An Algebraic Model for the Rearrangements of 2-Bicyclo[2.2.1]heptyl Cations[1]

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Abstract: Procedures for deriving and analyzing the multiple-rearrangement products of bicyclo[2.2.1]heptyl carbocation derivatives (norbornyl cations) are presented. Concepts from group and graph theory are utilized to provide insight and computational algorithms; however, the principal results are presented as coset graphs which can be derived and applied without group theory. The coset graphs act as road maps for determining sequences of Wagner–Meerwein rearrangements, 6,2-*endo*-hydride shifts, and 3,2-*exo*-hydride shifts which interconvert given norbornyl cations. Other rearrangements also may be incorporated into the model. Computer programs such as the PL/I coded ORNOCARE (Oak Ridge Norbornyl Cation Rearrangement Program) may be used instead of the coset graphs if desired. Operating instructions and a listing of ORNOCARE are included in the microfilm supplement.

The objective of this paper is to develop a model based on permutation group theory[2] which can be used to find sequences of rearrangements which will convert a given substituted 2-bicyclo[2.2.1]heptyl cation, herein called norbornyl cation, into any other given permutationally isomeric norbornyl cation. This chemical problem may be restated in terms of combinatorial group theory, and we will be concerned mainly with the aspects of group theory described by Magnus, Karrass, and Solitar[3] and by Coxeter and Moser.[4] In order to simplify the discussion, the derivation of the model is based on three rearrangement mechanisms which are backed by substantial experimental verification; however, additional rearrangements can be added to the mathematical framework. We will show that the three rearrangement mechanisms alone can be combined in various sequences to produce all possible rearrangement products.

Notations for Rearrangement Mechanisms

Norbornyl cations are known to undergo several unimolecular rearrangement reactions including the Wagner–Meerwein rearrangement,[5,6] the 6,2-*endo*-hydride shift,[7-22] and the 3,2-*exo*-hydride shift.[16,19-23]

Figures 1 and 2 illustrate the symbolism used herein. The rearrangements are illustrated in Figure 2, in which for convenience the carbocations are denoted as classical structures. The 11 substituent sites are designated (arbitrarily) by the letters A–K. The seven skeletal sites are numbered one–seven beginning at the bridgehead adjacent to the positive charge, proceeding through that site around the six-membered ring, and ending with the apex (*i.e.*, the usual numbering system). The location of the charge also determines the handedness of the skeleton which is designed (+) for the right-handed and (−) for left-handed form as shown in Figure 1. Symbols such as B(1) and 2(1) in the cation in the upper right-hand corner of Figure 2 specify that substituent site B contains substituent 1 and skeletal site 2 contains skeletal carbon atom 1. The eleven letters, seven digits, and one chirality descriptor in a full designator such as BAKJEGFIHDC2174563(−) in Figure 2 are read from left to right. The first letter specifies that substituent 1 is on site B; the second letter specifies that substituent 2 is on site A; . . . ; the eleventh letter

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

(2) The use of permutation operators to describe molecular rearrangements is well established in the chemical literature. See the following and the references quoted therein: (a) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem., Int. Ed. Engl.*, 9, 703 (1970); (b) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *ibid.*, 10, 687 (1971); (c) W. G. Klemperer, *J. Amer. Chem. Soc.*, 94, 6940 (1972); (d) *ibid.*, 95, 2105 (1973); (e) W. Hässelbarth and E. Ruch, *Theor. Chim. Acta*, 29, 259 (1973).

(3) W. Magnus, A. Karrass, and D. Solitar, "Combinatorial Group Theory: Presentations of Groups in Terms of Generators and Relations," Interscience, New York, N. Y., 1966.

(4) H. S. M. Coxeter and W. O. J. Moser, "Generators and Relations for Discrete Groups," Springer-Verlag, New York, N. Y., 1965.

(5) G. Wagner, *J. Russ. Phys. Chem. Soc.*, 31, 680 (1899).

(6) J. A. Berson, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.

(7) The 6,2-hydride shift in 2-bicyclo[2.2.1]heptyl cations is formally analogous to the 1,3-hydride shift and also to the type of 1,3 shift which occurs when hydrogen migrates in protonated cyclopropanes. See, for example, R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, 89, 880 (1967); D. Fărcasiu, C. Kascheres, and L. H. Schwartz, *ibid.*, 94, 180 (1972); C. J. Collins, *Chem. Rev.*, 69, 543 (1969).

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(9) W. E. Doering and A. R. Wolf, *Perfum. Essent. Oil Rec.*, 42, 414 (1951).

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(11) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, 86, 4913 (1964).

(12) A. Colter, E. C. Friederich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 378 (1965).

(13) J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, 87, 4016 (1965).

(14) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, 88, 1556, 1558 (1966).

(15) B. M. Benjamin and C. J. Collins, *Tetrahedron Lett.*, 5477 (1966).

(16) C. J. Collins and M. H. Lietzke, *J. Amer. Chem. Soc.*, 89, 6566 (1967).

(17) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, 89, 1652 (1967).

(18) V. F. Raaen, B. M. Benjamin, and C. J. Collins, *Tetrahedron Lett.*, 2613 (1971).

(19) M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, 86, 5680 (1964).

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(21) G. A. Olah, A. M. White, J. R. De Member, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 92, 4627 (1970).

(22) C. J. Collins and C. E. Harding, *J. Amer. Chem. Soc.*, 91, 7194 (1969); *Justus Liebigs Ann. Chem.*, 745, 124 (1971).

(23) Rearrangements involving 3,2-*exo*-methyl shifts (Nametkin rearrangements) also are known to occur; *e.g.*, S. S. Nametkin and L. Brüssoff, *Justus Liebigs Ann. Chem.*, 459, 144 (1927); *J. Prakt. Chem.*, [2] 135, 155 (1932). 3,2-Endo shifts in general are inhibited in 2-bicyclo[2.2.1]heptyl compounds but documented examples of 3,2-*endo*-hydride shifts do exist. See A. W. Bushell and P. Wilder, Jr., *J. Amer. Chem. Soc.*, 89, 5721 (1967); P. Wilder, Jr., and W. C. Hsieh, *J. Org. Chem.*, 36, 2552 (1971).
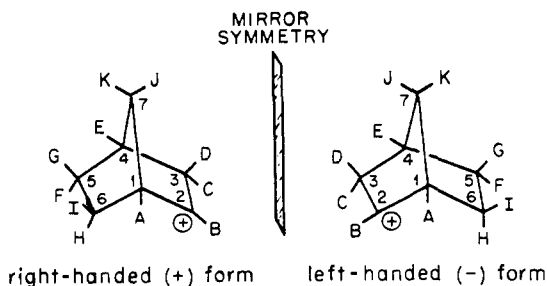
Figure 1. Notational conventions adopted to represent sites on the right- and left-handed norbornyl cations.

specifies that substituent 11 is on site C; the first digit specifies that skeletal carbon atom 1 is on site 2; . . . ; the seventh digit specifies that skeletal carbon atom 7 is on site 3; and the skeletal chirality is given as left handed $(-)$.

The full designators for the carbocations before and after a rearrangement provide an algebraic description of the rearrangement; for example, the Wagner–Meerwein rearrangement is defined by the permutation operator

$$W \equiv \begin{pmatrix} ABCDEFGHIJK1234567 + - \\ BAKJEGFIHDC2174563 - + \end{pmatrix}$$

To maintain permutation operator notation throughout, two chirality characters are appended to the designator to represent the chirality of the cation and its enantiomer. The operator may be read as substituent 1 goes from site A to site B, substituent 2 goes from site B to site A, . . . , skeletal carbon 1 goes from site 1 to site 2, . . . , and the skeletal chirality of a right-handed carbocation is reversed from $(+)$ to $(-)$ and vice versa for the left-handed cation. The permutation may also be resolved into cycles and rewritten as

$$W \equiv [(AB)(CK)(DJ)(FG)(HI)(E)$$
$$(12)(37)(4)(5)(6)(+ -)] \quad (1)$$

where two characters in parentheses indicate a transposition of the objects on the two sites (e.g., the substituents on sites A and B are interchanged) and a single character in parentheses indicates no change at that site. The transposition $(+ -)$ signifies a reversal of skeletal handedness. Similarly, rearrangements for the 6,2-hydride shift and 3,2-hydride shift may be written

$$6 \equiv [(BI)(CF)(DG)(JK)(A)(E)(H)$$
$$(26)(35)(1)(4)(7)(+ -)] \quad (2)$$

and

$$3 \equiv [(AE)(BC)(FH)(GI)(D)(J)(K)$$
$$(14)(23)(56)(7)(+ -) \quad (3)$$

respectively.

If the product from one rearrangement acts as the reactant for a consecutive rearrangement, the permutation operators are applied sequentially. For example, a Wagner–Meerwein rearrangement (W) followed by a 3,2-hydride shift (3) is denoted as a "word,"[3] $W3$ based on an alphabet composed of the characters W, 6, and 3.

Isomer Designation

The next step in defining the model is to develop a convention for designating the norbornyl isomers,
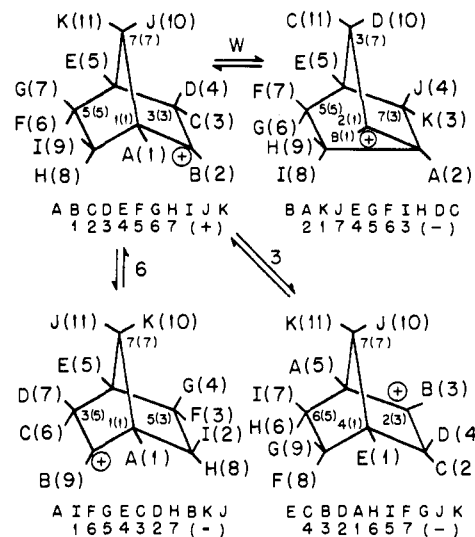
Figure 2. Norbornyl cation rearrangement mechanisms for the Wagner–Meerwein (W), 6,2-hydride shift (6), and 3,2-hydride shift (3) rearrangements. The drawing illustrates the derivation of the generator permutation operators (see text).

taking account of indistinguishable substituents and indistinguishable skeletal atoms. Following traditional organic structure notation, we omit positional information for the nonlabeled hydrogen atom substituents and the nonlabeled skeletal carbon atoms and let h and c designate the numbers of such unlabeled atoms. Consequently, a designator will require $l = 11 - h$ letters, $d = 7 - c$ digits, and one handedness indicator. This designator is based on an arbitrarily defined sequential ordering for the l substituents followed by the d labeled skeletal atoms. The site for the jth substituent $(j = 1, 2, \ldots, l)$ is given by the jth letter L_j of the designator, and the site for the mth labeled skeletal atom $(m = 1, 2, \ldots, d)$ is given by the mth digit D_m, which is the $(l + m)$th symbol of the designator. If two indistinguishable substituents are present in the jth and kth positions $(j < k)$ of the declared sequence, the position (site) letters L_j and L_k are ordered alphabetically. A similar rule holds for the numerical ordering of two skeletal site digits D_m and D_n $(m < n)$ when two indistinguishable labeled skeletal atoms are present. For example, a camphor cation with a labeled methyl group in the 7-syn position (J in Figure 1) and a labeled skeletal atom in the 3 position would be designated as BJAK3+

BJAK3+
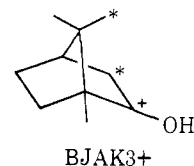
if the sequence is declared to be (OH, CH$_3$*, CH$_3$, CH$_3$, C*).

Group Presentations

The three permutation operators W, 6, and 3 are the generators for an intransitive permutation group[24,25] G

(24) A remarkably clear discussion of "substitution" (permutation) group theory is given in W. Burnside, "Theory of Groups of Finite Order," Cambridge University Press, Cambridge, England, 1897, Chapters 8 and 10 (a reprint from Dover Press is available).

(25) M. Hall, Jr., "The Theory of Groups," Macmillan, New York, N. Y., 1957, Chapter 5.

on the 20 characters of the set $S = S_1 + S_2 + S_3$, where $S_1 = (ABCDEFGHIJK)$, $S_2 = (1234567)$, $S_3 = (+ -)$. An intransitive permutation group is one which does not contain permutations changing a symbol into every other symbol of S. The sets of transitivity for an intransitive group are those subsets of symbols in which all symbols are interchanged, and the transitive subsets of G are S_1, S_2, and S_3. The intransitive group G may be considered a *subdirect product*[25] of the transitive groups G_1, G_2, and G_3 where G_i ($i = 1, 2, 3$) is the group formed when all symbols except those of set S_i are suppressed. In general, an intransitive permutation group may be considered to be a subgroup of the Cartesian product of transitive groups. The Cartesian product is a group composed of elements containing all possible combinations of elements from the substituent groups; however, in this case the intransitive group generated by W, 6, and 3 is the entire Cartesian product of G_1, G_2, and G_3.[26a] Furthermore, it may be shown that G_1, G_2, and G_3 are the symmetric permutation groups[26b] of degree 11, 7, and 2, respectively; as a consequence, the order of G is $11! \times 7! \times 2!$ or approximately 4×10^{11}. For convenience we define the group G_{13} as that which occurs when the set S_2 is suppressed and the group G_{23} as that which occurs when the set S_1 is suppressed.

The group G_{13} defines the permutations of the substituent set and of skeletal chirality. This group may be presented[3,4] in terms of the three generators

$$\tilde{W} \equiv [(AB)(CK)(DJ)(FG)(HI)(E)(+ -)] \qquad (4)$$

$$\tilde{6} \equiv [(BI)(CF)(DG)(JK)(A)(E)(H)(+ -)] \qquad (5)$$

$$\tilde{3} \equiv [(AE)(BC)(FH)(GI)(D)(J)(K)(+ -)] \qquad (6)$$

and the following defining relations, which describe many of the properties of the group in terms of this particular set of generators

$$\tilde{W}^2 = \tilde{6}^2 = \tilde{3}^2 = 1 \qquad (7)$$

$$(\tilde{W}\tilde{3})^{10} = (\tilde{W}\tilde{6})^{12} = (\tilde{6}\tilde{3})^{14} = 1 \qquad (8)$$

$$(\tilde{W}\tilde{6}\tilde{3}\tilde{W}\tilde{6})^3 \tilde{3}\tilde{W}\tilde{6}\tilde{W}\tilde{3} = 1 \qquad (9)$$

$$(\tilde{W}\tilde{3}\tilde{6}\tilde{3})^{10} = (\tilde{W}\tilde{6}\tilde{3}\tilde{6}\tilde{W}\tilde{6})^6 = (\tilde{W}\tilde{6}\tilde{3}\tilde{6}\tilde{W}\tilde{3})^5 =$$

$$(\tilde{W}\tilde{6}\tilde{3}\tilde{W}\tilde{6})^6 = (\tilde{6}\tilde{3}\tilde{W}\tilde{6}\tilde{3})^8 = (\tilde{W}\tilde{3}\tilde{6}\tilde{W}\tilde{3})^8 = 1 \qquad (10)$$

and

$$(\tilde{W}\tilde{6}\tilde{W}\tilde{6}\tilde{3}\tilde{6}\tilde{3})^9 = m \qquad (11)$$

where 1 is the identity operation and m is the mirror operation which changes chirality ($m^2 = 1$). The words $\tilde{W}^2$, $(\tilde{W}\tilde{3})^{10}$, etc., which are equivalent to the identity operation, are called relators.[3] The three relators $\tilde{W}^2$,

(26) (a) The presence of the entire Cartesian product was verified by forming the second level coset graph from Figures 4b and 4c (shown later) and noting that all 77 nodes are interconnected. (b) The connectiveness of the coset graphs in Figures 4b and 4d show that the sets S_1 and S_2 are transitive. To show that the corresponding groups G_1 and G_2 are the symmetric groups, we quote three theorems from H. Wielandt, "Finite Permutation Groups," Academic Press, New York, N. Y., 1964, pp 16, 34, 39. "Theorem 8.3. A transitive group of prime degree is primitive. Theorem 13.3. A primitive group which contains a transposition is a symmetric group. A primitive group which contains a 3 cycle is either alternating or symmetric." Since the permutation $\tilde{W}\tilde{6} = [(162)(375)(4)]$ is a 3 cycle and $\tilde{3}$ is an odd permutation, G_2 is the symmetric group SYM(7). "Theorem 13.9. Let p be a prime and G a primitive group of degree $n = p + k$ with $k \geqslant 3$. If G contains an element of degree and order p, then G is either alternating or symmetric (Jordan 1873)." Since the permutation $(\tilde{6}\tilde{3})^2 = [(BDCFGIH)(A)(E)-(J)(K)]$ is of degree and order 7 and $\tilde{W}$ is an odd permutation, the group G_1 is the symmetric group SYM(11).

$\tilde{6}^2$, and $\tilde{3}^2$ signify that each of the generators is involutory (*i.e.*, has a period of two); consequently, each generator is its own inverse (*e.g.*, $\tilde{W}^{-1} = \tilde{W}$). The relators describe the sequences of rearrangements which will transform any arbitrary norbornyl cation into itself. For example, the relator $(\tilde{W}\tilde{6})^{12}$ tells us that 12 pairs of steps alternating between Wagner–Meerwein rearrangements and 6,2-hydride shifts will reproduce the starting cation and thus produce a circuit (loop) of reactions. Because of the involutory nature of the generators, the inverse relator words also are valid and the reaction circuits can be traversed in either direction (*e.g.*, $[(\tilde{W}\tilde{6})^{12}]^{-1} = (\tilde{6}^{-1}\tilde{W}^{-1})^{12} = (\tilde{6}\tilde{W})^{12} = 1$). Each word in the defining relations 7–11 is cyclically reduced in that all cyclic permutations of the words produce valid relations (*e.g.*, $(\tilde{W}\tilde{3}\tilde{6}\tilde{3})^{10} = (\tilde{3}\tilde{6}\tilde{3}\tilde{W})^{10} = (\tilde{6}\tilde{3}\tilde{W}\tilde{3})^{10} = (\tilde{3}\tilde{W}\tilde{3}\tilde{6})^{10} = 1$). Relation 11 represents a mechanism for racemization containing 63 steps, but this may not be the shortest possible mechanism.

If all 11 substituents on the norbornyl cation are different, the shortest circuits possible are those described by relations 7–9. If, however, sets of indistinguishable substituents are present, many new circuits will appear; but all the circuits defined by the relations will still be present, though perhaps corresponding to multiple traverses of a smaller circuit. For every distinguishable isomer all these circuits are present in the coset graphs to be described later. The relators 7–10 and 15–17 were derived with the aid of a computer program (described later). The sufficiency of relations 8–11 as a complete abstract presentation of the group G_{13} has not been established rigorously and more relations may be required.

A presentation of the G_{23} permutation group for the skeletal carbon atom symbols and skeletal chirality symbols is

$$\hat{W} \equiv (12)(37)(4)(5)(6)(+ -) \qquad (12)$$

$$\hat{6} \equiv (26)(35)(1)(4)(7)(+ -) \qquad (13)$$

$$\hat{3} \equiv (14)(23)(56)(7)(+ -) \qquad (14)$$

$$\hat{W}^2 = \hat{6}^2 = \hat{3}^2 = 1 \qquad (15)$$

$$(\hat{W}\hat{3})^{10} = (\hat{W}\hat{6})^3 = (\hat{6}\hat{3})^2 = 1 \qquad (16)$$

$$(\hat{W}\hat{6}\hat{3})^{12} = (\hat{6}\hat{W}\hat{3}\hat{W})^{10} = 1 \qquad (17)$$

$$(\hat{W}\hat{3}\hat{6}\hat{W}\hat{3})^7 = m \qquad (18)$$

The order of the group is $2 \cdot 7! = 10,080$. We find by exhaustive enumeration that the 35-step path in (18) represents the shortest general racemization mechanism for the (hypothetical) fully labeled skeleton and that there are no pairs of products in G_{23} separated by more than 35 steps.

We shall not attempt to give a complete presentation for G; however, from (7), (8), (10), (15), and (16) we deduce that

$$W^2 = 6^2 = 3^2 = 1 \qquad (19)$$

$$(W3)^{10} = (W6)^{12} = (63)^{14} = 1 \qquad (20)$$

and

$$(W636W3)^5 = (63W63)^8 = 1 \qquad (21)$$

because the relators in (8) are all multiples of those in (16) and the fifth and third relators in (10) are multiples of the relators $(\hat{6}\hat{3}\hat{W}\hat{6}\hat{3})^2$ and $(\hat{W}\hat{6}\hat{3}\hat{6}\hat{W}\hat{3})^5$ derived from

(15) and (16). There are no relator words in G shorter than those in (19) and (20).

Additional Mechanisms

The above presentations are based on the rearrangements W, 6, and 3, but other arrangements such as the "double Wagner–Meerwein" rearrangement[27] D also may be operative. This mechanism operates through a 2-bicyclo[3.1.1]heptyl cation intermediate, but the overall result is described by the permutation

$$D = [(CK)(DJ)(FG)(HI)(A)(B)(E)$$
$$(37)(1)(2)(4)(5)(6)(+-)] \quad (22)$$

Although (22) is similar to (1), D cannot replace W, 6, or 3 in generating the group G. For example, the group generated by D, 6, and 3 is not transitive on subsets S_1 or S_2, because no paths from site A to site B or from site 1 to site 2 are possible. However, the generator sets $\{W, 6, 3\}$ and $\{W, 6, 3, D\}$ both generate the group G. Presentations based on the latter have relations such as

$$\hat{D}^2 = (\check{W}\hat{D})^2 = (\hat{D}\check{6})^3 = (\hat{D}\check{3})^6 = (\check{W}\hat{D}\check{3})^4 = 1 \quad (23)$$

and

$$\hat{D}^2 = (\hat{W}\hat{D})^2 = (\hat{D}\hat{6})^6 = (\hat{D}\hat{3})^6 = (\hat{W}\hat{D}\hat{3})^4 = 1 \quad (24)$$

in addition to all the relations described previously. Furthermore, D can be expressed in terms of W, 6, and 3. Two such relations for $\check{D}$ and $\hat{D}$ are the 23-step and 21-step processes

$$\check{D} = \check{3}(\check{6}\check{3})^3\check{W}\check{3}(\check{6}\check{3})^3\check{W}\check{3}(\check{6}\check{3})^3 \quad (25)$$

and

$$\hat{D} = (\hat{W}\hat{3})^2\hat{W}\hat{6}(\hat{W}\hat{3})^5\hat{6}(\hat{W}\hat{3})^2 \quad (26)$$

respectively. The extended generator set can produce appreciably shorter paths and the maximum number of steps in the shortest (most direct) path between remote pairs of fully labeled skeletal products is reduced from 35 to 14. The shortest skeletal racemization is the 13-step process

$$\hat{W}(\hat{D}\hat{6}\hat{W}\hat{3}\hat{W}\hat{6})^2 = m \quad (27)$$

whereas 35 steps are required in (18).

The double Wagner–Meerwein rearrangement will not be considered in the remaining sections of this paper.

Subgroups and Cosets

Up to this point, only the features of the problem which are common to rearrangements of all possible norbornyl cations have been discussed. We now consider the specializations which occur when some or all of the skeletal atoms or substituents are indistinguishable.[28]

(27) (a) W. Hückel and H. J. Kern, *Justus Liebigs Ann. Chem.*, **728**, 49 (1969). Aso see references quoted in (b) C. J. Collins and C. K. Johnson, *J. Amer. Chem. Soc.*, **95**, 4766 (1973).

(28) The number of distinguishable norbornyl cations depend on the type of substituents present. For example, if there are seven hydrogen atoms, three methyl atoms, one hydroxyl group, six unlabeled skeletal atoms, and one labeled skeletal atom the number of possible isomers is

$$\frac{11!}{7!\cdot3!\cdot1!}\frac{7!}{6!\cdot1!}\frac{2!}{1!\cdot1!} = 18,480$$

See R. S. Burington and D. C. May, "Handbook of Probability and Statistics with Tables," Handbook Publishers, Sandusky, Ohio, 1953, p 26.
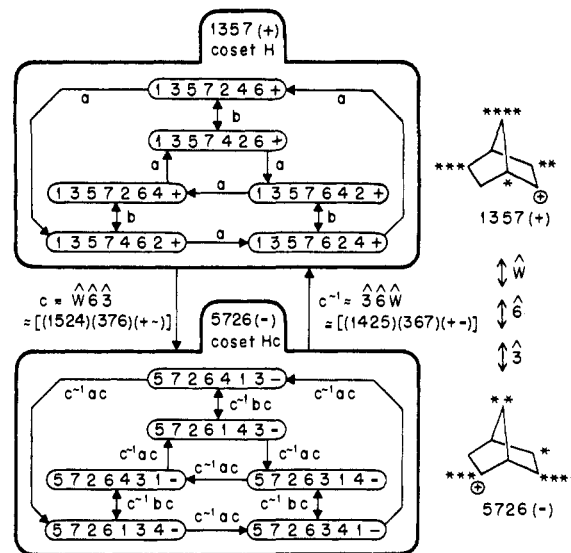
Figure 3

Figure 3. Graphical interpretation of coset and subgroup concepts. The subgroup H generated by permutations a and b (see text) interconverts the indistinguishable isomers of $1357(+)$. The coset-representative permutation c rearranges each isomer of $1357(+)$ into a correspondingly positioned isomer of $5726(-)$ (*e.g.*, $1357264+ \rightarrow 5726431-$). Thus the conversion of $1357(+)$ to $5726(-)$ may be accomplished by any of the permutations in the coset Hc (*e.g.*, $1357246+ \rightarrow 5726431-$) with abc, ba^2c, $a^{-1}bac$, etc., forming an equivalence class of words for the permutaton). The indistinguishable isomers of $5726(-)$, are interconverted by subroutine H' which is conjugate to H and generated by $c^{-1}ac$ and $c^{-1}bc$.

To illustrate the situation, suppose we have the arbitrary quadruply labeled starting cation $1357(+)$ with declared sequence [C*, C**, C***, C****] (see Figure 3). This cation will have three indistinguishable carbon atoms on skeletal sites 2, 4, and 6; consequently, there are $3! = 6$ quasi-isomers of $1357(+)$ which cannot be distinguished. The six permutations which interconvert these indistinguishable quasi-isomers are the identity [(1)(2)(3)(4)(5)(6)(7)]; the transpositions [(24)(1)(3)(5)(6)(7)], [(26)(1)(3)(4)(5)(7)], and [(46)(1)(2)(3)(5)(7)]; and the 3-cycle permutations [(246)-(1)(3)(5)(7)] (*i.e.*, atom at site 2 goes to site 4, etc.; 2 → 4 → 6 → 2) and [(264)(1)(3)(5)(7)], since these are the only permutations which leave the atoms on sites 1, 3, 5, and 7 unmoved. The six permutations form a group H which is a subgroup of G. This particular subgroup H is an intransitive permutation group with five transitivity sets (four sets with one character and one set with three characters). This subgroup which is a direct product of four SYM(1) and one SYM(3) permutation groups may be defined in terms of two subgroup generators

$$a = (246)(1)(3)(5)(7)$$

$$b = (24)(1)(3)(5)(6)(7)$$

and the defining relators

$$a^3 = b^2 = (ab)^2 = 1$$

Furthermore, the subgroup generators can always be expressed in terms of the group generators. We find

empirically that a and b in the above example can be expressed by the relations

$$a = \hat{6}(3\hat{W})^2(\hat{6}3\hat{W})^2 3\hat{W}3$$

and

$$b = (\hat{6}3\hat{W}3\hat{W}3\hat{W})^2(\hat{6}3\hat{W})^2 3\hat{W}\hat{6}3(\hat{W}3)^4$$

One systematic method for deriving subgroup generators is the Schreier method[3] which is described briefly in Appendix I.

Figure 3 is a portion of a graph showing two nodes, each of which contains six "subnodes." The nodes represent distinguishable norbornyl cations and the subnodes represent the indistinguishable quasi-isomers of the respective cations. The upper node, representing the arbitrary starting cation 1357(+), contains subnodes joined together by lines corresponding to the rearrangements produced by the subgroup generators a and b defined above. This pattern of lines and subnodes is the Cayley diagram[3,4,29] for the subgroup H generated by a and b. If the starting cation undergoes the arbitrary rearrangement sequence $c \equiv \hat{W}\hat{6}\hat{3} = [(1524)(367)(+-)]$, each of the indistinguishable isomers of 1357(+) will be converted into a specific indistinguishable isomer of 5726(−) at the corresponding position in the lower node of Figure 3. The indistinguishable isomers of 5726(−) may be interconverted by a subgroup H' generated by $a' = c^{-1}ac = [(134)(2)-(5)(6)(7)]$ and $b' = c^{-1}bc = [(14)(2)(3)(5)(6)(7)]$ with $a'^3 = b'^2 = (a'b')^2 = 1$. The subgroups H and H' are called conjugate subgroups of G.[24] The set of all permutations in G which will convert *any* arbitrary indistinguishable isomers of 1357(+) into *all* the different indistinguishable isomers of 5726(−) is the set $\{1c, ac, a^2c, bc, bac,$ and $ba^2c\}$, which is written more concisely as Hc. The sets of permutations H and Hc are right cosets of H in G. They are written as *right* cosets because (in this paper) the permutations in a word are evaluated from left to right. To transform one coset into another, we right multiply *all* the permutations of a coset by *any* generator sequence which transforms any member of the first coset into any member of the second coset (*e.g.*, $Hc \rightarrow H1$ by $Hcc^{-1} = H$). For this example in which there are $2\cdot7!/3! = 1680$ distinguishable cations, the $2\cdot7!$ permutations of G_{23} are divided into $r = 1680$ cosets with 3! permutations in each.

Although any member, j, of the distinguishable cations may be chosen as the starting cation, each new choice will produce a different subgroup H_j; however, the subgroups $H_j (j = 1, \ldots, r)$ are closely related in that they are conjugate subgroups of G. The significance of the subgroup H_j associated with cation C_j is that it contains all permutations which transform C_j into an indistinguishable isomer of itself. If H_j is defined by subgroup generators and relators written as words in the generators of G, combinations of the subgroup generators will provide sequences of norbornyl rearrangements which can, in combination with the relators of G, provide a description of all rearrangement circuits involving C_j.

In the general case, any choice of the subgroup H

permits the resolution of G into a union of disjoint cosets

$$G = H + Hu_2 + Hu_3 + \ldots + Hu_r$$

where u_j ($j = 2,3,\ldots, r$) are permutations from G but not from H and are called coset representatives. Any member of a coset Hu_j may be used as the coset representative u_j for that coset. Our present concern is to note how the complete set of cosets changes under the action of the group generators $\hat{W}$, $\hat{6}$, and $\hat{3}$. To do this we multiply each coset by a generator such as $\hat{W}$. The effect will be either to leave Hu_j unchanged or to change it into some other coset, thus yielding a *permutation* of the r cosets which we denote by the *representation*[30]

$$G^H(W) = \begin{pmatrix} H, & Hu_2, & \ldots, & Hu_r \\ HW, & Hu_2W, & \ldots, & Hu_rW \end{pmatrix}$$

The simplest nontrival example arises when there is only one distinguishable substituent (or skeletal atom) on the norbornyl cation. In this case the subgroup H fixes only one letter (or number) of the character set and the permutation of the representation is identical with the generator permutation. This fact will play a key role in the construction of coset graphs.
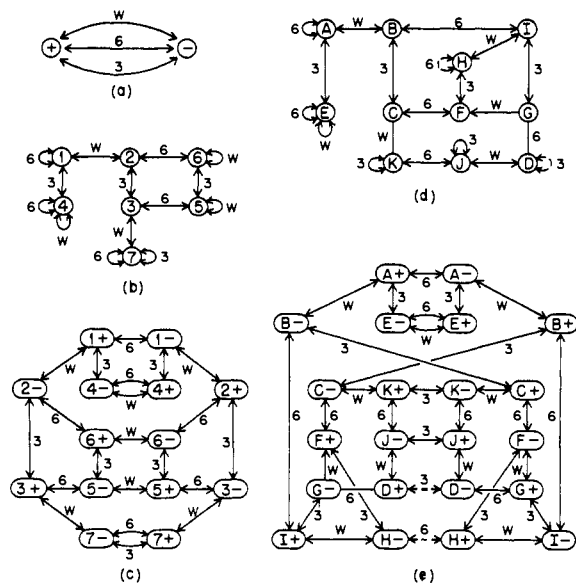
Coset Graphs

The interconversion of distinguishable norbornyl cations by the rearrangements (generator permutations) has a convenient graphical presentation in the form of a Schreier coset graph.[31] This coset graph is a graph $\Gamma(G, A, \{Hu_j\})$ for a group G with generating set $A = \{a_p\}$ acting *via* right multiplication upon the collection of right cosets $\{Hu_j\}$ of subgroup H in G. The vertices (nodes) of the graph are the cosets and the labeled and oriented edges (*i.e.*, the directed lines (arrows) used in chemical equations) depict the action of the elements of A upon the cosets. There is an edge labeled a_p from coset Hu_i to coset Hu_j if and only if $Hu_ia_p = Hu_j$. Each node of a coset graph is the initial point for p different edges and also is the terminal point for p different edges where p is the number of generators in the generator set. Any coset in the coset graph may be chosen as the origin node containing the identity permutation, and this assignment is made for the node representing the starting norbornyl cation.[32]

In this paper, the symbols placed within the nodes of the coset graphs represent the elements of the symbol set which are unchanged by the permutations of that particular coset acting upon the starting cation; consequently, the symbols within a node constitute the designator for a particular distinguishable norbornyl cation, and the designator is invariant to the choice of the starting cation.

(29) (a) A. Cayley, *Proc. London Math. Soc.*, **9**, 126 (1878); *Amer. J. Math.*, **1**, 174 (1878); (b) I. Grossman and W. Magnus, "Groups and Their Graphs," Random House, New York, N. Y., 1964.

(30) G. de B. Robinson, "Representation Theory of the Symmetric Group," University of Toronto Press, Toronto, 1961, pp 1–4.

(31) Schreier coset graphs are also called Schreier coset diagrams and *G* mod *H* graphs in the mathematical literature. They were introduced by (a) O. Schreier, *Abh. Math. Sem. Hamburgischen Univ.*, **5**, 161 (1927), and are discussed by (b) D. F. Stork, *Commun. Pure Appl. Math.*, **27**, 797 (1971). The first application of graph theory to a carbonium ion problem appears to be (c) A. T. Balaban, D. Fărcasiu, and R. Bănică, *Rev. Roum. Chim.*, **11**, 1205 (1966). Also see (d) A. Balaban, Ed., "Chemical Applications of Graph Theory," Academic Press, London, in press.

(32) The reason there is no preordained origin in a coset graph is the fact that coset graphs of *G* mod *H*₁ and *G* mod *H*₂ are graph isomorphic if and only if the subgroups *H*₁ and *H*₂ are conjugate in *G*.[31b] Two graphs are graph isomorphic if there is a one-to-one correspondence between the nodes of the two graphs and between the labeled, directed edges of the two graphs.

Figure 4. Coset graphs for norbornyl cation rearrangements. Dashed edges denote reaction in which the substituent on site H is shifted by a 6,2 shift or that D is shifted by a 3,2-shift; a nonhydrogen substituent may block the rearrangement. (a) Zero-level coset graph showing chirality permutation; (b) reduced first-level coset graph for the seven skeletal sites (1–7); (c) full first-level coset graph for the seven skeletal sites (1–7); (d) reduced first-level coset graph for the eleven substituent sites (A–K); and (e) full first-level coset graph for substituent sites.

The simplest nontrivial coset graph for the norbornyl cation problem is that shown in Figure 4a, which arises from the chirality operators of the generators. In this case there are no distinguishable substituents or skeletal atoms, and only two nodes occur corresponding to the right- and left-handed skeletons. The coset graphs shown in Figures 4b and 4d represent norbornyl cations with single distinguishable skeletal atoms and single distinguishable substituents, respectively, with the nodes for enantiomers superimposed. Figures 4c and 4e are coset graphs similar to 4b and 4d except that mirror image cations are presented as separate nodes. As a consequence, there are twice as many nodes in Figures 4c and 4e as there are in Figures 4b and 4d, respectively. The former are called full coset graphs and the latter reduced coset graphs. Figure 4a is a zero-level coset graph and Figures 4b–e are first-level coset graphs where the term "level" refers to the number of skeletal labels or distinguishable substituents in the norbornyl cation. All coset graphs in Figure 4 are determined directly from the group generators. To derive coset graph 4d, we first position 11 nodes containing the letters A–K in some pattern such as that shown in Figure 4d. By examination of the generator for W in eq 4, we see that we should connect A–B, C–K, D–J, F–G, H–I, and E–E. After labeling each of the connecting lines with a W, the process is repeated for the 6 and 3 generators of eq 5 and 6. Finally, the nodes are repositioned arbitrarily to make the graph as clear as possible. Note that Figure 4d presents nearly as much information as Figure 4e and requires only half as many nodes. In fact, we can keep track of handedness in a reduced graph by counting the reaction steps in a path to see if the number is even or odd. If the number is even, the final product has the same handedness as the starting product; otherwise the handedness is inverted.
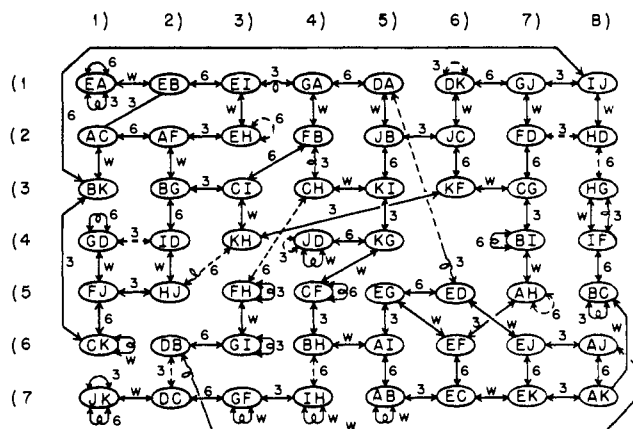
Figure 5. Reduced coset graph for disubstituted norbornyl cations. The chirality and transposition isomers are superimposed. If an "interchange symbol" (⇥) is encountered in a path, the two letters of subsequent nodes are read transposed until another interchange symbol is encountered. If the two substituents are indistinguishable, the interchange symbols may be ignored and all characters read in alphabetical order. If the number of steps in a path is even, the starting and final products have the same handedness, otherwise, they have opposite handedness (+, −). Dashed edges denote situations in which the substituent on site H is shifted by a 6,2 shift (6) or that on site D is shifted by a 3,2 shift (3); consequently, a nonhydrogen substituent may block the rearrangement. The following directory gives the row and column indices for the node labels ordered alphabetically

AB(7,5)	BD(6,2)	CG(3,7)	DK(1,6)	FK(3,6)
AC(2,1)	BE(1,2)	CH(3,4)	EF(6,6)	GH(3,8)
AD(1,5)	BF(2,4)	CI(3,3)	EG(5,5)	GI(6,3)
AE(1,1)	BG(3,2)	CJ(2,6)	EH(2,3)	GJ(1,7)
AF(2,2)	BH(6,4)	CK(6,1)	EI(1,3)	GK(4,5)
AG(1,4)	BI(4,7)	DE(5,6)	EJ(6,7)	HI(7,4)
AH(5,7)	BJ(2,5)	DF(2,7)	EK(7,7)	HJ(5,2)
AI(6,5)	BK(3,1)	DG(4,1)	FG(7,3)	HK(4,3)
AJ(6,8)	CD(7,2)	DH(2,8)	FH(5,3)	IJ(1,8)
AK(7,8)	CE(7,6)	DI(4,2)	FI(4,8)	IK(3,5)
BC(5,8)	CF(5,4)	DJ(4,4)	FJ(5,1)	JK(7,1)

The next case involves two substituents which may or may not be identical. By examining simultaneously two identical reaction sequences from two different starting nodes in a first-level coset graph, we derive a reduced second-level coset graph shown in Figure 5 with two fixed characters in each node. Figure 5 is reduced, with respect to handedness and to letter transposition, so that only 55 instead of 220 nodes are needed. A letter transposition is denoted by an "interchange symbol" (⟵⟋⟶) in a graph edge. If an interchange symbol is encountered in a path, the two letters of all subsequent nodes are read as if transposed until another interchange symbol is encountered. If the substituents are indistinguishable, the interchange symbols are ignored and the characters are read in alphabetical order. As an exercise in interpreting this "double-reduction" convention, the reader may verify that the semidetached subgraph with four nodes from the lower left corner of Figure 5 (reproduced as Figure 6a) is equivalent to the 16-node symmetrical coset graph shown in Figure 6b. Incidentally, this second-level subgraph represents all products with both substituents on the same carbon atom.

If more than two substituents are present, several copies of the first and second level coset graphs can be used jointly to play the game of "combinatorial chemistry." Objects such as chess pieces, each representing one or two of the substituents, are placed on the sub-
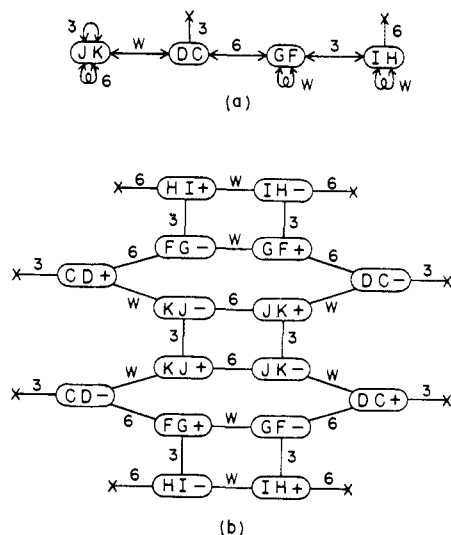
(a)

(b)

Figure 6. Comparison of reduced and full coset subgraphs for disubstituted norbornyl cation with both substituents on the same skeletal atom: (a) reduced coset subgraph from Figure 5; (b) full coset subgraph equivalent to part a.

stituent sites of the appropriate graphs and the objects are moved stepwise through a reaction sequence. Each object will operate under a different set of "blocking rules"[33] depending on which reactions, if any, are forbidden by the chemical properties of the substituents. Such techniques are simply graphical analogs for the blackboard manipulations organic chemists traditionally use, but the coset graphs provide a "roadmap" which makes the alternative routes more apparent.

Computer Implementation[34b]

A program ORNOCARE (Oak Ridge Norbornyl Cation Rearrangement) for the IBM-360 computer was coded by C. K. Johnson and P. R. Coleman using the dynamic array and string manipulation features of the PL/I language. The input parameters are the generator permutations, blocking conditions (based on substituent positions),[33] and path lengths[34a] for the reactions

(33) The "blocking rules" are logic specifications concerning the configurations of substituents which will essentially block a given rearrangement mechanism. For example, a 6,2-endo-shift rearrangement (6) will have a zero reaction rate constant if the shifting substituent on site H of the reactant cation is not a proton or deuteron. The same statement holds for site D in rearrangement 3 except that methyl groups also can shift (Nametkin rearrangement). The dashed lines in the coset graphs denote the paths where these problems can arise. Unfortunately, blocked reactions are not easily incorporated into the group theory treatment.

(34) (a) Many different reaction sequences (paths) connect the starting and terminal norbornyl cations, and we must have some basis for ranking the paths. The following discussion is kinetically indefensible. However, its only function is to provide an algorithm for determining the order in which the various pathways between cations (nodes) are printed out, leaving the final choice of the most appropriate routes to chemical intuition. The probability associated with a path is the product of probabilities p_e associated with each of the edges (reactions) in the path. If each edge is given a "length," l_e, defined by the equation $l_e = -\ln (p_e)$, the probability, P, for the path is

$$P = \prod_{\substack{\text{all edges} \\ e \text{ in path}}} p_e = \exp\left(-\sum_{\substack{\text{all edges} \\ e \text{ in path}}} l_e\right)$$

Consequently, a long path is less probable than a short path and the problem transforms to the computationally convenient shortest path problem. Oversimplifying even further, we ignore product and reactant specificity and assign "reaction path lengths" based on reaction type alone with $l(W) \leq l(6) \leq l(3)$. (b) The complete ORNOCARE program including program description, operating instructions, PL/I computer code, and example calculations is given in Appendix II. See paragraph at end of paper regarding supplementary material.

being used; the substituent sequence list; and the starting reactant (or reactants). As mentioned earlier, the program is not limited to the three rearrangements described previously. The output listing consists of a tabular form of the coset graph with columns for the reaction type and rows for the reaction products, an alphabetically ordered list of products with a shortest path[35-37] sequence of rearrangements leading from the reactant to each product and the overall permutation resolved into cycles for the algebraic product of the permutations in each path (i.e., the coset representative generated by the sequence). On option, the program internally forms an open tree (i.e., a graph without circuits) with duplicate nodes included, instead of a closed graph with duplicate nodes omitted, then sorts the products and prints out the p (say 10) shortest loop-free paths to each unique node. The program uses simple generator multiplication logic rather than coset enumeration procedures[35] from relators, so that the allowed list of reaction mechanisms and blocking conditions can be modified at will without recalculating a defining set of relators. The largest entire coset graph generated and analyzed by the program was the four-substituent coset graph with 15,840 nodes. About 4.5 min of IBM 360/91 time was required to form the graph and make the shortest path calculations and 500,000 bytes of core memory were used. Most of the time is spent checking for duplicate products. On the other hand, many questions of interest can be answered satisfactorily by simply computing the first few (say 6) reaction steps and by building the graph from the desired origin and terminal products simultaneously. All paths between the origin and terminal products up to a length of two times the number of reaction steps are found by this process, which uses only 10–15 sec of IBM 360/91 computer time and 150,000 bytes of core memory.

The result which is the most useful in practice is a listing of the 10 to 20 shortest loop-free paths between two given cosets, from which the chemist can select the most probable reaction path. The currently programmed approach of generating a tree of products (without eliminating duplicate products) followed by a sorting step can produce the desired result only if the cosets are sufficiently close together in terms of generator steps required, because the number of products grows geometrically with the number of steps. The range (number of steps) covered by this method can be improved by generating two smaller trees disjointly from roots at the starting and terminal nodes. The shortest paths are through nodes common to both trees (i.e., the nodes in the intersection) which may be identified by sorting and merging the products. An alternative is to generate as much of the closed graph as the computer can hold and to use one of the published methods[35,39] for finding multiple paths between nodes in a graph; a graph takes much more computing time (but much less memory) than a comparable tree. None of the above approaches utilize the group structure of

(35) S. E. Dreyfus, Oper. Res., 17, 395 (1969).

(36) R. B. Dial, Commun. ACM (Ass. Comput. Mach.), 12, 632 (1969).

(37) D. Braess, Computing, 8, 171 (1971).

(38) J. Leech, "Computational Problems in Abstract Algebra," Pergamon Press, Oxford, 1970, pp 21–36.

(39) S. Clarke, A. Krikorian, and J. Rausen, J. Soc. Ind. Appl. Math., 11, 1096 (1963).

the coset graph. A group-theoretic method which can find the paths without forming the coset graph or tree is described in Appendix I, but this algorithm has not been programmed.

Example

As an example of how the techniques developed here can be applied to a specific chemical problem, we examine the published results on the nitrous acid deamination of 3-*exo*-phenyl-3-hydroxyl- and 3-*endo*-phenyl-3-hydroxyl-2-*endo*-norbornylamines[40] which are shown in deuterated form as compounds I and II of Figure 7. The norbornyl cations formed by deamination of the nondeuterated analog of I and II are designated DC+ and CD−, respectively, with the declared sequence (phenyl, hydroxyl). Since both of the major substituents are on the same skeletal carbon atom, the coset subgraph in Figure 6 may be used to specify the complete set of allowed rearrangements assuming that the phenyl and hydroxyl substituents cannot undergo 3,2 or 6,2 shifts. In evaluating norbornyl reaction paths, there is good experimental evidence[19,21,22] that the probability ordering is $P(W) > P(6) \gg P(3)$. In the rearrangements of I and II the data[40] do not exclude a minute fraction of 3,2-hydride shift which we neglect, if it occurs, for present purposes. The six-membered circuit of alternating W and 6 reactions containing both DC+ and CD− is therefore the key feature of Figure 6 for this problem. However, note that racemization (*e.g.*, DC+ → DC−) cannot occur in this system unless a 3,2-hydride shift takes place.

Several deuterated derivatives of I and II were used in the study[40] with deuterium-labeled atoms herein designated as D_1, D_2, D_3, and D_4. Letters a–c attached to the compounds I–IV (see Figure 7) are used to specify specific deuterated isomers. The deuterated reactants used in this study are shown in Table I. The

Table I

Reactant	Substituents	Starting norbornyl cation
Ia	Ph, OH, D_1	DCB...(+)
IIa	Ph, OH, D_1	CDB...(−)
Ib	Ph, OH, D_2, D_3	DC·GI·(+)
Ic	Ph, OH, D_1, D_2, D_4	DCBG·K(+)

declared sequence for the cation designator is (Ph, OH, D_1, D_2, D_3, D_4). The dots in a cation designator denote items in the declared sequence which are not pertinent to that cation. With I fully labeled, the labeled atoms D_1, D_2, D_3, and D_4 would occur on sites B, G, I, and K, respectively, of a right-handed (+) skeleton. Examining the coset graph in Figure 4e, we find the following circuits in W and 6 involving these substituents considered individually.

Substituents
D_1, D_3 {$(B+)W(A-)6(A+)W(B-)6(\underline{I+})W(H-)6(H+)W-$
     $(\underline{I}-)6$}
D_2, Ph   {$(\underline{G+})W(F-)6(\underline{C+})W(K-)6(J+)W(D-)6$}
D_4, OH   {$(\underline{K+})W(C-)6(\underline{F+})W(G-)6(\underline{D+})W(J-)6$}

The underlined letters denote the sites occupied initially. From this we conclude that substituents on sites G, F,

(40) C. J. Collins, I. T. Glover, M. D. Eckart, V. F. Raaen, B. M. Benjamin, and B. S. Benjaminov, *J. Amer. Chem. Soc.*, **94**, 899 (1972).
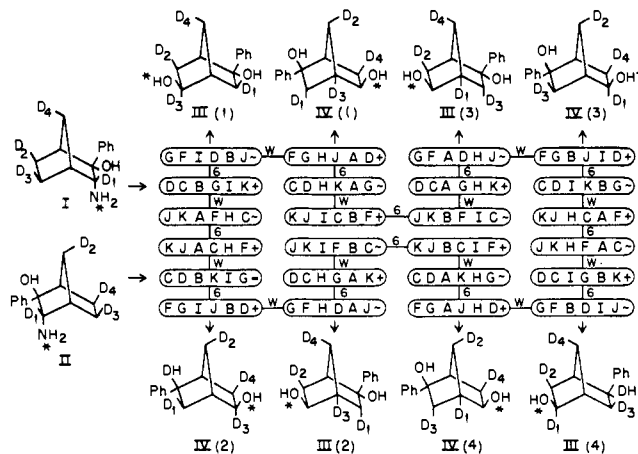

Figure 7. Coset circuit of alternating Wagner–Meerwein (W) and 6,2-hydride shift (6) rearrangements. The graph is used in tracing deuterium labels in the reactions I → III + IV and II → III + IV. The leaving amino and entering hydroxyl groups are marked by *'s.

C, K, J, and D are moved in circuits with 6 steps but substituents on A, B, H, and I require 8 steps; consequently, if distinguishable substituents are present on both types of sites, the circuit must contain 24 steps (*i.e.*, the last common multiple of 6 and 8). We also note that any substituent on site E is unmoved by the $W6$ series of reactions. The defining relation $(W6)^{12} = 1$ in (8) shows that 24 steps is the maximum number possible. If a reactant had both D_1 and D_3, and if they were indistinguishable, the circuit length would be 12 rather than 24 because the 8-step circuit would degenerate to a 4-step circuit since D_1 and D_3 are 4 steps apart in the 8-step circuit.

The 24-step coset circuit shown in Figure 7 is derived readily from Figures 4, 5, and 6 or from the coset circuits given above. Since each of the six original nodes of Figure 6 is repeated four times, there are now four times as many "source cations" which can produce different product molecules of types III and IV, as illustrated in Figure 7. Data on the yields of the deuterated isomers of III and IV obtained from Ia, IIa, and Ib are given in ref 40. In the actual experiment, reactant Ic was used instead of Ia to simplify the nmr analysis. The coset circuits show that the added deuterium atoms D_2 and D_4 move in circuits disjoint from the D_1 circuit; thus they do not introduce complications.

The methods developed herein also may be applied through computer programs such as ORNOCARE described previously. The advantages of computer implementation over coset graph implementation are that additional rearrangement mechanisms can be added easily if reasonable paths are not found with the three conventional mechanisms and that larger numbers of substituents can be handled. Example applications of the ORNOCARE program to chemical problems of current interest are described in the accompanying paper.[41]

In conclusion, we must stress the fact that the treatment in this paper is specifical to the 2-bicyclo[2.2.1]-heptyl cation system. The absence of three-dimensional point-group symmetry is the key factor which simplifies the treatment.

(41) C. J. Collins, C. K. Johnson, and V. F. Raaen, *J. Amer. Chem. Soc.*, **96**, 2524 (1974); also see ref 27b.
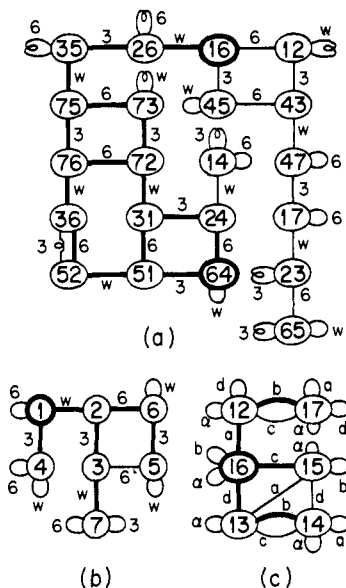
Figure 8. Coset graphs illustrating an algorithm for deriving the multiple paths between norbornyl cations. (a) Second-level reduced coset graph for norbornyl cations with two labeled skeletal atoms. The darkened lines indicate the five different paths with eight steps interconnecting nodes 16 and 64. (b) First-level reduced coset graph for one labeled skeletal atom. The darkened lines show the spanning tree of Schreier coset representatives with base at node one. (c) Reduced coset graph for subgroup with node number one fixed. The darkened lines indicate the subgroup coset representatives based on node 16.

Table II. Reidemeister-Schreier System of Subgroup Generators

(a1)	Group generators $W = (12)(37)(4)(5)(6)$ $6 = (26)(35)(1)(4)(7)$ $3 = (14)(23)(56)(7)$	(b2)	Schreier right coset representative relative to vertex 16
			$16 \to 12$ a
(b1)	Schreier right coset representatives relative to vertex 1		$16 \to 13$ d
			$16 \to 14$ db
			$16 \to 15$ c
	$1 \to 1$ ϕ		$16 \to 16$ ϕ
	$1 \to 2$ W		$16 \to 17$ ab
	$1 \to 3$ $W3$		
	$1 \to 4$ 3	(c2)	Schreier circuits for $16 \to 16$
	$1 \to 5$ $W63$		
	$1 \to 6$ $W6$		β_1 ϕ
	$1 \to 7$ $W3W$		β_2 α
			β_3 $a\alpha a$
(c1)	Schreier circuits for $1 \to 1$		β_4 $c\alpha c$
			β_5 $d\alpha d$
	α_1 ϕ		β_6 $ad\alpha da$
	α_2 $W6363W$		β_7 $db\alpha bd$
	α_3 $W3636W$		
			e_1 b
	a_1 6		e_2 cbc
	a_2 363		e_3 $ababa$
	a_3 $W6W6W$		
			f ada
	b $3W3$		
			g_1 $abca$
	c $W3W3W3W$		g_2 $acba$
	d_1 $W3W6W3W$		h $abdba$
	d_2 $W63W36W$		
			i cad
(a2)	Subgroup generators $\alpha = (1)(2)(3)(4)(5)(6)(7)$ $a = (26)(35)(1)(4)(7)$ $b = (27)(34)(1)(5)(6)$ $c = (27)(34)(56)(1)$ $d = (36)(45)(1)(2)(7)$		$j(=i^{-1})$ dac
			k_1 $cdbd$
			k_2 $dbdc$
			k_3 $dbcd$
			k_4 $dcbd$
			l $dbabd$

NOTE ADDED IN PROOF. **Other Chemical Systems.** The methods described herein have been used recently to formulate the rearrangement system for the 4-homoadamantyl (4-tricyclo[4.3.1.1^{3,8}]undecyl) cation described by J. E. Nordlander, F. Ying-Hsiueh Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3962 (1969). The permutation characters for this system are arranged in three orbits (sets of transitivity) with 11 skeletal, 17 substituent, and two counterion-handedness characters. The two postulated rearrangement mechanisms produce generators which are not involutory; thus the inverse generators are distinct from the forward generators. The generator set consists of left- and right-handed Wagner-Meerwein rearrangements (W and W^{-1}, respectively), and right- and left-handed 5,4-hydride shift rearrangements (5 and 5^{-1}, respectively). If a counterion (or if a bridged cation) is present, the presentation consists of the single relation $(W5)^{21} = 1$ and the order of the group is 42; however, if the counterion or a bridged cation can be neglected, the additional relations $W^6 = 5^6 = (5^2W^{-3})^4 = (5^2W^{-3})^4 = (W5^2W^{-1}5^2)^3 = (W5^{-2}W^{-1}5^2)^3 = (W5^{-1})^{21} = 1$ are required and the order of the group becomes $11! \times 17!$.

We also have found a simple method for extending the bicyclic norbornyl cation model to include the tricyclic brexyl [A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1613, 1615 (1965)] and longifolyl [G. Rücker, *Angew. Chem., Int. Ed. Engl.*, **12**, 798 (1973)] cations. These are related to the norbornyl cation by the addition of a two- to four-carbon bridge linking two substituent sites such as D-J, C-F, etc. The basic approach is to delineate a subgraph of the disubstituent coset graph (Figure 5) to include those site pairs sterically

reasonable for the bridge under consideration. The first two characters of the designator are then assigned to this bridge and the rearrangements restricted to keep those characters within the subgraph. An additional complication for the brexyl cation is the twofold axis of skeletal symmetry which occurs when the two-carbon-atom chain bridges sites D and J. This is taken into account by an additional generator which performs a twofold rotation of the cation. An extended, redundant character set with 9 skeletal site characters and 15 substituent site characters is used in order to maintain disjoint skeletal and substituent character sets. Double coset^{2e,3} graphs, G MOD (H and K) with K the subgroup of internal symmetry, are used to superimpose the cosets of G MOD H which are interconnected by the internal symmetry generators.

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Appendix I

A method for finding generator-sequence paths which does not require the calculation of the complete coset graph is described. For this method we utilize the

Schreier system of coset representatives and subgroup generators[3,42] and some techniques described by Sims[43] for manipulating permutation groups.

To illustrate the method, suppose we wish to find sequences of rearrangement reactions which will produce the hypothetical rearrangement

16+   64+
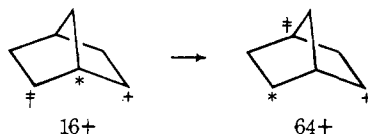
The second-level reduced coset graph for skeletal rearrangements, Figure 8a, shows that the five shortest paths are $W3W36W36$, $W3W63W36$, $W3W3W6W3$, $W3W63W63$, and $W3W36W63$. We now rederive these paths using the new method.

The basic generators given in Table IIa1 are used to construct the first-level coset graph shown in Figure 8b (which is identical with Figure 4b), and a Schreier system of coset representatives (Table IIb1) is selected by forming a shortest path spanning tree with root at node 1, as indicated by the darkened lines in Figure 8b. The "Schreier circuits" tabulated in Table IIc1 are defined by $\bar{K} \times g \times (\overline{Kg})^{-1}$ where $\bar{K}$ and $\overline{Kg}$ are coset representatives and g is a generator ($g = W, 6, 3$). For example, if $\bar{K}$ is $W63$ and g is 6, the path leads to node 3 which has the inverse coset representative $(\overline{Kg})^{-1} = (W3)^{-1} = 3^{-1}W^{-1} = 3W$, and the circuit is $W6363W$. Many of these circuits contract to the empty word ϕ; for example, $W6336W \rightarrow \phi$. The permutation for each Schreier circuit is evaluated explicitly, and those circuits which yield the same permutation are gathered into sets (equivalence classes). For example, the circuits 6, 363, and $W6W6W$ all yield the same permutation, a, when evaluated as follows

$$
\begin{array}{c|ccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
6 & 1 & 6 & 5 & 4 & 3 & 2 & 7 \\
\end{array}
\qquad
\begin{array}{c|ccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
3 & 4 & 3 & 2 & 1 & 6 & 5 & 7 \\
6 & 4 & 5 & 6 & 1 & 2 & 3 & 7 \\
3 & 1 & 6 & 5 & 4 & 3 & 2 & 7 \\
\end{array}
$$

$$
\begin{array}{c|ccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
W & 2 & 1 & 7 & 4 & 5 & 6 & 3 \\
6 & 2 & 6 & 5 & 4 & 7 & 1 & 3 \\
W & 6 & 2 & 3 & 4 & 7 & 1 & 5 \\
6 & 6 & 1 & 7 & 4 & 3 & 2 & 5 \\
W & 1 & 6 & 5 & 4 & 3 & 2 & 7 \\
\end{array}
$$

$$
a \equiv \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 6 & 5 & 4 & 3 & 2 & 7 \end{pmatrix} = [(26)(35)(1)(4)(7)]
$$

By evaluating all the Schreier circuits, we derive the permutations a, b, c, d, and α shown in Table IIa2. These permutations are the Schreier generators for the subgroup which fixes character 1; thus, all permutations of the subgroup will leave the atom at site 1 unmoved.

The subgroup generators a, b, c, d, and α (Table IIa2) are used to form another coset graph (Figure 8c) which has one node fewer than the previous coset graph (Figure 8b). The designators in the nodes of Figure 8c

(42) M. Hall, Jr., "Survey of Numerical Analysis," J. Todd, Ed., McGraw-Hill, New York, N. Y., 1962, pp 534–538.

(43) C. C. Sims, "Computational Problems in Abstract Algebra," J. Leech, Ed., p 169; also see the article by J. Neubüser, pp 1–20.

are written with two characters, the first of which is always a one (i.e., 12, 13, 14, 15, 16), because the atom at site one is fixed by the subgroup. We now choose node 16 of Figure 8c as the root node for another shortest path spanning tree as indicated by the darkened lines in Figure 8c, and a new set of Schreier coset representatives (Table IIb2) and Schreier circuits (Table IIc2) are tabulated. The new Schreier circuits fix characters 1 and 6 (the characters of the reactant cation); consequently, all sequences of the Schreier circuits of Table IIc2 will leave the reactant cation unchanged. In the general case, these Schreier circuits would be used as a new set of subgroup generators and the above process repeated until all characters for any given starting norbornyl cation are fixed.

Paths from node 16 to any other node are found by concatenation of words (path segments) from Tables IIc2, IIb2, and IIb1, which give paths from 16 to 16, paths from 16 to 12, 13, 14, 15, and 17, and paths from 1 to 2, 3, 4, 5, 6, and 7, respectively. In particular, the paths from node 16 to node 64 are found by choosing the final path segment ($W6$ in Table IIb1) so that the atom on site 6 of cation 64 originates from site 1 of some other cation. The "some other cation" in this case is cation 14 because the coset graph in Figure 8b shows that the path $W6$ which takes node 1 to node 6 also takes node 4 to node 4. The middle segment of the path (db in Table IIb2) goes from cation 16 to cation 14. The first segment of the path can be any Schreier circuit, s, from Table IIc2) which takes cation 16 to 16 including the empty word ϕ. Thus the "canonical," but not necessarily shortest, path from 16 to 64 is $\phi db W6$ which consists of the two alternative routes $d_1 b W6 = W3W6W3W3W3W6$ and $d_2 b W6 = W63W-36W3W3W6$. The complete path is then

$$
(16) \xrightarrow{s} (16) \xrightarrow{db} (14) \xrightarrow{W6} (64)
$$
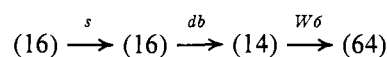
If we take s as the inverse of circuit $k_2 = dbdc$ in Table IIc2 and set $d = d_1$, we obtain the path $(d_1 b d_1 c)^{-1} d_1-b W6 = c^{-1} d_1^{-1} b^{-1} d_1^{-1} d_1 b W6 = c^{-1} d_1^{-1} W6 = W3W3W3-WW3W6W3WW6 = W3W36W36$, the first of the five paths noted previously.[44] The remaining four shortest paths are found by choosing the Schreier circuits $(db-cd_1)^{-1}$, $(c\alpha_2 c)(dbd_2 c)^{-1}$, $(d_1 cbd)(db\alpha_1 bd)^{-1}$, and $(cd_1 bd)-(db\alpha_2 bd)^{-1}$, respectively.

The practicality of computer implementation for this method remains to be demonstrated. All Schreier circuit combinations produce valid paths, and the problem is to design an algorithm to find efficiently the ones which lead to the shortest routes.

(44) The portion of a word containing crossed-out generators (i.e., W W) denotes a syllable which contracts to the empty syllable ϕ.