

# The Steric Courses of Chemical Reactions. 3. Computer Generation of Product Distributions, Steric Courses, and Permutational Isomers<sup>1</sup>

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**Abstract:** A rapid and generalized computer-assisted approach to the solution of complex problems in dynamic stereochemistry is described. Specifically, the generation of product distributions, steric courses, and permutational isomers is demonstrated by solving a variety of stereochemical problems involving symmetric molecules.

Dynamic stereochemistry has become an increasingly abstract discipline in recent years, relying heavily on topological, algebraic, and combinatorial concepts.<sup>1,3-8</sup> Although these formalisms have made possible the interpretation of complex experimental data, several less desirable features have also emerged. First of all, the abstract mathematical formalisms have tended to obscure fundamentally simple chemical concepts. The ability to approach complex problems in dynamic stereochemistry has therefore become dependent on an ability to grasp relatively complex mathematical formalisms. A second, equally serious situation has also resulted. Certain stereochemical problems are more amenable to abstract analysis than others, and the trend has been to analyze those of mathematical as opposed to chemical interest. For example, networks of reactions interconverting partially labeled, asymmetric molecules and networks of reactions interconverting completely labeled, symmetric molecules have been analyzed in detail.<sup>6,3c</sup> The chemically more realistic case of reactions interconverting partially labeled, symmetric molecules, however, has been largely ignored because of its mathematical complexity.

This paper represents an approach to the resolution of the above-mentioned difficulties by solving complex problems in dynamic stereochemistry with the aid of a computer. A user of the computer program need only understand the nature of his problem and the significance of its solution, not details of the computational procedures employed by the computer to obtain the solution. The computer, ideally suited to a "brute force" approach, can rapidly solve mathematically awkward problems not amenable to a more elegant approach. The main body of this paper is divided into three parts, dealing successively with species whose lifetime is increasingly short relative to the observational time scale. First, the generation of product distributions is discussed. Reaction products are assumed to be long lived on the observational time scale and thus subject to complete characterization. The following section treats the generation of steric courses of reactions interconverting symmetric molecules. Although these results have significance on any time scale, they are most useful for the interpretation of spectroscopic studies, dynamic nuclear magnetic resonance studies in particular. Reactions which occur very rapidly on the observational time scale are examined in the final section. Here, the identities of the individual species which undergo interconversion have merged, and one proceeds via the traditional methods of isomer enumeration. Molecular symmetry, however, must be generalized as to include the rapid dynamic processes.

Before discussing specific computer-assisted solutions to the

types of problems just mentioned, the mathematical procedures employed will be briefly reviewed.

**Background.** In the first two parts of this series,<sup>1</sup> group theoretical formalisms were derived which exhaustively generate the steric courses and product distributions of simple or multistep reactions interconverting symmetric molecules. These formalisms, however, can be applied directly to only the simplest problems involving small molecules. Consequently, combinatorial formulas were presented which allow the number of solutions to a given problem to be counted, without actually generating the solutions. With these formulas, non-trivial systems containing up to six or seven sites can be analyzed. Larger systems remain unapproachable owing to the difficulty of generating solutions when large numbers of reactions must be produced. In order to expand the domain of chemical systems which may be subjected to dynamic stereochemical analysis, the formalisms presented in parts 1 and 2 have been incorporated into a computer program<sup>9</sup> which allows systems containing up to 11 sites to be analyzed.

Four classes of problems discussed in the following sections may be treated using this computer-assisted approach. The most fundamental problem in dynamic stereochemistry, the generation of steric courses, is handled by a STRCRS statement which uses double coset formalisms<sup>1</sup> to generate differentiable reactions,<sup>1</sup> diastereomeric reactions,<sup>1</sup> enantiomeric reactions,<sup>1</sup> and NMR differentiable reactions<sup>2d</sup> interconverting symmetric molecules. If multistep reactions involving symmetric intermediate configurations are to be treated, a MULSTP statement is employed which embodies the formalisms used earlier<sup>1</sup> to generate the steric courses of processes such as dissociative or associative substitution reactions. The remaining two classes of problems treated below involve the structural implications of dynamic processes. A PRODIS statement is used to generate the isomeric configurations (product distribution) implied by a given set of reaction sequences.<sup>1</sup> In contrast to parts 1 and 2, however, product molecules need not be totally labeled. The methodology for treating partially labeled molecules is derived from Ruch, Hasselbarth, and Richter's<sup>5a</sup> double coset formalisms. This methodology is also incorporated into the ISOCNT statement which generates isomeric configurations for partially labeled molecules which have point group symmetry and/or symmetry implied by rapid dynamic processes.

The reader is assumed to be familiar with the double coset formalisms<sup>1,5a</sup> which are employed throughout this paper. Each section which follows below opens with the treatment of a specific problem in dynamic stereochemistry, and a description of the general procedure for solving analogous

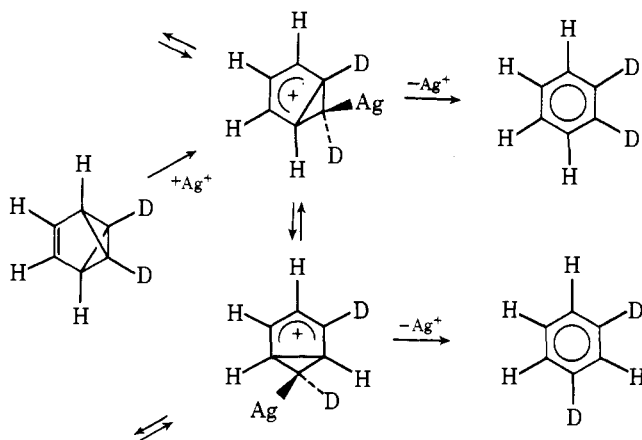
problems follows. For detailed discussion of the algorithms and data structures used to compute solutions, the reader is referred to the Appendix.<sup>9</sup>

**Generation of Product Distributions.** When dideuterio-benzvalene **1** is treated with  $\text{AgBF}_4$  in toluene solution, rapid



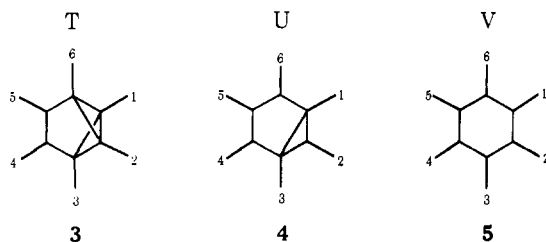
conversion to dideuteriobenzenes follows.<sup>10</sup> An interesting aspect of this reaction is its nonstatistical product distribution: 60% ortho, 30% meta, and 10% para. This distribution is consistent with the mechanism shown in Scheme I if rearrange-

Scheme I



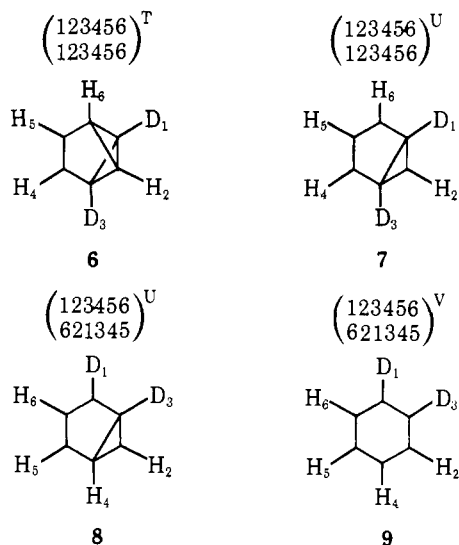
ment of the intermediate is about three times as rapid as decomposition of the intermediate into product.<sup>10</sup> To enforce the validity of this mechanism, one can envision the synthesis of an alternative dideuterio-benzvalene, **2**, and subsequent analysis of the  $\text{Ag}^+$  reaction products. The product distribution found may then be compared with the theoretical distribution implied by the mechanism shown in Scheme I. Generation of this product distribution is a very tedious problem owing to the difficulty of obtaining product distributions as a function of the number of intermediate rearrangements allowed. We shall address this problem here.

In order to present the problem to a computer, labeled configurations and reactions interconverting them must be represented in a nonpictorial fashion. Configurations are represented in terms of nuclear labels and labels of the sites which the nuclei occupy. By assigning a letter to each of the configurational skeletons and numbers to the nuclear sites on each skeleton, as in **3**, **4**, and **5**, each nuclear site is uniquely



defined by a number and a letter. Each nucleus is assigned the same label as the site it occupies in the reactant. For the case at hand, reactant **2** and site labeling **3** imply the labeled nuclei  $\text{D}_1$ ,  $\text{H}_2$ ,  $\text{D}_3$ ,  $\text{H}_4$ ,  $\text{H}_5$ , and  $\text{H}_6$ . Labeled configurations are represented by assigning each ligand label to a site label. The assignment is expressed by an  $\left(\begin{smallmatrix} j \\ i \end{smallmatrix}\right)$  matrix.<sup>11</sup> This matrix has two

rows, the top row always listing the nuclear labels in ascending order. Below each nuclear label is placed the label of the site which that nucleus occupies. An alphabetical superscript identifies the geometry of the configuration. Four examples of  $\left(\begin{smallmatrix} j \\ i \end{smallmatrix}\right)$  matrices are shown in **6**, **7**, **8**, and **9**, using the nuclear and site labels defined above.



Having provided a nonpictorial representation of labeled configurations, we turn to the representation of reactions which interconvert these configurations. Reactions are represented by superscripted permutation operations,<sup>1</sup> where the permutation operation acts on the site labels listed in the bottom row of the reactant  $\left(\begin{smallmatrix} j \\ i \end{smallmatrix}\right)$  matrix, converting it into the bottom row of the product  $\left(\begin{smallmatrix} j \\ i \end{smallmatrix}\right)$  matrix. The superscript consists of two letters, the first designating the geometry of the product configuration and the second designating the geometry of the reactant configuration. For example, the reaction of **6** to **7** is represented by  $(1)(2)(3)(4)(5)(6)^{\text{UT}}$ , **7** to **8** by  $(16543)(2)^{\text{UU}}$ , and **8** to **9** by  $(1)(2)(3)(4)(5)(6)^{\text{VU}}$ .<sup>12</sup> Note that these three reactions are implied by the mechanism shown in Scheme I.

Finally, configurational symmetry must be represented. If different  $\left(\begin{smallmatrix} j \\ i \end{smallmatrix}\right)$  matrices represent equivalent species, i.e., species which are physically indistinguishable, these equivalences must be represented by symmetry operations. Two types of symmetry may occur: configurational site symmetry and nuclear symmetry. The former occurs when a configuration has rotational point group symmetry, and the symmetry operations are represented by superscripted permutation operations as was done above for reactions. For example, the twofold rotational symmetry of benzvalene is represented by  $(12)(36)(45)^{\text{TT}}$ , using the site labeling defined in **3**. Nuclear symmetry arises when physically indistinguishable nuclei are assigned different labels. Any permutation which permutes the labels of identical nuclei is thus a nuclear symmetry operation. Here, the  $4! = 24$  permutations of the four hydrogen nuclei  $\text{H}_2$ ,  $\text{H}_4$ ,  $\text{H}_5$ , and  $\text{H}_6$  form the group  $S_4$  which acts on the labels 2, 4, 5, and 6. Similarly, the  $2! = 2$  permutations of the deuterium nuclei  $\text{D}_1$  and  $\text{D}_3$  form the group  $S_2$  which acts on the labels 1 and 3. Combining all possible permutations of the hydrogen and deuterium nuclei, the nuclear symmetry group  $S_2 + S_4$ , acting on the labels 1, 3, 2, 4, 5, and 6, is formed. This group contains  $2! \times 4! = 48$  operations.

Having appropriate representations of the relevant configurations, reactions, and symmetry groups, we can now turn to the problem at hand, namely, generation of the product distribution obtained when **2** is converted to dideuteriobenzenes via the mechanism shown in Scheme I assuming a given number of rearrangements of the intermediate. The computer first generates all the possible product configurations, then determines their symmetry equivalences, and finally prints out

(a) T=GROUP (1)(2)(3)(4)(5)(6), (1 2)(3 6)(4 5)  
 B=SET (1 3 4 5 6)(2), (1)(2)(3)(4)(5)(6)  
 A=SET (1 6 5 4 3)(2), (1 3 4 5 6)(2)  
 H=EXPAND A, A, A, A, B, T  
 V=GROUP (1)(2)(3)(4)(5)(6), (1 2 3 4 5 6), (1 3 5)(2 4 6),  
 (1 4)(2 5)(3 6), (1 5 3)(2 6 4), (1 6 5 4 3 2), (1)(2 6)(3 5)(4),  
 (1 3)(2)(4 6)(5), (1 5)(2 4)(3)(6), (1 2)(3 6)(4 5), (1 4)(2 3)(5 6),  
 (1 6)(2 5)(3 4)  
 L=S2+S4  
 RECODE L, 1, 3, 2, 4, 5, 6  
 PRODIS V, H, L

(b) ALL ISOMERIC PRODUCT CONFIGURATIONS ARE LISTED HERE. ENANTIOMERIC CONFIGURATIONS ARE SEPARATED BY SINGLE SPACES. DIASTEREOMERIC CONFIGURATIONS ARE SEPARATED BY DOUBLE SPACES. CONFIGURATIONS ARE PRECEDED BY INTEGERS WHICH INDICATE THE RELATIVE ABUNDANCE OF EACH PRODUCT ISOMER FOR THE REACTION SEQUENCE GIVEN.

22C1=1 2 3 4 5 6  
 37C2=2 3 1 6 5 4  
 5C3=2 6 5 4 3 1

**Figure 1.** Computer input (a) and output (b) for the generation of a product distribution of dideuterobenzenes from labeled benzvalene, assuming four rearrangements of the intermediate shown in Scheme I.

each isometric configuration together with a coefficient indicating the total number of product configurations equivalent to it. Computer input and output are shown in Figure 1.

The first part of the input instructs the computer to generate all possible product configurations by generating the permutations in  $H^{VT}$  which contains all possible net reactions  $h_i^{VT}$  implied by Scheme I, allowing for four rearrangements of the intermediate. These reaction steps and symmetry operations are defined above. First, the reactant **2** may rotate in space. The group **T** represents this rotation. Next, the reactant configuration is converted to the intermediate via one of the two reactions  $(13456)^{UT}$  and  $(1)(2)(3)(4)(5)(6)^{UT}$  in the set **B**. Both reactions are necessary since they are enantiomeric,<sup>1</sup> and even though they represent different steric courses, they must occur with equal probability in an achiral environment. Next, the intermediate rearranges four times via reactions represented by set **A**. Here again, two reactions must be indicated since they are enantiomeric. The conversion of the intermediate to product is represented by the achiral reaction  $(1)(2)(3)(4)(5)(6)^{VU}$ . Using these sets of symmetry operations and reactions, the set of net reactions  $H^{VT}$  is generated by the statement "H = EXPAND A, A, A, A, B, T". Note that the final step in the reaction sequence is omitted from the EXPAND statement because it is represented by the identity permutation and has no effect when reaction superscripts are ignored. The symmetry equivalences between product configurations are defined by the proper configurational symmetry group<sup>1</sup>  $V^{VV}$ , a representation of the rotational point group  $D_6$ , whose permutations are obtained using the site labeling **5**. Nuclear symmetry is defined by the nuclear symmetry group  $L$  as described above. Symmetry equivalent product configurations are determined and counted by the statement "PRODIS V, H, L" which also generates the output shown in Figure 1b.

In the output, each isomeric product configuration  $C_i$  is represented by the bottom row of its  $\binom{6}{j}$  matrix. Thus the  $j$ th number in the array indicates the site occupied by the  $j$ th nucleus. From the nuclear and site labeling defined above, the reader may verify that *o*-, *m*-, and *p*-dideuterobenzenes are represented by C2, C1, and C3, respectively. The coefficient of each  $C_i$  indicates its relative abundance, i.e., the number of product configurations equivalent to  $C_i$ .

Product distributions as a function of the number of intermediate rearrangements may be obtained by altering the definition of  $H$  in the input. If  $n$  rearrangements are desired, **A** is repeated sequentially  $n$  times in the EXPAND statement defining  $H$ . For the case of an infinite number of rearrangements (random rearrangement), the set **A** is used as the generator of a group and this group is used to represent intermediate rearrangements when defining  $H$ . Specifically, the

**Table I.** Product Distributions for the Conversion of Dideuteriobenzvalene into Dideuterobenzenes According to Scheme I

No. of rearrangements	Reactant 2			Reactant 1		
	% <i>o</i>	% <i>m</i>	% <i>p</i>	% <i>o</i>	% <i>m</i>	% <i>p</i>
0	50	50	0	100	0	0
1	63	25	13	50	50	0
2	56	38	6	50	25	25
3	63	25	13	38	50	13
4	58	34	8	44	31	25
5	62	27	12	38	47	16
6	59	33	9	43	34	23
7	61	28	11	38	45	17
8	59	32	9	41	36	22
Random	60	30	10	40	40	20

EXPAND statement in Figure 1a is replaced by the following two statements:

C = GEN A  
 H = EXPAND C, B, T

Table I displays the results of obtaining product distributions as a function of the number of intermediate rearrangements, assuming reactant **2**.

Consider now the case of reactant **1**. The site labels defined above may be retained intact, as may the representations of reactions and the proper configurational symmetry groups. Nuclear labels, however, must be redefined, since each nucleus is assigned the label of the site it occupies in the reactant. From **1** and **3** one obtains the labeled nuclei  $D_1, D_2, H_3, H_4, H_5$ , and  $H_6$ . This new nuclear labeling implies the nuclear symmetry group  $S_2 + S_4$  acting on the labels 1, 2, 3, 4, 5, 6. As a result, if the computer input in Figure 1a is altered by omitting the RECODE statement, product distributions for the reactant **1** may be obtained as was done for reactant **2** above. Results are shown in Table I.

For an arbitrary sequence of reactions involving partially labeled, symmetric species, the general procedure to be followed for the generation of product distributions is:

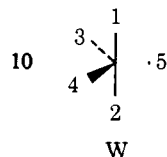
1. Label all relevant nuclear sites.
2. Label the relevant nuclei according to the sites they occupy in the reactant.
3. Express each reaction step in the reaction sequence as a permutation operation.
4. Express rotational symmetry groups as permutation groups, i.e., determine the proper configurational symmetry groups.
5. Generate all possible net reactions using an EXPAND statement, where reactions and proper configurational symmetry operations are listed in proper sequence.
6. Determine the nuclear symmetry group.
7. If enantiomeric product configurations are possible, express an improper symmetry element of the product configurations as a permutation operation.
8. Read into the computer the statement "PRODIS V, H, L, VPRIME", where  $V$  is the group of permutations in the proper configurational symmetry group of the product configurations, the set  $H$  is defined by the EXPAND statement in step 5,  $L$  is the nuclear symmetry group, and VPRIME is the permutation representing improper symmetry in the product configurations as defined in step 7. If step 7 is omitted, then VPRIME is omitted from the PRODIS statement.

**Generation of Steric Courses.** Two types of problems will be treated here, one dealing with the generation of a complete set of differentiable reactions<sup>13</sup> interconverting symmetric species, the other dealing with the generation of differentiable net re-

actions implied by a given sequence of reactions interconverting various symmetric species.

When traces of hydrogen fluoride are present, sulfur tetrafluoride undergoes rapid intermolecular fluorine exchange which averages the environments of all the fluorine nuclei.<sup>16</sup> Since the mechanism and steric course of this process are unknown, we shall first be concerned with the following questions: how many steric courses exist for fluorine exchange involving the impurity, which ones are enantiomeric or equivalent by microscopic reversibility, and which may be differentiated by a dynamic nuclear magnetic resonance (DNMR) experiment?

Site labeling is defined in **10**, where the axial SF<sub>4</sub> sites are



labeled 1 and 2, the equatorial sites are labeled 3 and 4, and the impurity fluorine nucleus occupies site 5. This labeling scheme forms the basis of the computer input shown in Figure 2a. First, the group of allowed reactions,  $H^{WW}$ , is defined. Here  $H = S_5$ , the permutation group which represents all possible 5! exchange reactions. Next, the proper configurational symmetry group  $W^{WW}$  is read in. The permutation group  $W$  represents all proper rotations of SF<sub>4</sub>. In order to determine NMR differentiable reactions, the effective NMR symmetry group,<sup>3e</sup>  $\hat{W}^{WW}$ , contains all permutations which leave the fluorine chemical shifts and coupling constants fixed. An improper configurational symmetry operation  $w'^{WW}$ , representing inversion of the configuration, is needed to determine enantiomeric reactions. The permutation  $w'$  used represents the reflection operation which exchanges the equatorial fluorines in SF<sub>4</sub>. To assist the interpretation of DNMR results, a permutation  $q$  is read in which exchanges all equatorial and axial fluorines. This operation will allow one to predict if a given reaction will imply symmetric or unsymmetric DNMR spectra.<sup>16</sup> The final STRCRS statement generates the output shown in Figure 2b. The integer 4 appearing in this statement defines intramolecular reactions as those which involve exchange of nuclei among sites one through four only.

In the computer output, the complete set of NMR differentiable reactions is listed in the left column. If two reactions are equivalent by microscopic reversibility, they are paired together between the long dashed lines. Intramolecular and intermolecular exchanges are identified by INTRA and INTER, respectively. A star appearing between the left and central columns indicates that the exchange processes between the long dashed lines may imply symmetric DNMR spectra.<sup>16</sup> A complete set of differentiable reactions is displayed in the central and right columns. Between the long dashed lines are listed those reactions which are NMR nondifferentiable from the reaction(s) listed in the left column. Within each group of reactions displayed between the short dashed lines, enantiomeric reactions are listed on the same line and reactions equivalent by microscopic reversibility are listed in the same column. If the reverse reaction and the enantiomer of a given reaction are nondifferentiable, the reaction and its enantiomer are listed on the same line and two stars appear on the far right.

To generate steric courses and NMR differentiable reactions for the general case where configurations having geometry X are converted into configurations having geometry Y, the following procedure must be followed.

1. Label the nuclear sites in reactant and product configurations.
2. Read into the computer the permutation representations

(a)

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H=55
W=GROUP (1) (2) (3) (4) (5), (1 2) (3 4) (5)
WCARET=GROUP (1) (2) (3) (4) (5), (1 2) (3) (4) (5), (1) (2) (3) (4) (5), (1 2) (3) (4) (5)
WPRIME=SET (1) (2) (3) (4) (5)
Q=SET (1 3) (2 4) (5)
STRCRS WCARET, W, H, W, WCARET, WPRIME, WPRIME, 4, Q
  
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(b)

ALL NMR DIFFERENTIABLE REACTIONS IN LEFT COLUMN; REACTIONS AND REVERSE REACTIONS ARE PAIRED TOGETHER.

ALL DIFFERENTIABLE REACTIONS IN CENTRAL AND RIGHT COLUMNS: THOSE WHICH ARE NMR NONDIFFERENTIABLE ARE COLLECTED BETWEEN LONG DASHED LINES. BETWEEN SHORT DASHED LINES, REACTIONS ARE ARRANGED AS FOLLOWS:

REACTION	(ENANTIOMER)	(ENANTIOMER OF REVERSE REACTION)
(REVERSE REACTION)		
INTRA H1=(1) (2) (3) (4) (5)	*	H1=(1) (2) (3) (4) (5) H2=(1) (2) (3) (4) (5)
INTER H2=(1) (2) (3) (4) (5)		H3=(1) (2) (3) (4) (5) H4=(1) (2) (3) (4) (5)
INTRA H3=(1) (2) (3) (4) (5)	*	H5=(1) (2) (3) (4) (5) H7=(1) (2) (3) (4) (5)
INTER H4=(1) (2) (3) (4) (5)		H6=(1) (2) (4) (3) (5) H8=(1) (2) (4) (3) (5) **
INTRA H5=(1) (2) (3) (4) (5) H6=(1) (2) (5) (4) (3)	*	H9=(1) (2) (3) (4) (5) H10=(1) (2) (4) (3) (5) H11=(1) (2) (3) (5) (4) H12=(1) (2) (4) (5) (3) **
INTER H7=(1) (2) (5) (3) (4)		H13=(1) (2) (3) (4) (5) H14=(1) (2) (5) (4) (3) H15=(1) (2) (4) (3) (5) H16=(1) (2) (5) (3) (4) H17=(1) (2) (3) (5) (4) H18=(1) (2) (5) (3) (4) H19=(1) (2) (4) (5) (3) H20=(1) (2) (5) (4) (3)
INTER H9=(1) (2) (3) (4) (5) H10=(1) (2) (5) (4)	*	H21=(1) (2) (5) (3) (4) H22=(1) (2) (5) (3) (4) H23=(1) (3) (2) (4) (5) H24=(1) (3) (2) (4) (5)
INTER H11=(1) (2) (3) (4) (5) H12=(1) (2) (5) (4)	*	H25=(1) (3) (2) (4) (5) H26=(1) (3) (2) (5) (4) H27=(1) (3) (2) (4) (5) H28=(1) (3) (2) (5) (4)
INTER H13=(1) (2) (3) (4) (5) H14=(1) (2) (5) (4) (3)	*	H29=(1) (3) (2) (5) (4) H30=(1) (3) (4) (2) (5) H31=(1) (3) (2) (5) (4) H32=(1) (3) (4) (2) (5) **

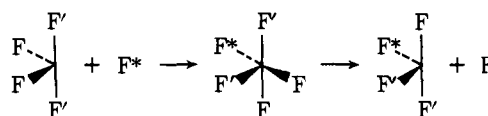
Figure 2. Computer input (a) and output (b) for the generation of a complete set of NMR differentiable and differentiable reactions implied by impurity fluoride exchange with sulfur tetrafluoride.

of the group of allowed permutations  $H^{YX}$ , the proper rotational symmetry groups  $X^{XX}$  and  $Y^{YY}$ , the effective NMR symmetry groups  $\hat{X}^{XX}$  and  $\hat{Y}^{YY}$ , and the improper symmetry operations  $x'^{XX}$  and  $y'^{YY}$ .

3. Finally, read into the computer the statement "STRCRS YCARET, Y, H, X, XCARET, YPRIME, XPRIME".

Output will always appear in the format shown in Figure 2b, but the symbols which identify intramolecular reactions and those which imply symmetric DNMR spectra will not appear unless specifically requested as in Figure 2a. Also, reactions and reverse reactions will not be paired together unless reactant and product configurations have the same geometry, i.e.,  $X = Y$ , and enantiomeric reactions will not be defined unless both reactant and product configurations have improper symmetry. If reactant or product configurations have no improper symmetry, the permutations XPRIME and YPRIME are omitted from the input.

When a chemical transformation occurs via one or more symmetric intermediate configurations, it may be necessary to represent the net steric course of the transformation by a combination of several differentiable reactions. Consider, for example, the fluorine exchange mechanism for sulfur tetrafluoride plus a fluoride impurity shown in Scheme II.<sup>3e</sup> Owing



to the symmetry of the  $C_{4v}$  intermediate, some of the net reactions implied by association followed by dissociation may

(a) A=SET (1)(2)(4)(3)(5),(1,4)(2)(3)(5)  
 X=GROUP (1)(2)(3)(4)(5),(1,3,2,5)(4),(1,2)(3,5)(4),(1,5,2,3)(4)  
 H=EXPAND A,X,A  
 W=GROUP (1)(2)(3)(4)(5),(1,2)(3,4)(5)  
 WCARET=GROUP (1)(2)(3)(4)(5),(1,2)(3)(4)(5),(1,2)(3,4)(5),(1,2)(3,4)(5)  
 WPRIME=SET (1)(2)(3)(4)(5)  
 MULSTP WCARET,W,H,W,WCARET,WPRIME,WPRIME

(b) EACH SET OF NMR NONDIFFERENTIABLE REACTIONS IS REPRESENTED BY A REACTION IN THE LEFT COLUMN. REACTIONS AND REVERSE REACTIONS ARE PAIRED TOGETHER. EACH REACTION IS PRECEDED BY AN INTEGER WHICH INDICATES HOW MANY OF THE (NET) REACTIONS ARE NMR NONDIFFERENTIABLE FROM THAT REACTION. NOTE THAT THE REACTION GIVEN NEED NOT BE ONE OF THE NET REACTIONS: IT MUST, HOWEVER, BE NMR NONDIFFERENTIABLE FROM ONE OR MORE OF THE NET REACTIONS IMPLIED BY THE REACTION SEQUENCE.

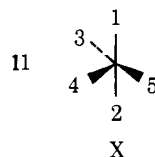
ALL DIFFERENTIABLE REACTIONS ARE IN CENTRAL AND RIGHT COLUMNS: THOSE WHICH ARE NMR NONDIFFERENTIABLE ARE COLLECTED BETWEEN LONG DASHED LINES. BETWEEN SHORT DASHED LINES, REACTIONS ARE ARRANGED AS FOLLOWS:

REACTION (REVERSE REACTION)	(ENANTIOMER OF REVERSE REACTION)
IF, FOR A GIVEN REACTION, ITS ENANTIOMER AND REVERSE REACTION ARE NONDIFFERENTIABLE, THE REACTION AND ENANTIOMER ARE WRITTEN ON THE SAME LINE AND TWO ASTERISKS APPEAR ON THE FAR RIGHT. THE INTEGER PRECEDING EACH REACTION INDICATES HOW MANY NET REACTIONS ARE NONDIFFERENTIABLE FROM THAT REACTION. HERE, THE REACTIONS LISTED MUST BE ONE OF THE NET REACTIONS IMPLIED BY THE REACTION SEQUENCE.	
2H1=(1)(2)(3)(4)(5)	2H1=(1)(2)(3)(4)(5)
2H2=(1)(2,3,4,5)	1H2=(1)(2,3,4,5)
2H3=(1)(2,5,4,3)	1H3=(1)(2,5,4,3)
4H4=(1)(2)(3)(4,5)	1H4=(1,3,4,5)(2) 1H5=(1,5,4,3)(2)
2H5=(1)(2)(3)(4,5)	1H6=(1)(2,4)(3,5) 1H7=(1,4)(2)(3,5) 1H8=(1,2,3)(4,5) 1H9=(1,3,2)(4,5) **
2H6=(1)(2,3)(4)(5)	1H10=(1,2)(3,5)(4) 1H11=(1,2,4)(3)(5) 1H12=(1,4,2)(3)(5) **
2H7=(1)(2,5)(3)(4)	2H13=(1,2,5)(3,4)

Figure 3. Computer input (a) and output (b) for the generation of net fluorine exchange reactions of sulfur tetrafluoride implied by the mechanism shown in Scheme II.

be differentiable reactions. This in turn means that DNMR line shape simulations based on this mechanism may need to be generated by a linear combination of reactions listed in the left column of Figure 2b. One is therefore interested in generating the differentiable net reactions and NMR differentiable net reactions implied by the reaction sequence shown in Scheme II.

First, sites in all relevant configurations must be labeled. Sites in the reactant and product configurations are labeled in **10** and sites in the intermediate configuration are labeled in **11**. Next, as was done when generating product distributions



above, a set of reactions  $H^{WW}$  must be generated which contains all the net reactions implied by the reaction sequence of Scheme II. This procedure is shown at the top of Figure 3a. The set A represents the two enantiomeric reactions (1)(24)(35)<sup>XW</sup> and (14)(2)(35)<sup>XW</sup> which convert reactant into intermediate. The possible rotations of the intermediate are represented by the proper configurational symmetry group  $X^{XX}$ . The conversion of intermediate into product is also represented by the set A, assuming microscopic reversibility. The set of net reactions  $H^{WW}$  is then generated by an EXPAND statement. In order to divide this set of net reactions into sets of differentiable reactions and NMR differentiable reactions, the proper configurational symmetry group  $W^{WW}$ , the effective NMR symmetry group  $\hat{W}^{WW}$ , and an improper configurational symmetry operation  $w^{WW}$  must be read into the computer as was done above in Figure 2a. Finally, output is generated by the MULSTP statement.

The left column of Figure 3b lists a set of NMR differentiable net reactions where each net reaction is preceded by a coefficient. The coefficient of  $H_i$  indicates the relative probability of a reaction occurring which is NMR nondifferentiable from  $H_i^{WW}$ . Note that each of the  $H_i$ 's listed in the left column of Figure 3b also appears in the left column of Figure 2b, and that reactions and reverse reactions are paired together. The central and right columns of Figure 3b are arranged in the

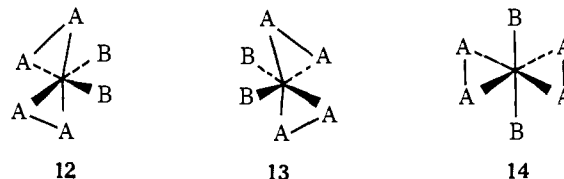
same fashion as Figure 2b. Here, however, the reactions listed are reactions in  $H^{WW}$  implied by Scheme II, and the coefficient of each  $H_i$  is the relative probability of a reaction occurring which is nondifferentiable from  $H_i$ .

For the general case of generating differentiable reactions implied by a multistep reaction sequence interconverting symmetric species, the following procedure is to be followed when reactant and product have geometries U and V, respectively:

1. Label all relevant nuclear sites.
2. Express each allowed reaction step as a permutation operation.
3. Express the rotational symmetry groups of all the intermediate configurations as permutations groups.
4. Read into the computer the expressions defined in steps 2 and 3, and follow these definitions with an EXPAND statement which defines  $H^{VU}$ , the collection of all net reactions.
5. For the reactant and product configurations, read in permutation representations of the proper configurational symmetry groups  $U^{UU}$  and  $V^{VV}$ , effective NMR symmetry groups  $\hat{U}^{UU}$  and  $\hat{V}^{VV}$ , and improper symmetry operations  $u^{UU}$  and  $v^{VV}$ . If reactant or product do not have improper symmetry, the improper symmetry operations are of course not defined.
6. Finally, read in the statement "MULSTP VCARET, V, H, U, UCARET, VPRIME, UPRIME".

Only if reactant and product configurations have the same geometry, i.e.,  $U = V$ , will reactions and reverse reactions be paired together in the output as in Figure 3b.

**Generation of Permutational Isomers.** The permutational isomerization mechanisms of six-coordinate bisbidentate chelate complexes  $M(A-A)_2B_2$  have been investigated by several workers in recent years.<sup>17</sup> Of particular interest has been the question of whether the chiral cis complexes **12** and **13** undergo permutational isomerization via the trans intermediate **14**. Since DNMR line shape analyses have failed to



yield definitive mechanistic information, we wish to show how an alternative approach may provide insight into the problem at hand. This approach involves comparing the number of permutational isomers of the rigid cis complex with the number of permutational isomers of the nonrigid cis complex, assuming that the nonrigidity arises via cis-trans isomerization. Since many of the complexes in this class may be observed as rigid molecules in the NMR low-temperature limit and as nonrigid molecules in the high-temperature limit, the predicted number of permutational isomers can be compared with the observed number.

Consider the partially labeled complex *cis*- $M(A-A')_2B_2$  where the chelate ligands are now unsymmetric because of labeling. We are interested first in determining the permutational isomers of the rigid complex. Although one can generate these isomers easily without the use of a computer, we shall take this opportunity to demonstrate the use of the program which generates permutational isomers. Sites in the two enantiomeric cis configurations are labeled in **15** and **16**. Note



(a) V=GROUP (1)(2)(3)(4)(5)(6), (1 3)(2 4)(5 6),  
 L=GROUP (1)(2)(3)(4)(5)(6), (1 3)(2 4)(5)(6), (1)(2 4)(3)(5)(6),  
 (1)(2)(3)(4)(5 6), (1 3)(2 4)(5)(6), (1 3)(2)(4)(5 6),  
 (1)(2 4)(3)(5 6), (1 3)(2 4)(5 6),  
 H=GROUP (1)(2)(3)(4)(5)(6), (1 2)(3)(4)(5)(6), (1)(2)(3 4)(5)(6),  
 (1)(2)(3 4)(5 6), (1 2)(3 4)(5)(6), (1 2)(3)(4)(5 6),  
 (1)(2)(3 4)(5 6), (1 2)(3 4)(5)(6), (1 3)(2 4)(5)(6), (1 4)(2 3)(5)(6),  
 (1 4 2 3)(5)(6), (1 3 2 4)(5)(6), (1 3)(2 4)(5)(6), (1 4)(2 3)(5)(6),  
 (1 4 2 3)(5)(6), (1 3 2 4)(5)(6)  
 ISOCNT V,H,L

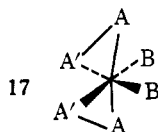
(b) ALL ISOMERS OF PARTIALLY LABELED CONFIGURATION ARE IN LEFT COLUMN;  
 ENANTIOMERS ARE PAIRED TOGETHER.

ALL ISOMERS OF FULLY LABELED CONFIGURATION ARE IN RIGHT COLUMN;  
 THOSE WHICH BECAME EQUIVALENT UPON PARTIAL DELABELING ARE COLLECTED  
 BETWEEN LONG DASHED LINES. THOSE WHICH ARE ENANTIOMERIC ARE PAIRED  
 TOGETHER BETWEEN THE SHORT DASHED LINES.

-----	
C1=1 2 3 4 5 6	C1=1 2 3 4 5 6
-----	
C2=1 2 4 3 5 6	C2=1 2 3 4 6 5
-----	
C3=1 2 4 3 5 6	C3=1 2 4 3 5 6
-----	
C4=1 2 4 3 6 5	C4=1 2 4 3 6 5
-----	
C5=2 1 3 4 5 6	C5=2 1 3 4 5 6
-----	
C6=2 1 3 4 6 5	C6=2 1 3 4 6 5
-----	
C7=2 1 4 3 5 6	C7=2 1 4 3 5 6
-----	
C8=2 1 4 3 6 5	C8=2 1 4 3 6 5
-----	

Figure 4. Computer input (a) and output (b) for the generation of the permutational isomers of *cis*-M(A-A')<sub>2</sub>B<sub>2</sub>.

that the labeling of the sites in **16** is obtained by inverting the skeleton and site labeling in **15**. Sites 2 and 4 will be referred to as axial sites, and sites 1 and 3 as equatorial sites. Nuclei occupying these sites are labeled by choosing an arbitrary permutational isomer, here **17**, and assigning each nucleus the



label of the site it occupies. From **15** and **17** one obtains the labeled ligands A<sub>1</sub>'-A<sub>2</sub>, A<sub>3</sub>'-A<sub>4</sub>, B<sub>5</sub>, B<sub>6</sub>.

Computer input is shown in Figure 4a. First, the proper configurational symmetry group  $V^{VV}$  is defined by permutations in  $V$  which represent rapid molecular motions, here rotations. Next, the nuclear symmetry group  $L$  is read in. Operations in  $L$  permute the labels of physically indistinguishable nuclei. Finally, the group of allowed permutations  $H$  is defined. Treated as reactions acting on the sites in **15**, the operations in  $H^{VV}$  represent all possible transformations which do not change the geometry of the configuration and do not imply bond breaking within a chelate ligand. The statement "ISOCNT V, H, L" generates the output shown in Figure 4b. Here, each isomeric configuration is represented by the bottom row of its  $(\frac{!}{!})$  matrix. Permutational isomers of the partially labeled compound are listed in the left column: C3 is the a-a isomer having both chelate labels in axial positions, C2 is the a-e isomer, and C1 is the e-e isomer.

Consider now the case where cis-trans isomerization occurs rapidly on the observational time scale. Retaining the labeling defined above, the groups  $H^{VV}$  and  $L$  defined in Figure 4a are still appropriate. The proper configurational symmetry group  $V^{VV}$ , however, must be redefined since it represents all motions which are immeasurably rapid on the observational time scale. This group will still contain a representation of the molecular rotational point group as a subgroup, but it must also contain additional operations which represent the rapid intramolecular rearrangements implied by rapid cis-trans isomerization. We shall now proceed to define these additional operations.

Labeling the sites of the trans configurations as in **19**, the reactions  $h_1^{WV} = (1)(2)(3)(4)(5)(6)^{WV}$ ,  $h_2^{WV} = (13)(24)(5)(6)^{WV}$ , and  $h_3^{WV} = (1)(2)(34)(5)(6)^{WV}$  form a complete set of cis-trans isomerization reactions. We shall first consider the case where  $h_1^{WV}$  represents the steric course of cis-trans isomerization. Three additional reactions must also occur when

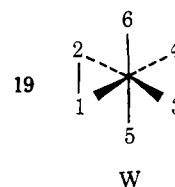
(a) A=SET (1)(2)(3)(4)(5)(6)  
 B=SET (1 3)(2 4)(5)(6)  
 U=GROUP (1)(2)(3)(4)(5)(6), (1 3)(2 4)(5)(6),  
 W=GROUP (1)(2)(3)(4)(5)(6), (1 4)(2 3)(5)(6), (1 2)(3 4)(5 6),  
 (1 3)(2 4)(5 6)  
 Q=EXPAND A,W,B,U,B,W,A  
 V=GEN U,Q  
 L=S2+S2+S2  
 RECODE L,1,3,2,4,5,6  
 H=S2<S2+S2  
 ISOCNT V,H,L

(b) ALL ISOMERS OF PARTIALLY LABELED CONFIGURATION ARE IN LEFT COLUMN;  
 ENANTIOMERS ARE PAIRED TOGETHER.

ALL ISOMERS OF FULLY LABELED CONFIGURATION ARE IN RIGHT COLUMN;  
 THOSE WHICH BECAME EQUIVALENT UPON PARTIAL DELABELING ARE COLLECTED  
 BETWEEN LONG DASHED LINES. THOSE WHICH ARE ENANTIOMERIC ARE PAIRED  
 TOGETHER BETWEEN THE SHORT DASHED LINES.

-----	
C1=1 2 3 4 5 6	C1=1 2 3 4 5 6
-----	
C2=1 2 4 3 5 6	C2=1 2 3 4 6 5
-----	
C3=1 2 4 3 5 6	C3=1 2 4 3 5 6
-----	
C4=1 2 4 3 6 5	C4=1 2 4 3 6 5
-----	

Figure 5. Computer input (a) and output (b) for the generation of the permutational isomers of *cis*-M(A-A')<sub>2</sub>B<sub>2</sub> undergoing rapid cis-trans isomerization.



$h_1^{WV}$  occurs in an achiral environment: its reverse reaction  $h_1^{-1 WV} = (1)(2)(3)(4)(5)(6)$ , its enantiomer  $\bar{h}_1^{WV*} = (13)(24)(5)(6)^{WV*}$ , and the enantiomer of its reverse reaction  $\bar{h}_1^{-1 V*W} = (13)(24)(5)(6)^{V*W}$ . Computer input for the case under discussion (see Figure 5a) begins with the construction of  $V^{VV}$ , the proper configurational symmetry group. The reactions  $h_1^{WV}$  and  $h_1^{-1 WV}$  are represented by A, and the reactions  $\bar{h}_1^{WV*}$  and  $\bar{h}_1^{-1 V*W}$  are represented by B. Whenever cis-trans isomerization occurs via  $h_1^{WV}$ , trans-cis isomerization will follow via  $h_1^{-1 WV}$ , but in the interim the rigid trans configuration will rotate in space. These rotations generate the symmetry group  $W^{WW}$ , a representation of the  $D_2$  rotational point group, which contains the permutations defined in Figure 5a as the group  $W$ . Thus the group of transformations  $h_1^{-1 WV}W^{WW}h_1^{WV}$  occurs rapidly and must be included in the proper configurational symmetry group  $V^{VV}$ . Finally, since  $\bar{h}_1^{-1 V*W}$  occurs rapidly, the rapid rotation of configurations having geometry  $V^*$  must be taken into account when defining  $V^{VV}$ . Rotations of configurations having geometries  $V$  and  $V^*$  are represented by the groups  $U^{VV}$  and  $U^{V*V*}$ , respectively, where  $U$  is defined in Figure 5a. Thus the set of operations  $h_1^{-1 WV}W^{WW}\bar{h}_1^{WV*}U^{V*V*}\bar{h}_1^{-1 V*W}W^{WW}h_1^{WV}$  must be included in  $V^{VV}$ . As a net result, the proper configurational symmetry group  $V^{VV}$  is generated, taking rapid rotations as well as rapid cis-trans isomerization into account, by operations in  $U^{VV}$  and  $Q^{VV}$ . The remaining symmetry groups  $H$  and  $L$  are identical with those used in the case of the rigid molecule. They are read into the computer in symbolic form in Figure 5a, and the computer generates the same groups which were read in explicitly in Figure 4a. Here again the ISOCNT statement generates the output shown in Figure 5b. Note that there are now only two permutational isomers of the partially labeled compound, an e-e isomer and an a-e isomer. By examining the group  $V$ , which the computer can print out, one sees that the ee and aa configurations are rapidly interconverting, but the ae configuration remains distinct.

The implications of cis-trans isomerization via  $h_2^{WV}$  or  $h_3^{WV}$  can be computed using the input of Figure 5a if A and B are suitably redefined in each case. The interesting result is that in both cases, two permutational isomers of the partially

labeled complex exist. As was the case for *cis-trans* isomerization via  $h_1^{WV}$ , the identities of the *a-a* and *e-e* isomers merge while that of the *a-e* isomer remains distinct. The final conclusion, therefore, is that no single *cis-trans* isomerization mechanism can lead to interconversion of all three permutational isomers of a rigid *cis*- $M(A-A')_2B_2$  complex, assuming of course that *cis-trans* isomerization does not involve any further symmetric intermediate configurations having connectivities greater than two.

For the general case of generating a complete set of permutational isomers of a partially labeled compound having geometry  $V$ , one must proceed in the following manner:

1. Label the nuclear sites in all relevant configurations.
2. Label the nuclei which may occupy them.
3. Define and read into the computer the permutations in the proper configurational symmetry group  $V^{VV}$ , an improper configurational symmetry operation  $v^{VV}$  (if the molecule has an achiral skeleton), the nuclear symmetry group  $L$ , and the group of allowed permutations  $H^{VV}$ .
4. Read in the statement "ISOCNT  $V, H, L, VPRIME$ ". If the molecule has a chiral skeleton and  $v^{VV}$  is undefined, the permutation  $v^{VV}$  is omitted from the input.

**Supplementary Material Available:** Complete description of the dynamic stereochemistry program and instructions for its use (23 pages). Ordering information is given on any current masthead page.

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- (13) We shall refer to reactions representing different steric courses as differentiable reactions<sup>1</sup> (or reactions differentiable in a chiral environment) and reactions representing the same steric course as nondifferentiable reactions<sup>1</sup> (or reactions nondifferentiable in a chiral environment). When treating permutational isomerization reactions, other authors have referred to a set of nondifferentiable reactions as a mode<sup>14</sup> or ring permutation.<sup>15</sup> Within their limited range of application, these terms differ in no way from the more general and precise terminology employed here.
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## A Molecular Orbital Analysis of Electronic Structure and Bonding in Chromium Hexacarbonyl

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**Abstract:** The SCF- $X\alpha$ -MSW method is used to calculate molecular orbitals in  $Cr(CO)_6$ , the ligand array  $(CO)_6$ , and free CO. Calculated ionization energies for  $Cr(CO)_6$  and CO are compared with experiment, as are calculated electronic transition energies for  $Cr(CO)_6$ . Correlation of orbital energies, charge distributions, and wave function contours in these three systems leads to the conclusions that (1) metal-carbon bonding in  $Cr(CO)_6$  is due primarily to  $Cr3d-CO5\sigma$  interactions, with only a minor contribution from  $Cr3d-CO2\pi$  interactions, (2)  $Cr4s$  and  $4p$  orbitals have negligible bonding interactions with ligand orbitals, and (3)  $Cr3d-CO2\pi$  interactions, although weak relative to  $Cr3d-CO5\sigma$  interactions, play a dominant role in determining the C-O bond order in  $Cr(CO)_6$  relative to free CO. Vibrational data, in particular interaction displacement coordinates, provide strong support for these conclusions.

An understanding of the interactions between carbon monoxide and transition metal atoms is essential to the understanding of structure and bonding in discrete organometallic carbonyl complexes and carbon monoxide adsorbed on metal surfaces. Chromium hexacarbonyl provides an ideal prototype system for the study of these interactions for several reasons: (1) Its octahedral symmetry implies equivalent orbital interactions at each ligand site. (2) Its symmetry also allows complete separation of metal-ligand  $d-\sigma$  and  $d-\pi$  interactions. (3) The relative simplicity of  $Cr(CO)_6$  leads to photoelectron and ultraviolet spectra which are more readily interpreted than those of more complex systems. (4) A complete vibrational

analysis of  $Cr(CO)_6$  has been carried out which provides detailed information regarding bonding relationships in the molecule.

Molecular orbital analyses of transition metal carbonyls have traditionally followed two general approaches. Following the first approach, molecular orbitals are generated using symmetry arguments and qualitative perturbation molecular orbital theory.<sup>1</sup> This approach has gained wide acceptance owing to its simplicity and transferability. The principles involved are of sufficient simplicity and generality to be readily transferred from system to system. The major drawback of this approach, however, is its dependence on preconceived notions