not very significant for practical applications. On the other hand, analytical expressions describing the precise behavior are dependent on the ΔJ value at 90° and it appears desirable to wait for more experimental results before attempting to evaluate empirically the constants involved in such expressions.[4,10b]

Accordingly, the relationship shown in Figure 2 illustrates clearly that many structural alternatives involving a carbonyl group can be identified confidently in a practical way and the great insight into the local environment of the carbonyl group of the BC conformation of cyclooctanone provided by the ^2J values of 2 further stresses the power of geminal couplings as a sensitive probe for specific conformational relationships.

Experimental Section

The VPC analyses and separation were carried out on a Varian Aerograph A90-P3 instrument using helium as carrier gas.

The ^{1}H NMR spectra were obtained at 100 MHz on a 5% solution of cyclooctanone-2,2,7,7-d_4 (2) in chlorodifluoromethane containing a small quantity of Me$_4$Si in a tube which had been degassed and sealed. The instrumental details and procedures are as described earlier[17] with the exception that temperatures are reported to ±1° since greater precision was not necessary in this work.

Preparation of Cyclooctanone-2,2,7,7-d_4 (2). Cycloheptanone (1.5 g), 60 ml of D$_2$O, and 6.0 g of K$_2$CO$_3$ were refluxed for 5 hr. After cooling, the ketone was extracted with ether. The ether solution was then dried with MgSO$_4$ and its volume was adjusted to 30 ml.

Freshly distilled boron trifluoride etherate (1 ml) was added to the solution followed by portions of a diazomethane solution in ether[13] while stirring adequately. Aliquots of the reaction mixture were taken periodically and analyzed by VPC using a Carbowax 20M column at 175° in order to monitor the extent of ring expansion. The reaction was stopped when the chromatogram suggested that about 60% of the mixture was cyclooctanone. Water (20 ml) was added and the ether layer was then separated and washed with a saturated solution of NaHCO$_3$ and with water and then dried over MgSO$_4$. The solution was concentrated and the cyclooctanone present was isolated by preparative VPC using a UC-W-98 column (15 ft × 0.375 in., 165°).

Reinjection of the isolated product on a Carbowax column showed it to be free of other ketones and to have the same retention time as an authentic commercial (Aldrich) sample of cyclooctanone. The ^{1}H NMR spectrum (Figure 1) shows that the isotopic purity of the cyclooctanone-2,2,7,7-d_4 (2) thus prepared is sufficient for the planned study.

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(12) (a) F. A. L. Anet, M. St-Jacques, P. M. Henrichs, A. K. Cheng, J. Krane, and L. Wong, *Tetrahedron*, **30**, 1629 (1974); (b) F. A. L. Anet, M. St-Jacques, and P. M. Henrichs, *Intra-Sci. Chem. Rep.*, **4**, 251 (1970).
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Formation and Interconversion of Allene Dimers via Bisallyl Diradicals. Possibilities on and Documentation of the Supergraph

Sidney I. Miller

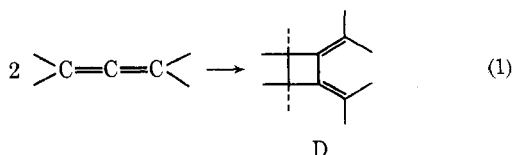*Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616*

A coding system is developed to handle interconversions among 1,2-dimethylenecyclobutanes (D) and associated planar (P) and orthogonal (O) bisallyl diradicals. In the most general case, a graph of 320 edges links the 64 D's, 32 P's, and 32 O's. Compact labels for the species and algorithms for interconversion steps DO, OP, etc., have been devised. Relationships among those D's, P's, and O's which formally originate in the allene KHC=C=CHK are summarized in several graphs.

Graph theory or systems analysis[1] has recently been applied to isomerizations. That is, given species ML$_n$, e.g., a trigonal bipyramid or octahedral complex, one can describe all of the permutational isomers and their isomerization paths either by a graph or in a topological representation.[2] For example, the graph of the 1,2 rearrangements of the carbocation R$_1$R$_2$R$_3$C–CR$_4$R$_5$$^+$ involves 30 distinct interconversions (edges) among the 20 isomers (points).[2a] Here we wish to focus on an example of complex genealogy in allene dimer chemistry in which three different structural types, each with its set of permutational isomers, are variously connected by bond-making, bond-breaking, and conformational interconversions. A graph derived for this system may be regarded as a projection of the energy hypersurface on which these species lie, through which reactant coordinates pass, and with which mechanisms must be consistent. The important feature that deserves emphasis is that the present approach can be generalized to even more complex systems in which groups of species of different symmetries are interconvertible.

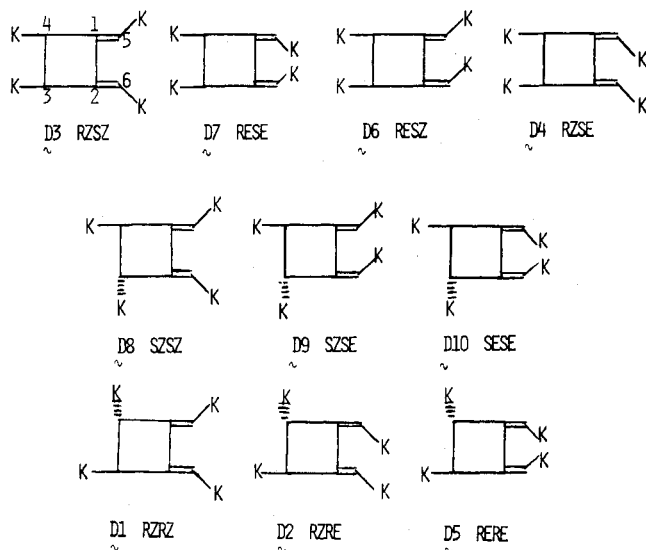A common entry into the 1,2-dimethylenecyclobutanes is via allene dimerization.[3]

$$2 \ \ce{>C=C=C<} \longrightarrow \quad \text{(1)}$$

D

There are, of course, other C_6 species which are isomeric with D, e.g., 1,3-dimethylenecyclobutane, biscyclopropylidene, 3,4-dimethylene-1-hexene, methylenespiropentane, etc., and other paths to D, e.g., from $\Delta^{1,4}$-bicyclo[2.2.0]hexene.[4] These possibilities are all interesting and often chemically significant but will be excluded to keep the problem at hand manageable. As it is, numerous isomeric dimers can be derived from various allenes in process 1: $K_2C=C=CH_2$ (3); $HKC=C=CH_2$ (10); $KLC=C=CH_2$ (10); $KHC=C=CKH$ (10); $KHC=C=CLH$ (36); $JHC=C=CKL$ (36); $abC=C=Ccd + efC=C=Cgh$ (64). This diversity is by no means hypothetical, since there are numerous examples of D mixtures resulting from the dimerization of allenes.[3]
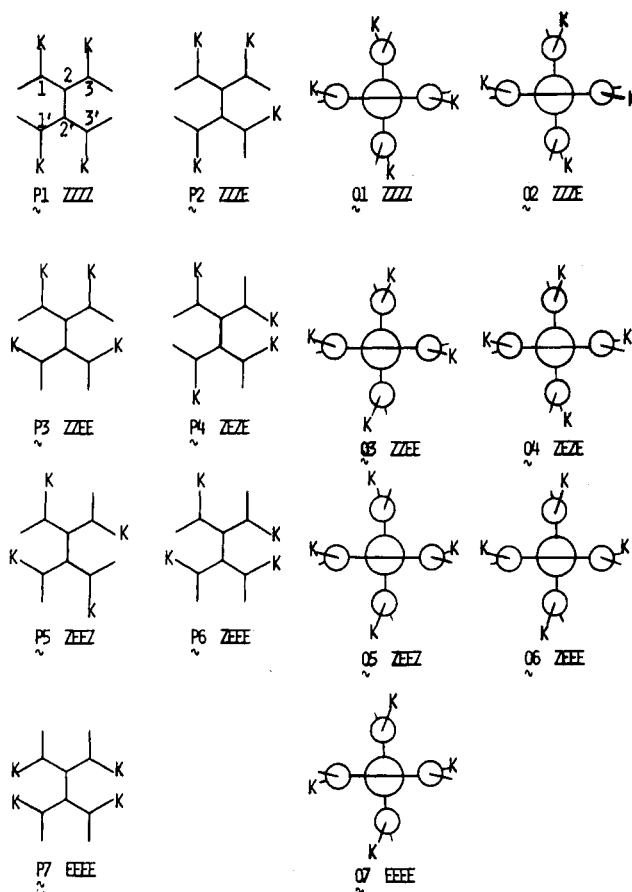
Evolution of a Typical Graph. The allene, $HKC=C=CKH$, leads to a dimer set of intermediate complexity, which will be used as the focus of this section. The isomers are set out in detail in Chart I. It is generally agreed that

Chart I

1,2-Dimethylenecyclobutanes, D, Derived from the Dimerization of KCH=C=CHK. Labels are R, Rectus; S, Sinister; E, Sequential Trans; Z, Sequential Cis

process 1 as well as the interconversions among D probably occur via 2,2'-bisallyl diradicals.[4-7] These radicals may take up an infinite number of conformations but we arbitrarily designate the wholly planar (P) and orthogonal (O) forms of bisallyl as the primarily interesting or pertinent ones for the problem at hand. To facilitate visualizing and manipulating O, we use a hybrid Fischer–Newman projection: the 2 and 2' carbon atoms are represented in projection at the center of the large circle, the 1 and 3 carbon atoms are at the centers of the top and bottom circles, respectively, and the 1' and 3' carbon atoms are at the centers of the left and right circles, respectively; as is customary, a circle defines a projection plane and lines (bonds) which cross the circle are projected from the front and those which do not cross are projected from behind onto the plane.[5] All of the P and O isomers are given in Chart II. With the aid of these projection formulas it is easily seen that, except for the enan-

Chart II

Planar (P) and Orthogonal (O) Bisallyl Diradicals Derived from KCH=C=CHK

tiomeric pair O4 and O5, the O's have a plane of symmetry perpendicular to the projection plane: no optical isomers are possible.

We proceed now to "connect" the isomers. That is, interconversions among them result from rotations about the middle (2,2') or end (1,2 or 2,3, etc.) bonds of the bisallyl diradical. Specifically, rotation around the middle bond interconverts P's and O's, while rotations around end bonds interconvert P's to P's or O's to O's. Either by inspection or the use of models one can find all of the rotation between the pairs of isomers. These are summarized in a PO graph (Figure 1). Note that the 14 species are linked by 25 edges.

Among the numerous processes open to the bisallyl diradical, e.g., dissociation, rearrangement, etc., we confine our attention to its collapse to 1,2-dimethylenecyclobutane (D). There are, however, several stereoelectronic restraints on the accessible modes of ring closure. The molecular orbitals of the P and O forms have been characterized[8] and ring closure to or ring opening from D have been specified as disrotatory for P and conrotatory for O.[8a,9] Four conrotatory *least motion* conversions of an O species, which involve ca. $\pi/4$ changes of the bonds, are given in Figure 2. (Non-least-motion closure involving ca. $3\pi/4$ bond changes were rejected.)

In Figure 1 we give the three PD graphs for the allowed disrotatory cyclizations from all P's to D's and two OD graphs for O to D openings. There are 16 PD and 18 OD edges or reaction steps represented in Figure 1.

The reaction steps in Figure 1 are, of course, energy limited. Because of electron delocalization in the allylic halves of P and O, barriers to end rotations (B_e) are somewhat higher than the usual single-bond barriers in hydrocarbons:
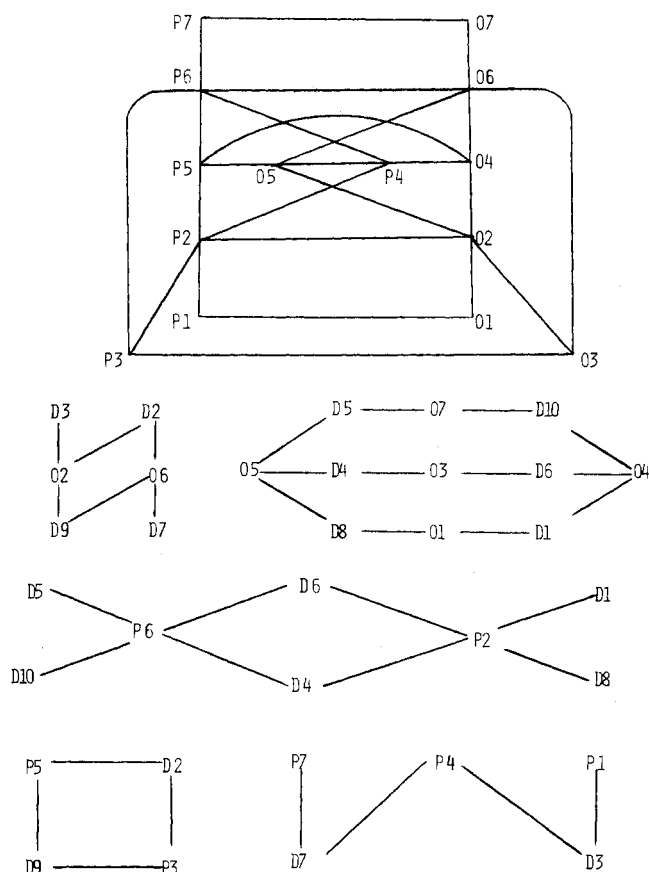
Figure 1. Graphs of the interconversions of dimeric species formed from the allene, HKC=C=CHK: 1,2-dimethylenecyclobutanes (D); planar (P) and orthogonal (O) bisallyl diradicals.

Table I
1,2-Dimethylenecyclobutane (D) Structures and Descriptive Labels

D(I)	Configuration	Code	D(J)	Configuration	Code
1	abcdefgh	RZ′rz′	1	abcdabcd	RZ′RZ′
2	abcdefhg	RZ′re′	2	abcdabdc	RZ′RE′
3	abcdfegh	RZ′sz′			
4	abcdfehg	RZ′se′	8	abcddcba	RZ′S′E
5	abcdghef	RZ′r′z	9	abdcabdc	RE′RE′
8	abcdhgfe	RZ′s′e	15	abdcdcba	RE′S′E
9	abdcefgh	RE′rz′	16	bacdbacd	SZ′SZ′
16	abdchgfe	RE′s′e	21	bacddcba	SZ′S′E
17	bacdefgh	SZ′rz′	22	badcbadc	SE′SE′
64	dcbahgfe	S′Es′e	26	badcdcba	SE′S′E
			27	cdbacdba	R′ZR′E
			36	dcbadcba	S′ES′E

framework D, P, and O, and by adopting certain IUPAC stereochemical conventions, we can code each species concisely. The following rules are used:[15] a has priority over b, c has priority over d, etc.; ab has priority over cd, which has priority over ef, etc; all of these substituents have priority over carbons; ab, cd, ef, and gh are associated with R, R′, r, and r′ or Z, Z′, z, and z′ configurations, respectively, depending on whether they are bonded to the ring or the methylene groups, ba, dc, fe, and hg are associated with S, S′, s, and s′ or E, E′, e, and e′ configurations, respectively, depending on whether they are bonded to the ring or the methylene groups. For a *normal* or *standard* label, ab and cd precede ef and gh; labels for the ring substituents of each pair precede those for the methylene substituents. Together with the letter D a four-letter label is adequate to characterize all of the isomers (Octal numbers could also have been used.[16]) Since it is sometimes useful to index D, we also use D(I) as a label, but this is simply a guide for listing rather than an indicator of structure.

In some of the interconversions, species may turn up with a nonstandard D label, e.g., Z′Ser′; this is equivalent to the standard label, SZ′r′e. Since the rules for interconversion were formulated for the standard format, normalization should be performed as soon as a nonstandard label appears. Captions in Figure 2 illustrate three labeling systems. In Table I we give the coding for the general case as well as for a simpler dimer set.

A related priority system holds for P(I) and O(I). Groups of higher priority which face outward are labeled Z or z, otherwise E or e. Primes on these letters distinguish cd from ab and gh from ef. One can always arrange to have the ab pair in the upper left quadrant and label from *left* to *right* across the top and then *left* to *right* across the bottom. The coding for Q(I) is identical with that of P(I), except that the potential chirality of the structure must be taken into account. We follow the IUPAC rules for a species with a chiral axis, that is, we use the Fischer convention, for an R structure.[15]

$$\text{ab} \overset{\text{gh}}{\underset{\text{ef}}{\overline{\bigoplus}}} \text{cd}$$

The four-letter label then follows the priority rules with the appropriate *unprimed* letter in the third position for R- and in the fourth position for S-bisallyl. O22 EZ′z′e and O19 EZ′ez′, for example, are enantiomers. A typical structure is illustrated in Figure 2. Detailed coding is given in Table II. Incidentally, if a nonstandard label turns up for

12 to 13 ± 2 kcal/mol has been suggested.[10] Secondly, it is probable that the O's are at, or close to, local energy minimums. Molecular orbital calculations indicate an energy difference (B_m) which places unsubstituted P ca. 4 or 10 kcal/mol above O.[8] Depending on the method of calculation, one may have to adjust B_m for the interaction of the 1,1′ and 3,3′ inward-facing hydrogen atoms. For unsubstituted bisallyl, crude limits on this steric energy can probably be set at <3.75 and >1 kcal/mol by the rotational barriers of 2,3-dimethylbutane and biphenyl.[11] (These considerations only permit one to assume a skew structure—we use the orthogonal geometry because of its simplicity and symmetry.) Thirdly, ring formation from diradicals, e.g., to cyclobutane, appears to have an energy barrier (E_c) of ca. 8 kcal/mol.[12] If such a barrier also holds for bisallyl, then it appears that $B_e > E_c > B_m$. All of these barriers become important when one confronts the complete graph of a given system and must make decisions relevant to specific reaction paths.[3-5]

Documentation of the Supergraph. In this section we consider P, O, and D and their interconversions as a topological problem. In the background is also the notion of storing in and retrieving from a computer sets of related species and reactions.[2h,13] The supergraph, which includes graphs of conformational (PP, PO) as well as chemical changes (PD, OD) and also contains this information, is too complex to picture, but one can obtain it or portions of it by means of a computer. Previous analyses of this type have often dealt with a single set of permutational isomers, but systems involving several kinds of isomerism and conversion processes are also on record.[2h,i]

Each species consists of a basic carbon framework and eight peripheral groups. There are a variety of representations of such structures.[14] However, by labeling the gross
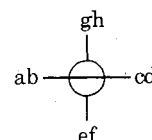
Table II
Planar (P) or Orthogonal (O) Bisallyl Structures and Descriptive Labels

(I)[a]	Configuration	Code	(J)[b]	Configuration	Code
1	abcdefgh	ZZ'zz'	1	abcdabcd	ZZ'ZZ'
2	abcdefhg	ZZ'ze'	2	abcdabdc	ZZ'ZE'
3	abcdfegh	ZZ'ez'	3	abcdbacd	ZZ'EZ'
4	abcdfehg	ZZ'ee'	4	abcdbadc	ZZ'EE'
5	abcdghef	ZZ'z'z	5	abcdcdab	ZZ'Z'Z
8	abcdhgfe	ZZ'e'e	8	abcddcba	ZZ'E'E
9	abdcefgh	ZE'zz'	9	abdcabdc	ZE'ZE'
16	abdchgfe	ZE'e'e	12	abdccdba	ZE'Z'E
17	bacdefgh	EZ'zz'			
			15	bacdbacd	EZ'EZ'
24	bacdhgfe	EZ'e'e			
25	badcefgh	EE'zz'	18	bacddcba	EZ'E'E
			19	badcbadc	EE'EE'
32	badchgfe	EE'e'e	20	badcdcba	EE'E'E

a P(I) or O(I). *b* P(J) or O(J).

O, e.g., Z'Eez', this indicates that the *normal* projection formula can be recovered by an inplane rotation of π: effectively this operation interchanges the order of the letters in each pair and yields the normal label for O22. Finally, by identifying the species deriving from KHC=C=CKH discussed earlier with those from abC=C=Cab and by using the conventions of Tables I and II, one can obtain the codes for D(K), P(K), and O(K) of Charts I and II.
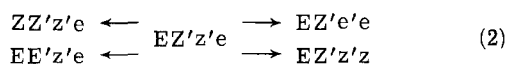
We denote interconversions between species by two-letter terms, e.g., DO (0601) indicates D6 → O1. It will also be convenient to use the following definitions for specific label pairs.

a (RS), (R'S'), (rs), (r's'), (ZE), (Z'E') (ze), (z'e')
b (RZ), (R'Z'), (rz), (r'z'), (SE), (S'E'), (se), (s'e')
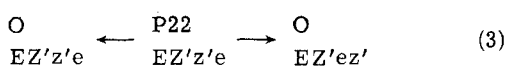*c* (RE), (R'E'), (re), (r'e'), (SZ), (S'Z'), (sz), (s'z')

a Conjugates. *b* Relates. *c* Inverts.

The main problem here is to formulate the interconversion rules in a manner consistent with the way the species have been coded. These are given first in words and then more compactly in symbolic form.
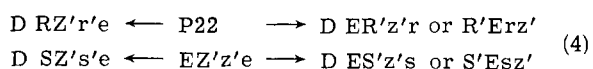
PP or OO. These involve a rotation of an outside bond in bisallyl: each O or P has access to four such steps. This isomerization, e.g., eq 2, is described by interchanging a and b *or* c and d, etc., i.e., change one of the four-letter labels to its conjugate.

$$\begin{array}{ccc}
ZZ'z'e \longleftarrow & & \longrightarrow EZ'e'e \\
 & EZ'z'e & \\
EE'z'e \longleftarrow & & \longrightarrow EZ'z'z
\end{array} \quad (2)$$

OP or PO. Each bisallyl has two such steps, e.g., eq 3: either retain the label or interchange the last two letters.

$$\begin{array}{ccc}
O & P22 & O \\
EZ'z'e \longleftarrow & EZ'z'e & \longrightarrow EZ'ez'
\end{array} \quad (3)$$

PD. There are two *disrotatory* interconversions, PD, e.g., eq 4. Keeping either the first and third or second and fourth letters the same, substitute one relate and one invert for the other two letters.

$$\begin{array}{ccc}
D RZ'r'e \longleftarrow & P22 & \longrightarrow D ER'z'r \text{ or } R'Erz' \\
D SZ's'e \longleftarrow & EZ'z'e & \longrightarrow D ES'z's \text{ or } S'Esz'
\end{array} \quad (4)$$

OD. The four conrotatory closures (OD) of Figure 2 are given in eq 5 as follows. Retain either the first and fourth

P19 SZ'sz'
bacdfegh

P48 S'Erz'
cdbaefgh

P22 EZ'z'e
bacdghfe

P8 RZ's'e
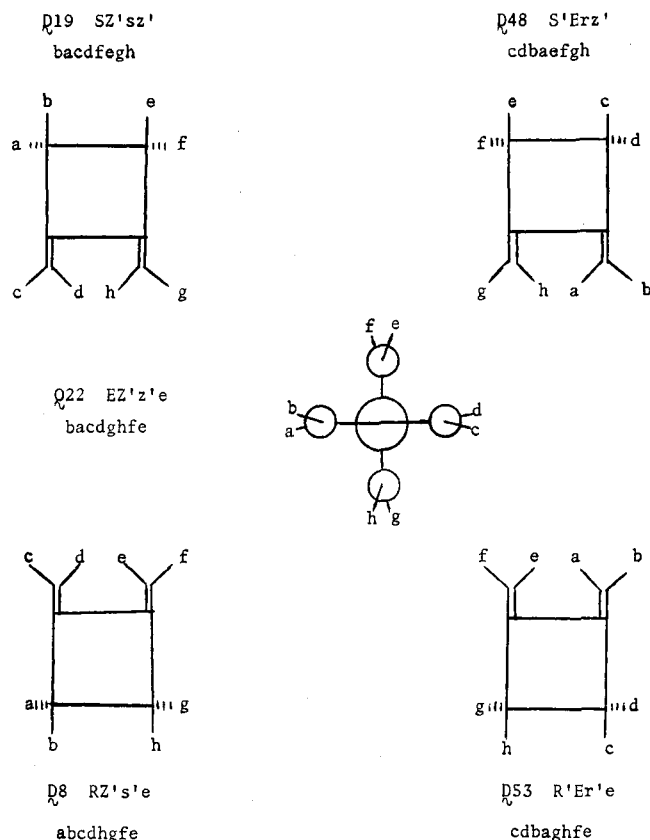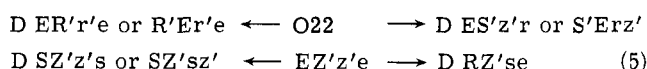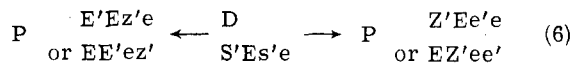abcdhgfe

P53 R'Er'e
cdbaghfe

Figure 2. Least Motion ($\pi/4$) conrotatory closures of an orthogonal bisallyl diradical to give four dimers. The labeling code is explained in the text.
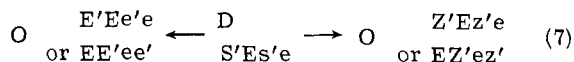
or second and third letter labels and interchange the other two with relates; or retain the first and third or second and fourth letter labels and interchange the other two with inverts.

$$\begin{array}{ccc}
D ER'r'e \text{ or } R'Er'e & \longleftarrow O22 & \longrightarrow D ES'z'r \text{ or } S'Erz' \\
D SZ'z's \text{ or } SZ'sz' & \longleftarrow EZ'z'e & \longrightarrow D RZ'se
\end{array} \quad (5)$$

DP. The disrotatory ring openings, DP, are illustrated in eq 6. Retain letters 2 and 4 of the label; invert one of the remaining letters and replace the other by the relate.

$$\begin{array}{ccc}
P & E'Ez'e & D & & Z'Ee'e \\
\text{or } EE'ez' & \longleftarrow & S'Es'e & \longrightarrow P & \text{or } EZ'ee'
\end{array} \quad (6)$$

DO. For the two conrotatory ring openings DO, retain letters 2 and 4 and either invert letters 1 and 3 or insert their relates; finally interchange the last two letters, e.g.

$$\begin{array}{ccc}
O & E'Ee'e & D & & Z'Ez'e \\
\text{or } EE'ee' & \longleftarrow & S'Es'e & \longrightarrow O & \text{or } EZ'ez'
\end{array} \quad (7)$$

The preceding statements may be expressed concisely, providing it is understood that 1234 is the four-letter label which is to be changed, that the slant (/) means "or", and that cnj, rel, and inv are read as "replace with the conjugate, relate, and invert", respectively, the letters that follow.

PP or OO cnj (1/2/3/4)
PO or OP 1234/1243
PD [13(rel 2 inv 4)/(rel 4 inv 2)]/
          [24(rel 1 inv 3)/(rel 3 inv 1)]
OD (14 rel 23)/(23 rel 14)/(13 inv 24)/(24 inv 13)
DP 24[(rel 1 inv 3)/(inv 1 rel 3)]
DO [24(inv 13)]/[(rel 1) 2 4 rel 3]

Some comments on the graph of our general case are of interest. The *degree* or *valency*[1b] of each vertex (species) is 4 for D and 10 for each of P and O. The total number of edges is 32 × 4 (OD) + 32 × 2 (OP) + 32 × ½ (OO) + 32 × 2 (PD) or 320. A minimum *path*[1b] (edge sequence) between Di and Dj can be evolved as follows. Open each D up along its OD's and compare the configurations of the O's deriving from each dimer. The maximum difference could be one in which each letter in the four-letter label as well as the order (chirality) for a pair, say Oi and On, are different. Of necessity, any other pairing of O's will have fewer differences and would be chosen. Suppose then that Oj and Om are to be linked. If their chirality is identical, three more edges, or less, will be needed; if their chirality is different, one P will have to be interposed in the sequence. Thus, *a minimum path* could consist of as few as two and as many as six edges.

Oi—Di$\diagdown$ $\diagup$Ok—Ol$\diagdown$ $\diagup$On
       $\diagdown$Oj—Pi$\diagup$ $\diagdown$Om—Dn$\diagup$
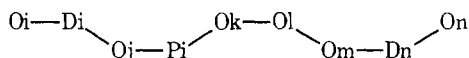
The reader is now in a position to compare the pictorial with the formal approach to this system of three type of species and their interconversions. Certainly, the pictorial approach is worth retaining in those systems with the simpler substitution patterns. At the level of the graphs which include D(I) or D(J), we believe that the formal approach has become a necessity. In any case, chemical information and/or judgments can now be introduced to analyze the problem further.

Registry No.—1,2-Dimethylenecyclobutane, 14296-80-1.

References and Notes

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