tion would give less crowding of the hydrogens in the inactive complex in which the cobalt(II) is coordinated to one *d* and one *l* tris chelate; work on that structure is in progress.

This complex represents the first example of a trigonal-prismatic complex with a coordination sphere of oxygen atoms; all previous examples[8] of discrete, trigonal-prismatic complexes have been based on the dithiolate ligand.

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[8] E. L. Muetterties, *J. Amer. Chem. Soc.*, **90,** 5097 (1968).

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On the Application of Orbital Symmetry Arguments to the Reactions of Transition Metal Complexes

Sir:

A recent paper[1] describes the application of the principles of orbital symmetry conservation[2] to some reactions of transition metal complexes. In this communication, we wish to amplify the conclusions of that paper, using a more rigorous method, and to point out certain very general limitations on the application of this approach to chemical problems.

The method of Woodward and Hoffmann involves the construction of orbital correlation diagrams for the one-electron energy levels of starting material and product, the correlations being made according to the symmetries of the activated complexes of two separate pathways. If these correlations predict substantial electronic destabilization of one transition state relative to the other, then the corresponding mechanism is disallowed; otherwise, it is allowed. A correctly constructed correlation diagram gives information concerning the energy of the activated complex of a reaction.

Merely correlating the orbitals of the starting material and the product without regard to the symmetry of the activated complex (the procedure followed by Eaton[1]) does not guarantee that this type of information will be obtained. The problems which can arise are illustrated by the treatment of the isomerization reactions of four-coordinate d^8 species given in ref 1, where it was concluded that square-planar to tetrahedral reactions are allowed, but that square-planar *cis–trans* isomerizations are disallowed. These two statements are contradictory, since attainment of tetrahedral geometry assures an allowed pathway for *cis–trans* isomerization. One reason for the contradiction is that the symmetry of the activated complex for the isomerization reaction (assumed to involve tetrahedral geometry) is higher than either the starting material or the product. The resulting increase in orbital degeneracy makes the correlation drawn in ref 1 of questionable value.[3] It is more informative in this case to look at the orbital correlation between the square plane and the tetrahedron.

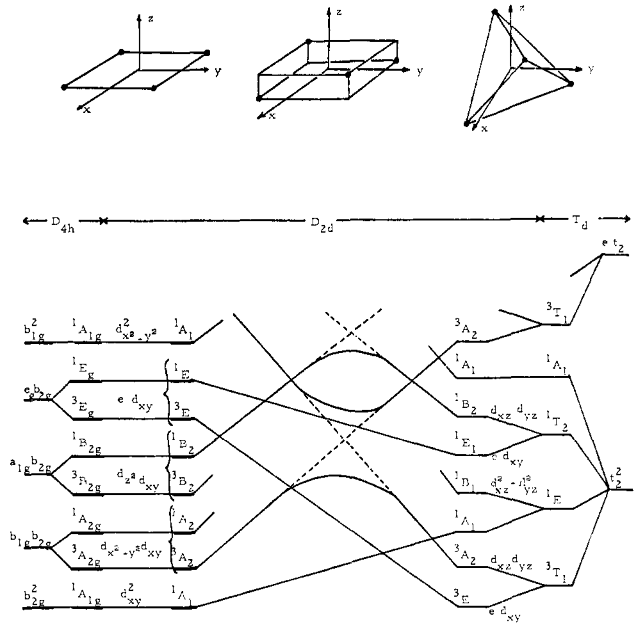

Figure 1. State correlation diagram for the isomerization of a square-planar to a tetrahedral d^8 complex. The symbol e stands for the degenerate set of orbitals (d$_{xz}$, d$_{yz}$). The orbital labels show the distribution of holes among the d orbitals for each state.

As pointed out by Longuet-Higgins and Abrahamson,[4] and acknowledged by Eaton,[1] a more elegant approach to this problem is to construct a state correlation diagram of the type shown in Figure 1.[5] Consideration of this diagram, which shows some of the correlations produced by the change of geometry for a d^8 system, leads to several conclusions. (a) Isomerization of a triplet tetrahedral complex to a square-planar complex is "disallowed," in the sense that the ground state of the tetrahedron correlates with an excited state of the square plane.[8] (b) The reverse reaction is "disallowed"

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[1] D. R. Eaton, *J. Am. Chem. Soc.*, **90,** 4272 (1968).

[2] R. B. Woodward and R. Hoffmann, *ibid.*, **87,** 4389 (1965); see also R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1,** 17 (1968).

[3] In particular, the distinction between the d_{xy}, d_{xz}, and the d_{yz} orbitals disappears in T_d symmetry. The d_{xy} orbital of one isomer cannot, therefore, be correlated uniquely with the d_{xy} orbital of the other.

[4] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87,** 2045 (1965).

[5] This diagram is similar to those used by Ballhausen, *et al.*,[6] and Martin, *et al.*,[7] to explain certain features of the spectra of square-planar compounds.

[6] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4,** 514 (1965).

[7] D. S. Martin, M. A. Tucker, and A. J. Kassman, *ibid.*, **4,** 1682 (1965).

[8] This definition of the term "disallowed" differs from that used in ref 1 or ref 4. In organic systems, where the ground states of starting material and product are almost always ^1A, a correlation of a ground with an excited state implies the existence of a crossing of states of the same symmetry, and the occurrence of such a crossing is used as the basis for the previous[4] definition. In inorganic systems, where ground states are not always totally symmetric singlets, a correlation of a ground with an excited state does not always produce this type of crossing. The extension of the definition of "disallowed" to cover any ground-state–excited-state correlation seems justified *conceptually* because such a correlation implies a barrier to reaction beyond that resulting from a difference in thermodynamic stability of starting material and product. Of course, as pointed out later, no definition has *experimental* meaning without a parallel "allowed" pathway for comparison.

for the same reason. (c) Excitation of a square-planar complex to the ^3E_g level makes the reaction allowed.

Thus, neither square-planar isomerization nor tetrahedral racemization are thermally allowed processes, if the mechanism involves a tetrahedral–square-planar interconversion. Photochemical *cis–trans* isomerization can, on the other hand, be allowed, in agreement with experiment.[9–11] Similar treatment of axial–equatorial interchange of the ligands of a trigonal-bipyramidal complex (through an intermediate or transition state with square-pyramidal geometry) shows that this reaction is, in agreement with Eaton's results, allowed, as is the substitution of square-planar complexes. Tetrahedral substitution is disallowed, in contrast to the results of the one-electron picture.[12] For a d^3 complex, racemization by way of a Bailar twist[13] is thermally allowed for weak ligand fields, but disallowed for strong fields. The same result is obtained for other mechanisms proposed for this reaction.[14,15]

Experimentally, there is little correlation between these predictions and observed reaction rates. This observation is hardly surprising, since the theory explicitly *ignores* changes in energy of the bonding levels of the complex.[16] The Woodward–Hoffmann treatment depends on the general assumption that if a reaction $A \rightarrow B$ can occur by two pathways, then, *other factors being equal*, the allowed pathway will have the lower activation energy. Implicit in this statement is the necessity for a comparison between two modes of reaction. For systems containing only carbon atoms, the energy difference between the two pathways appears, at least in one case, to be quite large,[17] but this empirical observation is not guaranteed by the qualitative arguments of the theory. Unfortunately, in the reactions of transition metal complexes, distinguishable pathways for the same reaction are usually not available, and the "allowedness" or "disallowedness" of any single reaction is not experimentally defined. In many of the reactions considered here (and particularly in substitution reactions), the rate will be determined by changes in binding energies, in over-all ligand field stabilization, and in the strengths of bonds being made or broken during the reaction. The contribution of orbital symmetry conservation might be expected to be much smaller.

Thus, orbital symmetry arguments concerning reactions of transition elements must be viewed with caution. The qualitative theory described herein may be useful in rationalizing differences in thermal and photochemical behavior of a complex with regard to the same reaction, or in the comparison of two distinguishable paths from the same starting material to slightly different products, if appropriate experiments can be devised. Verification of this limited theory is being sought.

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[11] J. R. Perumareddi and A. W. Adamson, *ibid.*, **72**, 414 (1968).

[12] Note that any reaction involving a change of spin multiplicity is disallowed in terms of the definition used here.

[13] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[14] P. Ray and K. Z. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[15] C. S. Springer and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

[16] Inclusion of these levels (or unoccupied p levels) in the configurations shown in Figure 1 would not change the appearance of this diagram at all, since, after the ordering of levels has been decided on, it depends entirely on symmetry properties of the complex.

[17] J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).

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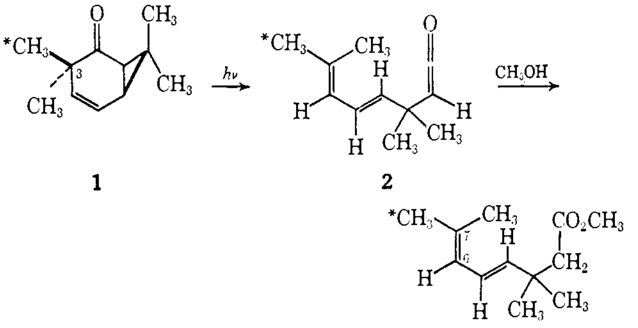
Stereoselective Photochemical Electrocyclic Valence Isomerization of 3-Methylcar-4-en-2-one

Sir:

One possible determinant of stereochemical selectivity in photochemical electrocyclic valence isomerizations for which the Hoffmann–Woodward generalizations seem to provide no unique predictions would be the ground-state geometry of the reactants.[1,2] The stereochemical outcome would be dictated by the conformation of the light-absorbing species, rather than by the character of the substituents on a terminus of the moiety suffering electrocyclic change. Even identical substituents, distinguishable only by geometrical disposition and an isotopic label, might retain stereochemical individuality during the conversion.

We now report discovery of such an example: the photochemical valence isomerization of 3-methylcar-4-en-2-one (**1**) in ether–methanol gives the *trans* isomer of methyl 3,3,7-trimethylocta-4,6-dienoate, and the 3-*endo*-methyl group of **1** becomes the 7-methyl *cis* to H-C(6) in **3**.



1 **2** **3**

3-Methylcar-4-en-2-one prepared from eucarvone (2,6,6-trimethylcyclohepta-2,4-dienone) using sodium amide and methyl iodide[3] was photolyzed (λ >300 nm) in ether containing 1.6% methanol to give after chromatography on silica gel 61% methyl 3,3,7-trimethylocta-4,6-dienoate.[4,5] Analysis of the nmr ab-

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[1] J. E. Baldwin and M. C. McDaniel, *J. Am. Chem. Soc.*, **90**, 6118 (1968), and references cited.

[2] S. M. Krueger, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., B*, in press.

[3] E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **78**, 174 (1956).

[4] Photolysis of **1** in a CH_2Cl_2–THF glass at liquid nitrogen temperatures generated the ketene intermediate **2** having a strong infrared absorption at 2110 cm^{-1}. Even at room temperature in ether the ketene may be generated and observed, and its reaction with added