December, 1988] *Bull. Chem. Soc. Jpn., 61, 4189—4206 (1988)*

# A Novel Approach to the Enumeration of Reaction Types by Counting Reaction-Center Graphs Which Appear as the Substructures of Imaginary Transition Structures

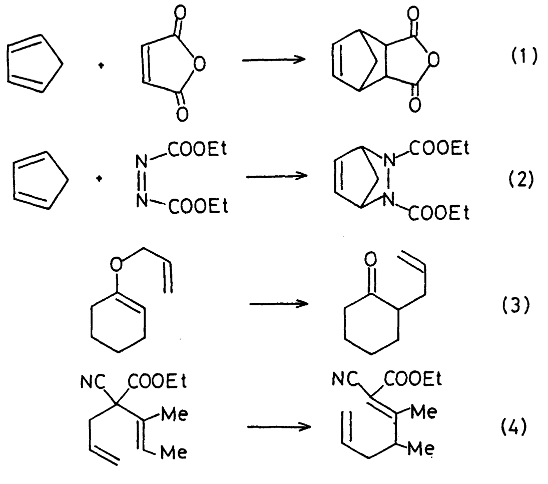
Shinsaku FUJITA
Research Laboratories, Ashigara, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa 250-01
(Received March 30, 1988)

A novel method of enumerating reaction types is presented. The reaction types are formulated as reaction-center graphs (RCGs) that are derived from a parent basic reaction graph (BRG) or from a parent reaction graph (RG) by the substitution of various atoms on the vertices and/or by the attachment of single, double, or triple par-bonds to the edges. The counting of the isomeric RCGs is solved by applying Pólya's theorem to the derivation of a cycle index, in which different variables are introduced to the different orbits of the permutation group of a parent BRG (or RG). Various atom-figure and bond-figure inventories are described in order to count the isomers of RCGs. The numbers of the RCGs are given in the form of the coefficients of a generating function called an RCG-counting polynomial series.

The collection of reaction types as a knowledge database is necessary for the construction of a computer system dealing with organic reactions.[1–12] The reaction data should be classified clearly and consistently in order to keep the database manageable. A well-defined classification of reaction types is also of fundamental importance for the purpose of retrieving organic reactions[13] as well as for the intention of providing organic chemistry with a more logical and systematic format.[14]

The classification of reaction types necessitates their enumeration, since the expanse of the information regarding them must be preestimated.[15] In addition, the enumeration implies the generation of new organic reactions that fundamentally supports a system of synthetic design.[2c]

The systematic enumeration of reaction types has been achieved only to a limited extent. This stems from the fact that an individual organic reaction is represented by a conventional reaction diagram which contains substrates and products combined with an arrow, as shown in Scheme 1.[16,17j] The conventional enumeration of reaction types thereby requires a multiple comparison among the molecules contained in both sides of the respective diagrams. The treatment of such dual representations is cumbersom and may lead to an overlooking of various possibilities and/or to duplicated counting.



Scheme 1.

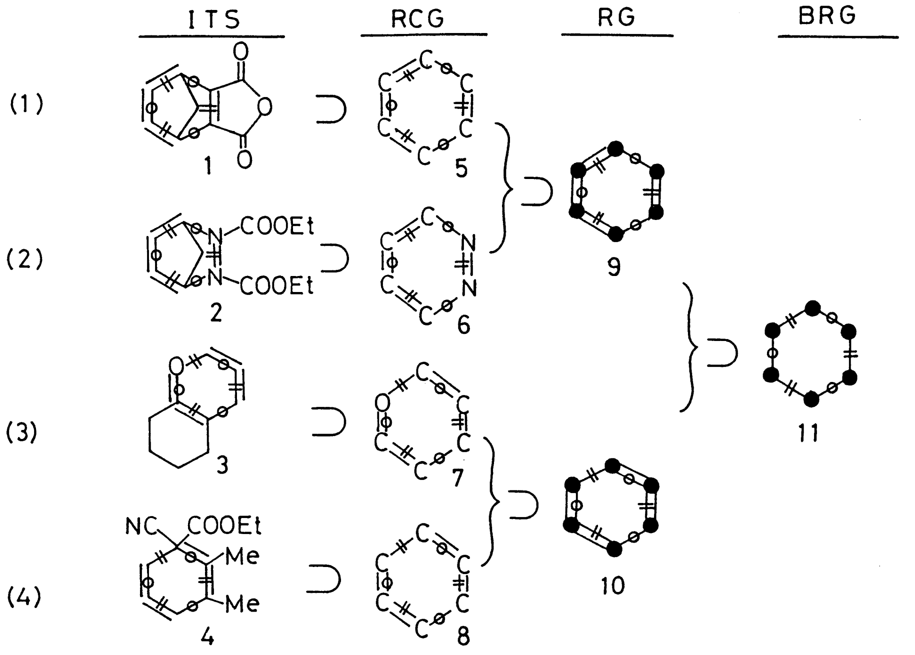
In previous papers,[17] we have proposed the concept of imaginary transition structures (ITS) which afford unitary representations of individual organic reactions. As a result, the manipulation of reaction data is transformed to that of ITSs as a kind of structural formulas. An abstraction of the reaction types is thereby accomplished by finding appropriate subgraphs or substructures of ITSs. Among the useful subgraphs, imaginary rings (ITS rings),[17a,i] reaction-center graphs (RCG),[17a] reaction graphs (RG),[17b,c,f,g] and three- or four-nodal subgraphs[17d,k] are especially effective for characterizing organic reactions.

By a formulation based on the ITSs, an enumeration of the reaction types is transformed into the counting of the subgraphs. In this connection, we have enumerated reaction graphs (RG) to afford a generic classification of reaction types.[17b,c,f,g] As a continuation of this work, the present report deals with a general method for counting reaction types and, especially, with an enumeration of the RC graphs (RCG) which provide us with more detailed information concerning reaction types than the reaction graphs do.

## Formulation and Methods

**Unique Representations of Reaction Types.** Scheme 2 summarizes the formulation of the reaction types discussed in this paper. These ITSs and the related substructures correspond to the diagrams shown in Scheme 1. Although the respective concepts have been reported in the previous papers,[17a,b] they should be restated and extended with the purpose of being applied to the present problem of enumeration.

The *imaginary transition structure (ITS)* of a given reaction contains the participating atoms (C, H, N, O, etc.) and three kinds of bonds (in- (—⊖—), out- (—╫—), and par-bonds (—)), which bonds correspond to the structural changes during the reaction.[17a]



Scheme 2.

A *reaction-center graph (RCG)* is defined as a substructure or a subgraph of a given ITS, in which all reaction centers and imaginary bonds between them are collected.[17b] For example, the RCGs (**5**—**8**) are extracted from the corresponding ITSs (**1**—**4**), as shown in Scheme 2. The RCGs (**5** and **6**) represent generic reaction types, both of which are called *Diels-Alder reactions.* They are discriminated from each other in the light of node values (i.e., $C_6$ and $C_4N_2$). The Claisen and Cope rearrangements are represented by the RCGs (**7** and **8**), which are the substructures of the ITSs (**3** and **4**) respectively. The RCGs (**7** and **8**) differ from each other in their node values (i.e. $C_5O$ vs. $C_6$).

A *reaction graph (RG)* is a more abstract substructure that disregards the node values of an RC graph.[17b] The RCGs (**5** and **6**) give the same RG (**9**), which coresponds to a generic class of the Diels-Alder reactions. The RCGs (**7** and **8**) afford another reaction graph (**10**) that represents a [3,3]sigmatropic rearrangement.

A *basic reaction graph (BRG)* is defined as a substructure that contains reaction centers without node values and has in- and out-bonds but no par-bonds on the edges.[17b] The BRG indicates an electron-shift pattern, which is a descriptor of a broad class of organic reactions. A common basic reaction graph (**11**) is obtained from the RGs (**9** and **10**) by deleting all of the par-bonds therefrom (Scheme 2).

A *reaction pair* consists of two graphs (ITSs, RCGs, RGs, or BRGs) interchangeable by an operation which exchanges all in-bonds and out-bonds with each other (*transformation to reverse reaction*: TRR). For example, the TRR operation on RG (**9**) affords the RG of the corresponding reverse reaction, i.e., retro-Diels-Alder reaction. We call a reaction pair of RG level *an RG pair,* and distinguish it from an RCG pair that is a reaction pair of the RCG level.

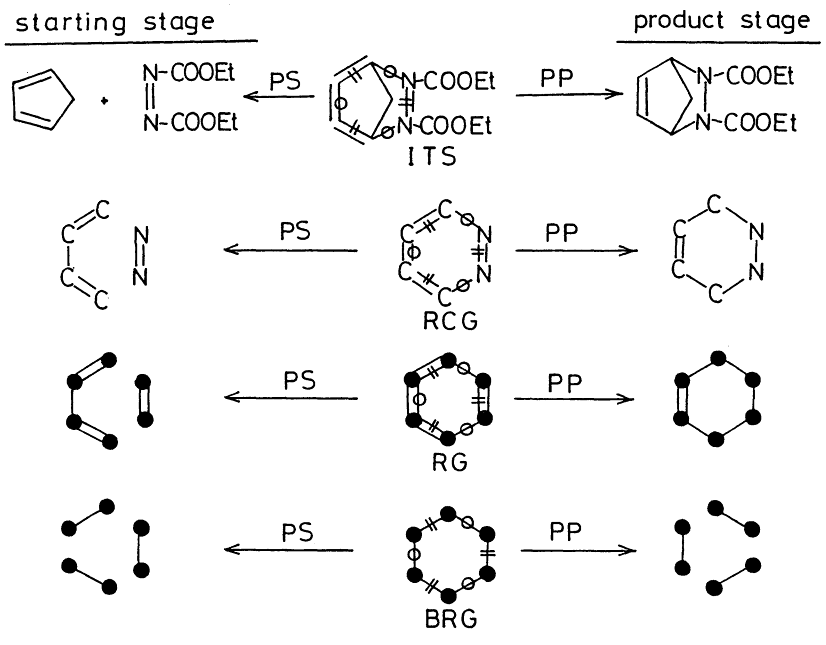
A *self reaction pair* is a special case of a reaction pair, the graph of which is invariant on the TRR operation. For example, RCG **8** and RG **10** are self-reaction pairs in the respective levels.

Scheme 2 indicates a hierarchical classification of organic reactions in terms of the ITS approach. It should be emphasized that the levels of the hierarchy, i.e., RCG, RG, and BRG, give explicit representations to the respective generic reaction types.

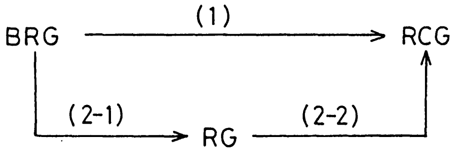
In order to avoid any unfamiliarity with the ITS approach, we introduce *projections to starting stage (PS)* and *to product stage (PP)* that derive conventional diagrams or general schemes from the corresponding ITS, RCG, RG, and BRG (Scheme 3). The PS operation involves a deletion of in-bonds (or taking up par- and out-bonds), and the PP operation involves a deletion of out-bonds (or the taking-up of par- and in-bonds).

**Formulation of the Enumeration Problem of Reaction Types.** In the light of the formulation described above, our subject to enumerate reaction types is now regarded as the counting of RCGs, RGs, and BRGs. In the present paper, we will discuss two approaches to the enumeration of RCGs (Scheme 4).

The first approach is a one-step method (Scheme 4(1)). An RC graph (RCG) is, thus, considered as being a derivative of a parent BRG that is attached by $l_1$ single par-bonds (—) and/or $l_2$ double par-bonds (=) on its edges and is substituted by an appropriate number of atoms on its vertices (nodes). The RCGs (**5**, **6**, **7**, and **8**) are derivatives based on BRG **11** in this sense.



Scheme 3.



Scheme 4.

An alternative approach consists of two steps (2-1 and 2-2 of Scheme 4). In the first step (2-1), a reaction graph (RG) is considered to be a derivative of a basic reaction graph (BRG) that is substituted by $l_1$ single par-bonds and/or $l_2$ double par-bonds on its edges. For example, the RGs (**9** and **10**) are isomers that contain 4 single par-bonds but differ from one another in their manner of substitution (Scheme 2). Several RGs have been enumerated in this line and reported in previous papers.[17b,c,f,g] The present paper affords a more general treatment regarding this step than the previous reports. The 2nd step (2-2) concerns an RCG as the derivative of a parent RG that is substituted by an appropriate number of atoms on its vertices.[18] For example, the RCGs (**5** and **6**) are derivatives that have $C_6$ and $C_4N_2$, respectively, on the vertices of the RG (**9**). Similarly, the RCGs (**7** and **8**) are derivatives having $C_5O$ and $C_6$, respectively, on the vertices of the RG (**10**).

**One-Step Enumeration.** In the one-step approach, an appropriate BRG is selected as a parent graph. Let **G** be the group of symmetry (order $g$) of the parent BRG, there being $p$ vertices (nodes) at which atoms can be substituted and being $q$ edges to which par-bonds can be attached. Let **H** (degree: $p+q$ and order: $g$) be a permutation group isomorphic to **G**. Let $h_C$ be the number of the permutations in **H** which have a cycle structure of the type:

$$C=[i_1+j_1, i_2+j_2, \cdots, i_r+j_r, \cdots],$$

wherein $i_r$ cycles of length $r$ are concerned with a substitution to the vertices and $j_r$ cycles or length $r$ are with respect to the edges; they satisfy the following relationships:

$$1i_1+2i_2+\cdots+pi_p=p$$
$$1j_1+2j_2+\cdots+qi_q=q$$

Since the edges and vertices obviously are not interchangeable by **H** (in other words, the two construct different classes or orbits), the cycle index of **H** is obtained by restating Pólya's theorem[19] in an applicable form to our cases:

$$Z(\mathbf{H})=(1/g)\sum_C h_C(s_1^{i_1}s_2^{i_2}\cdots s_p^{i_p})(t_1^{j_1}t_2^{j_2}\cdots t_q^{j_q}), \qquad (1)$$

where the summation is taken over all different types ($C$) of partitions (Appendix 1).

Then, let $s_r$ be an atom-figure inventory that indicates the manner of atom constitution (an atom figure). Also let $t_r$ be a bond-figure inventory that shows the mode of par-bond substitution (a bond-figure). They are defined as shown in the following equations:

$$s_r=1+u_1^r+u_2^r+u_3^r+\cdots \qquad (2)$$

$$t_r=1+x_1^r+x_2^r. \qquad (3)$$

By introducing $s_r$ (Eq. 2) and $t_r$ (Eq. 3) into the cycle index (Eq. 1), we obtain an RCG-counting polynomial series (Eq. 4) in the form of a generating function:

$$G(u_1, u_2, \cdots x_1, x_2)=Z(\mathbf{H}, 1+u_1+u_2+\cdots, 1+x_1+x_2)$$
$$=\sum A(k_1k_2\cdots l_1l_2)(u_1^{k_1}u_2^{k_2}\cdots)(x_1^{l_1}x_2^{l_2}). \qquad (4)$$

The coefficient $A(k_1k_2\cdots l_1l_2)$ of $(u_1^{k_1}u_2^{k_2}\cdots)(x_1^{l_1}x_2^{l_2})$ gives the number of RC graphs when $k_1$ atoms of the first kind, $k_2$ of the second kind and so on are introduced to the vertices of the parent BRG, and $l_1$ of single par-bonds and $l_2$ of double par-bonds are attached to the edges of the BRG. It should be noted that the two kinds of figure-counting series, which we call an *atom-figure inventory* and a *bond-figure one,* can take various forms according to the objects of enumeration. Although they are obviously equivalent from a mathematical point of view, the discrimination between them is convenient in chemical usage. This point will be exemplified in the following discussions.

The cycle index (Eq. 1) can be further generalized so as to be applicable to a case in which the vertices and/or edges subdivided to two or more intransitive orbits in a permutation group (Appendix 1).

An RCG pair-counting polynomial series $P(u_1, u_2, \cdots, x_1, x_2)$ can be obtained in a similar manner, except that the group of the parent BRG is replaced by that of a structure in which the difference between in- and out-bonds is disregarded.[20] The explicit forms for specific cases are listed in the discussions below.

**Two-Step Enumeration.** This approach contains two successive steps of enumeration (Scheme 4(2-1) and (2-2)). Suppose that a parent BRG has $p$ edges belonging to one orbit and $q$ edges to another different orbit of a permutation group $\mathbf{H}$ (degree: $p+q$ and order: $g$) and that the $p$ edges can be attached by single par-bonds and that the $q$ edges can be attached by single or double par-bonds. Variables $t_{ar}$ and $t_{br}$ are assigned to the respective orbits. The mathematical framework described above is thereby applicable to this case and, hence, the corresponding cycle index can be represented as

$$Z(\mathbf{H})=(1/g)\sum_{C} h_C(t_{a1}{}^{i_1}t_{a2}{}^{i_2}\cdots t_{ap}{}^{i_p})(t_{b1}{}^{j_1}t_{b2}{}^{j_2}\cdots t_{bq}{}^{j_q}), \quad (5)$$

wherein the other characters have the same meanings as stated above.

In order to obtain an RG-counting polynomial series, suppose that $t_{ar}$ is a bond-figure inventory of the first orbit ($a$) and $t_{br}$ is another bond-figure inventory of the second orbit ($b$):

$$t_{ar}=1+x_1{}^r \quad (6)$$

$$t_{br}=1+x_1{}^r+x_2{}^r \quad (7)$$

We obtain the polynomial $G_b(x_1, x_2)$ (Eq. 8) for counting RGs by introducing $t_{ar}$ (Eq. 6) and $t_{br}$ (Eq. 7) into the cycle index (Eq. 6):

$$\begin{aligned} G_b(x_1, x_2) &= Z(\mathbf{H}, 1+x_1, 1+x_1+x_2) \\ &= \sum B(l_1l_2)x_1{}^{l_1}x_2{}^{l_2} \end{aligned} \quad (8)$$

The coefficient $B(l_1l_2)$ of $x_1{}^{l_1}x_2{}^{l_2}$ gives the number of RGs in which $l_1$ of single par-bonds and $l_2$ of double par-bonds are attached to the edges of the parent BRG.

In the second step of the two-step method, we select an appropriate parent RG that has been derived at the first step described above. Suppose that $p$ and $q$ vertices of a parent RG belong to the two different orbits of a permutation group $\mathbf{H}$ (degree: $p+q$ and order: $g$), respectively. The $p$ of the vertices of the first orbit can be substituted by $n_1$ kinds of atoms. On the other hand, $q$ of the vertices of the second orbit can be substituted by $n_2$ kinds of atoms. Two different variables, $S_{ar}$ and $s_{br}$, are assigned to the respective orbits. We then obtain the following cycle index:

$$Z(\mathbf{H})=(1/g)\sum_{C} h_C(s_{a1}{}^{i_1}s_{a2}{}^{i_2}\cdots s_{ap}{}^{i_p})(s_{b1}{}^{j_1}s_{b2}{}^{j_2}\cdots s_{bq}{}^{j_q}), \quad (9)$$

wherein the other characters have the same meanings as stated above.

Let $s_{ar}$ and $s_{br}$ be the respective atom-figure inventories for orbits $a$ and $b$ and be defined as

$$s_{ar}=1+u_1{}^r+\cdots+u_{n1}{}^r \quad (10)$$

and

$$s_{br}=1+u_1{}^r+\cdots+u_{n2}{}^r \quad (11)$$

These equations are introduced to the cycle index (Eq. 9), which is, in turn, expanded into a generating function. An RCG-counting polynomial series $G_a(u_1, u_2, \cdots)$ is thus obtained:

$$\begin{aligned} G_a(u_1, u_2, \cdots) &= Z(\mathbf{H}, 1+u_1+\cdots+u_{n1}, 1+u_1+\cdots+u_{n2}) \\ &= \sum C(k_1k_2\cdots)(u_1{}^{k_1}u_2{}^{k_2}\cdots). \end{aligned} \quad (12)$$

The coefficient $C(k_1k_2\cdots)$ of the term $u_1{}^{k_1}u_2{}^{k_2}\cdots$ gives the number of RC graphs in which $k_1$ atoms of a first kind, $k_2$ of a second kind and so on are introduced to the vertices of the parent RG.

## Results and Discussion

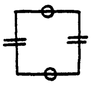
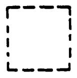
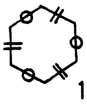
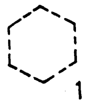
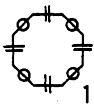
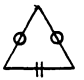
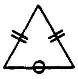
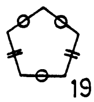
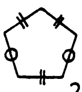
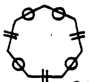
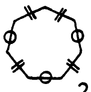
**Enumeration of RC Graphs Based on a Parent Basic Reaction Graph. Examples of the One-Step Method.** Table 1 summarizes representative BRGs selected as parent graphs and the corresponding cycle indices for the counting of RCGs and/or RCG pairs. These results have been obtained by applying Eq. 1 to the respective cases in accord with their permutation groups. The number of RCGs in each case is obtained where variables $s_r$ and $t_r$ of the cycle index collected in Table 1 are substituted by the figure-counting series (Eqs. 2 and 3).

To exemplify the derivation of cycle indices and of RCG-counting polynomial series, we examine the counting of isomers of hexagonal reaction graphs (Table 2).[21] Suppose that a parent BRG (**11**) is substituted by $l_1$ single par-bonds on its edges and attached by $k_1$ nitrogen atoms and $k_2$ oxygen atoms (and $6-k_1-k_2$ of implicit carbon or other atoms) on its vertices. The vertices of **11** are numbered as 1, 2, $\cdots$ 6 and the edges are designated as a, b, $\cdots$ f.

The symmetry of **11** is $\mathbf{D}_3$ (order 6). Hence, the permutation corresponding to each symmetry operation is obtained, as shown in Table 2, which permutation is represented by the product of cycles, e.g.,

$$\begin{aligned} C_{2(1)} &\sim \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} & \mathrm{e} & \mathrm{f} \\ 2 & 1 & 6 & 5 & 4 & 3 & \mathrm{a} & \mathrm{f} & \mathrm{e} & \mathrm{d} & \mathrm{c} & \mathrm{b} \end{pmatrix} \\ &= (1\ 2)\,(3\ 6)\,(4\ 5)\,(\mathrm{a})\,(\mathrm{d})\,(\mathrm{b}\ \mathrm{f})\,(\mathrm{c}\ \mathrm{e}). \end{aligned}$$

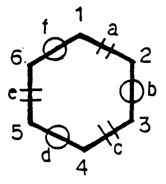
Table 1. Parent Basic Reaction Graphs and Cycle Indices for the One-Step Enumeration[a)]

| BRG | Symmetry | Cycle indes[b,c)] | Eq. |
|---|---|---|---|
|  12 | $D_2$ | G: $(1/4)(s_1^4t_1^4+2s_2^2t_1^2t_2+s_2^2t_2^2)$ | 13 |
|  13 | $D_4$ | P: $(1/8)(s_1^4t_1^4+2s_1^2s_2t_2^2+2s_2^2t_1^2t_2+s_2^2t_2^2+2s_4t_4)$ | 14 |
|  11 | $D_3$ | G: $(1/6)(s_1^6t_1^6+3s_2^3t_1^2t_2^2+2s_3^2t_3^2)$ | 15 |
|  14 | $D_6$ | P: $(1/12)(s_1^6t_1^6+s_2^3t_2^3+3s_1^2s_2^2t_2^3+3s_2^3t_1^2t_2^2+2s_3^2t_3^2+2s_6t_6)$ | 16 |
|  15 | $D_4$ | G: $(1/8)(s_1^8t_1^8+4s_2^4t_1^2t_2^3+s_2^4t_2^4+2s_4^2t_4^2)$ | 17 |
|  16 | $D_8$ | P: $(1/16)(s_1^8t_1^8+4s_2^4t_1^2t_2^3+s_2^4t_2^4+2s_4^2t_4^2+4s_1^2s_2^3t_2^4+4s_8t_8)$ | 18 |
|  17  18 | $C_2$ | G: $(1/2)(s_1^3t_1^3+s_1s_2t_1t_2)$ | 19 |
|  19  20 | $C_2$ | G: $(1/2)(s_1^5t_1^5+s_1s_2^2t_1t_2^2)$ | 20 |
|  21  22 | $C_2$ | G: $(1/2)(s_1^7t_1^7+s_1s_2^3t_1t_2^3)$ | 21 |

a) The cycle indices are obtained by applying Eq. 1 to the respective BRGs. b) A variable $s_r$ is assigned to the cycle of length $r$ which is concerned with a permutation of the vertices. On the other hand, a variable $t_r$ is with respect to a permutation of the edges. c) G: a cycle index for counting RCGs. P: a cycle index for counting RCG pairs.

Table 2. A Permutation Group Based on a Parent BRG (**11**)

Parent BRG:



11 ($D_3$)

| Symmetry operation | Permutation | Variable[a)] assigned |
|---|---|---|
| I | (1)(2)(3)(4)(5)(6) (a)(b)(c)(d)(e)(f) | $s_1^6t_1^6$ |
| $C_{2(1)}$ | (1 2)(3 6)(4 5) (a)(d)(b f)(c e) | $s_2^3t_1^2t_2^2$ |
| $C_{2(2)}$ | (1 6)(2 5)(3 4) (c)(f)(a e)(b d) | |
| $C_{2(3)}$ | (1 4)(2 3)(5 6) (b)(e)(a c)(d f) | |
| $C_3$ | (1 5 3)(2 6 4) (a e c)(b f d) | $s_3^2t_3^2$ |
| $C_3^2$ | (1 3 5)(2 4 6) (a c e)(b d f) | |

a) A variable is assigned to each permutation in acord with the cycle structure wherein $s_r$ and $t_r$ are concerned with vertices and edges, respectively. Strictly speaking, this example has three orbits, i.e., (1,2,⋯6), (a,c,e), and (b,d,f). However, the same variable $t_r$ can be assigned to the latter two orbits without losing generality.

Let us consider a permutation group of degree 12 (=6+6) that is isomorphic to the symmetry of the parent BRG. Obviously, the set of the six vertices and that of the six edges construct different orbits. In other words, the six vertices and six edges are not interchanged with each other by any permutation collected in Table 2. Hence, we introduce different variables, $s_r$ and $t_r$, to the respective orbits. The assigned variables collected in Table 2 are derived from the cycle structures of the permutations. Upon collecting these assigned variables over all the permutations, we found that the corresponding cycle index (Eq. 15 of Table 1) is a specific case of Eq. 1. Therefore, the variables of Eq. 15 are replaced by atom-figure and bond-figure inventories:

$$s_r = 1 + u^r + v^r \tag{22}$$

and

$$t_r = 1 + x^r. \tag{23}$$

As a result, the following equation is derived as a generating function called an RCG-counting polynomial series:

$$G(u, v, x) = (1/6)\ \{(1+u+v)^6(1+x)^6 + 3(1+u^2+v^2)^3(1+x)^2(1+x^2)^2 + 2(1+u^3+v^3)^2(1+x^2)^2\}. \qquad (24)$$

Since the parent BRG (**11**) is a self-reaction pair, the set of isomers counted by Eq. 24 contains one or more self-reaction pairs. The next problem is the counting of reaction pairs. The corresponding parent graph (**14**) has $\mathbf{D}_6$ symmetry (order 12) and affords the cycle index (Eq. 16) as collected in Table 1. Then, an RCG pair-counting polynomial $P(u, v, x)$ (Eq. 25) is derived by the introduction of Eqs. 22 and 23 into Eq. 16:

$$\begin{aligned} P(u, v, x) &= (1/12)\ \{(1+u+v)^6(1+x)^6 + (1+u^2+v^2)^3(1+x^2)^3 + \\ &\quad 3(1+u+v)^2(1+u^2+v^2)^2(1+x^2)^3 + \\ &\quad 3(1+u^2+v^2)^3(1+x)^2(1+x^2)^2 + \\ &\quad 2(1+u^3+v^3)^2(1+x^3)^2 + \\ &\quad 2(1+u^6+v^6)(1+x^6)\}. \end{aligned} \qquad (25)$$

The expansion of Eq. 24 gives a polynomial series in which the coefficient of the term $u^{k_1}v^{k_2}x^l$ indicates the number or isomers derived from the parent BRG (**11**) with $l$ single par-bonds on the edges along with $k_1$ of nitrogen and $k_2$ of oxygen atoms. Similarly, an expansion of Eq. 25 affords a polynomial series, the coefficients of which show the numbers of the corresponding RCG pairs. The coefficients derived from Eqs. 24 and 25 are found in Table 3.

Table 3. Enumeration of Reaction Types Based on BRG (**11**)[a)]

| $k_1k_2$ | Number of RCGs (RCG pairs) | | | |
|---|---|---|---|---|
| | $l$=0 or 6 | $l$=1 or 5 | $l$=2 or 4 | $l$=3 |
| 0 0 | 1 (1) | 2 (1) | 4 (3) | 6 (3) |
| 1 0 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 0 1 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 2 0 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 1 1 | 5 (3) | 30 (15) | 75 (39) | 100 (50) |
| 0 2 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 3 0 | 4 (3) | 20 (10) | 50 (28) | 68 (34) |
| 2 1 | 10 (6) | 60 (30) | 150 (78) | 200 (100) |
| 1 2 | 10 (6) | 60 (30) | 150 (78) | 200 (100) |
| 0 3 | 4 (3) | 20 (10) | 50 (28) | 68 (34) |
| 4 0 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 3 1 | 10 (6) | 60 (30) | 150 (78) | 200 (100) |
| 2 2 | 18 (11) | 96 (48) | 234 (123) | 312 (156) |
| 1 3 | 10 (6) | 60 (30) | 150 (78) | 200 (100) |
| 0 4 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 5 0 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 4 1 | 5 (3) | 30 (15) | 75 (39) | 100 (50) |
| 3 2 | 10 (6) | 60 (30) | 150 (78) | 200 (100) |
| 1 4 | 5 (3) | 30 (15) | 75 (39) | 100 (50) |
| 0 5 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 6 0 | 1 (1) | 2 (1) | 4 (3) | 6 (3) |
| 5 1 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 4 2 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 3 3 | 4 (3) | 20 (10) | 50 (28) | 68 (34) |
| 2 4 | 4 (3) | 18 (9) | 42 (24) | 56 (28) |
| 1 5 | 1 (1) | 6 (3) | 15 (9) | 20 (10) |
| 0 6 | 1 (1) | 1 (1) | 4 (3) | 6 (3) |

a) The numbers of RCGs with $k_1$ or nitrogens, $k_2$ of oxygens and one single par-bond are obtained as the coefficients of $u^{k_1}v^{k_2}x^l$ in Eq. 24. The numbers in the parentheses indicate the number of RCG pairs which are obtained by the expansion or Eq. 25.

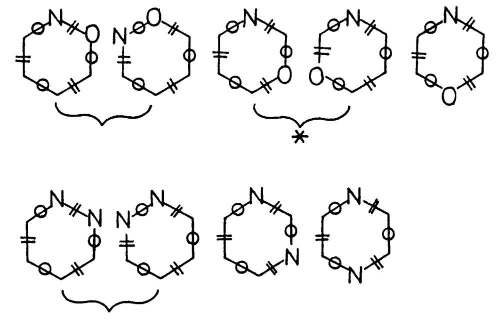
The results of Table 3 have been obtained by a mathematical treatment and, hence, affords a good probe to test the validity of manual enumeration. From this point of view, let us examine several examples derived from the parent BRG (**11**). Table 4 collects isomers with one nitrogen and one oxygen and no par-bonds ($k_1$=$k_2$=1, $l$=0) as well as isomers with two nitrogen ($k_1$=2, $k_2$=$l$=0).[22)] Each couple of the RCGs linked with a brace (Table 4) is a reaction pair. An isolated one is a self reaction pair. The number of NO isomers is 5; this number is obtained as the coefficient of the term $uv$ ($=u^1v^1x^0$) of Eq. 24 (Table 3, $k_1$=$k_2$=1, $l$=0). The number of RCG pairs is 3, which is obtained from Eq. 25 (the data in parentheses of Table 3 at $k_1$=$k_2$=1, $l$=0). The latter $N_2$ case affords 4 for RCGs and 3 for RCG pairs as the respective coefficients of the term $u^2$ ($=u^2v^0x^0$) in Eqs. 24 and 25 (Table 3). The results shown in Table 4 are, thus, confirmed by the values of Table 3.

A comparison between the NO and $N_2$ substitutions (Table 4) reveals that the RCG pair of the former NO case (marked by an asterisk) is degenerated to a self RCG pair in the latter $N_2$ case. This fact reflects the symmetries of the RCGs, which determine the values of the coefficients.

Table 5 shows the case of $k_1$=$k_2$=$l$=1. The number of isomers of RC graphs is 30 and that of RCG pairs is 15, which are in accord with the results obtained from the generating functions (Table 3).

It must be emphasized that *the number of reaction types is given in the form of the coefficient of a generating function such as Eq. 24 but not as a result of manual enumeration.* Therefore, the present method

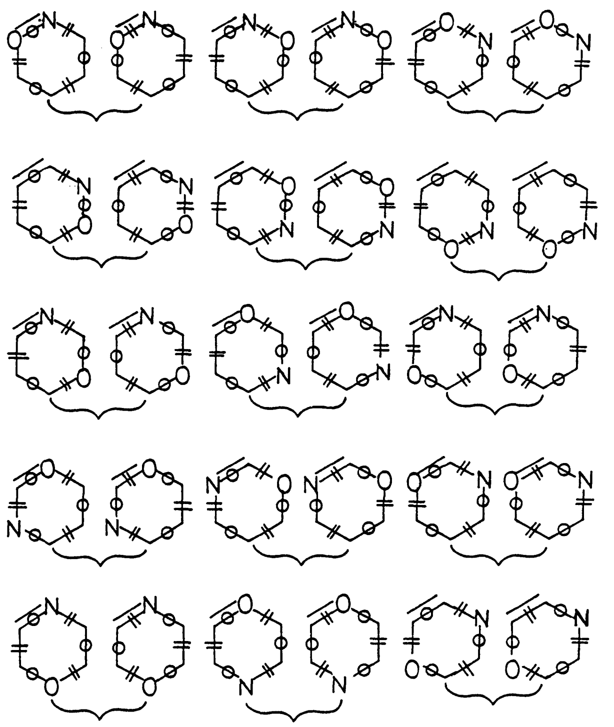
Table 4. Isomeric RCGs with NO or $N_2$ on the Vertices but No Par-Bonds on the Edges[a)]



a) Each couple of RCGs linked with a brace is a reaction pair. An isolated RCG is a self-reaction pair. The number of RCGs and that of RCG pairs are obtained as the coefficients of the respective generating functions (Eqs. 24 and 25). These numbers are listed in Table 3 ($k_1$=$k_2$=1, $l$=0; and $k_1$=2, $k_2$=$l$=0).

affords an assurance of the validity to a computer program for the enumeration of reaction types or for generating new reactions.

Table 5. Isomeric RCG$_s$ Substituted by One Nitrogen and One Oxygen on the Vertices and by One Single Par-Bond on the Edge[a)]



a) Each couple or RCGs linked with a brace is a reaction pair. The number of RCGs and that of RCG pairs are obtained as the coefficients of $u^1v^1l^1$ of Eqs. 24 and 25, respectively (Table 3, $k_1=k_2=l=1$).

**Enumeration of RC Graphs Based on a Parent Reaction Graph. The 2nd Step of the Two-Step Method.** The number of isomers obtained in the last section contains that of several RCGs in which the valency of the atoms exceeds chemically reasonable values. Hence, a more specific treatment than that mentioned above is necessary in order to avoid counting chemically unreasonable isomers. This approach starts from an appropriate reaction graph (RG) in place of the BRG described above.

Table 6 summarizes parent RGs of the hexagonal class having 0 to 6 single par-bonds along with the respective cycle indices for counting RCGs and/or RCG pairs. The two parent RGs in alignment are a reaction pair with one another (e.g. **23** and **24**). Contrarily, the RG coupled with a broken-lined graph is a self-reaction pair (e.g. **11** followed by **14**). The two cases are slightly different in a practical treatment, although the results are obtained by applying Eq. 9 to each of the parent RGs in a similar manner. In the former case, the number of RCGs derived from a parent RG is equal to the value based on the corresponding reverse RG. Hence, the number of RCG pairs is always half of the total number of RCGs, based on the RG and the reverse RG as parents. On the other hand, the latter case requires a separate treatment of counting the RCG pairs, since the parent RG is a self-reaction pair.

To exemplify the method of enumeration, let us work out the RG (**9**) as a parent and count the isomers having $k_1$ nitrogen and $k_2$ oxygen atoms. The six vertices, whose numbering is shown, are divided into three classes by the corresponding permutation group ($\mathbf{C}_2$), i.e., 1, 2; 3, 4; and 5, 6 (Table 7). The cycle index for **9** (Eq. 39) is obtained, as collected in Table 6, when we

Table 6. Hexagonal RGs as Parent Graphs and Their Cycle Indices[a,b)]

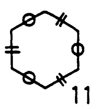
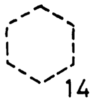
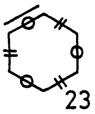
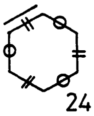
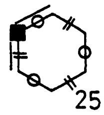
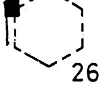
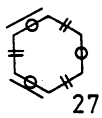
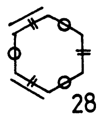
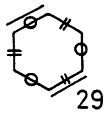
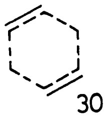
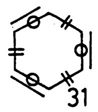
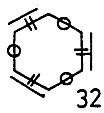
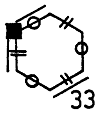
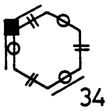
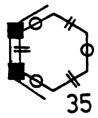
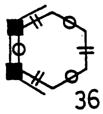
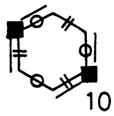
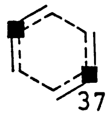
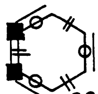
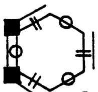
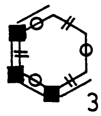
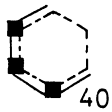
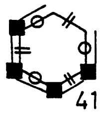
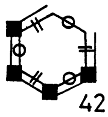
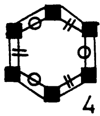
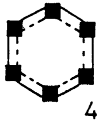
| RG | Symmetry | Cycle index | Eq. |
|---|---|---|---|
|  11 | $\mathbf{D}_3$ | G: $(1/6)(s_{b1}{}^6+3s_{b2}{}^3+2s_{b3}{}^2)$ | 26 |
|  14 | $\mathbf{D}_6$ | P: $(1/12)(s_{b1}{}^6+3s_{b1}{}^2s_{b2}{}^2+4s_{b2}{}^3+2s_{b3}{}^2+2s_{b6})$ | 27 |
|  23  24 | $\mathbf{C}_2$ | G: $(1/2)(s_{b1}{}^6+s_{b2}{}^3)$ | 28 |
|  25 | $\mathbf{C}_1$ | G: $s_{a1}s_{b1}{}^5$ | 29 |
|  26 | $\mathbf{C}_2$ | P: $(1/2)(s_{a1}s_{b1}{}^5+s_{a1}s_{b1}s_{b2}{}^2)$ | 30 |

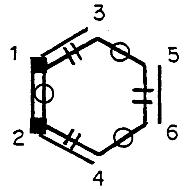
Table 6. (Continued)

| RG | Symmetry | Cycle index | Eq. |
|---|---|---|---|
|  27  28 | $C_2$ | G: $(1/2)(s_{b1}^6+s_{b2}^3)$ | 31 |
|  29 | $C_2$ | G: $(1/2)(s_{b1}^6+s_{b2}^3)$ | 32 |
|  30 | $D_2$ | P: $(1/4)(s_{b1}^6+s_{b1}^2s_{b2}^2+2s_{b2}^3)$ | 33 |
|  31  32 | $D_3$ | G: $(1/6)(s_{b1}^6+3s_{b2}^3+2s_{b3}^2)$ | 34 |
|  33  34 | $C_1$ | G: $s_{a1}s_{b1}^5$ | 35 |
|  35  36 | $C_2$ | G: $(1/2)(s_{a1}^2s_{b1}^4+s_{a2}s_{b2}^2)$ | 36 |
|  10 | $C_2$ | G: $(1/2)(s_{a1}^2s_{b1}^4+s_{a2}s_{b2}^2)$ | 37 |
|  37 | $D_2$ | P: $(1/4)(s_{a1}^2s_{b1}^4+s_{a1}^2s_{b2}^2+2s_{a2}s_{b2}^2)$ | 38 |
|  38  9 | $C_2$ | G: $(1/2)(s_{a1}^2s_{b1}^4+s_{a2}s_{b2}^2)$ | 39 |
|  39 | $C_1$ | G: $s_{a1}^3s_{b1}^3$ | 40 |
|  40 | $C_2$ | P: $(1/2)(s_{a1}^3s_{b1}^3+s_{a1}s_{a2}s_{b1}s_{b2})$ | 41 |
|  41  42 | $C_2$ | G: $(1/2)(s_{a1}^4s_{b1}^2+s_{a2}^2s_{b2})$ | 42 |
|  43 | $D_3$ | G: $(1/6)(s_{a1}^6+3s_{a2}^3+2s_{a3}^2)$ | 43 |
|  44 | $D_6$ | P: $(1/12)(s_{a1}^6+3s_{a1}^2s_{a2}^2+4s_{a2}^3+2s_{a3}^2+2s_{a6})$ | 44 |

a) The cycle indices are obtained by applying Eq. 9 to the respective RGs. A variable $s_{ar}$ is assigned to the cycle of length $r$ which is concerned with a permutation of the restricted vertices (■). A variable $s_{br}$ is with respect to a permutation of the unmarked vertices. b) G: a cycle index for counting RCGs. P: a cycle index for counting RCG pairs.

Table 7. Permutation Group Based on a Parent RG (**9**)

Parent RG:



9 ($C_2$)

| Symmetry operation | Permutation | Variable[a)] assigned |
|---|---|---|
| I | (1)(2) (3)(4) (5)(6) | $s_{a1}{}^2 s_{b1}{}^4$ |
| $C_2$ | (1 2) (3 4) (5 6) | $s_{a2} s_{b2}{}^2$ |

a) The vertices, 1 and 2, are distinguished from the others because of limitation of valency. The variable $s_{br}$ is given to the former vertices (marked by ■). The other vertices are assigned to $s_{br}$.

give a variable $s_{ar}$ to the first class and $s_{br}$ to the 2nd and 3rd classes. This treatment stems from the facts that vertices 1 and 2 (marked by boldface squares) are unable to be substituted by oxygen atoms due to a valency limitation and that the substituents on vertices 3 to 6 can be selected freely from a set of nitrogen, oxygen, and implicit carbon atoms.

We then introduce two kinds of atom-figure inventories:

$$s_{ar} = 1 + u^r \tag{45}$$

and

$$s_{br} = 1 + u^r + v^r, \tag{46}$$

the first of which is used for a substitution only by nitrogen atoms and the 2nd of which is used for a substitution by nitrogen and oxygen atoms. The variables of Eq. 39 are substituted by Eqs. 45 and 46 to afford an RCG-counting polynomial series (Eq. 47):

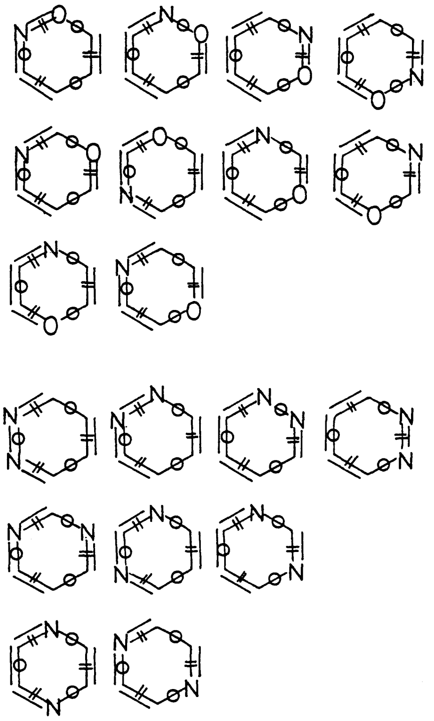
$$G(u, v) = (1/2)\{(1+u)^2(1+u+v)^4 + (1+u^2)(1+u^2+v^2)^2\}. \tag{47}$$

The expanded equation from Eq. 47 is a generating function in which the coefficient of $u^{k_1}v^{k_2}$ is the number of isomers with $k_1$ nitrogen and $k_2$ oxygen atoms.

Table 8 shows isomers in which one nitrogen and one oxygen atom substitute the vertices of the parent RG (**9**). The number of isomers collected is 10, the number of which is equal to the coefficient of the term $u^1v^1$ of Eq. 47. Table 8 also contains isomers having two nitrogen substituents on the RG (**9**). This list contains the isomers of the RCG (**6**) shown in Scheme 2. The number of $N_2$ isomers is 9, which is, again, confirmed by a comparison with the coefficient of $u^2v^0$ in Eq. 47.

The parent RG (**9**) is not a self-reaction pair and the TRR operation affords RG (**38**) of the reverse reaction (the retro Diels-Alder reaction). The enumeration of isomers based on RG (**38**) gives the same results as those of RG (**9**).

Table 8. Isomeric RCGs Derived by NO and $N_2$ Substitution on the Parent RG (**9**)[a)]



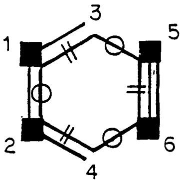
a) The numbers of RCGs are obtained as the coefficients of $uv$ for NO substitution (Table 9, **9**, $k_1$=$k_2$=1) and of $u^2$ for $N_2$ substitution (Table 9, **9**, $k_1$=2, $k_2$=0). See Appendix 2.

The Diels-Alder type addition of a triple bond is represented by the RG (**45**) that also has three classes of vertices (1, 2; 3, 4; and 5, 6). Since vertices 1, 2, 5, and 6 are unable to have oxygen substituents, the cycle index (Eq. 48) is different from Eq. 39.

$$Z(C_2) = (1/2)(s_{a1}{}^4 s_{b1}{}^2 + s_{a2}{}^2 s_{b2}) \tag{48}$$

By applying Eqs. 45 and 46 to Eq. 48, we obtain the following RCG-counting polynomial series (Eq. 49):

$$G(u, v) = (1/2)\{(1+u)^4(1+u+v)^2 + (1+u^2)^2(1+u^2+v^2)\}. \tag{49}$$



45($C_2$)

Let us next consider a case in which a parent RG is a self-reaction pair. The representative example is the RG (**10**) that has $C_2$ symmetry (Table 6). The six vertices are divided into three orbits. The vertices of the first orbit (marked by heavy squares) can take only C and N as a substituent because of a valency limitation.

Table 9. Enumeration of Reaction Types Based on Various Parent RGs[a)]

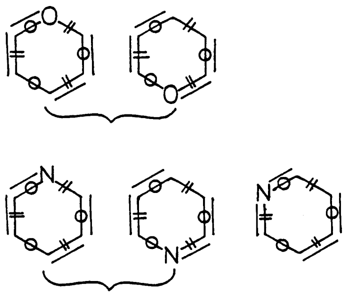
| $k_1k_2$ | Parent RG<br>**11** (**14**) | <br>**23** **25** (**26**)<br>**24** | <br>**27** **29** (**30**)<br>**28** | <br>**31** **33** **35** **10** (**37**)<br>**32** **34** **36** | <br>**38**[b)]**39** (**40**)<br>**9** | <br>**41** **43** (**44**)<br>**42** |
|---|---|---|---|---|---|---|
| | | | number of RCG's (RCG pairs) | | | |
| 0 0 | 1 (1) | 1 1 (1) | 1 1 (1) | 1 1 1 1 (1) | 1 1 (1) | 1 1 (1) |
| 1 0 | 1 (1) | 3 6 (4) | 3 3 (2) | 1 6 3 3 (2) | 3 6 (4) | 3 1 (1) |
| 0 1 | 1 (1) | 3 5 (3) | 3 3 (2) | 1 5 2 2 (1) | 2 3 (2) | 1 0 (0) |
| 2 0 | 4 (3) | 9 15 (9) | 9 9 (6) | 4 15 9 9 (6) | 9 15 (9) | 9 4 (3) |
| 1 1 | 5 (3) | 15 25(13) | 15 15 (8) | 5 25 10 10 (5) | 10 15 (8) | 5 0 (0) |
| 0 2 | 4 (3) | 9 10 (6) | 9 9 (6) | 4 10 4 4 (3) | 4 3 (2) | 1 0 (0) |
| 3 0 | 4 (3) | 10 20(12) | 10 10 (6) | 4 20 10 10 (6) | 10 20(12) | 10 4 (3) |
| 2 1 | 10 (6) | 30 50(26) | 30 30(16) | 10 50 20 20(10) | 20 30(16) | 10 0 (0) |
| 1 2 | 10 (6) | 30 40(22) | 30 30(16) | 10 40 12 12 (7) | 12 12 (7) | 2 0 (0) |
| 0 3 | 4 (3) | 10 10 (6) | 10 10 (6) | 4 10 2 2 (1) | 2 1 (1) | 0 0 (0) |
| 4 0 | 4 (3) | 9 15 (9) | 9 9 (6) | 4 15 9 9 (6) | 9 15 (9) | 9 4 (3) |
| 3 1 | 10 (6) | 30 50(26) | 30 30(16) | 10 50 20 20(10) | 20 30(16) | 10 0 (0) |
| 2 2 | 18(11) | 48 60(32) | 48 48(27) | 18 60 20 20(12) | 20 18(10) | 4 0 (0) |
| 1 3 | 10 (6) | 30 30(16) | 30 30(16) | 10 30 6 6 (3) | 6 3 (2) | 0 0 (0) |
| 0 4 | 4 (3) | 9 5 (3) | 9 9 (6) | 4 5 1 1 (1) | 1 0 (0) | 0 0 (0) |
| 5 0 | 1 (1) | 3 6 (4) | 3 3 (2) | 1 6 3 3 (2) | 3 6 (4) | 3 1 (1) |
| 4 1 | 5 (3) | 15 25(13) | 15 15 (8) | 5 25 10 10 (5) | 10 15 (8) | 5 0 (0) |
| 3 2 | 10 (6) | 30 40(22) | 30 30(16) | 10 40 12 12 (7) | 12 12 (7) | 2 0 (0) |
| 2 3 | 10 (6) | 30 30(16) | 30 30(16) | 10 30 6 6 (3) | 6 3 (2) | 0 0 (0) |
| 1 4 | 5 (3) | 15 10 (6) | 15 15 (8) | 5 10 1 1 (1) | 1 0 (0) | 0 0 (0) |
| 0 5 | 1 (1) | 3 1 (1) | 3 3 (2) | 1 1 0 0 (0) | 0 0 (0) | 0 0 (0) |
| 6 0 | 1 (1) | 1 1 (1) | 1 1 (1) | 1 1 1 1 (1) | 1 1 (1) | 1 1 (1) |
| 5 1 | 1 (1) | 3 5 (3) | 3 3 (2) | 1 5 2 2 (1) | 2 3 (2) | 1 0 (0) |
| 4 2 | 4 (3) | 9 10 (6) | 9 9 (6) | 4 10 4 4 (3) | 4 3 (2) | 1 0 (0) |
| 3 3 | 4 (3) | 10 10 (6) | 10 10 (6) | 4 10 2 2 (1) | 2 1 (1) | 0 0 (0) |
| 2 4 | 4 (3) | 9 5 (3) | 9 9 (6) | 4 5 1 1 (1) | 1 0 (0) | 0 0 (0) |
| 1 5 | 1 (1) | 3 1 (1) | 3 3 (2) | 1 1 0 0 (0) | 0 0 (0) | 0 0 (0) |
| 0 6 | 1 (1) | 1 0 (0) | 1 1 (1) | 1 0 0 0 (0) | 0 0 (0) | 0 0 (0) |

a) The coefficients of $u^{k1}v^{k2}$ indicate the numbers of isomeric RCG with $k_1$ of nitrogens and $k_2$ of oxygens on each of parent RG. These values are obtained by introducing Eqs. 45 and 46 to each of the cycle indices (Table 4). b) Obtained by the expansion of Eq. 47.

The other vertices are capable of taking a C, N, or O substituent. The cycle index for the parent RG (**10**) is obtained, as shown in Table 6 (Eq. 37), when we introduce a variable $s_{ar}$ to the first orbit and $s_{br}$ to the 2nd and 3rd orbits. In order to obtain an RCG-counting polynomial series, two kinds of atom-figure inventories (Eqs. 45 and 46) are introduced into the cycle index (Eq. 37). The result of the expansion of this polynomial is listed in Table 9.

Since the parent RG (**10**) is a self-reaction pair, the resulting set of isomers contains one or more self RCG pairs. The next problem is counting the RCG pairs. A parent graph (**37**) for counting RCG pairs is obtained by equalizing the in- and out-bonds of RG (**10**). This graph has $\mathbf{D}_2$ symmetry. The six vertices are divided into two orbits by this symmetry. We then obtain the cycle index of Eq. 38 (Table 6), in which two variables ($s_{ar}$ and $s_{br}$) are assigned to the orbits in accord with their limitation (maked by ■). The expansion of this polynomial gives a generating function that affords the number of RCG pairs with $k_1$ of oxygen and $k_2$ of nitrogen atoms as the coefficient of $u^{k_1}v^{k_2}$. The results are listed also in Table 9.

Table 10. Isomeric RCGs with O and N Substitution on the Parent RG (**10**)[a,b)]



a) The number of the O isomers is the coefficient of $v$ (Table 9, **10**, $k_1$=0, $k_2$=1). The number of RCG pairs is shown also in Table 9 (**37**, $k_1$=0, $k_2$=1). b) The number of the N isomers is the coefficient of $u$ (Table 9, **10**, $k_1$=1, $k_2$=0). The number of RCG pairs is found Table 9 (**37**, $k_1$=1, $k_2$=0). See Appendix 2.

Table 10 lists the isomers of $k_1$=0, $k_2$=1 (O substitution) and of $k_1$=1, $k_2$=0 (N substitution). The number of RCGs in the former case is 2 and that of RCG pairs is 1. These values are equal to the coefficients of the term $u^0v^1$ listed in Table 9. On making a substitution of one nitrogen, we obtain 3 isomers of RCG and 2

RCG pairs. These numbers are the same values as the coefficients of $u^1v^0$ collected in Table 9.

Table 9 also lists the other results that are obtained by applying atom-figure inventories (Eqs. 45 and 46) to the cycle indices shown in Table 6. When a parent RG is a self-reaction pair, the isomers, therefrom, contain one or more self-RCG pairs. In this case, Table 9 indicates the results of counting RCG-pairs as well as those of counting RCGs.[23]

In this section, we have dealt only with parent RGs of the hexagonal class. The method discussed, however, is applicable to the other types of parent RGs which are derived from the respective parent BRGs given in Table 1. Although the detailed results are abbreviated, full lists of the latter cases would be of essential importance for didactic and taxonomic purposes.

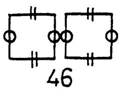
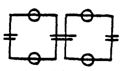
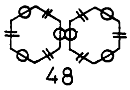
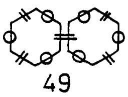
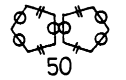
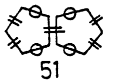
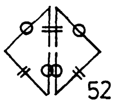
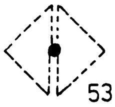
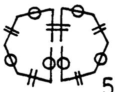
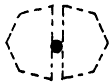
**Enumeration of RGs Based on a Fused BRG. Improved Examples of the First Step of the Two-Step Method.** In a previous paper,[17g] we reported an enumeration of RGs in which they are considered to be the isomers of basic reaction graphs given in Table 11. The previous treatment has not differenciated the fused bonds from the other pericyclic bonds. In light of the extension described in this paper, this subject can be discussed in a more detailed fashion.

Suppose that the fused positions can be attached only by a single par-bond and other pericyclic edges can be substituted by a singe or double par-bond. This formulation allows Eq. 5 to be applied to the various parent BRGs given in Table 11, in which the corresponding cycle indices are listed. Upon making the substitution $t_{ar}=1+x^r$ and $t_{br}=1+x^r+y^r$ and collecting like powers of $xy$, the coefficients of term $x^{l_1}y^{l_2}$ are obtained in order to indicate the number of isomers with $l_1$ single par-bonds and $l_2$ double par-bonds.

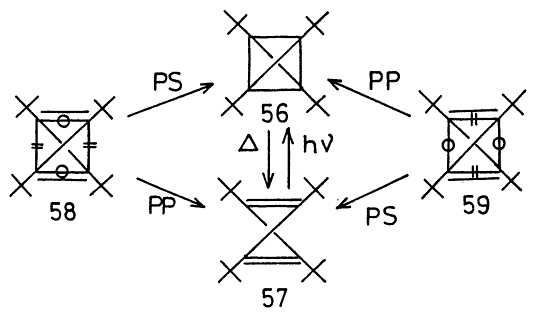
**Enumeration of RGs with Cross-Bonds. Extended Examples of the First Step of the Two-Step Method.** The above-mentioned treatment presumes that only in-bonds and out-bonds on edges are the positions of substitution. However, a more general enumeration is sometimes desirable. For example, tetra-*t*-butyltetrahedrane (**56**) and tetra-*t*-butylcyclobutadiene (**57**) have been reported to be interconvertible (Scheme 5).[24] The ITSs (**58** and **59**) represent these reactions. The corresponding reaction graphs (RGs) contain cross-bonds. The final problem discussed in this article is counting this type of reaction graph.

We select a basic reaction graph (**60**) as a parent, which has 4 usual edges and 2 phantom edges (cross-

Table 11. Fused BRG as Parent Graphs and Their Cycle Indices[a)]

| Fused BRG | Symmetry | Cycle index[b)] | Eq. |
|---|---|---|---|
|  46  47 | $\mathbf{D}_2$ | G: $(1/4)(t_{a1}t_{b1}^6+2t_{a1}t_{b2}^3+t_{a1}t_{b1}^2t_{b2}^2)$ | 50 |
|  48  49 | $\mathbf{D}_2$ | G: $(1/4)(t_{a1}t_{b1}^{10}+2t_{a1}t_{b2}^5+t_{a1}t_{b1}^2t_{b2}^4)$ | 51 |
|  50  51 | $\mathbf{D}_2$ | G: $(1/4)(t_{a1}t_{b1}^8+3t_{a1}t_{b2}^4)$ | 52 |
|  52 | $\mathbf{C}_2$ | G: $(1/2)(t_{a1}^2t_{b1}^4+t_{a1}^2t_{b2}^2)$ | 53 |
|  53 | $\mathbf{D}_2$ | P: $(1/4)(t_{a1}^2t_{b1}^4+2t_{a2}t_{b2}^2+t_{a1}^2t_{b2}^2)$ | 54 |
|  54 | $\mathbf{C}_2$ | G: $(1/2)(t_{a1}^2t_{b1}^8+t_{a1}^2t_{b2}^4)$ | 55 |
|  55 | $\mathbf{D}_2$ | P: $(1/4)(t_{a1}^2t_{b1}^8+2t_{a2}t_{b2}^4+t_{a1}^2t_{b2}^4)$ | 56 |

a) The cycle indices are obtained by applying Eq. 5 to the respective BRGs. b) A variable $t_{ar}$ is respect to the fused edges, whereas $t_{br}$ is assigned to the pericyclic edges.

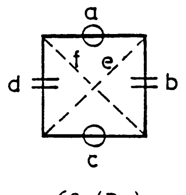


Scheme 5.

linkages of broken lines) as the positions of substitution (Table 12). The consideration of phantom edges is a new matter, compared with the previous enumeration.[17b)] When the six edges are marked as above, the 4 permutations of $\mathbf{D}_2$ group (degree 6) are easily obtained (Table 12). The edges are divided into three orbits, i.e., a, c; b, d; and e, f. The edges of the first and 2nd orbits are unable to have a triple par-bond (≡) as a substituent. On the other hand, the phantom edges of the 3rd orbit can be attached by either single, double or triple par-bond. Hence, we introduce a variable $t_{ar}$ to the former and another variable $t_{br}$ to the latter orbits. We thereby obtain a cycle index (Eq. 57), as shown in Table 13.

Table 12. Permutation Group Based on a Parent BRG (**60**)[a)]

Parent BRG:



60 ($D_2$)

| Symmetry operation | Permutation | Variable assigned[b)] |
|---|---|---|
| I | (a)(c) (b)(d) (e)(f) | $t_{a1}^4 t_{b1}^2$ |
| $C_{2(1)}$ | (a)(c) (b d) (e f) | $t_{a1}^2 t_{a2} t_{b2}$ |
| $C_{2(2)}$ | (a c) (b)(d) (e f) | $t_{a1}^2 t_{a2} t_{b2}$ |
| $C_{2(3)}$ | (a c) (b d) (e)(f) | $t_{a2}^2 t_{b1}^2$ |

a) A broken line indicates a phontom edge which can be substituted by a single, double, or triple par-bond. b) The pericyclic edges have a variable $t_{ar}$. A variable $t_{br}$ is respect to the phontom edges.

In order to obtain an RG-counting polynomial series $G(x, y, z)$, the variables of Eq. 57 are substituted by the following two kinds of bond-figure inventories:

$$t_{ar} = 1 + x^r + y^r \tag{61}$$

and

$$t_{br} = 1 + x^r + y^r + z^r, \tag{62}$$

wherein $t_{ar}$ is used for a substitution by a single or double par-bond and $t_{br}$ for a substitution by a single, double, or triple par-bond. The expansion of the polynomial affords the following generating function for the counting of RGs:

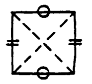
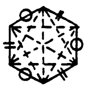
$$\begin{aligned} &G(x, y, z) \\ &= (1 + 3x + 3y + 6x^2 + 9xy + 6y^2 + 8x^3 + 18x^2y + 18xy^2 + \\ &\quad 8y^3 + 6x^4 + 18x^3y + 27x^2y^2 + 18xy^3 + 6y^4 + \cdots) + \\ &\quad z(1 + 3x + 3y + 6x^2 + 10xy + 6y^2 + \cdots) + \\ &\quad z^2(1 + 2x + 2y + 3x^2 + 4xy + 3y^2 + \cdots). \end{aligned} \tag{63}$$

The coefficient of $x^{l_1}y^{l_2}z^{l_3}$ of Eq. 63 is the number of RGs having $l_1$ single, $l_2$ double, and $l_3$ triple par-bonds on the edges.

Table 14 collects RGs of $l_1$=3, $l_2$=$l_3$=0 as an example. The number of the isomeric RGs is 6, which number is the coefficient of the term $x^3y^0y^0$ of the Eq. 63. Table 14 also shows isomeric RGs of $l_1$=4, $l_2$=$l_3$=0, the number of which is found as the coefficient of $x^4y^0z^0$ of Eq. 63. The two RGs connected with a brace construct a reaction pair and the isolated ones are self reaction pairs, respectively. The number of reaction pairs can be obtained by using the cycle index (Eq. 58) and the bond-figure inventories (Eqs. 61 and 62).

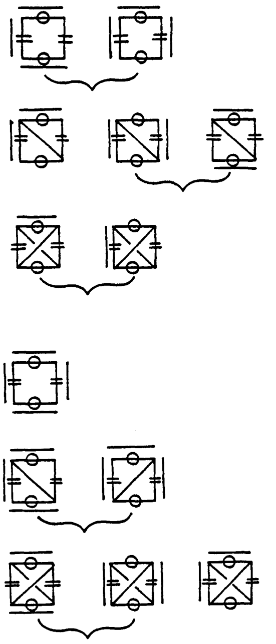
The BRG (**9**) has 9 additional phantom edges in light of the approach taken in this section. Hence we obtain the cycle index (Eq. 59) shown in Table 13. The degree and order of the permutation group obtained are 15 and 6, respectively. The cycle index (Eq. 60) for counting the corresponding reaction pairs

Table 13. Parent BRGs with Phantom Edges and Their Cycle Indices[a)]

| BRG | Symmetry | Cycle index[b,c)] | Eq. |
|---|---|---|---|
|  60 | $\mathbf{D}_2$ | G: $(1/4)(t_{a1}^2 t_{b1}^2 + 2t_{a1}^2 t_{a2} t_{b2} + t_{a2}^2 t_{b1}^2)$ | 57 |
|  | $\mathbf{D}_4$ | P: $(1/8)(t_{a1}^4 t_{b1}^2 + 2t_{a1}^2 t_{a2} t_{b2} + 3t_{a2}^2 t_{b1}^2 + 2t_{a4} t_{a2})$ | 58 |
|  61 | $\mathbf{D}_3$ | G: $(1/6)(t_{a1}^6 t_{b1}^9 + 3t_{a1}^2 t_{a2}^2 t_{b1} t_{b2}^4 + 2t_{a3}^2 t_{b3}^3)$ | 59 |
|  | $\mathbf{D}_6$ | P: $(1/12)(t_{a1}^6 t_{b1}^9 + 3t_{a1}^2 t_{a2}^2 t_{b1} t_{a2}^4 + 2t_{a3}^2 t_{b3}^2 + 3t_{a2}^3 t_{b1}^3 t_{b2}^3 + t_{a2}^3 t_{b1}^3 t_{b2}^3 + 2t_{a6} t_{b3} t_{b6})$ | 60 |

a) The cycle indices are obtained by applying Eq. 5 to the respective BRGs having phantom edges. b) A variable $t_{ar}$ is assigned to the pericyclic edges. The phantom edges have a variable $t_{br}$ assigned. c) G; a cycle index for counting RGs. P: a cycle index counting RG pairs.

Table 14. Isomeric RGs with Cross-Bonds[a)]



a) Out- and in-bonds are presumed to take pericyclic positions and thus the cross-bonds always consist of par-bonds. This table contains only two types of isomers, i.e. $l_1=3$, $l_2=l_3=0$, and $l_1=4$, $l_2=l_3=0$.

is also found in Table 13. When we introduced bond-figure inventories (Eqs. 61 and 62) to these cycle indices, we obtain generating functions for counting RGs and RG pairs, respectively, of hexagonal class.

## Conclusion

We have formulated an enumeration of reaction types as a counting of reaction graphs (RG) and of reaction-center graphs (RCG). The problem has been solved by applying Pólya's theorem in which different variables are introduced to different intransitive orbits of the graph in order to afford a cycle index. Various atom-figure inventories and bond-figure inventories are described for counting the isomers of RG and of RCG. Since the number of isomeric RCGs (or RGs) is obtained by such a mathematical equation as a generating function, the present approach affords a versatile probe for testifying the manual enumeration of reaction types.

## Appendix 1

This appendix is dovoted to a derivation of a generating function which enumerates the number of equivalence classes of configurations under the conditions of the present article.

**1.** Let $\mathbf{D}$ be a domain which consists of $p+q$ elements called *positions*. Let $\mathbf{H}$ (order $|\mathbf{H}|$) be a permutation group which acts on a domain $\mathbf{D}$. Suppose that $\mathbf{D}$ is partitioned by $\mathbf{H}$ into two orbits:

$$\mathbf{D}_1=\{d_{11}, d_{12}, \cdots d_{1p}\} \text{ and } \mathbf{D}_2=\{d_{21}, d_{22}, \cdots d_{2q}\}.$$

Let $\mathbf{X}$ be a codomain which contains $m$ elements called *figures*:

$$\mathbf{X}=\{X_1, X_2, \cdots X_m\}.$$

Let $f_\alpha$ and $f_\beta$ be two functions from the domain $\mathbf{D}$ to the codomain $\mathbf{X}$, i.e., $f_\alpha$: $\mathbf{D}\rightarrow\mathbf{X}$ and $f_\beta$: $\mathbf{D}\rightarrow\mathbf{X}$, wherein the functions are called *configurations*.

**Definition 1.** (binary relation). A relationship between $f_\alpha$ and $f_\beta$ is defined as a binary relation $(f_\alpha \sim f_\beta)$, if the following equation is fulfilled for $^{\exists}H$ $(\in\mathbf{H})$:

$$f_\alpha(d)=f_\beta(H(d)) \quad \text{for } ^{\forall}d\in\mathbf{D}.$$

**Theorem 1.** (The proof is abbreviated). The binary relation defined above is an equivalence relation. Therefore, the set of the functions are partitioned into equivalence classes by this relation.

**2.** We use the terms and notations defined in Definition 1. This section deals with the weight of a function (configuration).

**Defenition 2.** (the weight of a function). Suppose that two types of weights, $w_1(X_r)$ and $w_2(X_r)$ are assigned to each element $(X_r)$ of the codomain $\mathbf{X}$. We then define the weight $W(f)$ for each function ($f$: $\mathbf{D}\rightarrow X$) as follows:

$$W(f) = \prod_{d\in\mathbf{D}_1} w_1(f(d)) \prod_{d\in\mathbf{D}_2} w_2(f(d)).$$

**Theorem 2.** Let $f_\alpha$: $\mathbf{D}\rightarrow\mathbf{X}$ and $f_\beta$: $\mathbf{D}\rightarrow\mathbf{X}$ be equivalent. Then,

$$W(f_\alpha)=W(f_\beta).$$

*Proof.* Since $f_\alpha \sim f_\beta$, an appropriate $H$ $(\in\mathbf{H})$ is present which satisfies the follwing relationship:

$$f_\alpha(d)=f_\beta(H(d)) \text{ for } ^{\forall}d\in\mathbf{D}.$$

Then,

$$\begin{aligned} W(f_\alpha) &= \prod_{d\in\mathbf{D}_1} w_1(f_\alpha(d)) \prod_{d\in\mathbf{D}_2} w_2(f_\alpha(d)) \\ &= \prod_{d\in\mathbf{D}_1} w_1(f_\beta(H(d))) \prod_{d\in\mathbf{D}_2} w_2(f_\beta(H(d))). \end{aligned} \tag{a}$$

Because of Definition 2,

$$W(f_\beta)= \prod_{d\in\mathbf{D}_1} w_1(f_\beta(d)) \prod_{d\in\mathbf{D}_2} w_2(f_\beta(d)). \tag{b}$$

A comparison of the right-hand side of (a) with that of (b) shows their equality, since a set of $H(d)$'s is the same as that of $d$'s, except for the sequence. Hence, $W(f_\alpha)=W(f_\beta)$.

It should be noted that the converse of Theorem 2 is not always true: two functions (configurations) having the same weight do not always belong to the same equivalence class. Therefore, our goal is to obtain the number of equivalence classes having the same weight in the form of a generating function based on $W(f)$.

**3.** Let $\mathbf{F}_\mu$ is a set of functions ($f$: $\mathbf{D}\rightarrow\mathbf{X}$), all of which have the same weight $W_\mu(f)$. Let $H$ be a permutation of $\mathbf{H}$ on $\mathbf{D}$. This section shows that there is a permutation group on $\mathbf{F}_\mu$ onto which $\mathbf{H}$ is homomorphic.

**Theorem 3.** A function $H^{(\mu)}$: $\mathbf{F}_\mu\rightarrow\mathbf{F}_\mu$ is defined in accord with $H$ as follows:

$$H^{(\mu)}(f(d))=f(H(d)) \text{ for } ^{\forall}d\in\mathbf{D} \text{ and } ^{\forall}f\in\mathbf{F}_\mu.$$

Then,

(1) The function $H^{(\mu)}$ is a permutation on the set of $\mathbf{F}_\mu$.

(2) The mapping of $\mathbf{H}$ onto $\mathbf{H}^{(\mu)}$ defined above is homomorphic, wherein $\mathbf{H}^{(\mu)}$ is the set of all $H^{(\mu)}$.

*Proof.* (1) Suppose that both $f_\alpha$ and $f_\beta$ of $\mathbf{F}_\mu$ ($f_\alpha \neq f_\beta$) are mapped by $H^{(\mu)}$ to the same function, i.e.,

$$H^{(\mu)}(f_\alpha(d)) = H^{(\mu)}(f_\beta(d)) \text{ for } {}^\forall d \in \mathbf{D}.$$

Because of the above definition,

$$H^{(\mu)}(f_\alpha(d)) = f_\alpha(H(d)) \text{ and } H^{(\mu)}(f_\beta(d)) = f_\beta(H(d)).$$

Hence, $f_\alpha(H(d)) = f_\beta(H(d))$. This equation indicates that $f_\alpha = f_\beta$. This is contrary to the presumption. Thererore, $\forall f_\alpha$ ($\in \mathbf{F}_\mu$) is transformed by $H^{(\mu)}$ into a function different from itself. This fact shows that $H^{(\mu)}$ is a permutation on the set of $\mathbf{F}_\mu$.

(2) Let $H_\delta^{(\mu)}$ and $H_\varepsilon^{(\mu)}$ be the permutations on $\mathbf{F}_\mu$. They correspond to $H_\delta$ and $H_\varepsilon$ ($\in \mathbf{H}$), respectively. Then the following equations are obtained in the light of the definition:

$$H_\delta^{(\mu)}(f(d)) = f(H_\delta(d)) \tag{a}$$

and

$$H_\varepsilon^{(\mu)}(f(d)) = f(H_\varepsilon(d)). \tag{b}$$

Since $\mathbf{H}$ is a permutation group,

$$H_{\varepsilon\delta} = H_\varepsilon H_\delta. \tag{c}$$

Let $H_{\varepsilon\delta}^{(\mu)}$ correspond to $H_{\varepsilon\delta}$ ($\in \mathbf{H}$). Then,

$$\begin{aligned} H_{\varepsilon\delta}^{(\mu)}(f(d)) &= f(H_{\varepsilon\delta}(d)) \overset{\text{c}}{=} f(H_\varepsilon H_\delta(d)) = f(H_\varepsilon(H_\delta(d)) \\ &\overset{\text{b}}{=} H_\varepsilon^{(\mu)}(f(H_\delta(d))) \overset{\text{a}}{=} H_\varepsilon^{(\mu)} H_\delta^{(\mu)}(f(d)). \end{aligned}$$

That is, $H_{\varepsilon\delta}^{(\mu)} = H_\varepsilon^{(\mu)} H_\delta^{(\mu)}$, which indicates that the mapping of $\mathbf{H}$ onto $\mathbf{H}^{(\mu)}$ is homomorphic.

This theorem shows that $\mathbf{H}^{(\mu)} = \{H^{(\mu)}\}$ is a permutation group on $\mathbf{F}_\mu$ onto which the original permutation group $\mathbf{H}$ on $\mathbf{D}$ is homomorphic.

**4.** According to Definition 1, the domain $\mathbf{D}$ is partitioned by $\mathbf{H}$ into two orbits $\mathbf{D}_1$ and $\mathbf{D}_2$. Suppose that $H$ ($\in \mathbf{H}$) has the following cycle structure:

$[i_1, i_2, \cdots i_p]$ for a permutation of $\mathbf{D}_1$ part, and
$[j_1, j_2, \cdots j_q]$ for a permutation of $\mathbf{D}_2$ part, wherein
$i_1 + 2i_2 + \cdots + pi_p = p$ and
$j_1 + 2j_2 + \cdots + qj_q = q$.

The function $f$: $\mathbf{D} \rightarrow \mathbf{X}$, which has a weight defined in Definition 2, affords a configuration in which the orbit $\mathbf{D}_1$ has $p_1$ $X_1$, $p_2$ $X_2$, $\cdots$, and $p_m X_m$ on its positions and the orbit $\mathbf{D}_2$ has $q_1$ $X_1$, $q_2$ $X_2$, $\cdots$, and $q_m$ $X_m$ on its positions, wherein

$$p_1 + p_2 + \cdots + p_m = p \text{ and}$$
$$q_1 + q_2 + \cdots + q_m = q.$$

Then, the weight of the function $W(f)$ is obtained by Definition 2:

$$\begin{aligned} W(f) = {} & [w_1(X_1)^{p_1} w_1(X_2)^{p_2} \cdots w_1(X_m)^{p_m}] \cdot \\ & [w_2(X_1)^{q_1} w_2(X_2)^{q_2} \cdots w_2(X_m)^{q_m}]. \end{aligned}$$

Let $A_{p_1, \cdots p_m, q_1, \cdots q_m}$ be the total number of such functions (configurations) which are invariant on a permutation ($H$) of $\mathbf{H}$ and has $W(f)$ as the weight. Let $B_{p_1, \cdots p_m, q_1, \cdots q_m}$ be the total number of different classes of configurations which have the same weight $W(f)$. To begin with, let us examine the total number of functions.

**Theorem 4.** A generating function for counting $A_{p_1, \cdots p_m, q_1, \cdots q_m}$ is represented by:

$$\begin{aligned} \sum A_{p_1, \cdots p_m, q_1, \cdots q_m} & [w_1(X_1)^{p_1} \cdots w_1(X_m)^{p_m}] \cdot [w_2(X_1)^{q_1} \cdots w_2(X_m)^{q_m}] \\ & = (s_1^{i_1} s_2^{i_2} \cdots s_p^{i_p})(t_1^{j_1} t_2^{j_2} \cdots t_q^{j_q}), \end{aligned}$$

wherein $s_r = w_1(X_1)^r + w_1(X_2)^r + \cdots + w_1(X_m)^r$ and
$t_r = w_2(X_1)^r + w_2(X_2)^r + \cdots + w_2(X_m)^r$.

The summation is taken over all the partitions of $p$ ($p_1 + p_2 + \cdots + p_m = p$) and of $q$ ($q_1 + q_2 + \cdots + q_m = q$).

*Proof.* Let $\pi_1$ is a cycle of length $r_1$ which is involved in $H$ ($\in \mathbf{H}$) and is concerned with the permutation of $\mathbf{D}_1$. Let $\pi_2$ be a cycle of length $r_2$ which is contained in $H$ ($\in \mathbf{H}$) and is concerned with $\mathbf{D}_2$. When a function (configuration) is invariant on the permutation $H$, it is also invariant on the operations by $\pi_1$ and $\pi_2$. Then, the $r_1$ positions of $\mathbf{D}_1$ concerning with $\pi_1$ should have $r_1$ of the same figures, i.e., $r_1 X_1$ or $r_1 X_2 \cdots$ or $r_1 X_m$. Similarly, the $r_2$ positions of $\mathbf{D}_2$ should have $r_2 X_1$ or $r_2 X_2 \cdots$ or $r_2 X_m$. Hence, the corresponding generating function are represented by:

$$s_{r_1} = \sum_{k=1}^{m} w_1(X_k)^{r_1} \text{ and}$$

$$t_{r_2} = \sum_{k=1}^{m} w_2(X_k)^{r_2}$$

The same kinds of generating functions are obtained for all of the cycles involved in the permutation $H$. Therefore, a generating function for counting $A_{p_1, \cdots p_m, q_1, \cdots q_m}$ is obtained as follows:

$$\begin{aligned} \sum A_{p_1, \cdots p_m, q_1, \cdots q_m} & [w_1(X_1)^{p_1} \cdots w_1(X_m)^{p_m}] \cdot [w_2(X_1)^{q_1} \cdots w_2(X_m)^{q_m}] \\ & = (s_1^{i_1} s_2^{i_2} \cdots s_p^{i_p})(t_1^{j_1} t_2^{j_2} \cdots t_q^{j_q}) \\ & = \prod_{r=1}^{p} \Big(\sum_{k=1}^{m} w_1(X_k)^r\Big)^{i_r} \cdot \prod_{r=1}^{p} \Big(\sum_{k=1}^{m} w_2(X_k)^r\Big)^{j_r}, \end{aligned}$$

which is in accord with the cycle structure of $H$. When this polynomial is expanded, we obtained a generating function.

We call such summations as $s_r$ and $t_r$ figure inventories.

**5.** Let us work out $H$ ($\in \mathbf{H}$) which has been defined in Section 4. We introduced a formal variable $s_r$ which corresponds to a cycle of length $r$ of $\mathbf{D}_1$ part. Similarly, a variable $t_r$ is concerned with a cycle of lengh $r$ of $\mathbf{D}_2$ part. We then obtain the following product for $H$:

$$(s_1^{i_1} s_2^{i_2} \cdots s_p^{i_p})(t_1^{j_1} t_2^{j_2} \cdots t_q^{j_q}).$$

Since the same kind of products can be obtained for all the permutation of $\mathbf{H}$, these products are summed over $\mathbf{H}$.

**Definition 3.** (cycle index). The following equation is defined as a *cycle index* for $\mathbf{H}$:

$$Z(\mathbf{H}) = \frac{1}{|\mathbf{H}|} \sum_{H \in \mathbf{H}} (s_1^{i_1} s_2^{i_2} \cdots s_p^{i_p})(t_1^{j_1} t_2^{j_2} \cdots t_q^{j_q}).$$

**6.** We used the terms and notations described in Section 4. The purpose of this section is to derive a generating function of $B_{p_1, \cdots p_m, q_1, \cdots q_m}$.

**Theorem 5.** A generating function of counting $B_{p_1, \cdots p_m, q_1, \cdots q_m}$ which concerns with the total number of equivalence classes is represented by:

$$\begin{aligned} \sum B_{p_1, \cdots p_m, q_1, \cdots q_m} & [w_1(X_1)^{p_1} \cdots w_1(X_m)^{p_m}] \cdot [w_2(X_1)^{q_1} \cdots w_2(X_m)^{q_m}] \\ & = Z\Big(\mathbf{H}; \sum_{k=1}^{m} w_1(X_k)^r, \sum_{k=1}^{m} w_2(X_k)^r\Big), \end{aligned}$$

wherein the right-hand side indicates that the two terms denoted by the summations should be introduced to $s_r$ and $t_r$ of $Z(\mathbf{H})$ (Definition 3), respectively. The summation of the left-hand side is taken over all the partitions of $p$ $(p_1+p_2+\cdots+p_m=p)$ and of $q$ $(q_1+q_2+\cdots+q_m=q)$.

*Proof.* Let $\mathbf{F}_\mu$ be a set of functions which have the same weight

$$W_\mu=[w_1(X_1)^{p_1}\cdots w_1(X_m)^{p_m}]\cdot[w_2(X_1)^{q_1}\cdots w_2(X_m)^{q_m}]. \quad \text{(a)}$$

Let $\delta_\mu$ be the number of equivalent classes contained in $\mathbf{F}_\mu$. Then, a generating function for counting equivalence cases is obviously as follows:

$$\sum_\mu \delta_\mu W_\mu .$$

Since $\mathbf{H}_\mu$ is homomorphic to $\mathbf{H}$ (Theroem 3), the number $\delta_\mu$ is obtained by Burnside's lemma:[19c)]

$$\delta_\mu = \frac{1}{|\mathbf{H}|}\sum_{H\in\mathbf{H}} \psi(H^{(\mu)}).$$

wherein $\psi$ $(H^{(\mu)})$ is the number of invariant functions (configurations) of $\mathbf{F}_\mu$ on the operation of $H^{(\mu)}$. Since this lemma is true for all $\mu$,

$$\sum_\mu \delta_\mu W_\mu = \sum_\mu \left(\frac{1}{|\mathbf{H}|}\sum_{H\in\mathbf{H}} \psi(H^{(\mu)})\right)W_\mu$$
$$= \frac{1}{|\mathbf{H}|}\sum_{H\in\mathbf{H}}\sum_\mu \psi(H^{(\mu)})W_\mu . \quad \text{(b)}$$

Because of the definition of $\psi$ $(H^{(\mu)})$ and $W_\mu$, the term

$$\sum_\mu \psi(H^{(\mu)})W_\mu$$

indicates the total number of functions invariant on the permutation $H$ which corresponds to each $H^{(\mu)}$. The term is thus equal to the equation proved in Theorem 4. Therefore,

$$\sum_\mu \psi(H^{(\mu)})\,W_\mu$$
$$=\sum A_{p_1,\cdots p_m,q_1,\cdots q_m}[w_1(X_1)^{p_1}\cdots w_1(X_m)^{p_m}]\cdot[w_2(X_1)^{q_1}\cdots w_2(X_m)^{q_m}]$$
$$= (s_1^{i_1}s_2^{i_2}\cdots s_p^{i_p})\,(t_1^{j_1}\;t_2^{j_2}\cdots t_q^{j_q}), \quad \text{(c)}$$

wherein the summation of the second equation is taken over all the partitions of $p$ $(p_1+p_2+\cdots+p_{m,}=p)$ and of $q$ $(q_1+q_2+\cdots+q_m=q)$; and the variables $s_r$ and $t_r$ of the 3rd equation are represented by:

$$s_r = \sum_{k=1}^{m} w_1\,(X_k)^r$$

and

$$t_r = \sum_{k=1}^{m} w_2\,(X_k)^r.$$

Since Eq. (c) can be established for each $H$ corresponding to $H^{(\mu)}$, the following equation is obtained by the substitution of Eq. (b) by Eq. (c):

$$\sum_\mu \delta_\mu W_\mu = \frac{1}{|\mathbf{H}|}\sum_{H\in\mathbf{H}}(s_1^{i_1}s_2^{i_2}\cdots s_p^{i_p})\,(t_1^{j_1}t_2^{j_2}\cdots t_q^{j_q})$$
$$= Z(\mathbf{H}\,;\sum_{k=1}^{m} w_1(X_k)^r\;,\;\sum_{k=1}^{m} w_2(X_k)^r\,),$$

wherein the latter relationship comes from Definition 3. Since

$$\sum_\mu \delta_\mu W_\mu =$$
$$\sum B_{p_1,\cdots p_m,q_1,\cdots q_m}[w_1(X_1)^{p_1}\cdots w_1(X_m)^{p_m}]\cdot[w_2(X_1)^{q_1}\cdots w_2(X_m)^{q_m}]\,,$$

we obtain the relationship to be proved.

**7.** The weights $w_j(X_k)$ $(k=1, 2, \cdots, m)$ for $\mathbf{D}_j$ are determined in accord with the restrictive conditions, which are concerned with bond multiplicity (or complex bond number) or the valency of atoms in the present chemical application. The following examples show the effectiveness of Theorem 5.

**Example 1.** (the derivation of Eq. 4 of the text). The present domain $\mathbf{D}$ consists of edges and nodes which construct two different orbits on the operation of $\mathbf{H}$. Then, Eq. 1 of the text is easily obtained in the light of Definition 3. The codomain $\mathbf{X}$ contains atom-figures (A, B, C, $\cdots$) and bond-figures ($\phi$, $-$, $=$), i,e.,

$$\mathbf{X}=\{\mathrm{A, B, C}, \cdots; \phi, -, =\},$$

wherein the symbol ($\phi$) indicates no substitution of bonds on the edges, and the symbols, $-$ and $=$, denote single and double par-bonds, respectively. Then the weights of them are given as follows:

$$w_1(\mathrm{A})=1,\quad w_1(\mathrm{B})=u_1,\; w_1(\mathrm{C})=u_2, \cdots;$$
$$w_1(\phi)=0,\; w_1(-)=0,\; w_1(=)=0 \text{ and}$$
$$w_2(\mathrm{A})=0,\quad w_2(\mathrm{B})=0,\; w_2(\mathrm{C})=0, \cdots;$$
$$w_2(\phi)=1,\; w_2(-)=x_1,\; w_2(=)=x_2.$$

Hence, Eqs. 2 and 3 of the text are obtained easily:

$$s_r = \sum_{k=1}^{m} w_1(X_k)^r=1+u_1^r+u_2^r+\cdots \quad (2)$$

and

$$t_r = \sum_{k=1}^{3} w_2(X_k)^r=1+x_1^r+x_2^r. \quad (3)$$

Equation 4 is then derived by means of Theorem 5.

**Example 2.** (the derivation of Eq. 8 of the text). Equation 5 of the text is obtained easily by Definition 3. The codomain $\mathbf{X}$ contains bond-figures:

$$\mathbf{X}=\{\phi, -, =\}.$$

The weights of them are given as follows:

$$w_1(\phi)=1,\; w_1(-)=x_1,\; w_1(=)=0 \text{ and}$$
$$w_2(\phi)=1,\; w_2(-)=x_1,\; w_2(=)=x_2.$$

Hence, two type of bond-figure inventories are easily obtained:

$$s_r = \sum_{k=1}^{3} w_1(X_k)^r=1+x_1^r \quad (6)$$

and

$$t_r = \sum_{k=1}^{3} w_2(X_k)^r=1+x_1^r+x_2^r. \quad (7)$$

In the text, $s_r$ and $t_r$ are denoted as $t_{ar}$ and $t_{br}$, respectively. Theorem 5 gives Eq. 8 in this case.

**8.** Theorem 5 can be easily extended to the case in which the domain $\mathbf{D}$ has three or more orbits. All the proofs described above hold the generality in the extended case. Such extended items are given below:

Domain: $\mathbf{D}=(\mathbf{D}_j)$ for $j=1, 2, \cdots n$.

Orbits of the domain:

$\mathbf{D}_j=\{d_{jk}\}$ for $k=1, 2, \cdots |\mathbf{D}_j|, j=1, 2, \cdots n$.
Codomain: $\mathbf{X}=\{X_k\}$ for $k=1, 2, \cdots m$.
Function (Configuration): $f$: $\mathbf{D} \rightarrow \mathbf{X}$.
Weight of a function (conriguration):

$$W(f) = \prod_{j=1}^{n} \left( \prod_{d\in \mathbf{D}} w_j(f(d)) \right).$$

Cycle structure of $\mathbf{H}$:

$[i_{jk}]$ ($k=1$ to $|\mathbf{D}_j|$) for $\mathbf{D}_j$ ($j=1$ to $n$),

wherein

$$\sum_{k=1}^{|\mathbf{D}_j|} k i_{jk} = |\mathbf{D}_j| \quad (j = 1,\ 2, \cdots n).$$

Cycle index of $\mathbf{H}$:

$$Z(\mathbf{H}) = \frac{1}{|\mathbf{H}|} \sum_{H\in\mathbf{H}} \left( \prod_{j=1}^{n} \left( \prod_{r=1}^{|\mathbf{D}_j|} s_{jr}^{i_{jr}} \right) \right).$$

Counting polynomial:

$$\sum_{(p_{jk})} B_{(p_{jk})} \left( \prod_{j=1}^{n} \left( \prod_{k=1}^{m} w_j(X_k)^{p_{jk}} \right) \right)$$
$$= Z(\mathbf{H}, \sum_{k=1}^{m} w_j(X_k)^r \text{ (for all } j)).$$

The summation concerned with $(p_{jk})$ is taken over all partitions of $|\mathbf{D}_j|$ represented by:

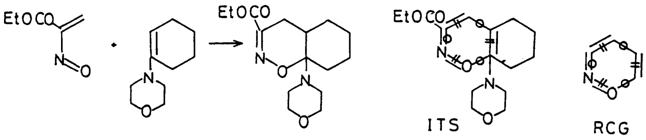
$$\sum_{k=1}^{m} p_{jk} = |\mathbf{D}_j| \quad \text{for } j = 1,\ 2, \cdots |\mathbf{D}_j|\ .$$

## Appendix 2

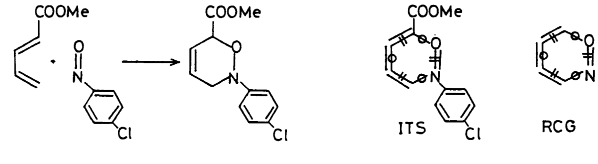
This appendix collects several reactions reported in the literature in order to exemplify the RC graphs of Tables 8 and 10. The examples have been taken from D. L. Boger, *Tetrahedron*, **39**, 2869 (1983); S. B. Needleman and M. C. C. Kuo, *Chem. Rev.*, **62**, 405 (1962); and some original articles. This list contains imaginary transition structures and RC graphs along with conventional reaction diagrams.

The RC graphs which do not appear in this list, but in Table 10, provide us with useful suggestions that would help in the development of new reactions. For example, the

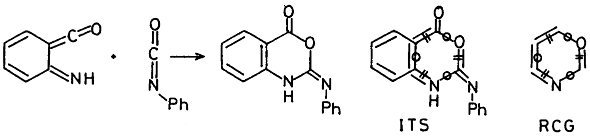
(1-1) Cycloaddition of a vinylnitroso compound with an enamine. (T. L. Gilchrist, D. A. Lingham, and T. G. Roberts, *J. Chem. Soc., Chem. Commun.*, **1979**, 1089).



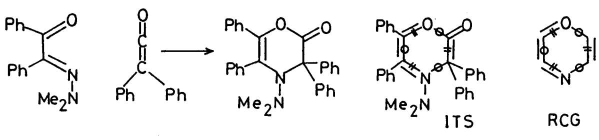
(1-2) Cycloadition of a diene with a nitroso compound. (G. Kreeze and J. Firl, *Tetrahedron Lett.*, **1965**, 1163).



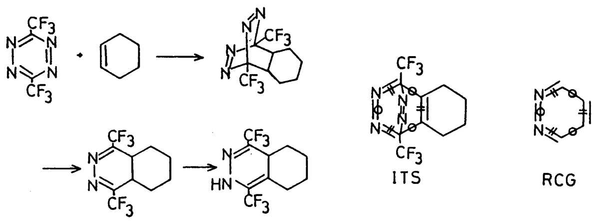
(1-3) Cycloaddition of a reactive *o*-quinone methide ketene with phenyl isocyanate. (H. Herlinger, *Angew. Chem.*, **76**, 437 (1964)).



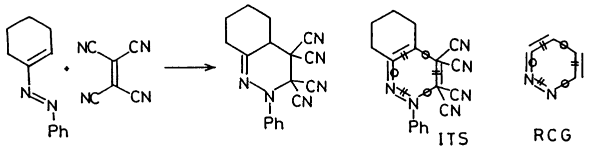
(1-4) Cycloaddition of a hydrazone with diphenylketene. (R. Gommper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969)).



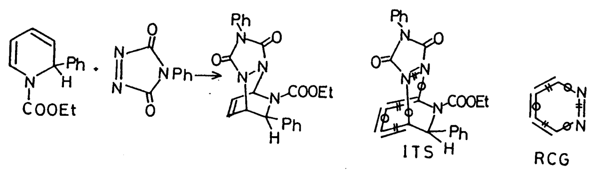
(1-5) The reaction of a 1,2,4,5-tetrazine with cyclohexene. (M. G. Barlow, R. N. Haszeldine, and J. A. Pickett, *J. Chem. Soc., Perkin Trans. 1*,**1978**, 378).



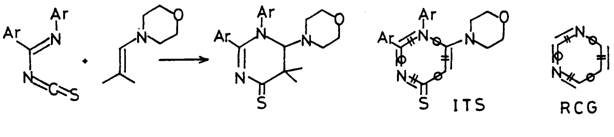
(1-6) Cycloaddition of 1-phenylazocyclohexene with a dienophile. (L. Caglioli, G. Rosini, P. Tundo, and A. Vigevari, *Tetrahedron Lett.*, **1970**, 2349).



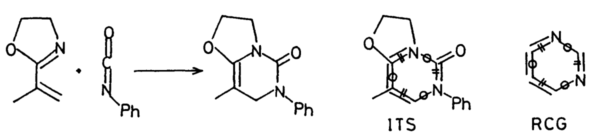
(1-7) Cycloaddition of *N*-ethoxycarbonyl-1,2-dihydropyridine with 4-phenyl-4*H*-1,2,4,-triazole-3,5-dione. (E. E. Knaus, F. M. Pasutto, C. S. Giam, and E. A. Swinyard, *J. Heterocycl. Chem.*, **13**, 481 (1976)).



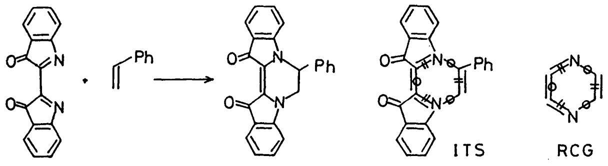
(1-8) The reaction of an imidoyl isothiocyanate with an enamine. (H. M. Blatter and H. Lukaszewski, *J. Org. Chem.*, **31**, 722 (1966)).



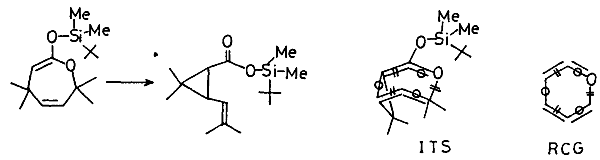
(1-9) Cycloaddition of 2-isopropenyl-2-oxazoline with phenylisocyanate. (A. E. Seelinger, W. Diepers, R. Feinauer, R. Nehring, W. Thier, and H. Hellmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 875 (1966)).



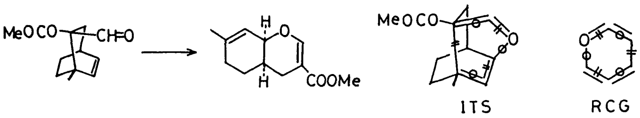
(1-10) Cycloaddition of dehydroindigo with an olefin. (R. Pummerer and E. Stieglitz, *Ber.*, **75**, 1072 (1942)).



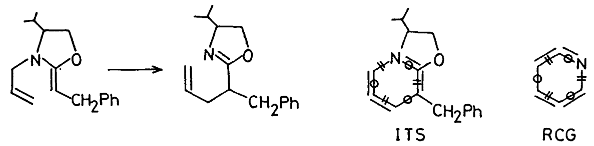
(2-1) The alicyclic Claisen rearrangement. (R. L. Funk and J. D. Munger, Jr., *J. Org. Chem.*, **50**, 707 (1985); A. G. Cameron and D. W. Knight *Tetrahedron Lett.*, **26**, 3503 (1985)).



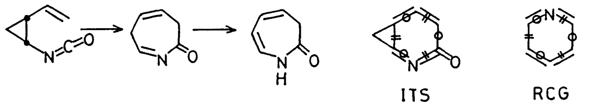
(2-2) The retro-Claisen rearrangement. (R. K. Boeckman, C. J. Flann, and K. M. Poss, *J. Am. Chem. Soc.*, **107**, 4359 (1985)).



(2-3) The Claisen rearrangement of a ketene *N*-allyl-*N*,*O*-acetal. (H. Hope and M. D. Yanuck, *J. Am. Chem. Soc.*, **107**, 443 (1985)).



(2-4) The rearrangement of a cyclopropane derivative. (E. Vogel and R. Erb, *Angew. Chem.*, **74**, 76 (1962)).



Claisen rearrangement (2-1) and the retro one (2-2) have already been investigated. Although the N-analog of the Claisen rearrangement is a known reaction (2-3), a retro-rearrangement has never been reported, to the best of our knowledge.

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21) For the treatment in which only edges are considered in the same parent BRG, see Ref. 17b.

22) The equivalent problem has been dealt with previously by a difrerent approach,[3a] but the result is different from ours.

23) Hendrickson's manual enumeration of reaction types (Table 1 of Ref. 3a) corresponds to the cases of $k_1$=0—3, $k_2$=0—3 collected in Table 9. His enumeration is limited only to that of RCG pairs in the present sense. Although his approach has introduced a $\sigma$-shell as a novel concept to solve the problem, a manual enumeration tends to overlook several possible reaction types. In fact, his list (Table 1) contains different values from the results of our work at $B$=0, NO, $C_4Z_2$(O); $B$=2 (O), O, $C_3Z_3$(V); $B$=2 (P), $N_2O$ and $NO_2$(V); $B$=3 (Δ), N and O, $C_4Z_2$ (O); $B$=3 (Δ), NO $C_4Z_2$ (M); and $B$=3 (Δ), N and O, $C_3Z_3$ (L). As a result, the total number of reaction types listed in Table 1 (Ref. 3a) is 957, although the corresponding number of RCG pairs in our result (Table 9) is calculated to be 964.

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