S. Swaminathan, B. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970); (b) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (c) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

[6] For reasons different than those given here, concert in symmetry-forbidden processes has been invoked by W. Schmidt, *Tetrahedron Lett.*, 581 (1972), and by N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972).

the original p orbital are hardly affected. The allyl ψ_2 orbital does not mix with the p orbital, and although ψ_1 and ψ_3 both mix with p, the interactions approximately cancel each other. Similar conclusions emerge from a corresponding treatment of reactions in which the migrating group retains configuration and rearranges either by an allowed antarafacial or a forbidden suprafacial one.[7]

In most geometries corresponding to the forbidden transition state of Figure 1, there is substantial overlap between the migrating p orbital and the orbital on the center carbon of the allyl system. This further depresses the energy of the subjacent level (to $2.56\beta_0$ if the interaction is assumed equal to the nearest-neighbor interactions) and reinforces the effect.

Subjacent orbital control of the transition state geometry normally would not be expected to become important until steric factors became unfavorable to the operation of Woodward–Hoffmann control. However, it must be kept in mind that even in the most favorable cases known, the allowed suprafacial inversion 1,3-sigmatropic transition state is only slightly preferred experimentally, the geometric distortions needed to achieve it being very severe.[8] Consequently, it should not be difficult to present steric or other extrasymmetric obstacles to its achievement and thereby bring the forbidden concerted reaction to the fore.[9] In such circumstances, the assumptions of equal interaction terms used to derive the orbital energies in Figure 1 become quite unsatisfactory, but perturbation theory provides a more realistic comparison of the two types of stabilization. Applied to the rearrangement of methylenecyclobutane for example, a Hückel-like perturbation calculation with resonance integrals assumed proportional to overlap and overlap integrals[10] evaluated from assumed molecular geometry yields stabilization energies of 2.9–5.8 (first order) and 1.6–3.2 kcal/mol (second order) for the allowed and forbidden reactions, respectively. The calculations are too crude to permit a prediction on the stereochemistry of the rearrangement but clearly suggest that the allowed and forbidden pathways are closely balanced in energy.

It may well be that the subjacent orbital effect plays an important role in facilitating the forbidden pathway in the rearrangements of thujene,[11] 2-cyano-3-methylethylidenecyclopropane,[12] and *trans*-1,2-dipropenylcyclobutanes.[13] In the latter two cases, steric factors do not heavily favor either the forbidden or allowed kind of motion. In several examples constructed to make the allowed pathway sterically difficult (1,3 rearrangements of *endo*-7-methylbicyclo[3.2.0]hept-2-enes[8c,14] and bicyclo[4.2.0]oct-2-enes[15]), it is now clear that rearrangement occurs not with the stereorandomness expected if the reactive sites were widely separated, but rather with high symmetry-forbidden stereospecificity (88% for one member of the series[8c,14] and 93–94% for the rest[15]).

Acknowledgment. We are indebted to Professor W. von E. Doering for helpful discussions.

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[7] Very similar arguments apply to electrocyclic reactions. For example, the transition state for the cyclobutadienoid forbidden reaction (disrotatory opening of cyclobutene) also has a stabilized subjacent level, the behavior of which may be seen by consultation of Figure 11 in the paper by H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

[8] (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5303 (1967); (b) J. A Berson, *Accounts Chem. Res.*, 1, 152 (1968); (c) 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 13–17, 1971, Abstracts, p 28.

[9] Our conclusions are based upon one-electron considerations. It is not inconceivable that the important two-electron energies characteristic of open shells[8c] could reverse, in certain cases, the ordering of the nonconcerted and forbidden transition state energies

[10] We are grateful to W. Jorgensen for values of the atomic integrals.

[11] W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971).

[12] W. von E. Doering and L. Birladeanu, *ibid.*, submitted for publication.

[13] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, submitted for publication.

[14] J. A. Berson and G. L. Nelson, *ibid.*, **92**, 1096 (1970).

[15] J. A. Berson and R. Holder, submitted for publication.

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Aliphatic Semidiones. XXI. Isomerization of Bicyclo[2.2.1]hept-5-ene-2,3-semidiones to Bicyclo[3.2.0]hept-2-ene-5,6-semidiones[1]

Sir:

An interest in the possibility of long-range interaction of nonconjugated π-electron systems led us to attempt the synthesis of **2**. Since α-hydroxy ketones in basic DMSO usually yield the semidione,[2,3] we prepared **1a** and **1b** by the addition of benzoyl nitrite[4] to norbornadiene and 1-methylnorbornadiene.[5] Hydrolysis of the first formed benzoyloxy nitrimines[6] gave **1** (**a**, $R_1 = R_4 = H$;[5] **b**, $R_1 = CH_3$, $R_4 = H$; **b′**, $R_1 = H$, $R_4 = CH_3$).[7]

Treatment of **1a** with potassium *tert*-butoxide in DMSO in a flow system[8] gave an unstable semidione detectable from ~1 to 20 sec after mixing, whose esr spectrum was inconsistent with the symmetry of **2a** (Chart I) but which was consistent with bicyclo[3.2.0]-hept-2-ene-5,6-semidione (**3a** or **4a**).[9]

Addition of acetoxyketene[10] to cyclopentadiene yielded **5a**. Pure samples of the endo isomer[7] (the major adduct) and exo isomer[7] yielded the same esr spectra as observed for the paramagnetic reaction product from **1a**.

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[1] Application of Electron Spin Resonance Spectroscopy to Studies of Valence Isomerization. IV. Work supported by a grant from the National Science Foundation.

[2] G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964).

[3] G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

[4] L. Francesconi and U. Cialdea, *Gazz. Chim. Ital.*, 34 (I), 435 (1904).

[5] Private communication from Dr. T. R. Sharpe, Du Pont Experimental Station.

[6] G. A. Boswell, *J. Org. Chem.*, **33**, 3699 (1968).

[7] Identification based on pmr, ir, elemental analysis, or high-resolution mass spectra.

[8] G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

[9] For example, INDO calculations using a logical set of bond lengths and a dihedral angle of 120° between planar rings gave values of $a_a{}^H = 10.2$, $a_b{}^H = 9.1$, $a_c{}^H = 1.5$, $a_d{}^H = -0.44$, $a_e{}^H = -0.47$, and $a_f{}^H = 0.2$ G (unpublished results with Mr. C. Chung). The positive sign of $a_c{}^H$ indicates that $\pi-\pi$ overlap is not the predominant delocalization mechanism since the negative value of $Q_{CH}{}^H$ predicts a negative sign of $a_c{}^H$ for homoconjugation. Similar calculations for **2** lead to small negative values for $a_{vinyl}{}^H$ indicating that in **2** homoconjugation predominates over spin polarization mechanisms.

[10] Generated from acetoxyacetyl chloride by the procedure of W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35**, 3733 (1970).