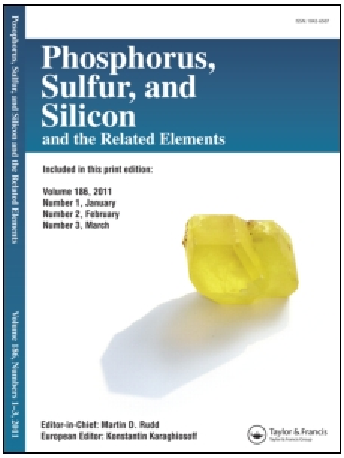

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE S_N2 REACTION AT A TETRAHEDRALLY SUBSTITUTED 3rd (4th, 5th,...) ROW ATOM: THE MINIMUM CONSTRAINTS FOR STEREOSPECIFICITY

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To cite this Article Gielen, Marcel and Willem, Rudi(1977) 'THE S_N2 REACTION AT A TETRAHEDRALLY SUBSTITUTED 3rd (4th, 5th,...) ROW ATOM: THE MINIMUM CONSTRAINTS FOR STEREOSPECIFICITY', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 3, 339 — 344

To link to this Article: DOI: 10.1080/03086647708079944

URL: http://dx.doi.org/10.1080/03086647708079944

Phosphorous and Sulfur
1977, Vol. 3, pp. 339–344

THE S_N2 REACTION AT A TETRAHEDRALLY SUBSTITUTED 3rd (4th, 5th,...) ROW ATOM: THE MINIMUM CONSTRAINTS FOR STEREOSPECIFICITY

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(*Received January 17, 1977*)

The addition-elimination matrix **AE** is used to define the minimum constraints for stereospecificity for S_N2 reactions at a tetrahedrally substituted 3rd (4th, 5th, . . .) row atom. Since these reactions seem to occur via trigonal bipyramidal five-co-ordinate intermediates undergoing possibly intramolecular rearrangements, the possibility of ligand scrambling at this intermediate stage must be considered. Therefore, several specific cases are examined in which the different rearrangement modes P1, P2, P3, P4 of the idealized trigonal bipyramid TBP can occur separately. Graphical or matrix E(Px) descriptions are given which allow us to see if the minimum constraints are sufficient to obtain a stereospecific substitution. The conditions for stereospecificity are discussed.

INTRODUCTION

A possible mechanism for S_N2 reactions at tetrahedrally substituted 3rd (4th, 5th, . . .) row metal atoms, which explains many experimental results,[1] is the succession of:

i) the addition of the nucleophile at the metal by attack of a face or an edge of the tetrahedral molecule;

ii) intramolecular rearrangements;[2]

iii) the elimination of the leaving group by axial or equatorial departure from the TBP complex.

The intramolecular rearrangements can be classified according to the concept of mode of rearrangement.[2] It is worthwhile to emphasize that all the rearrangements which can be described by permutations belonging to the same mode of the ideal TBP (with five identical ligands) will be said to belong to the same "mode" even if, strictly speaking, they are neither rotationally nor symmetry equivalent as they should be.[2] A reason for this procedure is that a more subtle classification is not necessary to define the criteria of stereospecificity for S_N2 reactions at metal centres. It has the additional advantage to give a better idea of the possible rearrangement scheme of the intermediate complex than would a classification according to the "full" mode concept.

All these possible reactions can be described by an exchange matrix E(Px) with x = 0, 1, 2, 3, 4 or 5,[2a] which contains two types of submatrices: **AE**, describing the addition-elimination reactions (independent of the mode Px which is used)[2a] and **R**(Px) describing the intramolecular rearrangements of the TBP species belonging to mode Px.[2a]

If intramolecular rearrangements of a given mode are allowed, then any reaction sequence containg *no* intramolecular rearrangement will also be allowed, since the TBP obtained by an addition of the nucleophile on the tetrahedral molecule may lose the leaving group, this TBP having undergone intramolecular rearrangements or not. Thus the minimum constraints for stereospecificity[3] are easy to define: they are those constraints for which a reaction occurring *without any intramolecular rearrangement* is stereospecific. Let us consider, for instance, the reaction $\overset{+}{4} \rightarrow \bar{5}$ (or $\bar{4} \rightarrow \overset{+}{5}$)[4] proceeding with inversion of the relative configuration,[2a, 5] and $\overset{+}{4} \rightarrow \overset{+}{5}$ (or $\bar{4} \rightarrow \bar{5}$) proceeding with retention of the relative configuration. When we want a reaction proceeding with inversion of configuration, the allowed intermediate TBP's must connect $\overset{+}{4}$ and $\bar{5}$ (or $\bar{4}$ and $\overset{+}{5}$) *and may not connect* $\overset{+}{4}$ *and* $\overset{+}{5}$ (or $\bar{4}$ and $\bar{5}$). When we want a reaction proceeding with retention of configuration, the allowed intermediate TBP's must connect $\overset{+}{4}$ and $\overset{+}{5}$ (or $\bar{4}$ and $\bar{5}$) and may not connect $\overset{+}{4}$ and $\bar{5}$ (or $\bar{4}$ and $\overset{+}{5}$).

Minimum Constraints for Inversion of Configuration

All the TBP's for which the coefficients of lines $\overset{+}{4}$ and $\bar{5}$ of submatrix **AE** are different (1 and . or . and 1) will cause a substitution reaction transforming $\overset{+}{4}$ into $\overset{+}{5}$, thus proceeding with retention of configuration, and must be discarded to define the minimum constraints for inversion i.e. $\overset{(-)}{14}$, $\overset{(-)}{15}$, $\overset{(-)}{24}$, $\overset{(-)}{25}$, $\overset{(-)}{34}$ and $\overset{(-)}{35}$.[6]

$$\begin{array}{c|cccccccccccccccccccc|}
 & \overline{12} & 13 & \overline{14} & 15 & \overline{23} & 24 & \overline{25} & \overline{34} & 35 & \overline{45} & 12 & \overline{13} & 14 & \overline{15} & 23 & \overline{24} & 25 & 34 & \overline{35} & 45 \\
\overset{+}{4} & 1 & 1 & . & 1 & 1 & . & 1 & . & 1 & . & . & . & 1 & . & . & 1 & . & 1 & . & 1 \\
\bar{5} & 1 & 1 & 1 & . & 1 & 1 & . & 1 & . & . & . & . & . & 1 & . & . & 1 & . & 1 & 1
\end{array}$$

Of course, these constraints are not necessarily sufficient to get a stereospecific substitution reaction if intramolecular rearrangements are allowed. They will be sufficient if, and only if, none of $\overline{12}$, 13, $\overline{23}$ or 45 connected to $\overset{+}{4}$ and to $\bar{5}$ are allowed to undergo intramolecular rearrangements connecting them to one of the trigonal bipyramids of the enantiomeric set, 12, $\overline{13}$, 23 or $\overline{45}$ from which $\overset{+}{5}$ and $\bar{4}$ could be reached.

The **E**(PO) matrix describing the case where $\overset{\pm}{1} = \overset{\pm}{2} = \overset{\pm}{3} = 0$ and $\overset{(-)}{14} = \overset{(-)}{15} = \overset{(-)}{24} = \overset{(-)}{25} = \overset{(-)}{34} = \overset{(-)}{35} = 0$ is the adjacency matrix of the graph described in Figure 1.

From this graph, it is obvious that the reaction is stereospecific as expected: it is indeed formed by two disjoined (enantiomeric) subgraphs or, in other words, **E**(PO) can be written as a block-diagonalized matrix.

The **E**(P1) matrix describing the same specific case also gives two disjoined enantiomeric graphs, as shown in Figure 2:[2a] the substitution reaction is still stereospecific if mode P1 is allowed.

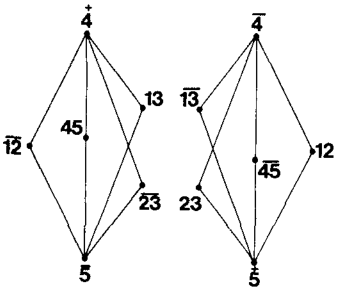


FIGURE 1 Minimum constraints for inversion applied to E(PO).

The **E**(P2) matrix valid for the same constaints again gives two disjoined enantiomeric graphs (see Figure 2) showing that the substitution reaction is also stereospecific if mode P2 is allowed.

Obviously, **E**(P3) and **E**(P4) [and **E**(P5)] must then give graphs showing that the substitution is no more stereospecific: indeed, the pair of modes [P2P3] or [P1P4] or [P0P5] constitute what is called a pair of enantiomeric modes[2b] [if a given mode Px transforms a TBP into a set of isomers, then the enantiomeric mode of P(x), P(5-x), transforms the same TBP into the enantiomers of the set of isomers obtained by mode P(x)]. These graphs are given in Figure 3.

The case of substitution reactions for which the nucleophile 5 and the leaving group 4 are the most electronegative ligands and for which no cyclic constraints are introduced (see for instance Ref. 2a) is a case which can be deduced from this one by introducing three extra-constraints: $\overset{(-)}{12} = \overset{(-)}{13} = \overset{(-)}{23} = 0$.

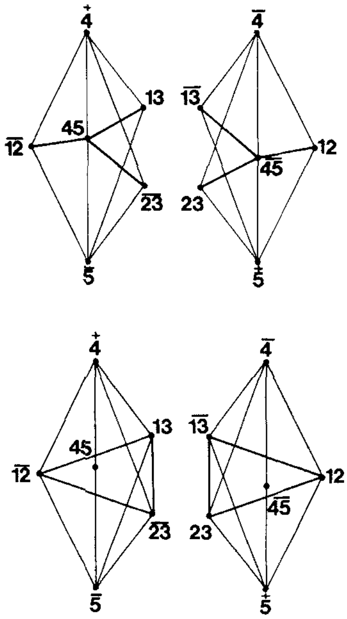


FIGURE 2 Minimum constraints for inversion applied to E(P1) and to E(P2): the substitution reaction is still stereospecific.

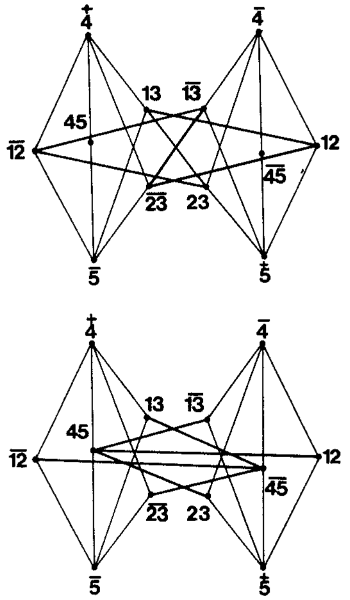


FIGURE 3 Minimum constraints for inversion applied to E(P3) and to E(P4): the substitution reaction is no more stereospecific.

Minimum Constraints for Retention of Configuration

All the TBP's for which the coefficients of lines $\overset{+}{4}$ and $\bar{5}$ of the **AE** matrix are identical, i.e. $\overset{(-)}{12}$, $\overset{(-)}{13}$, $\overset{(-)}{23}$ and $\overset{(-)}{45}$ (*vide supra*), will cause a substitution reaction proceeding with inversion of configuration and must be discarded to define the minimum constraints for a reaction proceeding with retention of configuration.

As for the minimum constraints for inversion, these constraints will not necessarily be sufficient for a stereospecific reaction if intramolecular rearrangements are allowed.

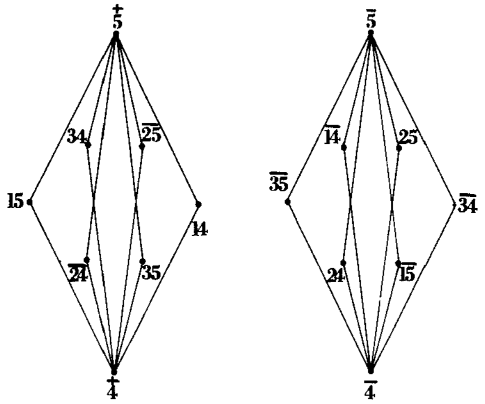


FIGURE 4 Minimum constraints for retention applied to E(PO).

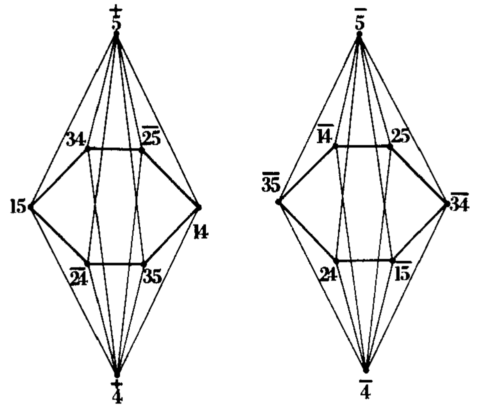


FIGURE 5 Minimum constraints for retention applied to E(P1): the substitution reaction is still stereospecific.

The E(PO) matrix describing the case where $\overset{\pm}{1} = \overset{\pm}{2} = \overset{\pm}{3} = 0$ and $\overset{(-)}{12} = \overset{(-)}{13} = \overset{(-)}{23} = \overset{(-)}{45} = 0$ is the adjacency matrix of the disjoined enantiomeric graphs of Figure 4.

$$\begin{array}{c|cccccccccccccccc|}
 & \overset{+}{4} & \overset{+}{5} & 14 & 15 & \overline{24} & \overline{25} & 34 & 35 & \overline{4} & \overline{5} & \overline{14} & \overline{15} & 24 & 25 & \overline{34} & \overline{35} \\
\overset{+}{4} & . & . & 1 & 1 & 1 & 1 & 1 & 1 & . & . & . & . & . & . & . & . \\
\overset{+}{5} & . & . & 1 & 1 & 1 & 1 & 1 & 1 & . & . & . & . & . & . & . & . \\
14 & 1 & 1 & . & . & 1 & . & 1 & . & . & . & . & 1 & . & . & . & . \\
15 & 1 & 1 & . & . & . & 1 & . & 1 & . & . & 1 & . & . & . & . & . \\
\overline{24} & 1 & 1 & 1 & . & . & . & 1 & . & . & . & . & . & . & 1 & . & . \\
\overline{25} & 1 & 1 & . & 1 & . & . & . & 1 & . & . & . & . & 1 & . & . & . \\
34 & 1 & 1 & 1 & . & 1 & . & . & . & . & . & . & . & . & . & . & 1 \\
35 & 1 & 1 & . & 1 & . & 1 & . & . & . & . & . & . & . & . & 1 & . \\
\overline{4} & . & . & . & . & . & . & . & . & . & . & 1 & 1 & 1 & 1 & 1 & 1 \\
\overline{5} & . & . & . & . & . & . & . & . & . & . & 1 & 1 & 1 & 1 & 1 & 1 \\
\overline{14} & . & . & . & 1 & . & . & . & . & 1 & 1 & . & . & 1 & . & 1 & . \\
\overline{15} & . & . & 1 & . & . & . & . & . & 1 & 1 & . & . & . & 1 & . & 1 \\
24 & . & . & . & . & . & 1 & . & . & 1 & 1 & 1 & . & . & . & 1 & . \\
25 & . & . & . & . & 1 & . & . & . & 1 & 1 & . & 1 & . & . & . & 1 \\
\overline{34} & . & . & . & . & . & . & . & 1 & 1 & 1 & 1 & . & 1 & . & . & . \\
\overline{35} & . & . & . & . & . & . & 1 & . & 1 & 1 & . & 1 & . & 1 & . & .
\end{array}$$

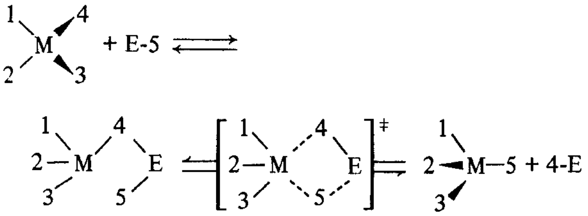
FIGURE 6 E(P2) matrix valid for the minimum constraints for retention: the substitution is not stereospecific because 14 is connected to $\overline{15}$, $\overline{24}$ to 25 and 34 to $\overline{35}$. In the "full" description of modes, each intramolecular rearrangement represents a mode in itself. It is thus possible to discard some of the rearrangements belonging to the same mode of the ideal TBP, for instance $14 \rightleftarrows \overline{15}$, $\overline{24} \rightleftarrows 25$ and $34 \rightleftarrows \overline{35}$. The extra-constraints making those intramolecular rearrangements unfeasible will be the minimum constraints necessary (and sufficient) to render the reaction $\overset{+}{4} \rightarrow \overset{+}{5}$ stereospecific.

The **E**(P1) matrix describing the same specific case also gives two disjoined enantiomeric graphs, as shown in Figure 7:[2] the substitution reaction is still stereospecific if mode P1 is allowed.

On the contrary, neither the **E**(P2) matrix nor the **E**(P3) valid for the same constraints can be block-diagonalized by permutations of lines (and of columns). The minimum constraints for retention are thus not sufficient to impose a stereospecificity if modes P2 or P3 are allowed. The graphs corresponding to these matrices (see Figure 6) are rather complex and are not formed by disjoined enantiomeric subgraphs.

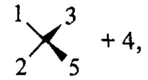
Since **E**(P1) can be block-diagonalized by permutations of lines (and of the corresponding columns) and since P1 and P4 are enantiomeric modes, it will not be possible to block-diagonalize **E**(P4).

The case of substitution reactions in which a four-membered ring is formed which contains the central atom, the incoming nucleophile and the leaving group, i.e.

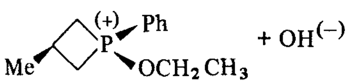


is exactly described by the minimal constraints for retention if 4 and 5 are more electronegative than 1, 2 and 3.[2,7]

The cases of substitution reactions on phosphetanes,[1] and of analogous reactions



symbolizing for instance



can be derived from these minimum constraints for retention by introducing two extra-constraints: $\overset{(-)}{34} = \overset{(-)}{35} = 0$,[2a] since 1 and 2 may not simultaneously be equatorial or axial because of the presence of the four-membered ring and since 4 and 5 may not simultaneously be equatorial because of the electronegativity constraints.[1]

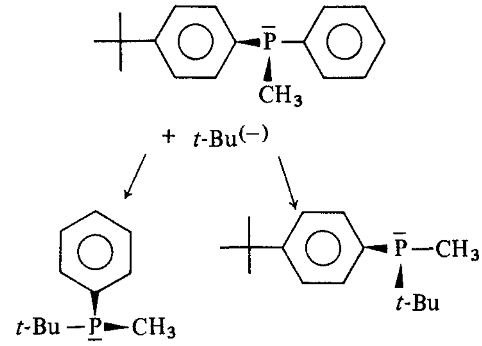
Minimum Constraints for Two Parallel Substitution Reactions Proceeding both with Inversion of Configuration

The minimum constraints for $\overset{+}{5} \leftarrow \overset{+}{3} \rightarrow \overset{-}{4}$ (or for $\overset{-}{5} \leftarrow \overset{-}{3} \rightarrow \overset{+}{4}$) can be found by discarding all the TBP's x which allow the transformations $\overset{+}{3} \rightleftarrows x \rightleftarrows \overset{+}{4}$, $\overset{-}{3} \rightleftarrows x \rightleftarrows \overset{-}{4}$, $\overset{+}{3} \rightleftarrows x \rightleftarrows \overset{-}{5}$ and $3 \rightleftarrows x \rightleftarrows \overset{+}{5}$, i.e. $\overset{(-)}{13} = \overset{(-)}{14} = \overset{(-)}{23} = \overset{(-)}{24} = \overset{(-)}{35} = \overset{(-)}{45} = 0$ and $(\overset{(-)}{14}=)\ \overset{(-)}{15} = (\overset{(-)}{24}=)\ \overset{(-)}{25} = \overset{(-)}{34} = (\overset{(-)}{35}=)\ 0$.

The only possible TBP compatible with this case is $\overset{(-)}{12}$.

Of course, no intramolecular rearrangement is allowed for this case (except that belonging to mode P5).

An application of this specific situation has been described in Ref. 8:



Minimum Constraints for Two Parallel Substitution Reactions Proceeding both with Retention of Configuration

The minimum constraints for $\overset{-}{5} \leftarrow \overset{+}{3} \rightarrow \overset{+}{4}$ (or $\overset{+}{5} \leftarrow \overset{-}{3} \rightarrow \overset{-}{4}$) can be found by discarding all the TBP's y which allow the transformations $\overset{+}{3} \rightleftarrows y \rightleftarrows \overset{-}{4}$, $\overset{-}{3} \rightleftarrows y \rightleftarrows \overset{+}{4}$, $\overset{+}{3} \rightleftarrows y \rightleftarrows \overset{+}{5}$ and $\overset{-}{3} \rightleftarrows y \rightleftarrows \overset{-}{5}$, i.e. $\overset{(-)}{12} = \overset{(-)}{15} = \overset{(-)}{25} = \overset{(-)}{34} = 0$ and $(\overset{(-)}{12}=)\ \overset{(-)}{14} = \overset{(-)}{24} = \overset{(-)}{35} = 0$.

The **E**(PO) matrix valid for this specific case can be written in a block-diagonalized form and is the adjacency matrix of the two disjoined enantiomeric graphs shown in Figure 7.

The **E**(P1) matrix valid for these constraints also gives two disjoined enantiomeric graphs (see Figure 8). The substitution reactions are still stereospecific if mode P1 is allowed.

The **E**(P2) matrix valid for the same constraints can also be transformed into two disjoined enantiomeric graphs (see Figure 8).

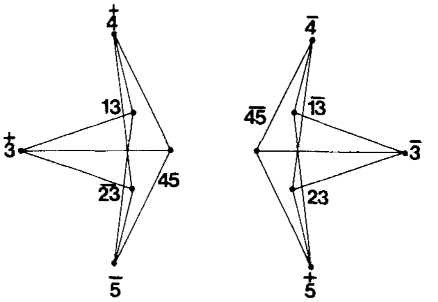
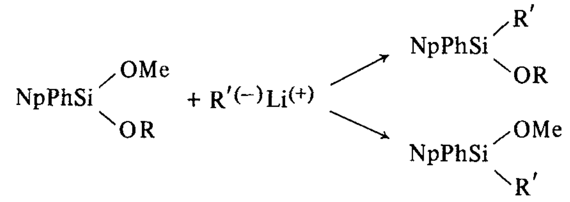


FIGURE 7 Minimum constraints for two parallel substitution reactions proceeding both with retention applied to E(PO).

The E(P4) matrix valid for the same case will thus not be block-diagonalizable by permutations of lines (and of columns), neither will the E(P3) matrix.

Two parallel substitution reactions proceeding with retention have already been described in the literature:[9]



$$\mathrm{NpPhSi}\begin{matrix}\diagup \mathrm{OMe}\\ \diagdown \mathrm{OR}\end{matrix} + \mathrm{R}'^{(-)}\mathrm{Li}^{(+)} \begin{matrix}\nearrow \mathrm{NpPhSi}\begin{matrix}\diagup \mathrm{R}'\\ \diagdown \mathrm{OR}\end{matrix}\\ \searrow \mathrm{NpPhSi}\begin{matrix}\diagup \mathrm{OMe}\\ \diagdown \mathrm{R}'\end{matrix}\end{matrix}$$

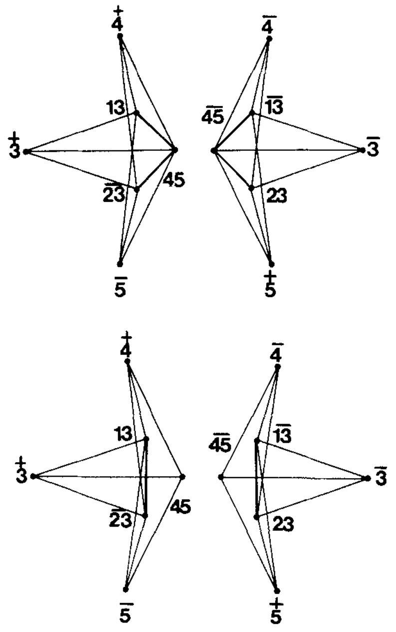


FIGURE 8 Minimum constraints valid for two parallel substitution reactions proceeding with retention applied to E(P1) and to E(P2): the reactions are still stereospecific.

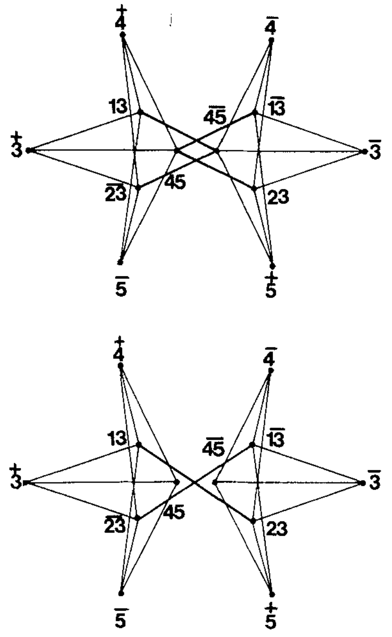


FIGURE 9 Minimum constraints for two parallel substitution reactions proceeding with retention applied to E(P4) and to E(P3): the reactions are no more stereospecific.

The chemical constraints for this reaction are more drastic than those described in this section ($\overset{(-)}{13}$ and $\overset{(-)}{23}$ are also discarded because OMe and OR, i.e. ligands 4 and 5, are the most electronegative ones and are thus expected to prefer the apical positions, which means that the only reasonable bipyramidal molecules are probably 45 and $\overline{45}$).

It is worth mentioning that the case of two parallel substitution reactions proceeding with retention of configuration also simultaneously describes the case of two parallel reactions proceeding with different stereochemistries, one with retention and the other one with inversion. Indeed, if $\overset{+}{3}$ reacts with retention to give $\overset{+}{4}$ (and $\bar{5}$) (with a change of parity[2]), then the reaction from $\overset{+}{4}$ to $\bar{5}$ proceeds with inversion (conservation of parity) and is thus automatically already described.

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† Compare also the contribution of Dugnudii, Gillespie, Marquarding and I. Ugi in the same monograph.