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Drawing Methods for Lowest Energy Boat and Pentane Conformations

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Abstract. Pentane and boat conformations help predict and understand the stereochemical outcome of several chemical reactions. This report presents two methods that teach the processes of drawing the lowest energy boat conformations and pentane conformations. Both techniques use cyclohexane drawings that students learn in undergraduate organic chemistry courses. We provide step-by-step instructions for both techniques and show that implementing these methods results in improved student performance in questions related to boat and pentane conformations.

Keywords: upper-division undergraduate, graduate education, boat conformation, pentane conformations, *syn*-pentane interactions.

1 Introduction

Students first learn different conformations of cyclohexanes when they take Organic I in the United States. Later, these concepts help them understand reactivity and mechanisms, especially in advanced courses, such as Organic Synthesis and Physical Organic Chemistry. Graduate students quickly learn how important it is to draw chair or chair-like transition states to predict stereochemical outcomes of chemical reactions [1]. Due to this significance, undergraduate textbooks describe the conversion of planar projections of cyclohexanes into chair structures (Figure 1) (Hornback, 2006; Karty, 2018). Substituents with solid wedged lines in the planar form are up (higher) in the chair conformation. Substituents represented with hashed wedged lines are down (lower).

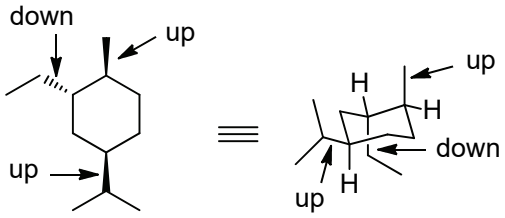


Figure 1. Conversion of a planar cyclohexane drawing into a chair structure.

However, when it comes to other typical conformers of cyclohexane, i.e., half-chair, twist-boat, and boat, textbooks do not provide enough information for students to draw these conformations quickly. Even the terminology for cyclohexane conformers remains inconsistent in introductory organic chemistry texts [4]. Chemists have addressed this gap in information for twist-boat conformers [5]. How can students draw the lowest energy boat conformation quickly? In this publication, we describe such a method which addresses this question. We acknowledge that the use of molecular models (physical or computer) enables better visualization of conformers. We recommend their use when teaching boat conformations. However, building models requires significant time, making them impractical in a traditional time-restricted, paper-style examination.

Chemists use boat conformations and other cyclohexane conformations to understand the stereochemical outcome of reactions going through a cyclohexane transition state. As multiple boat conformations are feasible (vide infra), one needs to know how to draw the lowest energy boat

conformation. One typical example where chemists use boat and chair conformations to understand the stereochemical outcome is the Doering–Roth experiment [6]. This experiment is mentioned in textbooks to discuss the mechanism of Cope rearrangement (Anslyn, 2004; Eliel, 1994; Kalsi, 2015). Boat conformations are also useful in understanding the stereochemical outcome of Claisen rearrangement [10], and aldol reactions, where *E* -enolates at times prefer a boat conformation (Gawley, 1996) [12–13]. Boat conformations also help explain Cope and oxy-Cope reactions' stereochemical outcomes that provide seven-membered rings (Grossman, 2002) [15–16].

Study of *syn*-pentane (a.k.a. gauche pentane or g^+g^- pentane) interactions (Anslyn, 2004; Nasipuri 1994) [19] is another area where cyclohexane projections are helpful for stereochemical drawings. Indeed, *syn*-pentane interactions are introduced by their analogy to the $A^{1,3}$ strain using chair conformations [19] (Burgess, 2009). However, students still have difficulty translating a perspective formula into a conformation devoid of *syn*-pentane interactions (examples given below). This difficulty is due to an absence of step-by-step instructions on using cyclohexane conformations to draw an acyclic perspective formula devoid of *syn*-pentane interactions.

Syn-pentane interactions are routinely invoked in transition states to rationalize the stereochemical outcome of products in aldol reactions, and conjugate cuprate additions (Gawley, 1996; Nicolaou, 2003) [22–23]. Pentane conformers are labeled using Klyne-Prelog terminology (e.g., g+g-) utilizing Newman projections. However, Newman projections representation of these conformers is not as informative as the zig-zag extended sawhorse formulae, and chemists prefer using zig-zag extended sawhorse formulae to draw pentane conformers (Figure 2) (Anslyn, 2004 [17]; Nasipuri 1994; Burgess, 2009) [19]. This manuscript describes step-by-step instructions that use cyclohexane projections to help draw the lowest energy pentane conformers.

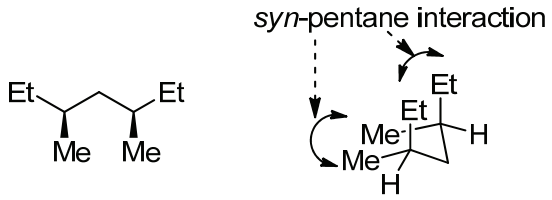


Figure 2. A conformer of the structure of the left showing *syn*-pentane interactions.

2 Procedure

2.1 Lowest Energy Boat Conformation

The most common boat representation in textbooks is the one on the left in Figure 3 [5]. From the perspective of reaction mechanisms, a more useful drawing of boat conformation is the one on the right (Anslyn, 2004 [7]) [24]. Students can draw this picture of a boat quickly as axial and equatorial bonds are drawn the same way they are in a usual chair conformation [25].

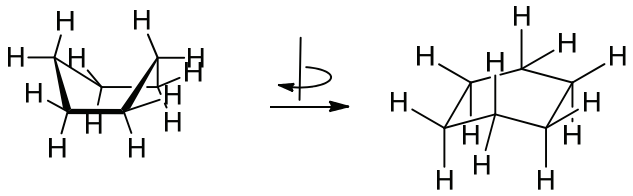


Figure 3. Two views of a boat conformation.

Consider (1*S*,3*S*)-3-methylcyclohexanol (**1**) (Figure 4). Three boat conformations of (**1**) are selected to show different energy profiles of boat conformations of the same molecule. The highest energy is the one where both OH and CH_3 are at axial positions (**2**) and the highest axial strain energy (A value) possessing substituent (i.e., CH_3) [26] is situated on the flagpole position.

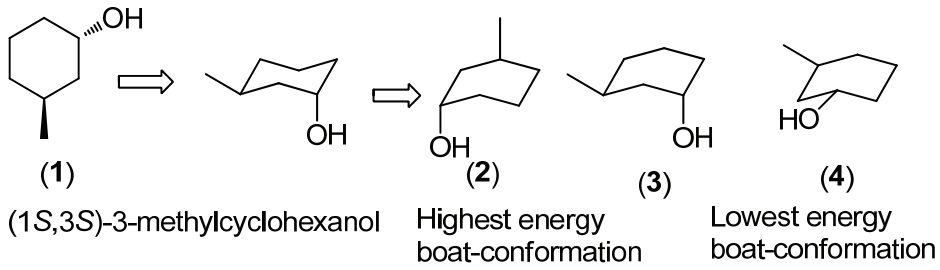


Figure 4. Different boat conformation of (1).

Students can quickly draw the lowest-energy boat conformation by knowing two things: 1) How to draw a boat (Figure 3) and 2) knowing that, if possible, the lowest energy boat conformation, just like chair conformations, should have groups with large A values situated at the equatorial positions. The method is shown for (**1**) (Figure 5). It is as follows:

1. Convert a planar cyclohexane structure into the lowest energy chair conformation.

2. In a chair conformation, all carbons of the cycle are either up or down (zig-zag). Pull up one carbon that is down or push down one carbon that is up in a chair conformer. The pulling up of one carbon is shown with an empty arrow in figure 5 sequence a, while the pushing down of one carbon is shown in figure 5 sequences b, and c. This process will give a boat conformation. Any carbon that is pulled up or pushed down will impact the adjacent two carbon atoms as well, and all axial bonds on these three carbon atoms will change to equatorial bonds. For pushing down or pulling up, only select that carbon, which will put substituents in such a way that the conformer has the lowest A value. In the case of Figure 5 sequence a, this is shown by pulling up the indicated carbon. This operation will not change methyl's equatorial position as it is not on the carbon that is pulled up, or on a carbon adjacent to the carbon that is pulled up. However, it will make OH equatorial. Now both OH and the methyl will be equatorial (lowest A value conformer) in the boat conformation, making it the lowest energy boat conformation. In the case of Figure 5 sequences b and c, pushing down the indicated carbon next to the OH will make the OH equatorial in the boat conformation. However, this operation will not change the equatorial position of the methyl group. Again both OH and the methyl will be equatorial (lowest A value conformer) in the boat conformation.

3. Draw the skeleton (no axial equatorial bonds) of the boat. The carbon atom, pulled up or pushed down, is either the flagpole carbon a or b. These are the two carbons initially shown with a solid dot in the chair conformer. At this point, it is not decided which of these dots is a and which is b.

4. Place the substituent, which was initially on the carbon pulled up (Figure 5, sequence a) (or down) on a or b. Ensure that all axial bonds are changed to equatorial bonds on the three carbon atoms affected by the pulling up or pushing down a carbon. All other carbon atoms will retain their equatorial and axial positions in the boat conformation. If no substituent is present on the carbon that is pushed down or pulled up (Fig. 5 sequence b and c), see if another substituent is present on the other carbon with a solid dot in the chair conformation. This is the carbon that we choose as a or b in the boat conformation. If such a group is present (Figure 5 sequence b), then place that group on either position a or b.

5. Place other substituents in relation to the first group. How do we do this? We check if the first group on carbon a or b of the boat still has the same up or down direction as it did in the chair. If the answer is yes, then the other group is placed in the same clockwise or anticlockwise orientation as it was in the chair. In Fig. 5 sequence a, the methyl is placed clockwise to the OH group. This is because it is down in the chair and the boat conformation. It is also clockwise to the OH group in the chair conformation. What if the first group on carbon a or b has a different direction than it did in its chair? In such a case, place the next group in the opposite sense than how it is in the chair. This situation is shown in Fig. 5, sequence b. Here, the OH group is placed clockwise to the methyl group in the boat conformation. This is because the methyl group is down in the boat conformation and up in the chair conformation. The boat drawing can be understood by knowing that the carbon is pushed down during

steps 2 & 3 of Fig. 5 sequence b, and the whole boat has been turned upside down. Instructors are encouraged to show this operation to curious students with the help of a model.

Figure 5, sequence c, shows the process where both OH and the methyl groups are not on a thick dot. Here, the placement of OH and the methyl group requires more care. Their relative positions should be such that they both are equatorial. Here the OH should change from axial to equatorial as the thick dot carbon is pushed down, and the methyl should not as it is not adjacent to the carbon that is pushed down. Neither OH nor the methyl should occupy the flagpole carbon atoms as they were not on the thick dot carbon atoms in the chair conformation.

Instructors can easily show this method to students, using a model. Pushing one carbon up or down changes axial and equatorial groups on three carbons; the carbon pulled up or pushed down and its two adjacent carbons.

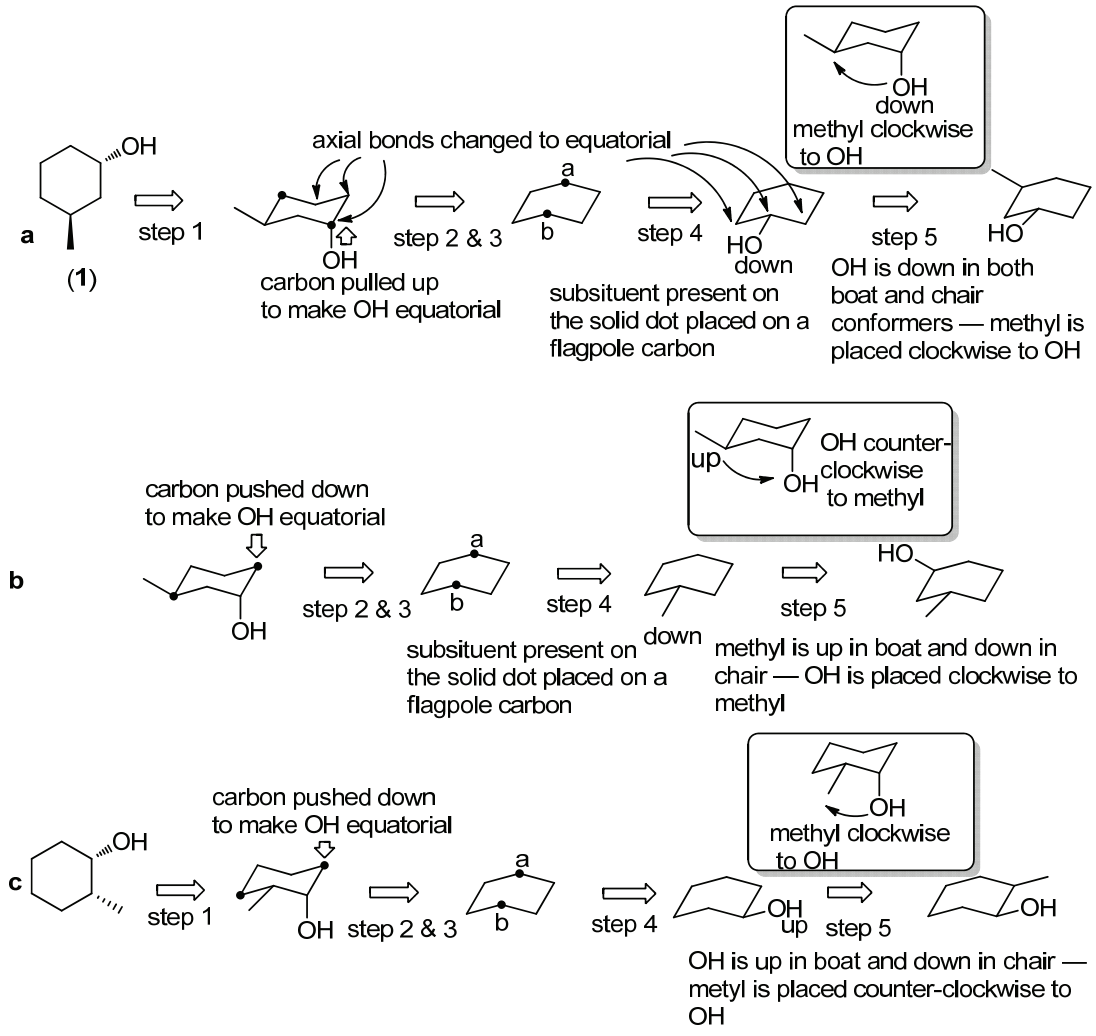


Figure 5. The sequence of steps to draw the lowest energy boat conformations.

An example [27] below (Figure 6) shows how this technique could predict a Claisen rearrangement reaction's stereochemical outcome. It follows the steps mentioned for the sequence 5b. The method also helps with the drawing of the transition state.

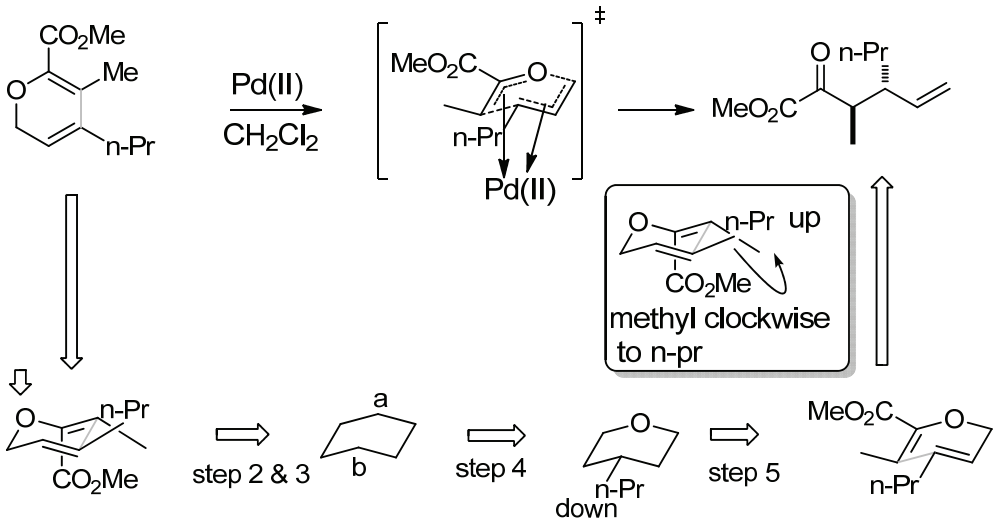


Figure 6. Application of the boat conformation method in predicting the stereochemical outcome of a Claisen rearrangement reaction. Grey lines are not actual bonds. They indicate similarity with cyclohexane conformers.

2.2 Conformation that Avoids *syn*-pentane Interactions

A technique introduced by Wyatt and Warren, known as change of bond in the plane (CBP), for manipulating a tetrahedral carbon can be handy here [1] (Wyatt, 2007). Briefly, any of the three bonds drawn in Figure 7 can be shown with a hashed wedged line as long as the groups are not swapped. The same process can be conducted if the stereochemistry is shown with a solid wedged line.

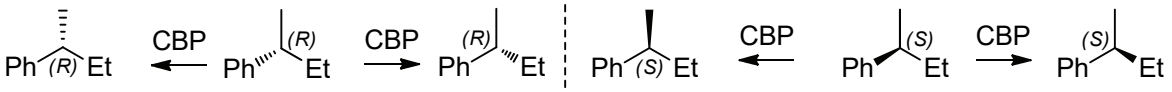


Figure 7. Process of CBP technique for the manipulation of tetrahedral stereocenters.

The method for drawing conformational drawings of pentane that avoid *syn*-pentane interactions uses the CBP technique. The method is presented with the help of examples below:

1. Convert (**5**) into (**6**) using the CBP technique mentioned above. This operation will result in the structure resembling the cyclohexane planar drawing (shown in the box). In Organic I, students are taught to convert such drawings into chair conformations.

2. Draw a chair conformation and place substituents on the chair conformation. All substituents with a solid wedged line or a hashed wedge line will be placed on either the axial or equatorial positions. Substituents with solid wedged lines will be up, and substituents with hashed wedged lines will be down. All other bonds will be part of the chair conformation.

3. Erase the extra bonds from the chair conformation (shown in grey) to arrive at a conformation that may or may not have *syn*-pentane interactions.

4. If the structure is a high energy conformer with *syn*-pentane interactions, rotate the groups on carbon atoms that carry substituents. It may be necessary to perform rotations on all such carbon atoms. Do one rotation at a time on only one carbon to avoid any mistakes. In the example shown (Figure 8 sequence a), this is done on the back carbon. The rotation is done by keeping the sawhorse skeleton and moving all substituents on the back carbon in one direction (clockwise in this case: ethyl taking H's position, H taking methyl's position and methyl taking ethyl's place). Continue these rotations until one arrives at a conformer with no *syn*-pentane interactions.

Figure 8, sequence b, shows the process for (**7**), which carries both substituents on solid wedged bonds. This change in stereochemistry between (**5**) and (**7**) is reflected in step 1. The other significant difference is in step 4, where both front and back carbon atoms are rotated. The back carbon is rotated clockwise (first empty arrow of step 4) and the front carbon counter-clockwise (second empty arrow of step 4) to arrive at the conformer with no *syn*-pentane interactions.

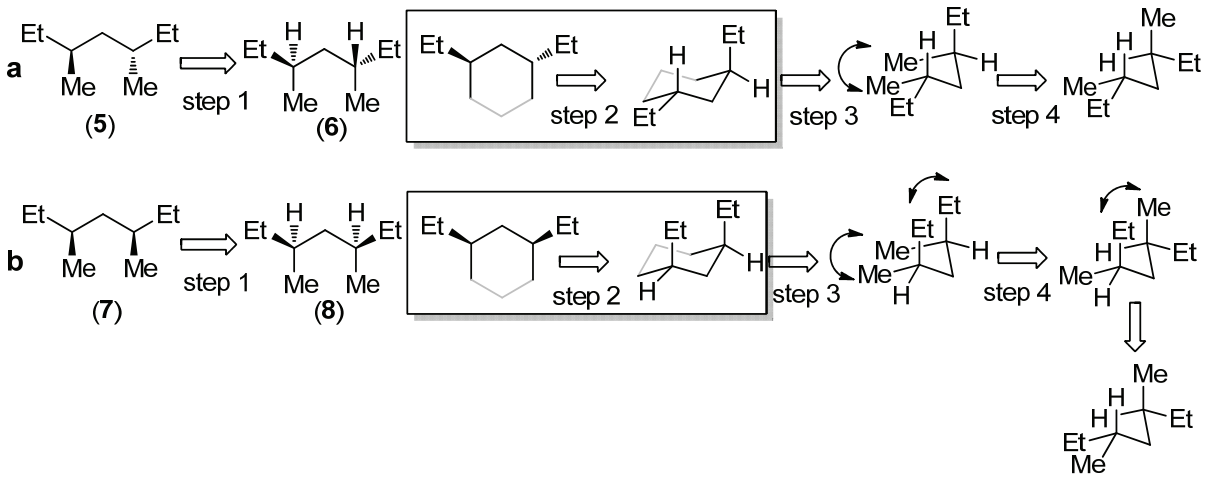
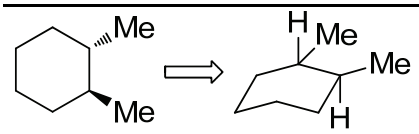
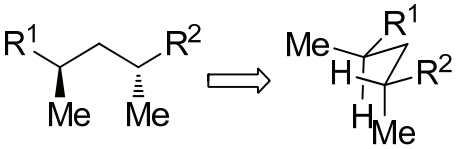


Figure 8. The sequence of steps for drawing pentane conformers devoid of *syn*-pentane interaction. Double-ended arrows indicate *syn*-pentane interactions.

The two methods were evaluated for their effectiveness during the graduate-level Physical Organic Chemistry course at The University of Tulsa in 2019. After introducing the boat and pentane conformers and before introducing their drawing methods mentioned above, students were asked to draw the lowest energy boat and lowest energy pentane conformers (Table 1). Most of the students were not able to draw the lowest energy conformers. The students were then taught the drawing methods and given one problem for the boat ((*R,S*)-1,3-dimethylcyclohexane) and pentane conformers (Burgess, 2009) as a homework assignment. In the final exam, most students answered questions concerning boat and pentane conformers correctly, thus proving an increase in student performance.

Table 1. Student performance before and after the introduction of drawing methods.





R^1 and R^2 have greater axial strain energies than Me

Student Success Rate				
Students participated	Before introducing the boat drawing method	After introducing the boat drawing method	Before introducing the pentane drawing method	After introducing the pentane drawing method
N = 6	**0%**	**100%**	**17%**	**83%**

3 Conclusion

Pentane and boat conformations have been widely used to understand and predict the stereochemical outcome of reactions. However, no systematic instructions existed to help students draw the lowest energy boat and pentane conformers until now. In this paper, we have described two methods to help students draw these stereochemical drawings. Both methods use cyclohexane drawings (planar and chair) that students routinely utilize during their undergraduate organic chemistry courses. Assessment data

have shown that boat and pentane drawing methods improved student performance in questions related to drawing the lowest energy boat and pentane conformers. Therefore, implementing these methods will help teachers increase their student scores in a Physical Organic Chemistry course.

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