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## Converting Chair-like Transition States into Zig-Zag Projections A Method of Drawing Stereochemical Structures

**A short and easy method for the conversion of chair-like transition states into zig-zag projections using planar cyclohexane structures, and also the concepts of change of bond in the plane and group swap by rotation are described. Some common reactions where this method could be used to draw products include: aldol reaction, [3,3] sigmatropic rearrangements, allylation and crotylation of aldehydes, and formation of lithium enolates.**

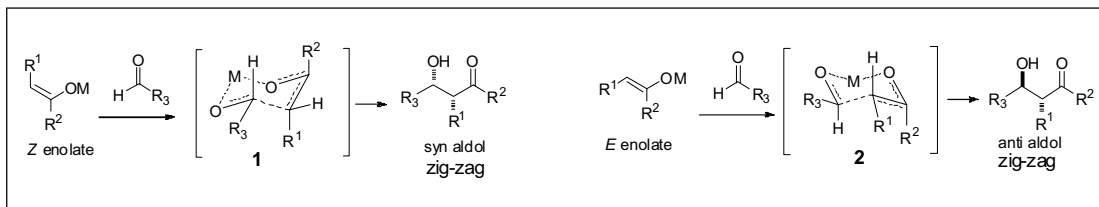
### Introduction

From early instruction, chemistry students learn that cyclohexane exists mainly in the chair conformation as it is virtually strain free. This is why chair-like transition states are low in energy and, therefore, are commonly employed to understand the stereochemical outcome of numerous organic reactions, which include: allylation and crotylation of aldehydes, formation of lithium enolates, aldol reactions, and [3,3] sigmatropic rearrangements. Many books clearly describe the process of drawing chair-like transition states [1–2]. However, students struggle to convert these transition state structures into zig-zag projections. Such a conversion is important because, generally, the product is shown in a zig-zag conformation. Linear chains are drawn in a zig-zag projection because it represents the most stable conformation. In a zig-zag projection, all carbon–carbon bonds are anti to each other. For example, in aldol reactions, after drawing the Zimmerman–Traxler model, products are drawn in zig-zag projections (*Scheme 1*). Therefore, there is a need for a method that will clearly describe the step-by-step conversion of chair-like transition states into zig-zag structures.

### Keywords

Stereochemistry, synthesis, chair-like transition states, zig-zag projections.



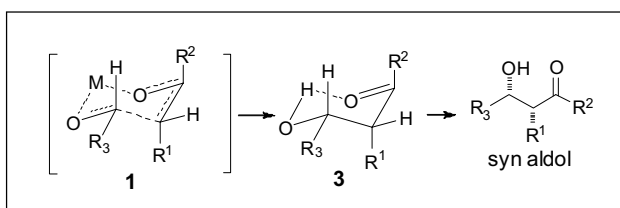


## Procedure

### Drawing Chair-like Transition States

The process of drawing correct chair-like transition states is clearly described in the literature [1–2]. Briefly, the enolate geometry is fixed, causing  $R^1$  and  $R^2$  to occupy axial positions in *Z* enolates, and axial and equatorial positions in *E* enolates (*Scheme 1*, Structures **1** and **2**). In the transition state leading to the formation of the major product, the aldehydic substituent  $R^3$  occupies the equatorial position, while the minor product is obtained when  $R^3$  is axial (not shown for clarity).

The conversion of the chair-like transition state (**1**) into the zig-zag projection is commonly explained by drawing the product in the chair conformation which is flattened out to give the zig-zag projection (*Scheme 2*) [1–2]. However, many students find it difficult to convert the flattened structures into zig-zag projections. Computer or molecular models are generally used to understand stereochemical concepts and they should be employed to transform the flattened structures into zig-zag projections when possible. However, it is often impractical to build molecular or computer models either due to time constraints or due to the non-availability of computers or molecular model kits. One method that uses Newman projections for the conversion is available online [3].

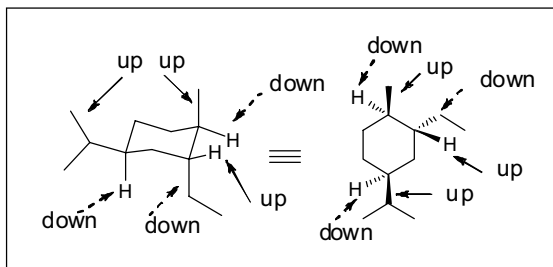


**Scheme 1.** Implications of the stereochemistry of enolates in aldol reactions.

Stereochemical outcome of numerous organic reactions is understood with the help of chair-like transition states.

**Scheme 2.** Common method for the conversion of chair-like transition states into zig-zag projections.

**Figure 1.** Conversion of chair into planar structures.



Z enolates provide syn aldol while E enolates provide anti aldol products.

The author wishes to present an alternative that uses planar cyclohexane structures and utilizes the concepts of change of bond in the plane (CBP) and group swap by rotation (GSR) [4].

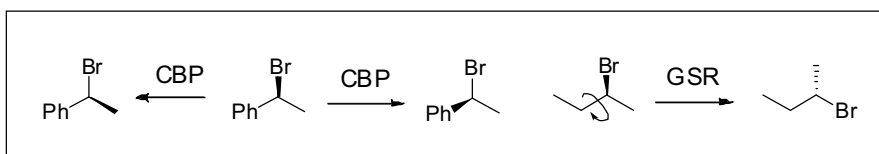
### *Conversion of Chair Conformation into Planar Structures*

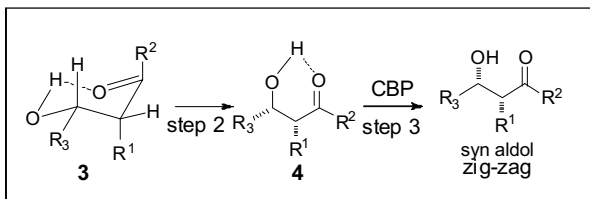
Undergraduate textbooks describe how chair conformation can be represented in flat form (e.g., *Figure 1*) [5–6]. Substituents that are up (higher) relative to their partners on the same carbon are represented with bold wedges ( $\blacktriangle$ ) in the planar structure. Substituents which are down (lower) relative to their partners on the same carbon are represented with hashed wedges ( $\cdots$ ) in planar structures.

### *Manipulation of Tetrahedra*

Wyatt and Warren have shown the technique of CBP and GSR (*Figure 2*) for the manipulation of tetrahedra [4]. These two concepts are used in our method of converting chair-like transition states into zig-zag projections. The CBP changes bonds which are in the plane. In the example shown in *Figure 2*, any one of the three bonds that are drawn could be shown with a thick wedged line as long as groups are not swapped. The GSR technique exhibits how rotation could be shown by swapping the position of two groups.

**Figure 2.** The processes of CBP and GSR.





**Scheme 3.** Author's method for the conversion of chair-like transition states into zig-zag projections.

**Method for converting chair-like transition states into zig-zag projections (Scheme 3)**

Consider the aldol reaction of *Z*-enolates (Scheme 1).

- 1) Draw the product of the reaction in chair form (**3**) [1–2].
- 2) Draw a planar cyclohexane structure of the chair product, keeping the H atom at the north-most position (**4**). All of the axial and equatorial bonds that are pointing up in the chair conformation are represented with thick lines (—) in the planar structure and all such bonds that are pointing down are represented with dashed lines (.....). Erase the H...O=C hydrogen bond.
- 3) Apply the change of bond in the plane (CBP) technique to arrive at the zig-zag projection.

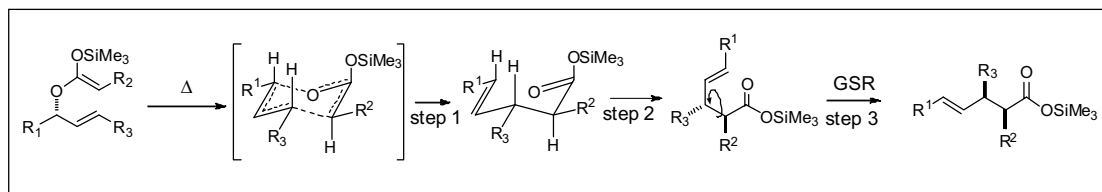
The technique should be explained to students with the help of models so that students know how it works. The method can be modified for other reactions where chair-like transition states are used to explain the stereochemical outcome of the product. As an example, the process is shown for the Ireland–Claisen rearrangement reaction (Scheme 4).

**Conclusions**

The method described here is concise and it builds upon the concepts that are familiar to undergraduate and graduate students

All of the axial and equatorial bonds that are pointing up in the chair conformation are represented with thick lines in the planar structure.

**Scheme 4.** Application of the new method in the Ireland–Claisen rearrangement reaction.



The method is useful for students taking Physical Organic Chemistry and Synthetic Organic Chemistry courses.

taking upper level organic chemistry courses such as Physical Organic Chemistry and Synthetic Organic Chemistry. Both these courses have many reactions where chair-like transition states are involved and where the products are written in zig-zag projections. The author has found that students in his class, who use this method, score better on questions regarding the stereochemical outcome of reactions that undergo chair-like transition states. The technique is also expected to help students understand the current literature, where chair-like transition states are commonly invoked to describe the stereochemical outcome of reactions. Therefore, it can be especially useful for the teaching of upper level undergraduate and graduate organic chemistry courses.

### Suggested Reading

- [1] J Clayden, N Greeves, S Warren and P Wothers, *Organic Chemistry*, Oxford University Press, Oxford, p.900, 2007.
- [2] G Procter, *Stereoselectivity in Organic Synthesis*, Oxford Chemistry Primer no. 63, Oxford University Press, Oxford, pp.43–51, 1998.
- [3] A Mehta, Directed Aldol Synthesis: Part 2 – Syn and Anti control using Zimmerman Traxler principle. <http://pharmaxchange.info/press/2011/08/directed-aldol-synthesis-part-2-syn-and-anti-control-using-zimmerman-traxler-principle/> (accessed June 2013).
- [4] P Wyatt, S Warren, *Organic Synthesis: Strategy and Control*, Wiley, Chichester, pp.380–381, 2007.
- [5] J M Hornback, *Organic Chemistry*, 2nd Ed., Thomson Brooks/Cole, U.S., pp. 205–214, 2006.
- [6] D Klein, *Organic Chemistry*, John Wiley & Sons, Inc., U.S., pp.167–174, 2012.

