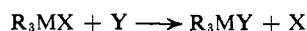


## The Steric Courses of Chemical Reactions. I

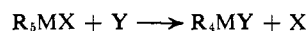
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**Abstract:** Procedures for classifying, enumerating, and representing topologically the steric courses of chemical reactions which interconvert symmetric molecules are presented. Reactions are defined in terms of permutation operations, and the symmetry of reactant and product configurations is then used to define classes of symmetry-equivalent reactions. The resulting classification schemes are shown to be readily interpretable in terms of traditional stereochemical concepts. Topological representations of reaction pathways are discussed, and procedures for calculating various properties are provided. Finally, some examples are treated which demonstrate the utility of this approach.

The steric course of a chemical reaction is defined by the stereochemical relationship between reactants and products. Once this relationship is established, mechanistic information is obtained in that certain mechanisms are ruled out. Traditionally, mechanistic studies of tetrahedral substitution reactions have relied heavily on the stereochemical relationship between reactants and products. Since there exist only  $3!/3 = 2$  permutational isomers of a "tetrahedral"  $C_{3v}$  molecule  $R_3MY$ , the substitution reaction



may proceed either with "inversion of configuration" or "retention of configuration." No other distinct possibility exists, assuming that both reactant and product have the same symmetry. For more complex systems, the situation is far less clear. Consider for example the case of octahedral substitution. Although there exist  $5!/4 = 30$  permutational isomers of  $C_{4v}$  "octahedral" molecule  $R_3MY$ , one might expect 30 distinct steric courses for the reaction



assuming both reactant and product have the same symmetry. It will be shown below, however, that this number is too large.

This paper addresses the problem of defining, classifying, enumerating, and representing all distinct changes of stereochemistry which may accompany the reactions of symmetric molecules. In the first section, the concept of configuration is generalized and reactions are defined in terms of stereochemical change. Then two simple exchange reactions are examined closely in order to clarify the physical significance of these definitions. In the next section, the relationship between reaction mechanism and steric course is discussed. Finally, three examples are treated.

## I. Definitions

When symmetric molecules undergo chemical reactions, the steric course is not uniquely defined by the stereochemical relationship between reactants and products unless labeling techniques are employed. This is because permutational isomers of molecules are not physically distinguishable unless chemically identical ligands are labeled. Labeling may be achieved by

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nuclear spin states, isotopic substitution, or chemical substitution such that the effect of the labels on the chemical properties of a molecule is negligible. We say that the ligands are chemically identical but distinguishable by labels. Accordingly, the point group of a molecule is defined by neglecting the labeling of chemically identical ligands and considering only the symmetry of the unlabeled molecule. Molecules which are identical when labeling is ignored are called chemically identical molecules even though the labeled molecules may in fact be distinguishable by physical techniques.

Consider for example Figure 1a, which may represent permutational isomerization of the  $C_{2v}$  molecule  $(CH_3)_2NPF_4$ . Mathematically, the chemically identical F ligands are distinguishable by the indexed labels  $B_2$ ,  $B_3$ ,  $B_4$ , and  $B_5$ . Physically, the steric course of the reaction has been studied by nmr spectroscopy using the spin states of the  $^{19}F$  nuclei as labels.<sup>2</sup> Figure 1b may represent the cis-trans isomerization of  $Ru(PR_3)_4H_2$ .<sup>3</sup> Here again, the steric course might be studied by nmr spectroscopy using the  $^{31}P$  and  $^1H$  nuclear spin states as labels. Figure 1b may also represent the cis-trans isomerization of  $Ru(CO)_4(SiCl_3)_2$ .<sup>4</sup> The steric course of this reaction might be studied using isotopic labeling, i.e.,  $^{13}CO$  and  $^{12}CO$  as labeled ligands.

The dynamic stereochemistry of isomerization reactions has been investigated in detail.<sup>5-8</sup> Reactions are defined by permutation operations, and sets of symmetry equivalent reactions, reactions formally non-differentiable in a chiral environment, are defined such that the steric course of equivalent reactions is identical. Thus the number of classes of symmetry equivalent reactions is the number of theoretically measurable changes in stereochemistry which might accompany a given isomerization. Different definitions of symmetry equivalent reactions are necessary since the nature of the environment and the nature of the experimental measuring techniques used determine whether or not certain changes in stereochemistry may be differentiated.

Figure 1c-f may represent reactions of  $Mn(CO)_5X$

(2) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

(3) J. P. Jesson in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 187.

(4) R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, **94**, 274 (1972).

(5) W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

(6) W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 6940 (1972).

(7) W. G. Klemperer, *Inorg. Chem.*, **11**, 2668 (1972).

(8) W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 8360 (1972).

+ CO,<sup>9</sup> Pt(NH<sub>3</sub>)<sub>3</sub>Cl<sup>+</sup> + Cl<sup>-</sup>,<sup>10</sup> PCl<sub>3</sub> + Cl<sub>2</sub>,<sup>11</sup> and SF<sub>4</sub> + SF<sub>4</sub>,<sup>12</sup> respectively. The types of reactions shown in Figure 1 are closely related. Two successive exchange reactions shown in (c) may result in permutational isomerization. In (d), forward reaction followed by reverse reaction may also result in permutational isomerization. Similarly, association followed by dissociation as in (e), (f), or (g) may result in a net exchange reaction. If the dissociation reaction shown in (f) is followed by association according to (g), polytopal isomerization reactions result. The purpose of this section is to express the relationship between these reactions in mathematical terms. Then the techniques already used to treat isomerization reactions may be applied to more complicated sequences of reactions. We begin by generalizing the definitions of concepts used in the treatment of isomerization reactions.

**A. Configurations and Their Symmetry.** A configuration is defined here as a set of labeled ligands which have been assigned to labeled sites called skeletal positions. Assume that a set of  $n$  (unidentate) ligands contains  $n_1$  ligands of a given chemical identity,  $n_2$  ligands of another chemical identity, and  $n_3$  ligands of a third chemical identity. Thus,  $n = n_1 + n_2 + n_3$ . These ligands are assigned labels from the set  $L = \{A_1, A_2, \dots, A_{n_1}, B_{n_1+1}, B_{n_1+2}, \dots, B_{n_1+n_2}, C_{n_1+n_2+1}, C_{n_1+n_2+2}, \dots, C_n\}$  such that the letter indicates the chemical identity of each ligand and the integral subscript provides a unique index for each ligand. The skeletal positions of a configuration are assigned labels from the set  $S^W = \{s_1^W, s_2^W, \dots, s_n^W\}$  such that ligands of types A, B, and C occupy skeletal positions labeled by  $\{s_1^W, s_2^W, \dots, s_{n_1}^W\}$ ,  $\{s_{n_1+1}^W, s_{n_1+2}^W, \dots, s_{n_1+n_2}^W\}$ , and  $\{s_{n_1+n_2+1}^W, s_{n_1+n_2+2}^W, \dots, s_n^W\}$ , respectively. Here, the superscript W identifies the geometry of the configuration, while the integral subscript provides a unique index for each skeletal position.

Chemically speaking, a configuration is a set of labeled, rigid molecules having a definite orientation in space. Mathematically, a configuration is conveniently described by a  $2 \times n$  matrix

$$\begin{pmatrix} l \\ s \end{pmatrix}_i^W = \begin{pmatrix} 123 \dots n \\ jkp \dots q \end{pmatrix}^W$$

where ligand indices are listed in the top row, and below each ligand index is written the index of the skeletal position which that ligand occupies. The superscript W identifies the geometry of the configuration, and the subscript  $i$  is an integral label for each matrix. The reference configuration is defined by

$$\begin{pmatrix} l \\ s \end{pmatrix}_e^W = \begin{pmatrix} 123 \dots n \\ 123 \dots n \end{pmatrix}^W$$

Examples of this nomenclature are shown in Figure 2.

Although a configuration is defined in terms of oriented molecules, we shall be concerned here with molecules which are free to rotate and translate in space. Therefore, different configurations having the same geometry may be equivalent in that they represent the same set of labeled molecules oriented differently in

(9) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968), and references therein.  
 (10) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 5.  
 (11) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972), and references therein.  
 (12) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

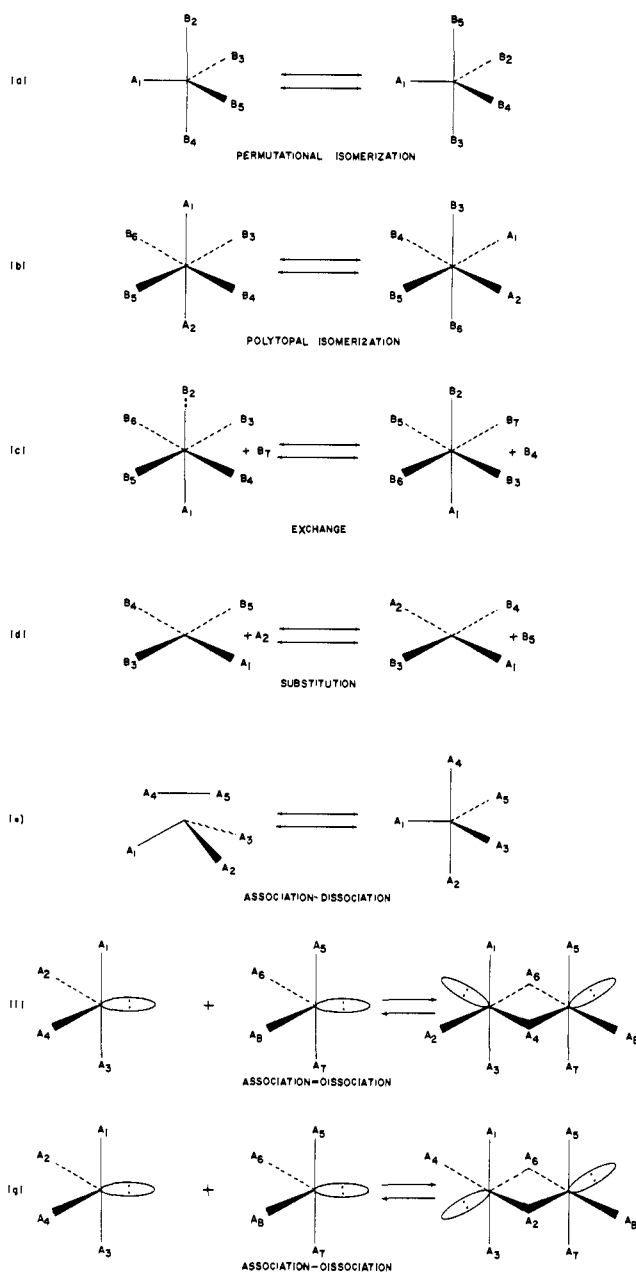


Figure 1. Some representative types of chemical reactions interconverting symmetric molecules.

space. Such is the case in Figure 2 for the pairs of configurations shown in (b), (f), (j), (l), and (n). Equivalence between two configurations  $\begin{pmatrix} l \\ s \end{pmatrix}_i^W$  and  $\begin{pmatrix} l \\ s \end{pmatrix}_j^W$  may be defined by a permutation operation which represents translation and/or rotation of molecules in the configuration. By "translation" we mean permutation of chemically identical molecules. Since the indices of the skeletal positions serve as "ligand coordinates," we let the permutation operations act on these indices. Thus the permutation represents a "coordinate transformation." For example, the equivalence of configurations  $\begin{pmatrix} l \\ s \end{pmatrix}_e^Q$  and  $\begin{pmatrix} l \\ s \end{pmatrix}_1^Q$  shown in Figure 2a is expressed by the relation

$$\begin{pmatrix} l \\ s \end{pmatrix}_e^Q = q_i^{QQ} \begin{pmatrix} l \\ s \end{pmatrix}_1^Q$$

where  $q_i^{QQ} = (1)(24)(35)^{QQ}$ , acting on the indices of the skeletal positions, represents a twofold rotation opera-

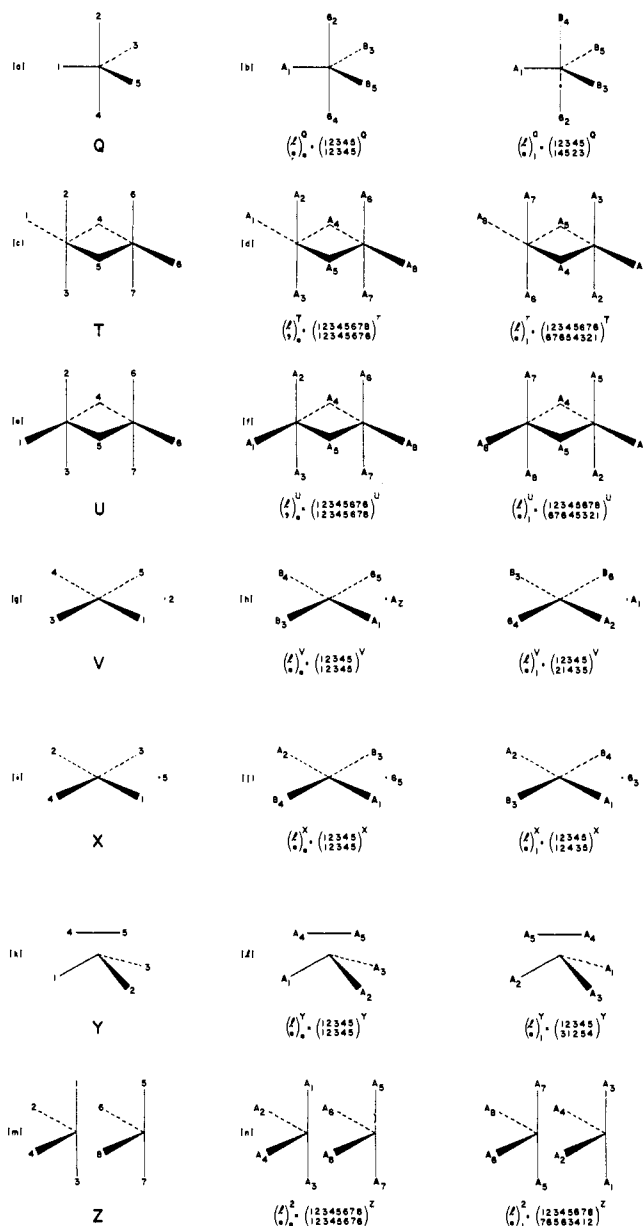


Figure 2. Six pairs of configurations having different geometries are shown in the two columns on the right. To the left of each pair is shown the indexing of skeletal positions which allows definition of the appropriate  $(\begin{smallmatrix} 1 \\ 2 \end{smallmatrix})$  matrices.

tion. When  $q_i^{\text{QQ}}$  acts on the bottom row of  $(\begin{smallmatrix} 1 \\ 2 \end{smallmatrix})_1^{\text{Q}}$ , the bottom row of  $(\begin{smallmatrix} 1 \\ 2 \end{smallmatrix})_s^{\text{Q}}$  is generated

$$\begin{pmatrix} 12345 \\ 12345 \end{pmatrix}^{\text{Q}} = (1)(24)(35)^{\text{QQ}} \begin{pmatrix} 12345 \\ 14523 \end{pmatrix}^{\text{Q}}$$

Mathematically, the permutation operation  $(1)(24)(35)^{\text{QQ}}$  means "leave 1 fixed, replace 2 with 4, replace 4 with 2, replace 3 with 5, and replace 5 with 3." Chemically speaking, the operation  $(1)(24)(35)^{\text{QQ}}$  means "the ligand in position  $s_1^{\text{Q}}$  is left fixed, the ligand in position  $s_2^{\text{Q}}$  is moved to position  $s_4^{\text{Q}}$ , the ligand in position  $s_4^{\text{Q}}$  is moved to position  $s_2^{\text{Q}}$ , the ligand in position  $s_3^{\text{Q}}$  is moved to position  $s_5^{\text{Q}}$ , and the ligand in position  $s_5^{\text{Q}}$  is moved to position  $s_3^{\text{Q}}$ ."

All the operations  $w_i^{\text{WW}}$  which represent rotation and/or translation of molecules in a configuration having geometry W form a group  $W^{\text{WW}}$  called the *proper configurational symmetry group*. Note that the

same letter is used to identify this group and the geometry of the configurations which the group acts on. Since  $W^{\text{WW}}$  represents rotations and/or translations of molecules, we now seek a more precise definition of  $W^{\text{WW}}$  in terms of permutation group representations of the rotational point groups of the molecules in a configuration.

If a configuration contains only one molecule, then the proper configurational symmetry group is a permutation group representation of that molecule's rotational point group which acts on the indices of the skeletal positions. The rotational point group of the molecules in configurations shown in Figure 2f is  $C_2$ . It contains two operations: the identity operation  $u_1$  and a two-fold rotation operation  $u_2$ . When  $u_1$  and  $u_2$  act on the indices of the skeletal positions shown in Figure 2e, the operations  $u_1^{\text{UU}} = (1)(2)(3)(4)(5)(6)(7)(8)^{\text{UU}}$  and  $u_2^{\text{UU}} = (18)(27)(36)(4)(5)^{\text{UU}}$  are generated. These two operations form the group  $U^{\text{UU}}$ , and we say  $U^{\text{UU}} = C_2^{\text{UU}}$ .

If a configuration having geometry W contains  $m$  chemically nonidentical molecules, and  $R_i$  is the rotational point group of the  $i$ th molecule, then  $W^{\text{WW}}$  is generated by letting all possible combinations of permutations in  $R_1^{\text{WW}}, R_2^{\text{WW}}, \dots$ , and  $R_m^{\text{WW}}$  operate. Letting  $|A|$  denote the number of elements in an arbitrary set A, we have  $|W^{\text{WW}}| = |R_1^{\text{WW}}| \cdot |R_2^{\text{WW}}| \cdot \dots \cdot |R_m^{\text{WW}}|$ . Formally, the proper configurational symmetry group is defined by

$$W^{\text{WW}} = \sum_{i=1}^m R_i^{\text{WW}}$$

where the summation implies direct sums.<sup>13</sup> For the configurations shown in Figure 2l,  $R_1 = C_3$  and  $R_2 = D_\infty$ .  $C_3^{\text{YY}}$  contains the operations  $(1)(2)(3)^{\text{YY}}, (123)^{\text{YY}}$ , and  $(132)^{\text{YY}}$ , while  $D_\infty^{\text{YY}}$  contains the operations  $(4)(5)^{\text{YY}}$  and  $(45)^{\text{YY}}$ . Thus  $Y^{\text{YY}} = C_3^{\text{YY}} + D_\infty^{\text{YY}}$  contains  $|C_3^{\text{YY}}| \cdot |D_\infty^{\text{YY}}| =$  six operations.

$$y_1^{\text{YY}} = (1)(2)(3)(4)(5)^{\text{YY}}$$

$$y_2^{\text{YY}} = (1)(2)(3)(45)^{\text{YY}}$$

$$y_3^{\text{YY}} = (123)(4)(5)^{\text{YY}}$$

$$y_4^{\text{YY}} = (123)(45)^{\text{YY}}$$

$$y_5^{\text{YY}} = (132)(4)(5)^{\text{YY}}$$

$$y_6^{\text{YY}} = (132)(45)^{\text{YY}}$$

Assume a configuration having geometry W contains  $m$  molecules and all  $m$  molecules are chemically identical. Therefore all these molecules have the same rotational point group R, and the group  $W^{\text{WW}}$  will contain  $|R^{\text{WW}}|^m$  operations representing all possible combinations of proper rotations of molecules in the configuration. In addition, however, there will be  $m!$  operations in  $W^{\text{WW}}$  which represent all possible permutations of the  $m$  chemically identical molecules. Since any combination of rotations can be combined with any one of the  $m!$  permutations of entire molecules, the group  $W^{\text{WW}}$  will contain a total of  $m!|R^{\text{WW}}|^m$  operations. Using standard notation,  $W^{\text{WW}} = S_m[R^{\text{WW}}]$ , the composition of "S<sub>m</sub> around R<sup>WW</sup>,"<sup>13</sup> where  $S_m$  is the symmetric permutation group degree  $m$

(13) For a rigorous definition of this operation see: R. W. Robinson, *J. Combinatorial Theory*, 4, 184 (1968), or F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, pp 163-164.

which contains all  $m!$  possible permutations of the  $m$  chemically identical molecules. The configurations shown in Figure 2n contain two chemically identical molecules having rotational point groups  $C_2$ . Here,  $m = 2$  and  $R = C_2$ . Thus  $Z^{ZZ} = S_2[C_2^{ZZ}]$  contains  $m! \cdot |R^{ZZ}|^m = 2! \cdot 2^2 = 8$  operations.

$$z_1^{ZZ} = (1)(2)(3)(4)(5)(6)(7)(8)^{ZZ}$$

$$z_2^{ZZ} = (13)(24)(5)(6)(7)(8)^{ZZ}$$

$$z_3^{ZZ} = (1)(2)(3)(4)(57)(68)^{ZZ}$$

$$z_4^{ZZ} = (13)(24)(57)(68)^{ZZ}$$

$$z_5^{ZZ} = (15)(26)(37)(48)^{ZZ}$$

$$z_6^{ZZ} = (1735)(2846)^{ZZ}$$

$$z_7^{ZZ} = (1537)(2648)^{ZZ}$$

$$z_8^{ZZ} = (17)(28)(35)(46)^{ZZ}$$

The first four operations represent rotations of the molecules in the configuration, while the last four represent rotations combined with permutation of the two chemically identical molecules, *i.e.*, rotations combined with translations.

In the most general case, a configuration having geometry  $W$  will contain  $m$  molecules having different chemical identities and  $m_i$  molecules of chemical identity  $i$  having rotational point group  $R_i$ . Thus  $\sum_{i=1}^m m_i$  equals the number of molecules in the configuration. Applying the definitions given in the preceding paragraphs, the *proper configurational symmetry group* is defined by

$$W^{WW} = \sum_{i=1}^m S_{m_i}[R_i^{WW}] \quad (1)$$

and the number of operations in this group is

$$|W^{WW}| = \prod_{i=1}^m m_i! |R_i^{WW}|^{m_i} \quad (2)$$

Two configurations  $(^i_s)_t^W$  and  $(^i_s)_j^W$  having the same ligand set and the same geometry  $W$  are defined to be *equivalent* if

$$w_k^{WW} \begin{pmatrix} l \\ s \end{pmatrix}_i^W = \begin{pmatrix} l \\ s \end{pmatrix}_j^W \quad (3)$$

for some  $w_k^{WW} \in W^{WW}$ . These configurations are *nonequivalent* if eq 3 does not hold.

Another useful permutation group may be generated which represents the operations in the full point groups of molecules in a configuration. The *full configurational symmetry group*  $\bar{W}^{WW}$  is defined by

$$\bar{W}^{WW} = \sum_{i=1}^m S_{m_i}[\bar{R}_i^{WW}] \quad (4)$$

where  $\bar{R}_i$  is the full point group of molecules in the configuration having chemical identity  $i$ . The number of operations in  $\bar{W}^{WW}$  is

$$|\bar{W}^{WW}| = \prod_{i=1}^m m_i! |\bar{R}_i^{WW}|^{m_i} \quad (5)$$

Clearly,  $W^{WW}$  is a subgroup of  $\bar{W}^{WW}$

If  $w_i^{WW} \in W^{WW}$ , we say  $w_i^{WW}$  represents *rotation of configuration*. If  $\bar{w}_i^{WW} \in \bar{W}^{WW}$ , then  $\bar{w}_i^{WW}$  may represent improper rotation (and possibly translation) of

one or more molecules in the configuration. If  $\bar{w}_i^{WW}$  represents improper rotation (and possibly translation) of *all* molecules in the configuration, we say  $\bar{w}_i^{WW}$  represents *inversion of configuration*. Accordingly, two nonequivalent configurations  $(^i_s)_t^W$  and  $(^i_s)_j^W$  are defined to be *enantiomeric* if eq 6 holds for some  $\bar{w}_k^{WW} \in \bar{W}^{WW}$  which represents inversion of configuration.

$$\begin{pmatrix} l \\ s \end{pmatrix}_i^W = \bar{w}_k^{WW} \begin{pmatrix} l \\ s \end{pmatrix}_j^W \quad (6)$$

If eq 6 does not hold, then nonequivalent configurations  $(^i_s)_t^W$  and  $(^i_s)_j^W$  are *diastereomeric*.

Two examples should make the physical significance of these definitions clear. For the configurations shown in Figure 2d, the operation  $t_i^{TT} = (18)(27)-(36)(45)^{TT}$  represents inversion of configuration. Since  $(^i_s)_e^T = t_i^{TT} (^i_s)_1^T$  and  $(^i_s)_e^T \neq t_j^{TT} (^i_s)_1^T$  for any  $t_j^{TT} \in T^{TT}$ , the configurations  $(^i_s)_e^T$  and  $(^i_s)_1^T$  are enantiomeric. For the configurations shown in Figure 2j, the operation  $\bar{x}_i^{XX} = (1)(2)(34)(5)^{XX}$  represents inversion of configuration, here, reflection operations acting on both molecules.<sup>14</sup> However, the operation  $(1)(2)(34)(5)^{XX}$  also represents rotation of configuration. Thus the configurations  $(^i_s)_1^X$  and  $(^i_s)_e^X = \bar{x}_i^{XX} (^i_s)_1^X$  are equivalent configurations. Whenever all molecules in a configuration are planar, operations which represent rotation of configuration also represent inversion of configuration.

**B. Reactions and Their Symmetry.** A *reaction* is defined here as a transformation which converts one configuration into another configuration such that stereochemical change occurs. Mathematically, this transformation is defined by an operation  $h_i^{VW}$  which transforms  $(^i_s)_j^V$ , the *reactant configuration*, into  $(^i_s)_k^W$ , the *product configuration*, by letting the permutation operation  $h_i$  act on the indices of the skeletal positions listed in the bottom row of  $(^i_s)_j^V$  and replacing the superscript  $V$  by  $W$ .<sup>15</sup> The reactant and product configurations may have the same geometry, *i.e.*, the case  $V = W$  is allowed. The only restriction is that reactant and product configurations must have the same ligand set.

The reactant and product configurations of the reaction shown in Figure 1a both have the same geometry. Using the indexing of skeletal positions defined in Figure 2a, the reactant configuration is defined by

$$\begin{pmatrix} l \\ s \end{pmatrix}_e^Q = \begin{pmatrix} 12345 \\ 12345 \end{pmatrix}^Q$$

and the product configuration is defined by

$$\begin{pmatrix} l \\ s \end{pmatrix}_2^Q = \begin{pmatrix} 12345 \\ 13452 \end{pmatrix}^Q$$

The reaction is defined by  $h_i^{QQ} = (1)(2345)^{QQ}$  since  $(^i_s)_2^Q$  is generated when  $h_i$  acts on the indices of the skeletal positions listed in the bottom row of  $(^i_s)_e^Q$

$$(1)(2345)^{QQ} \begin{pmatrix} 12345 \\ 12345 \end{pmatrix}^Q = \begin{pmatrix} 12345 \\ 13452 \end{pmatrix}^Q$$

Chemically speaking,  $(1)(2345)^{QQ}$  means "the ligand in

(14) It is assumed that ligands may be represented by points and therefore must have reflection symmetry, *i.e.*, be achiral.

(15) In common usage, the word "reaction" may refer collectively to a set of "reactions," *i.e.*, permutations, as defined here. The intended meaning of the word should be clear from context.

position  $s_1^Q$  is left fixed, the ligand in position  $s_2^Q$  is moved to position  $s_3^Q$ , the ligand in position  $s_3^Q$  is moved to position  $s_4^Q$ , the ligand in position  $s_4^Q$  is moved to position  $s_5^Q$ , and the ligand in position  $s_5^Q$  is moved to position  $s_2^Q$ .

In Figure 1d, the reactant configuration is defined by

$$\begin{pmatrix} l \\ s \end{pmatrix}_e^v = \begin{pmatrix} 12345 \\ 12345 \end{pmatrix}^v$$

and the product configuration by

$$\begin{pmatrix} l \\ s \end{pmatrix}_1^x = \begin{pmatrix} 12345 \\ 12435 \end{pmatrix}^x$$

if skeletal positions are labeled as in Figure 2g and i, respectively. The reaction is defined by  $h_i^{xv} = (1)(2)(34)(5)^{xv}$  since

$$(1)(2)(34)(5)^{xv} \begin{pmatrix} 12345 \\ 12345 \end{pmatrix}^v = \begin{pmatrix} 12345 \\ 12435 \end{pmatrix}^x$$

We describe the reaction  $h_1^{xv} = (1)(2)(34)(5)^{xv}$  by saying "the ligand in position  $s_1^v$  is moved to position  $s_1^x$ , the ligand in position  $s_2^v$  is moved to position  $s_2^x$ , the ligand in position  $s_3^v$  is moved to position  $s_4^x$ , the ligand in position  $s_4^v$  is moved to position  $s_3^x$ , and the ligand in position  $s_5^v$  is moved to position  $s_5^x$ ."

The reader may verify that the reactions shown in Figure 1f and g are defined by  $(12)(3)(456)(7)(8)^{uz}$  and  $(12564)(3)(7)(8)^{tz}$ , respectively, if skeletal positions are labeled as shown in Figure 2.

Given the set of  $n$  ligands labeled by  $L = \{A_1, A_2, \dots, A_{n_1}, B_{n_1+1}, B_{n_1+2}, \dots, B_{n_1+n_2}, C_{n_1+n_2+1}, C_{n_1+n_2+2}, \dots, C_n\}$  as above, we define a permutation group  $H$ , the group of allowed permutations, which acts on the set of numbers  $\{1, 2, \dots, n\}$ . Operations in  $H$  permute the numbers in the sets  $\{1, 2, \dots, n_1\}$ ,  $\{n_1 + 1, n_1 + 2, \dots, n_1 + n_2\}$ , and  $\{n_1 + n_2 + 1, n_1 + n_2 + 2, \dots, n\}$  among themselves in all possible ways.  $H$  therefore contains  $n_1!n_2!n_3!$  operations. Formally,  $H$  is defined by

$$H \equiv S_{n_1} + S_{n_2} + S_{n_3}$$

where  $S_{n_i}$  is the symmetric group degree  $n_i$  and the sums imply direct sums.

The set of all possible reactions  $h_i^{vw}$  which transform configurations having geometry V into configurations having geometry W is defined by the permutation operations in  $H$ , the group of allowed permutations. This set is called  $H^{vw}$ , the superscript indicating the geometry of product and reactant configurations. Unless  $V = W$ , products of the type  $h_i^{vw} \cdot h_j^{vw}$  are undefined, since

$$h_i^{vw} \cdot h_j^{vw} \begin{pmatrix} l \\ s \end{pmatrix}_k^v = h_i^{vw} \begin{pmatrix} l \\ s \end{pmatrix}_l^v$$

and  $h_i^{vw}$  by definition may only act on configurations having geometry V. Thus  $H^{vw}$  is not a group. The inverse of  $h_i^{vw}$ , called the reverse reaction of  $h_i^{vw}$ , is defined by

$$(h_i^{vw})^{-1} \equiv (h_i^{-1})^{vw}$$

The product of  $h_i^{vw}$  and  $h_j^{vw}$  is defined by

$$h_i^{vw} \cdot h_j^{vw} \equiv (h_i \cdot h_j)^{vw}$$

and indicates reaction  $h_j^{vw}$  followed by reaction  $h_i^{vw}$ .

$H^{ww}$  is a group with a product operation defined by  $h_i^{ww} \cdot h_j^{ww} \equiv (h_i \cdot h_j)^{ww}$ .  $H^{ww}$  contains  $W^{ww}$  and  $\overline{W}^{ww}$  as subgroups. If each operation in  $H^{ww}$  acts on  $\begin{pmatrix} l \\ s \end{pmatrix}_e^w$

$$|H^{ww}| = n_1!n_2!n_3!$$

different configurations are generated, and this set of configurations contains all possible configurations having geometry W. There is therefore a one-to-one correspondence between configurations having geometry W and operations in the group  $H^{ww}$ . Two configurations  $h_i^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_e^w$  and  $h_j^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_e^w$  are equivalent if

$$h_i^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_e^w = w_k^{ww} \cdot h_j^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_e^w = (w_k \cdot h_j)^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_e^w$$

for some  $w_k^{ww} \in W^{ww}$ . A complete set of equivalent configurations therefore contains  $|W^{ww}|$  configurations. The group  $H^{ww}$  can be partitioned into disjoint sets of operations  $W^{ww} h_i^{ww}$  such that each set corresponds to a complete set of equivalent configurations. The set of permutations  $W^{ww} h_i^{ww}$  is called a right coset of  $W^{ww}$  in  $H^{ww}$ . If we select one element from each right coset of  $W^{ww}$  in  $H^{ww}$ , we form a set of coset representatives  $C^w$ . Each  $c_i^w \in C^w$  thus uniquely specifies a complete set of equivalent configurations, and the set  $C^w$  represents a complete set of nonequivalent configurations having geometry W. Since a complete set of equivalent configurations contains  $|W^{ww}|$  operations, if we let  $I_w$  be the total number of nonequivalent configurations having geometry W, then  $I_w \cdot |W^{ww}| = |H^{ww}| = n_1!n_2!n_3!$ . Accordingly, we define  $I_w$  to be the configuration count and

$$I_w = \frac{|H^{ww}|}{|W^{ww}|} = \frac{n_1!n_2!n_3!}{\prod_{i=1}^m m_i! |R_i^{ww}|^{m_i}} \quad (7)$$

using eq 2 to calculate  $|W^{ww}|$ . Equation 7 may be rigorously derived noting that  $I_w = |C^w|$  and following well-known procedures outlined in ref 6.

Since reactions are defined in terms of oriented molecules but reactant and product molecules are assumed here to be free to rotate and translate in space, different reactions may in fact represent the same change in stereochemistry. For example, let

$$h_i^{vw} \begin{pmatrix} l \\ s \end{pmatrix}_j^v = \begin{pmatrix} l \\ s \end{pmatrix}_k^v \quad (8)$$

and

$$h_0^{vw} \begin{pmatrix} l \\ s \end{pmatrix}_p^v = \begin{pmatrix} l \\ s \end{pmatrix}_q^v \quad (9)$$

If

$$\begin{pmatrix} l \\ s \end{pmatrix}_j^w = w_j^{ww} \begin{pmatrix} l \\ s \end{pmatrix}_p^w \quad (10)$$

and

$$\begin{pmatrix} l \\ s \end{pmatrix}_k^v = v_i^{vv} \begin{pmatrix} l \\ s \end{pmatrix}_q^v \quad (11)$$

then  $h_i^{vw}$  and  $h_0^{vw}$  represent the same change in stereochemistry since the reactant configurations as well as product configurations in eq 8 and 9 are equivalent.

Mathematically, we substitute eq 10 and 11 into eq 8

$$h_i^{vW} \cdot w_r^{wW} \binom{l}{s}_p^W = v_i^{vV} \binom{l}{s}_q^V$$

This implies

$$(v_i^{vV})^{-1} \cdot h_i^{vW} \cdot w_r^{wW} \binom{l}{s}_p^W = (v_i^{-1} \cdot h_i \cdot w_r)^{vW} \binom{l}{s}_p^W = \binom{l}{s}_q^V$$

and comparing with eq 9

$$h_o^{vW} = (v_i^{-1} \cdot h_i \cdot w_r)^{vW}$$

In general,  $h_i^{vW}$  and  $h_j^{vW}$  are defined to be *nondifferentiable in a chiral environment* if eq 12 holds for some  $v_k^{vV} \in \mathcal{V}^{vV}$  and  $w_l^{wW} \in \mathcal{W}^{wW}$ .

$$h_i = v_k \cdot h \cdot w_l \quad (12)$$

The reactions  $h_i^{vW}$  and  $h_j^{vW}$  are *differentiable in a chiral environment* if eq 12 does not hold. In less precise chemical terms, reactions which are nondifferentiable in a chiral environment represent the same stereochemical change, *i.e.*, have the same steric course.

Just as the concept of equivalent configurations implies the concept of reactions differentiable in a chiral environment, the concept of enantiomeric configurations implies a corresponding relationship between reactions. Let  $\binom{l}{s}_i^W$  and  $\binom{l}{s}_j^W$  as well as  $\binom{l}{s}_k^V$  and  $\binom{l}{s}_o^V$  be enantiomeric configurations. Thus

$$\binom{l}{s}_i^W = \bar{w}_p^{wW} \binom{l}{s}_j^W \quad (13)$$

where  $\bar{w}_p^{wW}$  represents inversion of configuration, and

$$\binom{l}{s}_k^V = \bar{v}_q^{vV} \binom{l}{s}_o^V \quad (14)$$

where  $\bar{v}_q^{vV}$  represents inversion of configuration. If

$$\binom{l}{s}_k^V = h_r^{vW} \binom{l}{s}_i^W \quad (15)$$

and

$$\binom{l}{s}_o^V = h_s^{vW} \binom{l}{s}_j^W \quad (16)$$

then reactions formally nondifferentiable from  $h_r^{vW}$  and  $h_s^{vW}$  occur with equal probability in an achiral environment. Substituting eq 13 and 14 into eq 15 we obtain

$$\begin{aligned} \bar{v}_q^{vV} \binom{l}{s}_o^V &= h_r^{vW} \cdot \bar{w}_p^{wW} \binom{l}{s}_j^W \\ \binom{l}{s}_o^V &= (\bar{v}_q^{vV})^{-1} \cdot h_r^{vW} \cdot \bar{w}_p^{wW} \binom{l}{s}_j^W = \\ &= (\bar{v}_q^{-1} \cdot h_r \cdot \bar{w}_p)^{vW} \binom{l}{s}_j^W \end{aligned}$$

Comparing this result with eq 16

$$h_s^{vW} = (\bar{v}_q^{-1} \cdot h_r \cdot \bar{w}_p)^{vW}$$

Accordingly, a "mirror image"  $h_p^{vW}$  of a reaction  $h_q^{vW}$  is defined by eq 17, where  $\bar{v}_i^{vV}$  and  $\bar{w}_j^{wW}$  both represent inversion of configuration. If  $h_p^{vW}$  and

$$h_p = \bar{v}_i \cdot h_q \cdot \bar{w}_j \quad (17)$$

$h_q^{vW}$  are also differentiable in a chiral environment, they are defined to be *enantiomeric reactions* or simply *enantiomeric*. We then say that  $h_p^{vW}$  (or  $h_q^{vW}$ ) is a *chiral reaction*. If  $h_p^{vW}$  is nondifferentiable from its "mirror images" in a chiral environment, then  $h_p^{vW}$  is an *achiral reaction*. If two reactions are differentiable in a chiral environment and are not enantiomeric, they are defined to be *diastereomeric reactions* or simply *diastereomeric*.

One further type of symmetry equivalence between reactions is of interest. Two reactions  $h_i^{vW}$  and  $h_j^{vW}$  are *nondifferentiable in a totally symmetric environment* if eq 18 holds for some  $\bar{v}_k^{vV} \in \bar{\mathcal{V}}^{vV}$  and some  $\bar{w}_l^{wW} \in \bar{\mathcal{W}}^{wW}$ . If eq 18 does not hold,  $h_i^{vW}$  and  $h_j^{vW}$  are

$$h_i = \bar{v}_k \cdot h_j \cdot \bar{w}_l \quad (18)$$

*differentiable in a totally symmetric environment*. Note that eq 17 and 18 differ in that  $\bar{v}_i^{vV}$  and  $\bar{w}_j^{wW}$  both represent inversion of configuration, while  $\bar{v}_k^{vV}$  and  $\bar{w}_l^{wW}$  are arbitrary operations in  $\bar{\mathcal{V}}^{vV}$  and  $\bar{\mathcal{W}}^{wW}$ , respectively.

As was discussed above, the set  $H^{vW}$  contains all possible reactions which interconvert configurations having geometries V and W. Since we are concerned here with the steric course of reactions, we are interested primarily in different sets of reactions nondifferentiable in a chiral environment as defined by eq 12. The number of these disjoint sets contained in  $H^{vW}$  is called the number of reactions differentiable in a chiral environment. A complete set of reactions differentiable in a chiral environment is generated by selecting one reaction from each set of reactions nondifferentiable in a chiral environment. A complete set of reactions differentiable in a totally symmetric environment and a complete set of diastereomeric reactions may be similarly generated.

It is often a great help when dealing with complex problems in dynamic stereochemistry to determine the number of diastereomeric reactions or reactions differentiable in a chiral or totally symmetric environment before actually identifying the reactions. Accordingly, formulas are provided here which enumerate these reactions. These formulas will not be discussed in detail at this point. Their application and significance will be explained later in the context of specific examples.

First, we define the *generalized cyclic type*  $(j_1, j_2, \dots, j_n; k_1, k_2, \dots, k_n; l_1, l_2, \dots, l_n)$  of a permutation  $h_i \in H$ . Recall that elements in  $H$  permute numbers in the sets  $\{1, 2, \dots, n_1\}$ ,  $\{n_1 + 1, n_1 + 2, \dots, n_1 + n_2\}$ , and  $\{n_1 + n_2 + 1, n_1 + n_2 + 2, \dots, n_1 + n_2 + n_3\}$  among themselves. The array  $(j_1, j_2, \dots, j_n; k_1, k_2, \dots, k_n; l_1, l_2, \dots, l_n)$  indicates that the permutation  $h_i$  contains  $j_p$  cycles of length  $p$  which permute the numbers  $\{1, 2, \dots, n_1\}$  among themselves,  $k_q$  cycles of length  $q$  which permute the numbers  $\{n_1 + 1, n_1 + 2, \dots, n_1 + n_2\}$  among themselves, and  $l_r$  cycles of length  $r$  which permute the numbers  $\{n_1 + n_2 + 1, n_1 + n_2 + 2, \dots, n_1 + n_2 + n_3\}$  among themselves.

To count the number of reactions  $h_i^{vW}$  in the set  $H^{vW}$  differentiable in a chiral environment, eq 19 is used if  $V \neq W$ , *i.e.*, the reactant and product configurations have different geometries.<sup>16</sup>

(16) Equations 19-21 may be derived following procedures outlined in ref 5, 7, and 8. Equation 22 is derived in the Appendix.

$$D_{VW} = \frac{1}{|\overline{V^{VV}}||\overline{W^{WW}}|} \sum_{V^{VV}, \overline{W^{WW}}} (h^{V_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) \times (h^{W_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) \times \prod_{p=1}^{n_1} (i_p! p^{j_p}) \prod_{q=1}^{n_2} (k_q! q^{k_q}) \prod_{r=1}^{n_3} (l_r! r^{l_r}) \quad (19)$$

Here,  $D_{VW}$  is the number of reactions differentiable in a chiral environment, the summation extends over all generalized cyclic types of permutations in  $V^{VV}$  and  $W^{WW}$ , and  $h^{V_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}$  and  $h^{W_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}$  are the numbers of operations in  $V^{VV}$  and  $W^{WW}$ , respectively, having cyclic type  $(j_1, j_2, \dots, j_{n_1}; k_1, k_2, \dots, k_{n_2}; l_1, l_2, \dots, l_{n_3})$ .

If reactant and product configurations have the same geometry  $W$ , the number of reactions differentiable in a chiral environment is  $D'_{WW}$

$$D'_{WW} = D_{WW} - 1 \quad (20)$$

where  $D_{WW}$  is calculated using eq 19.

To count the number of reactions  $h_i^{VW} \in H^{VW}$  differentiable in a totally symmetric environment, eq 21 is

$$D_{\overline{V}\overline{W}} = \frac{1}{|\overline{V^{VV}}||\overline{W^{WW}}|} \sum_{\overline{V^{VV}}, \overline{W^{WW}}} (h^{\overline{V}_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) \times (h^{\overline{W}_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) \times \prod_{p=1}^{n_1} (j_p! p^{j_p}) \prod_{q=1}^{n_2} (k_q! p^{k_q}) \prod_{r=1}^{n_3} (l_r! r^{l_r}) \quad (21)$$

used if reactant and product configurations have different geometries. In eq 21,  $D_{\overline{V}\overline{W}}$  is the number of reactions differentiable in a totally symmetric environment, and all other symbols were defined above for eq 19. When reactant and product configurations have the same geometry  $W$ ,  $D_{\overline{W}\overline{W}}$  is given by eq 21 if  $\overline{W^{WW}} \neq W^{WW}$  and  $D'_{\overline{W}\overline{W}} = D'_{WW}$  if  $\overline{W^{WW}} = W^{WW}$ .

If reactant and product configurations have different geometries, eq 22 is used to count the number of diastereomeric reactions in the set  $H^{VW}$ . Here,  $D_{V'W'}$  is

$$D_{V'W'} = \frac{1}{|\overline{V^{VV}}||\overline{W^{WW}}| + |\overline{V^{VV}}||\overline{W^{WW}}|} \sum_{V^{VV}, \overline{W^{WW}}; \overline{V^{VV}}, \overline{W^{WW}}} \times \{ (h^{V_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) (h^{W_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) + (h^{V'_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) (h^{W'_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}) \} \times \left\{ \prod_{p=1}^{n_1} (j_p! p^{j_p}) \prod_{q=1}^{n_2} (k_q! q^{k_q}) \prod_{r=1}^{n_3} (l_r! r^{l_r}) \right\} \quad (22)$$

the number of diastereomeric reactions;  $|\overline{V^{VV}}|$  and  $|\overline{W^{WW}}|$  are the number of operations in  $\overline{V^{VV}}$  and  $\overline{W^{WW}}$ , respectively, which represent inversion of configuration; the summation extends over all generalized cyclic types of operations in  $\overline{V}$  and  $\overline{W}$  which represent rotation and/or inversion of configuration;  $h^{V_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}$  and  $h^{W_{j_1 j_2 \dots j_{n_1}, k_1 k_2 \dots k_{n_2}, l_1 l_2 \dots l_{n_3}}}$  are the numbers of operations in  $\overline{V}$  and  $\overline{W}$ , respectively, having cyclic type  $(j_1, j_2, \dots, j_{n_1}; k_1, k_2, \dots, k_{n_2}; l_1, l_2, \dots, l_{n_3})$  which represent inversion of configuration; and all other symbols were defined above for eq 19. When reactant and product configurations have the same geometry,  $D'_{W'W'} = D_{W'W'}$  - 1 is the number of diastereomeric reactions.

From the symmetry of eq 19, 21, and 22, it is clear that  $D_{WV} = D_{VW}$ ,  $D_{\overline{W}\overline{V}} = D_{\overline{V}\overline{W}}$ , and  $D_{V'W'} = D_{W'V'}$ .

**Table I.** Definitions Relating the Structural Stereochemistry of Configurations and the Dynamic Stereochemistry of Reactions

Configurations <sup>a,b</sup>	Reactions <sup>b,c</sup>
I. Equivalent	I. Nondifferentiable in a Chiral Environment
$\binom{l}{s}_i^W = w_h^{WW} \binom{l}{s}_j^W$	$h_p^{VW} = v_k^{VV} \cdot h_q^{VW} \cdot w_h^{WW}$
II. Nonequivalent	II. Differentiable in a Chiral Environment
$\binom{l}{s}_i^W \neq w_h^{WW} \binom{l}{s}_j^W$	$h_p^{VW} \neq v_k^{VV} \cdot h_q^{VW} \cdot w_h^{WW}$
A. Enantiomeric	A. Enantiomeric
$\binom{l}{s}_i^W = \bar{w}_n^{WW} \binom{l}{s}_j^W$	$h_p^{VW} = \bar{v}_m^{VV} \cdot h_q^{VW} \cdot \bar{w}_n^{WW}$
B. Diastereomeric	B. Diastereomeric
$\binom{l}{s}_i^W \neq \bar{w}_n^{WW} \binom{l}{s}_j^W$	$h_p^{VW} \neq \bar{v}_m^{VV} \cdot h_q^{VW} \cdot \bar{w}_n^{WW}$

<sup>a</sup>  $\binom{l}{s}_i^W$  and  $\binom{l}{s}_j^W$  are two configurations having the same geometry  $W$ . <sup>b</sup>  $w_h^{WW}$  and  $v_k^{VV}$  are elements in the proper configurational symmetry groups  $W^{WW}$  and  $V^{VV}$ , respectively.  $\bar{w}_n^{WW}$  and  $\bar{v}_m^{VV}$  are operation in the full configurational symmetry groups  $\overline{W^{WW}}$  and  $\overline{V^{VV}}$ , respectively, which represent inversion of configuration. <sup>c</sup>  $h_p^{VW}$  and  $h_q^{VW}$  are reactions in the set  $H^{VW}$ .

**C. Summary.** Table I summarizes the more important definitions provided in this section. The definitions relating the structural stereochemistry of configurations retain the physical significance of the words equivalent, nonequivalent, enantiomeric, and diastereomeric as conventionally used to describe the stereoisomeric relationships between molecules or groups in molecules.<sup>17</sup> Equivalent configurations are physically indistinguishable if molecules in the configuration are free to rotate and translate in space, while nonequivalent configurations are in theory distinguishable. Within a set of nonequivalent configurations, however, certain pairs of configurations are physically indistinguishable in an achiral environment. These configurations are called enantiomeric. Diastereomeric configurations are nonequivalent configurations which are in theory physically distinguishable in an achiral environment.

The definitions relating the dynamic stereochemistry of reactions are based on the same physical criteria, as shall be made clear in the next section. Reactions nondifferentiable in a chiral environment are precisely those reactions which are physically indistinguishable if reactant and product molecules are free to rotate and translate in space. Reactions differentiable in a chiral environment are in theory distinguishable by physical methods and may be described as representing different steric courses. Within a set of reactions differentiable in a chiral environment, certain pairs of reactions are physically indistinguishable in an achiral environment in that they must occur with equal probability. These reactions are called enantiomeric. Diastereomeric reactions are reactions differentiable in a chiral environment which are in theory physically distinguishable in an achiral environment.

## II. Discussion

In this section we shall examine the steric courses of some very simple exchange reactions in order to dem-

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

onstrate the physical significance of the definitions given above.

We consider first the exchange reactions interconverting configurations having the geometry shown in Figure 3a. Here, the ligands are labeled by  $L = \{A_1, A_2, A_3, B_4, B_5\}$  and the skeletal positions are indexed as shown in Figure 3b. The proper configurational symmetry group is  $W^{WW} = C_3^{WW} + R_3^{WW}$ ,<sup>18</sup> and the full configurational symmetry group is  $\bar{W}^{WW} = C_{3v}^{WW} + R_3^{WW}$ .<sup>18</sup> These groups are representations of the permutation groups  $W$  and  $\bar{W}$  defined by the following operations.

$$w_1 = \bar{w}_1 = (1)(2)(3)(4)(5)$$

$$w_2 = \bar{w}_2 = (123)(4)(5)$$

$$w_3 = \bar{w}_3 = (132)(4)(5)$$

$$\bar{w}_4 = (12)(3)(4)(5)$$

$$\bar{w}_5 = (13)(2)(4)(5)$$

$$\bar{w}_6 = (1)(23)(4)(5)$$

Operations  $w_1^{WW}$ ,  $w_2^{WW}$ , and  $w_3^{WW}$  represent rotation of configuration, while  $\bar{w}_4^{WW}$ ,  $\bar{w}_5^{WW}$ , and  $\bar{w}_6^{WW}$  represent inversion of configuration. The group of allowed permutations  $H = S_3 + S_2$  contains  $3! \cdot 2! = 12$  operations. Three of the 12 operations in  $H^{WW}$  represent rotation of configuration and the remaining nine operations represent exchange reactions and permutational isomerization reactions. The configuration count  $I_W$  equals  $3! \cdot 2! / 3 = 4$  (see eq 7). A complete set of four nonequivalent configurations is shown in Figure 1c. Note that a complete set of nonequivalent configurations is not uniquely defined, but represents an arbitrary choice of one configuration from each of the  $I_W$  sets of equivalent configurations.

The number of reactions differentiable in a chiral environment,  $D'_{WW}$ , equals  $D_{WW} - 1$  (see eq 20). To calculate  $D_{WW}$  using eq 19, we need the generalized cyclic types of operations in  $W^{WW}$ : for  $w_1^{WW}$ ,  $(j_1, j_2, j_3; k_1, k_2) = (3, 0, 0; 2, 0)$  and for  $w_2^{WW}$  and  $w_3^{WW}$ ,  $(j_1, j_2, j_3; k_1, k_2) = (0, 0, 1; 2, 0)$ . Therefore  $h_{300,20}^{WW} = 1$  and  $h_{001,20}^{WW} = 2$ . Substituting in eq 19

$$D_{WW} = \{1/(3 \cdot 3)\} \{1 \cdot 1 \cdot 3! \cdot 1^3 \cdot 2! \cdot 1^2 + 2 \cdot 2 \cdot 1! \cdot 3! \cdot 2! \cdot 1^2\} = 4$$

and therefore  $D'_{WW} = 3$ . Since we are only interested in exchange reactions, not permutational isomerization reactions, we calculate  $D'_{C_3C_3} = 1$ , the number of permutational isomerization reactions differentiable in a chiral environment<sup>7</sup> which interconvert the permutational isomers of the  $C_{3v}$  molecule in the configuration.  $H^{WW}$  therefore contains only  $D'_{WW} - D'_{C_3C_3} = 2$  exchange reactions differentiable in a chiral environment. Figure 3d shows a complete set of exchange reactions differentiable in a chiral environment. Note that a complete set of reactions differentiable in a chiral environment is not uniquely defined, but represents an arbitrary choice of one reaction from each set of reactions nondifferentiable in a chiral environment. The arrows drawn in Figure 3d connecting ligands in the reactant configurations do not represent mechanistic

(18)  $R_{3i}$  is the infinite point group consisting of all proper rotations, all reflections and inversion at a point.  $R_3$  is the subgroup of  $R_{3i}$ , which contains only proper rotations.

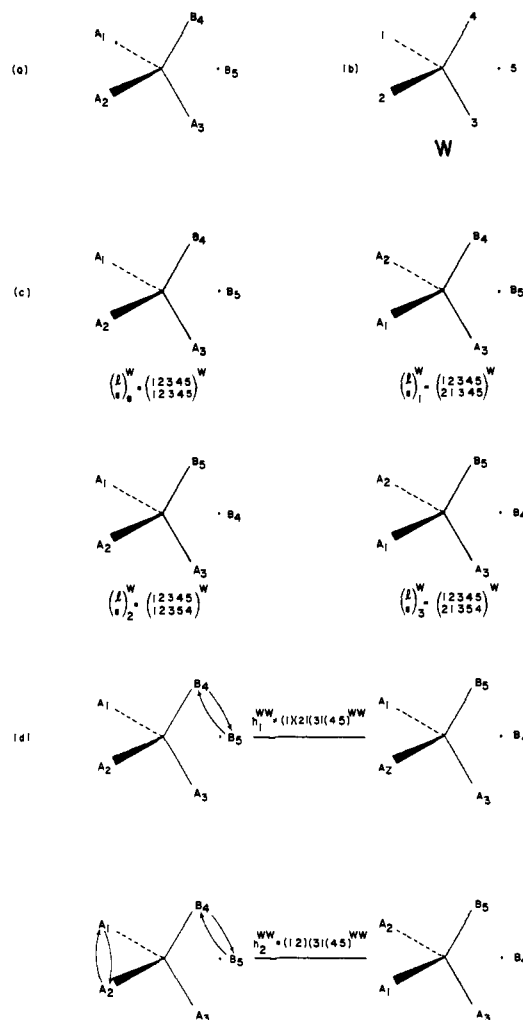


Figure 3. Configurations and reactions defining the stereochemistry of exchange reactions discussed in the text.

pathways but merely provide a convenient description of the stereochemical change involved. We see that  $h_1^{WW}$  implies "retention of configuration" while  $h_2^{WW}$  implies "inversion of configuration."

For completeness' sake, we note that both  $h_1^{WW}$  and  $h_2^{WW}$  are achiral since

$$\bar{w}_4^{WW} \cdot h_1^{WW} \cdot w_4^{WW} = h_1^{WW}$$

$$\bar{w}_4^{WW} \cdot h_2^{WW} \cdot w_4^{WW} = h_2^{WW}$$

Thus  $h_1^{WW}$  and  $h_2^{WW}$  are diastereomeric reactions and form a complete set of diastereomeric exchange reactions. We verify this by calculating the number of diastereomeric reactions in  $H^{WW}$ ,  $D'_{W'W'} = D_{W'W'} - 1$ , and calculating  $D'_{C_3C_3'} = D_{C_3C_3'} - 1$ , the number of diastereomeric permutational isomerization reactions in  $H^{WW}$ . Then  $D'_{W'W'} - D'_{C_3C_3'}$  must equal two. From eq 22,

$$D_{W'W'} = \{1/(3 \cdot 3 + 3 \cdot 3)\} \{(1 \cdot 1 + 0 \cdot 0) \cdot 3! \cdot 1^3 \cdot 2! \cdot 1^2 + (2 \cdot 2 + 0 \cdot 0) \cdot 1! \cdot 3! \cdot 2! \cdot 1^2 + (0 \cdot 0 + 3 \cdot 3) \cdot 1! \cdot 1! \cdot 1! \cdot 2! \cdot 1^2\} = 4$$

$$D_{C_3C_3'} = 2$$

and therefore

$$D_{W'W'} - D'_{C_3C_3'} = 3 - 1 = 2$$



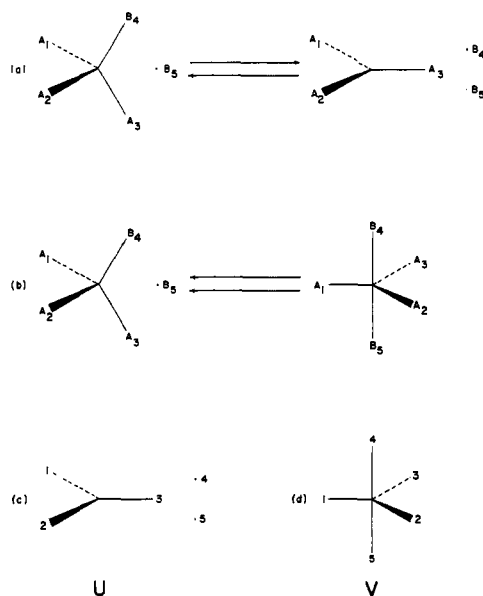


Figure 4. Association-dissociation reactions implying exchange reactions shown in Figure 3.

The number of reactions differentiable in a totally symmetric environment equals  $D_{\bar{w}\bar{w}}$  since  $|\bar{w}^{\text{WW}} \neq W^{\text{WW}}$ . From eq 21

$$D_{\bar{w}\bar{w}} = \{1/(6 \cdot 6)\} \{1 \cdot 1 \cdot 3! \cdot 1^3 \cdot 2! \cdot 1^2 + 2 \cdot 2 \cdot 1! \cdot 3^1 \cdot 2! \cdot 1^2 + 3 \cdot 3 \cdot 1! \cdot 1^1 \cdot 1! \cdot 2^1 \cdot 2! \cdot 1^2\} = 1/36\{12 + 24 + 36\} = 2$$

The number of permutational isomerization reactions differentiable in a totally symmetric environment,<sup>7</sup>  $D_{C_3, C_3, C_3}$ , is one. Hence,  $D_{\bar{w}\bar{w}} - D_{C_3, C_3, C_3} = 1$ , and all exchange reactions are nondifferentiable in a totally symmetric environment. The reactions  $h_1^{\text{WW}}$  and  $h_2^{\text{WW}}$  are since  $w_4^{\text{WW}} \cdot h_1^{\text{WW}} = h_2^{\text{WW}}$ . In general, reactions nondifferentiable in a totally symmetric environment are those which cannot be distinguished by physical techniques incapable of discerning enantiomeric molecules. Thus the steric course of two reactions nondifferentiable in a totally symmetric environment may be different, but this difference will not be measurable by certain physical techniques.

It is well known in carbon chemistry that "tetrahedral" exchange reactions of the type being discussed may proceed with "inversion" ( $h_2^{\text{WW}}$ ) or "racemization" (a combination of  $h_1^{\text{WW}}$  and  $h_2^{\text{WW}}$ ) depending on whether the mechanism is associative or dissociative. To show the formal relationship between association-dissociation reactions and exchange reactions, we will discuss these two possibilities in detail.

Consider first the sets of reactions  $H^{\text{UW}}$  and  $H^{\text{WU}}$  which interconvert configurations having geometries W and U shown in Figure 4a. Skeletal positions are indexed in Figures 3b and 4c.  $U^{\text{UU}} = D_3^{\text{UU}} + S_2 \cdot [R_3^{\text{UU}}]$  and therefore  $|U^{\text{UU}}| = |D_3^{\text{UU}}| \cdot 2! \cdot |R_3^{\text{UU}}|^2 = 6 \cdot 2 = 12$ . Also,  $I_U = |H^{\text{UU}}|/|U^{\text{UU}}| = 3! \cdot 2!/12 = 1$ . This implies that  $D^{\text{WU}} = D^{\text{UW}}$  must equal one and all reactions  $h_i^{\text{UW}} \in H^{\text{UW}}$  are nondifferentiable in a chiral environment. Discussion may therefore proceed in terms of the achiral dissociation reaction  $h_3^{\text{UW}} = (1)(2)(3)(4)(5)^{\text{UW}}$  and association reaction  $(h_3^{\text{UW}})^{-1} = (h_3^{-1})^{\text{WU}} = (1)(2)(3)(4)(5)^{\text{WU}}$  shown in Figure 4a. Of

interest here is the set of operations generated when the reaction  $h_3^{\text{UW}}$  is followed by the reaction  $h_3^{\text{WU}}$ . If the molecules in the configuration having geometry U are assumed to be free to rotate and translate in space, this set of operations is defined by  $h_3^{\text{WU}} U^{\text{UU}} h_3^{\text{UW}} = (h_3 U h_3)^{\text{WW}} = U^{\text{WW}}$ . The permutation group U, defined by the representation  $U^{\text{UU}}$ , contains these operations.

$$u_1 = (1)(2)(3)(4)(5)$$

$$u_2 = (123)(4)(5)$$

$$u_3 = (132)(4)(5)$$

$$u_4 = (1)(2)(3)(45)$$

$$u_5 = (123)(45)$$

$$u_6 = (132)(45)$$

$$u_7 = (12)(3)(45)$$

$$u_8 = (13)(2)(45)$$

$$u_9 = (1)(23)(45)$$

$$u_{10} = (12)(3)(4)(5)$$

$$u_{11} = (13)(2)(4)(5)$$

$$u_{12} = (1)(23)(4)(5)$$

We now examine the set of operations  $U^{\text{WW}}$ . This set contains operations in  $W^{\text{WW}}$  as well as reactions in  $H^{\text{WW}}$ . Three operations are identical with the three operations in  $W^{\text{WW}}$ :  $u_1^{\text{WW}} = w_1^{\text{WW}}$ ,  $u_2^{\text{WW}} = w_2^{\text{WW}}$ , and  $u_3^{\text{WW}} = w_3^{\text{WW}}$ . There are in addition three sets of operations, each set containing three reactions nondifferentiable in a chiral environment, namely:  $u_4^{\text{WW}}$ ,  $u_5^{\text{WW}}$ , and  $u_6^{\text{WW}}$ ;  $u_7^{\text{WW}}$ ,  $u_8^{\text{WW}}$ , and  $u_9^{\text{WW}}$ ;  $u_{10}^{\text{WW}}$ ,  $u_{11}^{\text{WW}}$ , and  $u_{12}^{\text{WW}}$ . Each of these sets may be represented by a reaction in  $H^{\text{WW}}$ , i.e.,  $u_4^{\text{WW}} = h_1^{\text{WW}}$ ,  $u_5^{\text{WW}} = h_2^{\text{WW}}$ , and  $u_{10}^{\text{WW}} \equiv h_4^{\text{WW}}$ . We thus partition  $U^{\text{WW}}$  into four sets, each containing three operations. This result is summarized in the relationship

$$\Psi^{\text{WW}}((h_3^{-1})^{\text{WU}}; h_3^{\text{UW}}) = 3e^{\text{WW}} + 3h_4^{\text{WW}} + 3h_1^{\text{WW}} + 3h_2^{\text{WW}} \quad (23)$$

Here  $\Psi^{\text{WW}}((h_3^{-1})^{\text{WU}}; h_3^{\text{UW}})$  represents the unique partition of  $(h_3^{-1})^{\text{WU}} U^{\text{UU}} h_3^{\text{UW}}$  into sets containing operations in  $W^{\text{WW}}$  or reactions in  $H^{\text{WW}}$  which are nondifferentiable in a chiral environment.

Let us consider the situation where the configurations having geometry U represent metastable reaction intermediates and the ligands occupying skeletal positions  $s_4^{\text{U}}$  and  $s_5^{\text{U}}$  are present in equal concentrations. Since the coefficients of the terms in  $\Psi^{\text{WW}}((h_3^{-1})^{\text{WU}}; h_3^{\text{UW}})$  are identical, each of the following possibilities will occur with equal probability every time dissociation is followed by association: (i) operations in  $W^{\text{WW}}$  (no net reaction), (ii) reactions nondifferentiable from  $h_4^{\text{WW}}$  in a chiral environment (permutational isomerization reactions), (iii) reactions nondifferentiable from  $h_2^{\text{WW}}$  in a chiral environment (exchange reactions with "retention of configuration"), (iv) reactions nondifferentiable from  $h_1^{\text{WW}}$  in a chiral environment (exchange reactions with "inversion of configuration"). If the ratios of the coefficients of the terms in  $\Psi^{\text{WW}}((h_3^{-1})^{\text{WU}}; h_3^{\text{UW}})$  do not represent the actual probabilities, i.e., do not have physical significance, we say that "memory effects" are present. Crudely, this means that a molecule remem-

bers its past history and because of this it is more likely to follow one reaction path than another. The most usual type of memory effect for dissociation–association reactions is incomplete dissociation. Here, the molecules in the configurations having geometry U are not free to rotate and translate in space and therefore the proper configurational symmetry group  $U^{UU}$  is not physically meaningful.

We now turn to the association–dissociation reactions of the type shown in Figure 4b. The skeletal positions of the configurations shown in Figure 4b are indexed as shown in Figures 3b and 4d. We examine only the operations implied by the achiral association reaction  $h_3^{vw} = (1)(2)(3)(4)(5)^{vw}$  followed by the reverse reaction  $(h_3^{-1})^{wv} = (1)(2)(3)(4)(5)^{wv} = h_3^{vw}$ , *i.e.*, the set of operations  $h_3^{wv}V^{vv}h_3^{vw} = V^{ww}$ . The permutation group  $V$ , defined by the representation  $V^{vv} = D_3^{vv}$ , contains these operations.

$$v_1 = (1)(2)(3)(4)(5)$$

$$v_2 = (123)(4)(5)$$

$$v_3 = (132)(4)(5)$$

$$v_4 = (1)(23)(45)$$

$$v_5 = (12)(3)(45)$$

$$v_6 = (13)(2)(45)$$

Following the procedure used above, we find

$$\bar{V}^{ww}((h_3^{-1})^{wv}; h_3^{vw}) = 3e^{ww} + 3h_2^{ww} \quad (24)$$

This means that if association is followed by dissociation as shown in Figure 4b, the only stereochemical change possible is that implied by  $h_2^{ww}$ , *i.e.*, “inversion of configuration.” Permutational isomerization and exchange with “retention of configuration” are ruled out.

A slightly more complicated example should clarify the physical significance of enantiomeric reactions. For configurations having the geometry shown in Figure 5a, the configurational symmetry group  $X^{xx} = C_1^{xx} + R_3^{xx}$  contains but one operation,  $x_1^{xx} = (1)(2)(3)(4)(5)^{xx}$  and  $\bar{X}^{xx} = C_s^{xx} + R_3^{xx}$  contains two operations,  $\bar{x}_1^{xx} = x_1^{xx}$  and  $\bar{x}_2^{xx} = (1)(2)(34)(5)^{xx}$ , if skeletal positions are indexed as in Figure 5b. The ligand set is labeled by  $L = \{A_1, B_2, C_3, C_4, C_5\}$  and therefore the group of allowed permutations  $H = S_1 + S_1 + S_3$  contains  $n_1!n_2!n_3! = 1! \cdot 1! \cdot 3! = 6$  operations. Since  $X^{xx}$  contains only one operation,  $I_X = |H^{xx}|/|X^{xx}| = 6$ .  $D'_{xx} = 5$ ,  $D'_{C_1C_1} = 1$ , and therefore  $H^{xx}$  contains only four exchange reactions differentiable in a chiral environment. A complete set of exchange reactions differentiable in a chiral environment is shown in Figure 5c. If we choose to view “tetrahedral” exchange reactions in terms of “inversion or retention of configuration,”  $h_1^{xx}$  and  $h_2^{xx}$  both represent “retention” while  $h_3^{xx}$  and  $h_4^{xx}$  both represent “inversion.” Reactions  $h_1^{xx}$  and  $h_2^{xx}$  as well as  $h_3^{xx}$  and  $h_4^{xx}$  nevertheless represent different changes in stereochemistry (steric courses) since ligands in skeletal positions  $s_3^x$  and  $s_4^x$  are enantiotopic and are therefore not equivalent in a chiral environment. Chiral catalysts or enzymes may provide a chiral environment which allows preferential substitution of one of the enantiotopic ligands.<sup>19</sup>

(19) Cf. K. Mislow and M. Raban, *Top. Stereochem.*, **4**, 127 (1969).

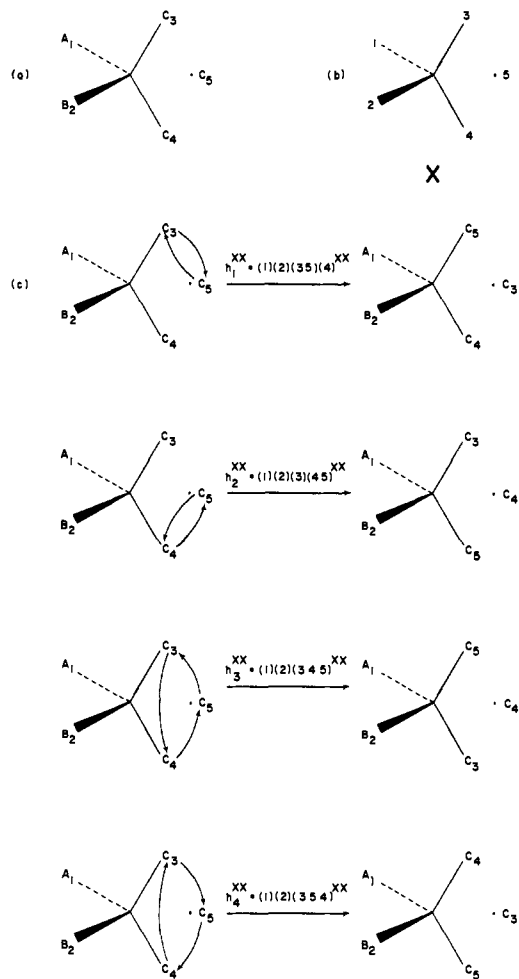


Figure 5. Configurations and reactions defining the stereochemistry of exchange reactions discussed in the text.

The operation  $\bar{x}_2^{xx}$  represents inversion of configuration and

$$h_2^{xx} = \bar{x}_2^{xx} \cdot h_1^{xx} \cdot \bar{x}_2^{xx} = (\bar{x}_2 \cdot h_1 \cdot \bar{x}_2)^{xx}$$

$$h_3^{xx} = \bar{x}_2^{xx} \cdot h_4^{xx} \cdot \bar{x}_2^{xx} = (\bar{x}_2 \cdot h_4 \cdot \bar{x}_2)^{xx}$$

Thus  $h_1^{xx}$  and  $h_2^{xx}$  as well as  $h_3^{xx}$  and  $h_4^{xx}$  are enantiomeric reactions. As was pointed out above, enantiomeric reactions have equal probabilities of occurring in an achiral environment and are physically indistinguishable. We see that in the case at hand, this fact is related to the enantiotopic relationship between ligands occupying positions  $s_3^x$  and  $s_4^x$ .

As in the previous example, we now examine the reactions implied by dissociation followed by association. Consider the configurations shown in Figure 6a. If skeletal positions are labeled as in Figures 5b and 6b, the groups  $X^{xx}$ ,  $\bar{X}^{xx}$ ,  $Y^{yy}$ , and  $\bar{Y}^{yy}$  are representations of the groups  $X$ ,  $\bar{X}$ ,  $Y$ , and  $\bar{Y}$  defined by the following operations.

$$x_1 = \bar{x}_1 = (1)(2)(3)(4)(5)$$

$$\bar{x}_2 = (1)(2)(34)(5)$$

$$y_1 = \bar{y}_1 = (1)(2)(3)(4)(5)$$

$$y_2 = \bar{y}_2 = (1)(2)(3)(45)$$

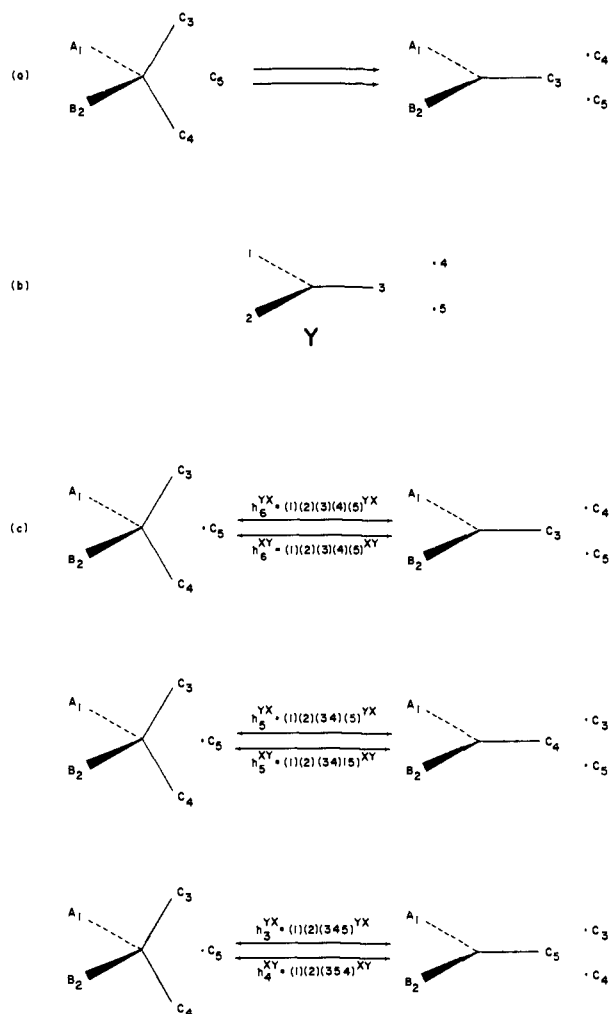


Figure 6. Dissociation-association reactions implying exchange reactions shown in Figure 5.

$x_1^{XX}$ ,  $y_1^{YY}$ , and  $y_2^{YY}$  represent rotation of configuration, while  $\bar{x}_2^{XX}$ ,  $\bar{y}_1^{YY}$ , and  $\bar{y}_2^{YY}$  represent inversion of configuration. Using eq 19

$$D_{XY} = D_{YX} = \{1/(1 \cdot 2)\} \{1 \cdot 1 \cdot 1! \cdot 1! \cdot 1! \cdot 1! \cdot 3! \cdot 1^3\} = 3$$

is the number of reactions differentiable in a chiral environment. Complete sets of reactions differentiable in a chiral environment are shown in Figure 6c. Using eq 22, we find  $D_{X'Y'} = D_{Y'X'} = 2$ . The reader may verify that  $h_6^{YX}$  and  $h_5^{YX}$  as well as  $h_6^{XY}$  and  $h_5^{XY}$  are enantiomeric reactions, while  $h_3^{YX}$  and  $h_4^{XY}$  are achiral. The fact that  $h_6^{YX}$  and  $h_5^{YX}$  are enantiomeric again reflects the enantiotopic relationship between ligands occupying positions  $s_3^X$  and  $s_4^X$ , while the fact that  $h_6^{XY}$  and  $h_5^{XY}$  are enantiomeric reflects the enantiotopic relationship between the two faces of the three-coordinate molecule in the configuration having geometry Y.<sup>19</sup>

Assuming that the reactions take place in an achiral environment, we examine the reactions implied by the dissociation reaction  $h_6^{YX}$  followed by the reverse reaction  $h_6^{XY}$ . Since  $h_6^{YX}$  and  $h_5^{YX}$  as well as  $h_6^{XY}$  and  $h_5^{XY}$  must occur with equal probability in an achiral environment, the set of operations  $(h_6 Y h_6)^{XX}$ ,  $(h_6 Y h_5)^{XX}$ ,  $(h_5 Y h_5)^{XX}$ , and  $(h_5 Y h_6)^{XX}$  is implied by dissociation

followed by association. These operations are

$$\begin{aligned} (h_6 \cdot y_1 \cdot h_6)^{XX} &= (1)(2)(3)(4)(5)^{XX} = x_1^{XX} \\ (h_6 \cdot y_2 \cdot h_6)^{XX} &= (1)(2)(3)(45)^{XX} = h_2^{XX} \\ (h_6 \cdot y_1 \cdot h_5)^{XX} &= (1)(2)(34)(5)^{XX} = h_5^{XX} \\ (h_6 \cdot y_2 \cdot h_5)^{XX} &= (1)(2)(354)^{XX} = h_4^{XX} \\ (h_5 \cdot y_1 \cdot h_5)^{XX} &= (1)(2)(3)(4)(5)^{XX} = x_1^{XX} \\ (h_5 \cdot y_2 \cdot h_5)^{XX} &= (1)(2)(35)(4)^{XX} = h_1^{XX} \\ (h_5 \cdot y_1 \cdot h_6)^{XX} &= (1)(2)(34)(5)^{XX} = h_5^{XX} \\ (h_5 \cdot y_2 \cdot h_6)^{XX} &= (1)(2)(345)^{XX} = h_3^{XX} \end{aligned}$$

and therefore

$$\Psi^{XX}((h_1^{-1})^{XY}; h_1^{YX}) = 2e^{WW} + 2h_5^{WW} + h_1^{WW} + h_2^{WW} + h_3^{WW} + h_4^{WW}$$

### III. Reaction Mechanism and Steric Course

A chemical reaction mechanism is usually defined in terms of a potential energy surface in multidimensional space which indicates the potential energy of every possible geometric arrangement of the atoms comprising the system in question. "Low regions" on this surface correspond to stable or metastable configurations, and the mechanistic pathways are defined by "paths" on this surface which interconnect the low regions. It is possible that these "paths" are "forked" and there exist "junctions" at which more than two paths meet. Instead of actually considering the relevant parts of the potential energy surface and defining reaction mechanisms in terms of "paths" and "junctions," it is more convenient from a stereochemical point of view to represent reaction mechanisms topologically by constructing a graph where points represent junctions, and lines represent the "paths" which interconnect them. These lines may be further subdivided by points which represent other configurations of interest.

Such topological representations<sup>20, 21</sup> may be described in terms of the formalisms developed above. Consider the topological representation of a simple system where each point represents equivalent configurations having geometry V, W, or X. These points are labeled by coset representatives from the sets  $C^V$ ,  $C^W$ , and  $C^X$ , and the total number of points thus equals  $I_V + I_W + I_X$ . Assume that lines connect points representing configurations having geometry V and W as well as points representing configurations having W and X, but no (single) lines connect points representing configurations having geometries V and X. Such a graph represents the case where reactant configurations, intermediate configurations, and product configurations have geometry V, W, and X, respectively. If only one mechanism interconverts reactant and intermediate configurations, and only one mechanism interconverts intermediate and product configurations, then two reactions,  $h_p^{VW}$  and  $h_q^{WX}$ , define the lines of the topological representation: points  $c_i^V$  and  $c_j^W$  are connected by a line if and only if

$$h_i^{VW} \cdot v_m^{VW} \cdot c_i^V = w_k^{WW} \cdot c_j^W \quad (25)$$

holds for some  $v_m^{VW} \in V^{VW}$ , some  $w_k^{WW} \in W^{WW}$ , and  $h_l^{VW} \in H^{VW}$  where  $h_l^{VW} = h_p^{VW}$  if  $h_p^{VW}$  is achiral and

(20) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(21) For a recent review, see: M. Gielen, *Ind. Chim. Belge*, **36**, 815 (1971).

$h_i^{WV} = h_p^{WV}$  or a "mirror image" of  $h_p^{WV}$  if  $h_p^{WV}$  is chiral. Points  $c_j^W$  and  $c_k^X$  are connected by a line if and only if

$$h_i^{XW} \cdot w_m^{WW} \cdot c_j^W = x_i^{XX} c_k^X \quad (26)$$

holds for some  $w_m^{WW} \in W^{WW}$ , some  $x_i^{XX} \in X^{XX}$ , and  $h_i^{XW} \in H^{XV}$  where  $h_i^{XW} = h_q^{XW}$  if  $h_q^{XW}$  is achiral and  $h_i^{XW} = h_q^{XW}$  or a "mirror image" of  $h_q^{XW}$  if  $h_q^{XW}$  is chiral.

As was shown in ref 6 for the case of permutational isomerization reactions, eq 25 and 26 define topological representations such that two reactions are represented topologically in an identical fashion if the following conditions exist. (a) The reactions are nondifferentiable in a chiral environment. Reactions nondifferentiable in a chiral environment must occur with equal probability if molecules rotate and translate freely in their environment. (b) One reaction and the reverse reaction of the other reaction are nondifferentiable in a chiral environment. If a given reaction occurs in an equilibrium situation, the principle of microscopic reversibility demands that its reverse reaction also occur. (c) Any "mirror image" of one reaction is nondifferentiable from the other reaction or its reverse reaction in a chiral environment. When reactions occur in an achiral environment, a reaction and its "mirror images" must occur with equal probability.

The connectivity  $\delta_V$  of a point  $c_i^V$  is defined as the total number of lines which meet at that point. The number of these (single) lines which connect different points representing configurations having geometry W to the point  $c_i^V$  is denoted  $\delta_{WV}$  and thus for the case under discussion,  $\delta_V = \delta_{WV}$ . For the connectivity  $\delta_W$ , however,  $\delta_W = \delta_{VW} + \delta_{XW}$ , since  $c_i^W$  is connected by single lines to points representing configurations having geometry V as well as points representing configurations having geometry X. Also,  $\delta_X = \delta_{WX}$ . Connectivities may be calculated using formulas derived elsewhere.<sup>8</sup> If  $h_p^{WV}$  is achiral

$$\delta_{WV} = \frac{|V|}{|V \cap h_p^{-1} W h_p|} \quad (27)$$

and if  $h_p^{WV}$  is chiral

$$\delta_{WV} = \frac{2|V|}{|V \cap h_p^{-1} W h_p|} \quad (28)$$

Here,  $|V|$  is the number of operations in the group  $V$  and  $|V \cap h_p^{-1} W h_p|$  is the number of operations which the groups  $V$  and  $h_p^{-1} W h_p$  have in common. Note that in general,  $\delta_{VW} \neq \delta_{WV}$ . If  $h_p^{WV}$  represents the transformation of configurations having geometry V into configurations having geometry W, then by microscopic reversibility,  $(h_p^{WV})^{-1} = (h_p^{-1})^{VW}$  represents the transformation of configurations having geometry W into configurations having geometry V. If  $(h_p^{-1})^{VW}$  is achiral

$$\delta_{VW} = \frac{|W|}{|W \cap h_p V h_p^{-1}|}$$

and comparing with eq 27,  $\delta_{VW}$  does not necessarily equal  $\delta_{WV}$ .

In eq 23 and 24 we provided means of expressing the steric course of exchange reactions which proceeded *via* intermediate configurations having connectivities

greater than two. If we wish to express the net stereochemical changes implied by the sequence  $h_p^{WV}$  followed by  $h_q^{XW}$  discussed above, we define

$$\Psi^{XV}(h_q^{XW}; h_p^{WV}) = \sum_{i=1}^{D_{XV}} a_i h_i^{XV} \quad (29)$$

Here,  $D_{XV}$  is the number of reactions in  $H^{XV}$  differentiable in a chiral environment, and  $a_i$  is the relative probability of reactions nondifferentiable from  $h_i^{XV}$  occurring if these reactions occur *via* intermediate configurations having geometry W. Note that if  $X = V$  as in eq 23 and 24,  $\Psi^{XX}(h_q^{XW}; h_p^{WX})$  includes an extra term  $a_0 e^{XX}$  which indicates the relative probability of no net reaction occurring each time the sequence  $h_p^{WX}$  followed by  $h_q^{XW}$  occurs. If "memory effects" are ruled out,  $\Psi^{XV}(h_q^{XW}; h_p^{WV})$  may be calculated as follows. (i) Assuming  $h_q^{XW}$  and  $h_p^{WV}$  are both achiral, the set of  $|W|$  reactions  $h_q^{XW} W^{WW} h_p^{WV} = (h_q W h_p)^{XV}$  is partitioned into subsets of reactions nondifferentiable in a chiral environment. Then  $a_i$  is the number of reactions in the subset containing reactions nondifferentiable from  $h_i^{XV}$  in a chiral environment. (ii) If  $h_q^{XW}$  is achiral but  $h_p^{WV}$  is chiral, the coefficients  $a_i$  are derived by partitioning the set of  $2|W|$  reactions in  $(h_q W h_p)^{XV}$  and  $(h_q W h_r)^{XV}$  where  $h_r^{WV}$  is a "mirror image" of  $h_p^{WV}$ . (iii) If  $h_p^{WV}$  is achiral, but  $h_q^{XW}$  is chiral and  $h_s^{XV}$  is a "mirror image" of  $h_q^{XW}$ , then the coefficients  $a_i$  are derived from the set of  $2|W|$  reactions in  $(h_q W h_p)^{XV}$  and  $(h_s W h_p)^{XV}$ . (iv) If both  $h_p^{WV}$  and  $h_q^{XW}$  are chiral,  $h_r^{WV}$  is a "mirror image" of  $h_p^{WV}$ , and  $h_s^{XV}$  is a "mirror image" of  $h_q^{XW}$ , then the coefficients  $a_i$  are derived from the set of  $4|W|$  reactions in  $(h_p W h_q)^{WV}$ ,  $(h_r W h_q)^{XV}$ ,  $(h_p W h_s)^{XV}$ , and  $(h_r W h_s)^{XV}$ .

To consider more complicated sequences of reactions, e.g.,  $h_i^{UV}$  followed by  $h_j^{VU}$ , ..., followed by  $h_k^{XW}$

$$\Psi^{XT}(h_k^{XW}; \dots, h_j^{VU}; h_i^{UV}) = \sum_{i=1}^{D_{XT}} a_i h_i^{XT}$$

may be derived in a similar fashion.

#### IV. Examples

**A. Trigonal-Bipyramidal Substitution.** This example concerns reactions of the type shown in Figure 7a, where reactant configurations have geometry V and product configurations have geometry X. Skeletal positions are indexed in Figure 7b and c. The proper configurational symmetry groups are defined by  $V^{VV} = C_2^{VV} + R_3^{VV}$  and  $X^{XX} = C_2^{XX} + R_3^{XX}$ , while  $\bar{V}^{VV} = C_{2v}^{VV} + R_3^{VV}$  and  $\bar{X}^{XX} = C_{2v}^{XX} + R_3^{XX}$ . The groups  $V$ ,  $\bar{V}$ ,  $X$ , and  $\bar{X}$  contain the following operations

$$v_1 = \bar{v}_1 = x_1 = \bar{x}_1 = (1)(2)(3)(4)(5)(6)$$

$$v_2 = \bar{v}_2 = x_2 = \bar{x}_2 = (14)(23)(5)(6)$$

$$\bar{v}_3 = \bar{x}_3 = (14)(2)(3)(5)(6)$$

$$\bar{v}_4 = \bar{x}_4 = (1)(23)(4)(5)(6)$$

The group of allowed permutations  $H = S_4 + S_1 + S_1$  contains  $4! \cdot 1! \cdot 1! = 24$  operations. Configuration counts  $I_V$  and  $I_X$  both equal  $24/2 = 12$ .

The number of reactions differentiable in a chiral environment,  $D_{XV}$ , is calculated using eq 19

$$D_{XV} = \{1/(2 \cdot 2)\} \{1 \cdot 1 \cdot 4! \cdot 1^4 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + 1 \cdot 1 \cdot 2! \cdot 2^2 \cdot 1! \cdot 1! \cdot 1^1\} = 8$$

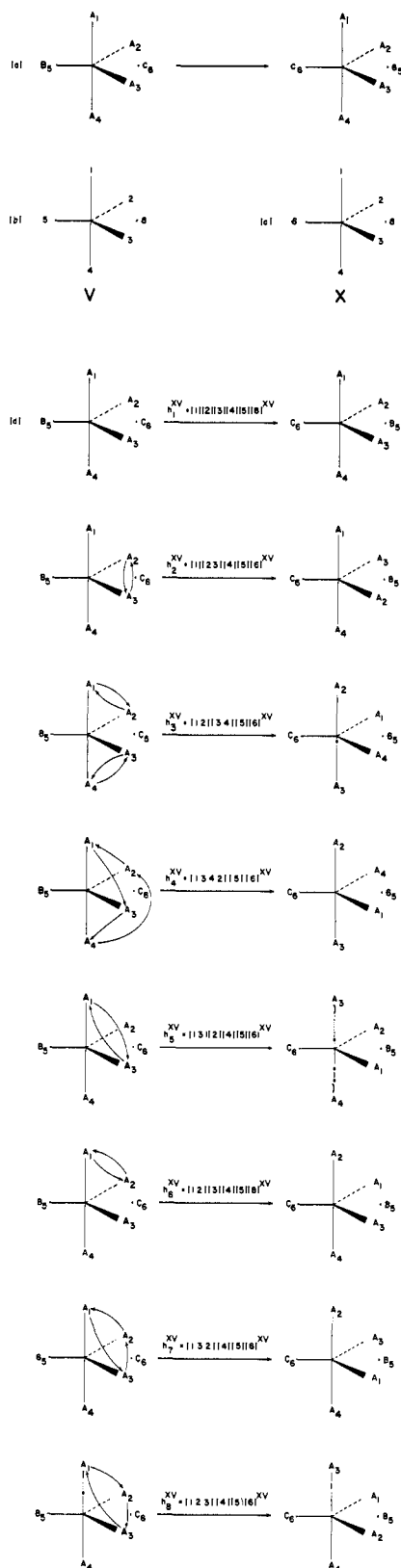


Figure 7. Configurations and reactions defining the stereochemistry of "trigonal bipyramidal" substitution reactants discussed in the text.

Eight appropriate reactions are most easily derived following a procedure justified elsewhere:<sup>8</sup> the set of 12 operations which convert  $(\text{trigonal bipyramidal})^V$  into the 12 non-equivalent configurations having geometry X must contain a complete set of reactions differentiable in a

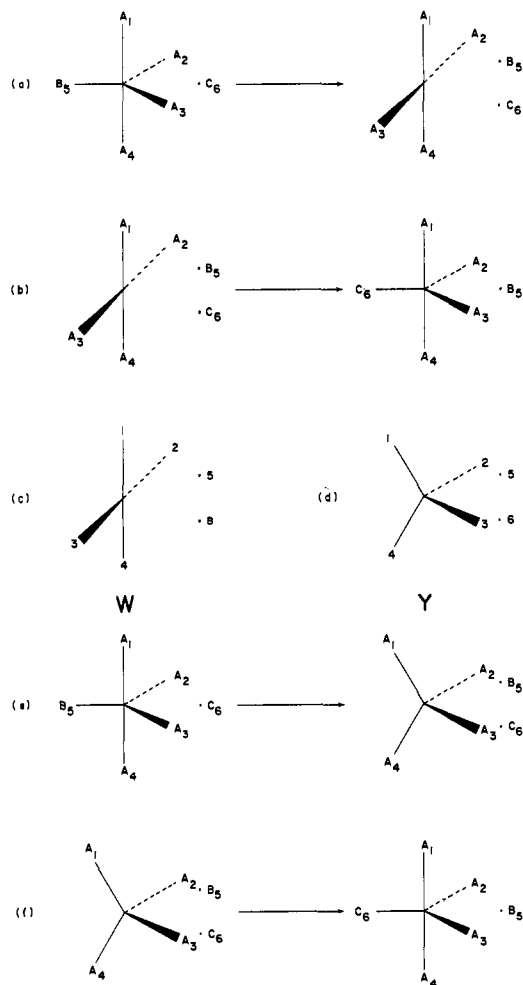


Figure 8. Dissociation and association reactions implying substitution reactions shown in Figure 7.

chiral environment. Eight differentiable reactions selected from this set of 12 reactions are shown in Figure 7d. The arrows drawn in the reactant configuration connecting the ligand labels crudely represent the permutation of ligands which each reaction implies. Since the reactant and product configurations have different geometries, these arrows are somewhat ill-defined from a mathematical and physical point of view, but they are very useful for quickly identifying the stereochemical relationships between various reactions. For example, they indicate the enantiomeric relationship between  $h_5^{XV}$  and  $h_6^{XV}$  as well as  $h_7^{XV}$  and  $h_8^{XV}$ , which is verified by the fact that

$$h_5^{XV} = \bar{x}_4^{XX} \cdot h_6^{XV} \cdot \bar{v}_4^{VV}$$

and

$$h_7^{XV} = \bar{x}_4^{XX} \cdot h_8^{XV} \cdot \bar{v}_4^{XV}$$

Using eq 22

$$D_{X'V'} =$$

$$\left\{ \frac{1}{2 \cdot 2 + 2 \cdot 2} \right\} \{ (1 \cdot 1 + 0 \cdot 0) \cdot 4! \cdot 1^4 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + (1 \cdot 1 + 0 \cdot 0) \cdot 2! \cdot 2 \cdot 2 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + (0 \cdot 0 + 2 \cdot 2) \cdot 1! \cdot 1^2 \cdot 1! \cdot 2 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 \} = 6$$

and therefore the reactions  $h_1^{XV}$ ,  $h_2^{XV}$ ,  $h_3^{XV}$ ,  $h_4^{XV}$ ,  $h_5^{XV}$ ,

and  $h_7^{XV}$  form a complete set of diastereomeric reactions.

We now examine the steric course of substitution reactions for two cases where intermediate configurations have a connectivity greater than two.

First, consider the sequence of reactions shown in Figure 8a and b. If the skeletal positions of the reactant, intermediate, and product configurations are indexed as shown in Figures 7b, 8c, and 7c, respectively, the dissociation reaction is described by  $h_1^{WV} = (1)(2)(3)(4)(5)(6)^{WV}$ , while  $h_1^{XW} = (1)(2)(3)(4)(5)(6)^{XW}$  describes the subsequent association reaction. The groups  $W^{WW} = D_4^{WW} + R_3^{WW} + R_3^{WW}$  and  $\bar{W}^{WW} = D_{4h}^{WW} + R_{3i}^{WW} + R_{3i}^{WW}$  are representations of the groups  $W$  and  $\bar{W}$  defined by the operations

$$w_1 = \bar{w}_1 = (1)(2)(3)(4)(5)(6)$$

$$w_2 = \bar{w}_2 = (1243)(5)(6)$$

$$w_3 = \bar{w}_3 = (1342)(5)(6)$$

$$w_4 = \bar{w}_4 = (14)(23)(5)(6)$$

$$w_5 = \bar{w}_5 = (1)(23)(4)(5)(6)$$

$$w_6 = \bar{w}_6 = (14)(2)(3)(5)(6)$$

$$w_7 = \bar{w}_7 = (12)(34)(5)(6)$$

$$w_8 = \bar{w}_8 = (13)(24)(5)(6)$$

Since  $|W^{WW}| = 8$ ,  $I_W = 24/8 = 3$ . Reactions  $h_1^{WV}$  and  $h_1^{XW}$  are achiral since  $h_1^{WV} = \bar{w}_5^{WW} \cdot h_1^{WV} \cdot \bar{v}_4^{VW}$  and  $h_1^{XW} = \bar{x}_4^{XW} \cdot h_1^{XW} \cdot \bar{w}_5^{WW}$ . From eq 27

$$\delta_{WV} = \frac{|V|}{|V \cap W|} = 2/2 = 1$$

$$\delta_{VW} = \frac{|W|}{|W \cap V|} = 8/2 = 4$$

$$\delta_{XW} = \frac{|W|}{|W \cap X|} = 8/2 = 4$$

$$\delta_{WX} = \frac{|X|}{|X \cap W|} = 2/2 = 1$$

and consequently,  $\delta_V = \delta_{WV} = 1$ ,  $\delta_W = \delta_{VW} + \delta_{XW} = 8$ , and  $\delta_X = \delta_{WX} = 1$ . These results may be checked using a relation derived elsewhere,<sup>8</sup>  $I_V \delta_{WV} = I_W \delta_{VW}$  and  $I_X \delta_{WX} = I_W \delta_{XW}$ . The isomer counts and connectivities just calculated are of great help in constructing a topological representation. We shall however determine the steric course of this reaction sequence using the techniques presented in the previous section. The substitution reactions implied by  $h_1^{WV}$  followed by  $h_1^{XW}$  are contained in the set of reactions  $h_1^{XW} \cdot W^{WW} \cdot h_1^{WV} = W^{XV}$ . Consulting Figure 7d, we note that  $w_1^{XV} = h_1^{XV}$ ,  $w_2^{XV} = h_4^{XV} \cdot v_2^{XV}$ ,  $w_3^{XV} = h_4^{XV}$ ,  $w_4^{XV} = h_1^{XV}$ ,  $v_2^{VW}$ ,  $w_5^{XV} = h_2^{XV}$ ,  $w_6^{XV} = h_2^{XV} \cdot v_2^{VW}$ ,  $w_7^{XV} = h_3^{XV}$ , and  $w_8^{XV} = h_3 \cdot v_2^{VW}$ , and therefore

$$\Psi^{XV}(h_c^{XW}; h_p^{WV}) = 2h_1^{XV} + 2h_2^{XV} + 2h_3^{XV} + 2h_4^{XV}$$

Note that the implicit assumption has been made that the reaction sequence is "irreversible," *i.e.*, dissociation always leads to substitution.

Now consider an alternative reaction sequence shown in Figure 8e and f. Here, the skeletal positions of reactant, intermediate, and product configurations are indexed as shown in Figures 7b, 8d, and 7c, respectively.

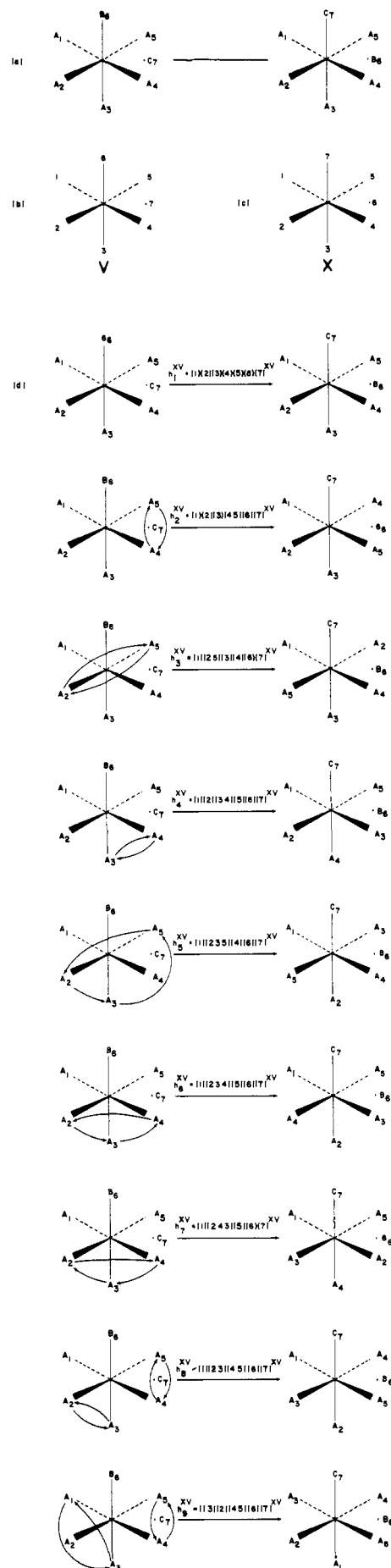


Figure 9. Configurations and reactions defining the stereochemistry of "octahedral" substitution reactions discussed in the text.

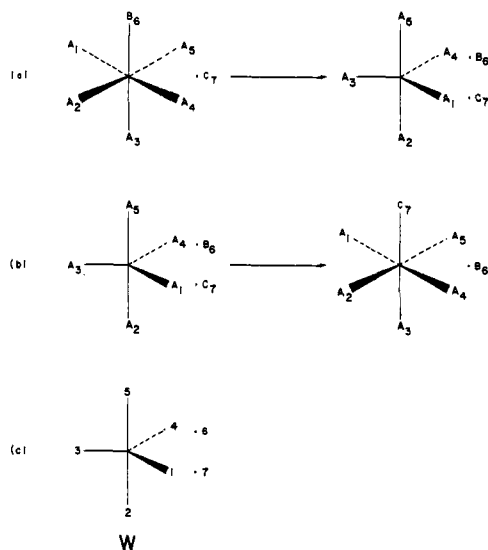


Figure 10. Dissociation and association reactions implying substitution reactions shown in Figure 9.

The dissociation reaction is described by  $h_1^{YV} = (1)(2)(3)(4)(5)(6)^{YV}$  and the subsequent association reaction by  $h_1^{XY} = (1)(2)(3)(4)(5)(6)^{XY}$ . The proper configurational symmetry group of the intermediate configuration is  $Y^{YY} = T^{YY} + R_3^{YY} + R_3^{YY}$ . Following the procedure used in treating the reaction sequence examined in the preceding paragraphs, the reader may verify that

$$\Psi^{XV}(h_1^{XY}; h_1^{YV}) = 2h_1^{XV} + 2h_3^{XV} + 4h_7^{XV} + 4h_8^{XV}$$

**B. Octahedral Substitution.** The type of "octahedral" substitution reactions considered here is shown in Figure 9a. Skeletal positions are labeled as in Figure 9b and c. The group of allowed permutations,  $H = S_3 + S_1 + S_1$ , contains  $5! \cdot 1! \cdot 1! = 120$  operations. The groups  $V^{VV} = C_4^{VV} + R_3^{VV}$ ,  $X^{XX} = C_4^{XX} + R_3^{XX}$ ,  $\bar{V}^{VV} = C_{4v}^{VV} + R_{3i}^{VV}$  and  $\bar{X}^{XX} = C_{4v}^{XX} + R_{3i}^{XX}$  are representations of the groups  $V$ ,  $X$ ,  $\bar{V}$ , and  $\bar{X}$  defined by

$$\begin{aligned} v_1 = \bar{v}_1 = x_1 = \bar{x}_1 &= (1)(2)(3)(4)(5)(6)(7) \\ v_2 = \bar{v}_2 = x_2 = \bar{x}_2 &= (1245)(3)(6)(7) \\ v_3 = \bar{v}_3 = x_3 = \bar{x}_3 &= (1542)(3)(6)(7) \\ v_4 = \bar{v}_4 = x_4 = \bar{x}_4 &= (14)(25)(3)(6)(7) \\ \bar{v}_5 = \bar{x}_5 &= (15)(24)(3)(6)(7) \\ \bar{v}_6 = \bar{x}_6 &= (12)(3)(45)(6)(7) \\ \bar{v}_7 = \bar{x}_7 &= (14)(2)(3)(5)(6)(7) \\ \bar{v}_8 = \bar{x}_8 &= (1)(25)(3)(4)(6)(7) \end{aligned}$$

Thus configuration counts  $I_V$  and  $I_X$  both equal  $120/4 = 30$ .

$D_{XV}$ , the number of reactions differentiable in a chiral environment, is calculated using eq 19

$$\begin{aligned} D_{XV} = \{1/(4 \cdot 4)\} \{ &1 \cdot 1 \cdot 5! \cdot 1^3 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + \\ &2 \cdot 2 \cdot 1! \cdot 4^1 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 \cdot 1^1 + \\ &1 \cdot 1 \cdot 2! \cdot 2^2 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 \cdot 1^1 \cdot 1^1 \} = 9 \end{aligned}$$

A complete set of reactions differentiable in a chiral environment may be derived using the procedure fol-

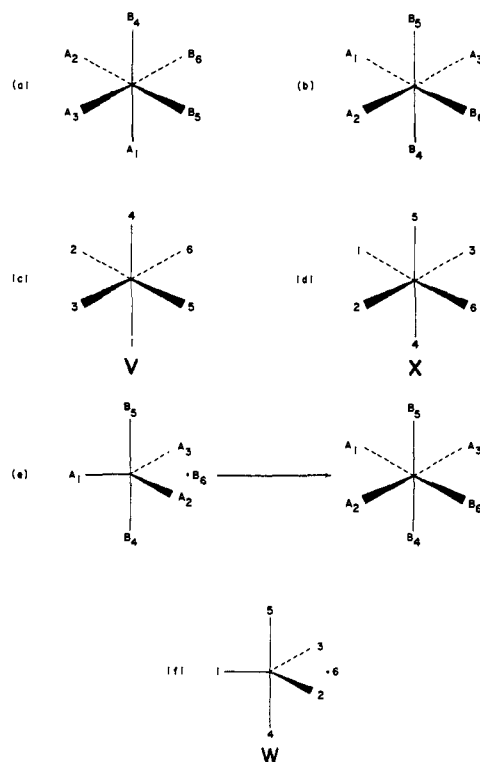


Figure 11. Configurations describing isomerization reactions of  $\text{IrH}_3(\text{PR}_3)_3$ .

lowed in the previous example. Such a set is shown in Figure 9d. The number of diastereomeric reactions,  $D_{X'V'}$ , is

$$\begin{aligned} D_{X'V'} = \{1/(4 \cdot 4) + 4 \cdot 4\} \{ &(1 \cdot 1 + 0 \cdot 0) \cdot \\ &5! \cdot 1^5 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + (2 \cdot 2 + 0 \cdot 0) \cdot 1! \cdot 4^1 \cdot 1! \cdot \\ &1^1 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 + (1 \cdot 1 + 2 \cdot 2) 2! \cdot 2^2 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 \cdot 1^1 \cdot \\ &1^1 + (0 \cdot 0 + 2 \cdot 2) 3! \cdot 1^3 1! \cdot 2^1 \cdot 1! \cdot 1^1 \cdot 1! \cdot 1^1 \} = 7 \end{aligned}$$

As the arrows drawn in Figure 9d suggest,  $h_6^{XV}$  and  $h_7^{XV}$  as well as  $h_8^{XV}$  and  $h_9^{XV}$  are enantiomeric. The seven reactions  $h_1^{XV}$ ,  $h_2^{XV}$ ,  $h_3^{XV}$ ,  $h_4^{XV}$ ,  $h_5^{XV}$ ,  $h_6^{XV}$ , and  $h_8^{XV}$  thus form a complete set of diastereomeric reactions.

We now determine the stereochemical implications of substitution which proceeds by dissociation as shown in Figure 10a followed by association as shown in Figure 10b. The skeletal positions are indexed as shown in Figures 9b, 10c, and 9c, and therefore  $h_p^{WV} = (1)(2)(3)(4)(5)(6)(7)^{WV}$  describes the dissociation reaction, while  $h_q^{XW} = (1)(2)(3)(4)(5)(6)(7)^{XW}$  describes the association reaction. The group  $W^{WW} = D_3^{WW} + R_3^{WW} + R_3^{WW}$  is a representation of the group  $W$  defined by the operations

$$\begin{aligned} w_1 &= (1)(2)(3)(4)(5)(6)(7) \\ w_2 &= (134)(2)(5)(6)(7) \\ w_3 &= (143)(2)(5)(6)(7) \\ w_4 &= (1)(25)(34)(6)(7) \\ w_5 &= (14)(3)(25)(6)(7) \\ w_6 &= (13)(4)(25)(6)(7) \end{aligned}$$

Both  $h_p^{WV}$  and  $h_q^{XW}$  are achiral, and the steric course of this reaction sequence is therefore derived from the set

of six reactions,  $h_q^{xw}W^{ww}h_p^{wv} = W^{xv}$ . Consulting Figure 9d, we note that  $w_1^{xv} = h_1^{xv}$ ,  $w_2^{xv} = x_3^{xx}$ ,  $h_3^{xv} \cdot v_2^{vv}$ ,  $w_3^{xv} = x_2^{xx} \cdot h_3^{xv} \cdot v_3^{vv}$ ,  $w_4^{xv} = x_3^{xx} \cdot h_5^{xv} \cdot v_3^{vv}$ ,  $w_5^{xv} = h_1^{xv} \cdot v_4^{vv}$ , and  $w_6^{xv} = x_2^{xx} \cdot h_3^{xv} \cdot v_2^{vv}$ . Consequently

$$\Psi^{xv}(h_q^{xw}, h_p^{wv}) = 2h_1^{xv} + 4h_5^{xv}$$

**C. Polytopal Isomerization of  $\text{IrH}_3(\text{PR}_3)_3$ .** Certain phosphino iridium hydrides of the type  $\text{IrH}_3(\text{PR}_3)_3$  exist in two polytopal forms, facial (see Figure 11a and meridial (see Figure 11b).<sup>22</sup> Upon heating in solution, the facial isomer rearranges to the meridial isomer, and Muetterties<sup>23</sup> has suggested that this process may proceed *via* five-coordinate intermediates,  $\text{IrH}_3(\text{PR}_3)_2$ . We shall examine the possibility of checking the validity of this mechanism using labeling techniques.

Hydride ligands are labeled  $A_1$ ,  $A_2$ , and  $A_3$  and phosphine ligands are labeled  $B_4$ ,  $B_5$ , and  $B_6$ . The skeletal positions are indexed in Figure 11c and d. Assuming that the isomers have  $C_{3v}$  and  $C_{2v}$  symmetry,  $V^{vv} = C_3^{vv}$  and  $X^{xx} = C_2^{xx}$ . The groups  $V$  and  $X$  contain the operations

$$v_1 = (1)(2)(3)(4)(5)(6)$$

$$v_2 = (123)(456)$$

$$v_3 = (132)(465)$$

$$x_1 = (1)(2)(3)(4)(5)(6)$$

$$x_2 = (1)(23)(45)(6)$$

The final step of Muetterties' proposed mechanism is shown in Figure 11e, and the skeletal positions of the postulated intermediate configuration are indexed in Figure 1. Thus  $W^{ww} = D_3^{ww} + R_3^{ww}$ , and  $W$  is defined by

$$w_1 = (1)(2)(3)(4)(5)(6)$$

$$w_2 = (123)(4)(5)(6)$$

$$w_3 = (132)(4)(5)(6)$$

$$w_4 = (1)(23)(45)(6)$$

$$w_5 = (13)(2)(45)(6)$$

$$w_6 = (12)(3)(45)(6)$$

Neglecting any further intermediate configurations, we examine the reactions in  $H^{ww}$  to ascertain the possible changes in stereochemistry which might accompany transformations of the reactant configurations into intermediate configurations having geometry  $W$ . Using eq 19 and 22

$$D_{wv} = \{1/(3 \cdot 6)\} \{1 \cdot 1 \cdot 3! \cdot 1^3 \cdot 3! \cdot 1^3\} = 2$$

$$D_{w'v'} = \{1/(3 \cdot 6 + 3 \cdot 6)\} \times \\ \{1 \cdot 1 + 0 \cdot 0\} 3! \cdot 1^3 \cdot 3! \cdot 1^3\} = 1$$

Thus regardless of the mechanistic pathway connecting the reactant and the postulated intermediate configurations, only two steric courses exist, and in an achiral environment they will be indistinguishable. Ligands will become completely "scrambled," and should the postulated intermediate exist, the net isomerization reaction will completely lack stereospecificity.

(22) J. Chatt, R. W. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

(23) E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

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## Appendix

In this section eq 22, which enumerates diastereomeric reactions, is derived. A similar result has been derived by Ruch, Hässelbarth, and Richter.<sup>24</sup> The derivation provided here is analogous to the proofs of theorems given in the Appendices of ref 5 and 7 which provide formulas which enumerate differentiable permutational isomerization reactions. Familiarity with these proofs should aid in understanding the present derivation. Although eq 22 is a general result, the following derivation does not allow for the case where all operations in  $\bar{V}^{vv}$  and  $\bar{W}^{ww}$  which represent inversion of configuration also represent rotation of configuration. In this case, two reactions are diastereomeric if and only if they are differentiable in a chiral environment, and the limitation is therefore of no consequence.

We shall assume that the group of allowed permutations is defined by

$$H \equiv \sum_{i=1}^l S_{n_i}$$

$l \leq 3$ , but the case for an arbitrary  $l > 3$  may be treated in the same fashion. Before proceeding with the derivation, we must express the relationship between diastereomeric reactions in a mathematically concise manner. If reactions in the set  $H^{vw}$  are to be enumerated,  $V$  and  $W$  are the permutation groups whose representations  $V^{vv}$  and  $W^{ww}$  are proper configurational symmetry groups. We define the sets  $V'$  and  $W'$  to be subsets of the groups  $\bar{V}$  and  $\bar{W}$ , respectively, such that  $v_i' \in V'$  and  $w_j' \in W'$  if and only if  $v_i'^{vv}$  and  $w_j'^{ww}$  represent inversion of configuration. Next, we define a permutation group  $\Pi'(\bar{V}, \bar{W})$ ,  $\Pi'(\bar{v}_i, \bar{w}_j) \in \Pi'(\bar{V}, \bar{W})$ , whose elements permute elements  $h_k^{vw}$  in  $H^{vw}$  according to

$$\Pi'(\bar{v}_i, \bar{w}_j)h_k \equiv \bar{v}_i \cdot h_k \cdot \bar{w}_j^{-1}$$

where  $\bar{v}_i \in \bar{V}$  and  $\bar{w}_j \in \bar{W}$  must either both be elements in  $V$  and  $W$ , respectively, or both be elements in  $V'$  and  $W'$ , respectively. Thus

$$|\Pi'(\bar{V}, \bar{W})| = |V||W| + |V'||W'| \quad (\text{A1})$$

The reader may verify that  $\Pi(\bar{V}, \bar{W})$  is a well defined group with a product operation defined by

$$\Pi'(\bar{v}_i, \bar{w}_j) \cdot \Pi'(\bar{v}_k, \bar{w}_l) = \Pi'(\bar{v}_i \cdot \bar{v}_k, \bar{w}_j \cdot \bar{w}_l)$$

The group  $\Pi'(\bar{V}, \bar{W})$  may be used to rigorously define diastereomeric reactions;  $h_k^{vw}$  and  $h_l^{vw}$  are diastereomeric reactions if and only if

$$\Pi'(\bar{v}_i, \bar{w}_j)h_k \neq h_l$$

for all  $\Pi'(\bar{v}_i, \bar{w}_j) \in \Pi'(\bar{V}, \bar{W})$ . The number of diastereomeric reactions,  $D_{V'W'}$ , is the number of equivalency classes generated in  $H$  if  $h_k, h_l \in H$  are equivalent when

$$\Pi'(\bar{v}_i, \bar{w}_j)h_k = h_l$$

for some  $\Pi'(\bar{v}_i, \bar{w}_j) \in \Pi'(\bar{V}, \bar{W})$ . The number  $D_{V'W'}$

(24) E. Ruch, W. Hässelbarth, and B. Richter, *Theor. Chim. Acta*, 19, 288 (1970); E. Ruch and W. Hässelbarth, private communication.



may be calculated using Burnside's Lemma<sup>25</sup>

$$D_{V'W'} = \frac{1}{|\Pi'(\bar{V}, \bar{W})|} \sum_{\Pi'(\bar{v}_i, \bar{w}_j) \in \Pi'(\bar{V}, \bar{W})} \chi(\bar{v}_i, \bar{w}_j) \quad (\text{A2})$$

where  $\chi(\bar{v}_i, \bar{w}_j)$  is the number of  $h_k$  in  $H$  which  $\Pi'(\bar{v}_i, \bar{w}_j)$  leaves fixed, *i.e.*, the number of  $h_k$  in  $H$  for which

$$h_k = \Pi'(\bar{v}_i, \bar{w}_j)h_k \equiv \bar{v}_i \cdot h_k \cdot \bar{w}_j^{-1}$$

or equivalently

$$v_i = h_k \cdot \bar{w}_j \cdot h_k^{-1}$$

Accordingly,  $\chi(\bar{v}_i, \bar{w}_j) = 0$  unless  $\bar{v}_i$  and  $\bar{w}_j$  have identical generalized cyclic type, and if  $\bar{v}_i$  and  $\bar{w}_j$  both have generalized cyclic type  $(i_1, j_2, \dots, j_{n_1}; k_1, k_2, \dots, k_{n_2}; l_1, l_2, \dots, l_{n_3})$ , then

$$\chi(\bar{v}_i, \bar{w}_j) = \prod_{p=1}^{n_1} (j_p! p^{j_p}) \prod_{q=1}^{n_2} (k_q! q^{k_q}) \prod_{r=1}^{n_3} (l_r! r^{l_r}) \quad (\text{A3})$$

(25) F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, p 181.

Since  $\chi(\bar{v}_i, \bar{w}_j)$  is dependent only on the generalized cyclic type of  $\bar{v}_i$  and  $\bar{w}_j$ , and  $\chi(\bar{v}_i, \bar{w}_j) \neq 0$  if and only if  $\bar{v}_i$  and  $\bar{w}_j$  have identical generalized cyclic type, the summation in eq A2 may be changed to one over the generalized cyclic types of the operations in  $V$ ,  $W$ ,  $V'$ , and  $W'$ . Let  $h^{V_{j_1 j_2 \dots j_{n_1} k_1 k_2 \dots k_{n_2} l_1 l_2 \dots l_{n_3}}}$ ,  $h^{V'_{j_1 j_2 \dots j_{n_1} k_1 k_2 \dots k_{n_2} l_1 l_2 \dots l_{n_3}}}$ ,  $h^{W_{j_1 j_2 \dots j_{n_1} k_1 k_2 \dots k_{n_2} l_1 l_2 \dots l_{n_3}}}$ , and  $h^{W'_{j_1 j_2 \dots j_{n_1} k_1 k_2 \dots k_{n_2} l_1 l_2 \dots l_{n_3}}}$  be the number of operations in  $V$ ,  $V'$ ,  $W$ , and  $W'$ , respectively, having generalized cyclic type  $(i_1, j_2, \dots, j_{n_1}; k_1, k_2, \dots, k_{n_2}; l_1, l_2, \dots, l_{n_3})$ . Then by substituting eq A1 and A3 into eq A2 and using the new summation extending over all generalized cyclic types of permutations in  $V$ ,  $W$ ,  $V'$ , and  $W'$ , we obtain eq 22.

During the course of this derivation we have assumed that all elements in  $H^{VW}$  represent reactions. For the case  $V = W$ , some elements in  $H^{VW}$  do not represent reactions but represent rotation of configuration, and therefore the number of diastereomeric reactions is  $D_{W'W'} - 1$ .

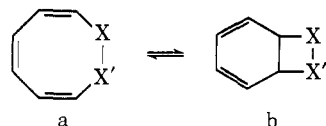
## Effects of Additional Ring Fusions and Binding to Metal Atoms upon the Cyclooctatriene–Bicyclooctadiene Equilibrium<sup>1</sup>

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**Abstract:** The hydrocarbons bicyclo[6.3.0]undeca-2,4,6-triene (**1**) and bicyclo[6.4.0]dodeca-2,4,6-triene (**3**) have been prepared by reaction of dithiocyclooctatetraene with 1,3-dibromopropane and 1,4-dibromobutane, respectively. **1** and **3** could not be isolated pure, but instead **1** was obtained mixed with its tautomer tricyclo[6.3.0.0<sup>2,7</sup>]undeca-3,5-diene (**2**) and **3** was obtained mixed with its tautomer tricyclo[6.4.0.0<sup>2,7</sup>]dodeca-3,5-diene (**4**). The kinetics and equilibrium of the **1** → **2** conversion have been studied. The rate constant at 20° (extrapolated from measurements at 34 and 58°) is  $1.6 \times 10^{-5} \text{ sec}^{-1}$ . Assuming a frequency factor of  $10^{13}$  the Arrhenius activation energy is  $24 \pm 1 \text{ kcal/mol}$ . At 58° the equilibrium constant,  $K = [\mathbf{2}]/[\mathbf{1}]$ , is  $\sim 33$ . The equilibrium molar ratio **3**:**4** at 114° is approximately unity. From pmr spectra and other considerations the probable molecular structures and ring conformations are deduced. The systems **1**–**2** and **3**–**4** react with  $\text{Fe}_2(\text{CO})_9$  and  $\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$  to form a variety of crystalline derivatives, all of which have been characterized as to gross structure (*i.e.*, connexity of bonds but not conformational details) by ir and pmr spectra. These derivatives, which will be suitable for X-ray crystallographic studies of structural details, are the following: (2) $\text{Fe}(\text{CO})_3$ , (2) $_2\text{Mo}(\text{CO})_2$ , (1) $\text{Mo}(\text{CO})_3$ , (4) $\text{Fe}(\text{CO})_3$ , (4) $_2\text{Mo}(\text{CO})_2$ , (3) $\text{Fe}_2(\text{CO})_6$ , (3) $\text{Mo}(\text{CO})_3$ . Yields of the various derivatives run parallel to the intrinsic relative stabilities of the tautomers in each of the pairs, **1**–**2** and **3**–**4**.

It was nearly 20 years ago that Cope and coworkers<sup>4</sup> first studied an equilibrium of the type



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(4) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4876 (1952).

for the case where  $X = X' = \text{CH}_2$ , *i.e.*, for cyclooctatriene and its tautomer bicyclooctadiene. They reported that the equilibrium ratio  $a/b$  is  $\sim 6$  at 80–100°. More recently, Huisgen and coworkers<sup>5</sup> reinvestigated this system (for which they found a ratio of  $\sim 8$  at 60°) and 11 others with a variety of  $X$  and  $X'$  groups. Variations in  $X$  and  $X'$  were found to influence the ratio greatly, changing it over a range of  $\sim 10^4$ . Huisgen and coworkers considered several factors which might be expected to influence the position of equilibrium, but concluded that no entirely satisfactory explanation for the observed facts could be found within the framework of their considerations.

(5) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtel, *Tetrahedron Lett.*, 5215 (1968).