Teaching Reaction Mechanisms Using the Curved Arrow Neglect (CAN) Method

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Understanding reaction mechanisms is fundamentally important to the mastery of organic chemistry. Evidence of this comes from every textbook used in organic chemistry *(1)* and from anecdotal evidence from most individuals teaching organic chemistry. Emphasis on reaction mechanisms stems from the importance of having students understand and then predict future behavior of chemical reactants *(2, 3)*. Current ideas about drawing reaction mechanisms can be traced to Ingold *(4)* who showed the flow of electrons in a reaction using "curved arrows" to indicate the origin of reacting electrons flowing to their final location. Given the importance of reaction mechanisms and the convention for drawing the reaction mechanism, the question addressed in this article is "How can we get the students to learn and express these mechanisms in the way that organic chemists understand reactions, thereby passing on the knowledge of organic chemistry to the students?"

Background

Previous studies on the strategies of teaching organic reaction mechanisms seem to be limited to single reaction types, with no studies seeming to lead to something that could be generally used in a computer-assisted instruction (CAI) environment. Karty *(5),* used a modified Hendrickson, Cram, and Hammond approach to teach mechanisms and reported increased student competence with mechanisms and increased long-term retention. Another suggestion to enhance understanding of organic reaction mechanisms emphasized balanced chemical reactions to teach mechanisms and proved to be a powerful technique in helping students understand molecular reactivity *(6)*. Further, a study concerning mechanistic insights of competitive substitution and elimination reactions was provided by Hagen *(7)*. In this work, he developed a flow chart that used a series of hierarchical questions to direct the students' knowledge about possible substitution or elimination reactions. An alternative, and more visual approach to teaching mechanisms, with only S_N2 reactions being exemplified, can be found in the work of Neeland *(8)* who discovered that bar magnets are ideal to demonstrate the electron flow of a chemical reaction. Using an overhead projector as a visualization device, Neeland substituted bar magnets for the nucleophile and the leaving group in an S_N2 reaction. As the nucleophile approached, the leaving group was pushed away quite forcefully. An interesting, and yet, fundamentally simplistic method for teaching mechanisms was described by Erdik *(9),* who created a thought-provoking, paper-and-pencil fill-in-the-blanks activity to aid students in writing organic reaction mechanisms. In this activity, organic groups and functional groups were presented as the building blocks in a puzzle that must be fit together properly to come to a compete, and correct, mechanism.

A more general approach to teaching and understanding the pedagogy of reaction mechanisms has been undertaken by Bodner. Based on a study of graduate students and their ability to predict the mechanisms of reactions, Bhattacharyya and Bodner *(10)* reached the conclusion that "*the curved-arrows used in the electron-pushing formalism held no physical meaning for the graduate students involved in this study*". In related work that emphasized how undergraduate students in an organic chemistry class understand arrow pushing, Ferguson and Bodner *(11)* found that students defend their mechanistic route based on the given structures and used their own rules to compensate for an incomplete understanding of the fundamental concepts. Finally, Bhattacharyya *(12)* investigated how students develop into practicing organic chemists by interviewing graduate students concerning their mental models of organic acids. His data suggested that the participants' mental models of organic acids showed little evidence of the anticipated hybridization of theoretical constructs and lacked the predictive capability needed to produce new science.

Research in our group has been directed toward the development of a CAI system for organic chemistry *(13)*. In our initial published work in this area, we reported on the WE_LEARN computer system for organic chemistry, which is a method for students to practice their homework via repetition until they master the concepts of a given assignment. This was accomplished through the creation of a database of questions, from which the computer could randomly select a single question each time that the assignment was performed. We term this approach as a "practice makes perfect" CAI strategy *(14)*. With this strategy in mind, we sought a way to have the computer evaluate the results of the student answer as part of a general teaching and learning methodology for reaction mechanisms. Unfortunately, only the method of Erdik *(9)* seems viable to the generalization of a method that can be used with CAI. Limited results with the Erdik-type of methodology will be described later in the manuscript. However, technical issues (e.g., lack of randomizibility of answer choices and screen size) led us to abandon this approach as a completely generalizable CAI methodology for teaching and learning reaction mechanisms. We describe here a new, generalizable method and then discuss the testing and evaluation of the methodology.

Curved Arrow Neglect (CAN) Method

A new and generalizable CAI method for teaching and learning organic reaction mechanisms has several requirements: (i) the method must be consistent with current technology; (ii) the method must be implemented with a minimum of effort from an existing starting point; and (iii) the method must be flexible enough to permit the generation of a large number of similar examples within a reasonable period of time.

When we started this research, the students were able to draw the structures of compounds online and have them graded by the computer *(15)*. The computer grading of organic structures was accomplished by converting the structures into canonical strings (e.g., SMILES) and comparing these canonical strings to canonical strings that have been independently gener-

ated as the correct answers to the question. This methodology has been utilized by several different groups *(16–18)* and leads to online structure drawing CAI methods for organic chemistry. In the ideal limit, we would like to evaluate student-drawn mechanisms, complete with curved arrows. In fact, online structure drawing methods are available for the drawing of the "curved arrows". However, while the arrows can be drawn, there are not yet methods available that allow computers to evaluate the placement of these arrows for accuracy.

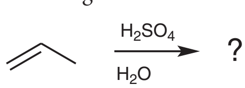
Given the success of our "practice makes perfect" CAI strategy, but cognizant of the fact that we could not get the computer to evaluate a student-drawn reaction with curved arrows, we sought to develop a compromise solution for the CAI-based teaching of reaction mechanisms. Since computers are unable to evaluate the curved arrows (at least at this point in time), we decided to have the students learn the sequence of chemical intermediates along the reaction coordinate in a way that we can provide testing of their knowledge base at a future time. We have termed this method to be the CAN method for learning reaction mechanisms, where CAN stands for "curved arrow neglect". The strategy is shown using the hydration of alkenes as an example. The goal is to have the students draw the reaction scheme shown in Figure 1. The question becomes how to get the students to think of this "moving picture", or storyboard, in a linear, understandable fashion.

In a simplistic view of this mechanism, each of the intermediates represents a potential energy minimum along the reaction coordinate, while the "curved-arrows" represent bond-making and bond-breaking. This picture helps the organic chemist to understand the reaction. Therefore, if one were to simply omit the "curved arrows" from the drawing of Figure 1, a process that we are naming CAN, one would obtain the scheme shown in Figure 2. A careful observer might note that we really have deleted more than the curved arrows showing the flow of electrons in this reaction. Anecdotal evidence from the author's (JHP) classroom suggests that students often utilize subtle cues to help them identify the correct answers to questions on quizzes or tests. Therefore, we have also deleted other clues (e.g., $+H^+$, $-H_2O$), which might help the students to find methods for determining the correct answer to the question. Additional examples of the methodology have been provided in the online materials for both the questions to the students and the feedback provided to students after they have submitted their answers.

Since each of the intermediates can be drawn and evaluated via online techniques, CAI methods can now be utilized to assist in teaching and learning of this reaction mechanism. In our WE_LEARN system *(13),* these capabilities lead to a series of questions (examples shown in Figure 3). These questions are ideally suited for random selection and presentation to students as part of practice problems or testing.

Question:

Give an electron arrow pushing mechanism for the following reaction.



Desired Answer:

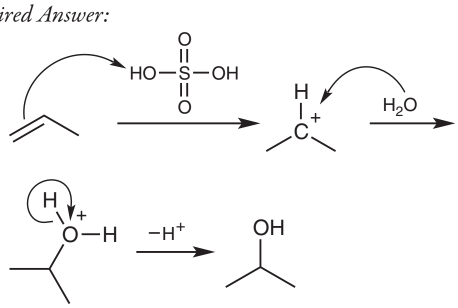


Figure 1. Complete mechanism for hydration of propene, including "curved arrows".

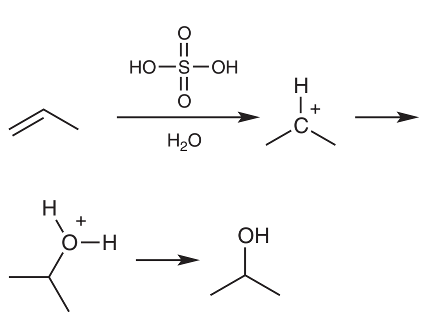
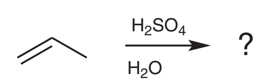


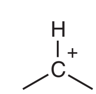
Figure 2. Mechanism for propene hydration using CAN (curved arrow neglect).

Question:

Give the structure of the next intermediate that is proposed to be in the mechanism of the following reaction.

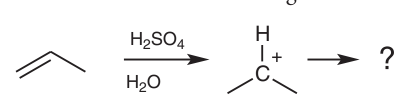


Answer:

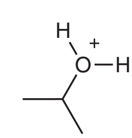


Question:

Give the structure of the next intermediate that is proposed to be in the mechanism of the following reaction.

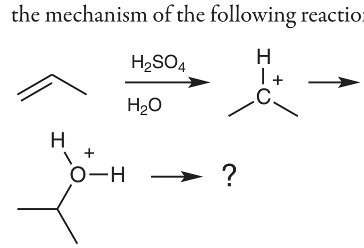


Answer:



Question:

Give the structure of the next intermediate that is proposed to be in the mechanism of the following reaction.



Answer:

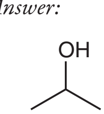


Figure 3. Potential questions for evaluating mechanism knowledge.

Evaluation of the CAN Approach

To test the viability of the CAN methodology for teaching mechanisms, we used a modified "pre-treatment" and "post-treatment" strategy.

Pre-Treatment Strategy

In the "standard" WE_LEARN approach *(13),* a large number of example reactions are contained within a database, from which a single question is chosen randomly when a student requests a question. The database of questions is carefully constructed to ensure that no concept is emphasized relative to another concept. For example, in the case of alkene hydration reactions, the database was carefully structured to give a similar number of example reactions of symmetrical alkenes, alkenes with electron-donating groups, and alkenes with an electron-withdrawing group (Figure 4). This strategy was based on the "inquiry" approach to learning *(19–22)* in which students would formulate their own mechanisms to get the observed products of a reaction. In this approach, students would see a diverse population of example compounds and, hopefully, would learn to apply proper mechanistic reasoning to obtain the correct product, either from a list of potential compounds (i.e., multiple-choice or multiple-select questions) or by drawing the compound directly. Either method would be a proper CAI approach. Again, we emphasize that it is the balancing of the number of examples of each type that is important in this methodology.

The "pre-treatment" learning results were determined by asking the students to draw complete arrow-pushing mechanisms on exams. This was done for three semesters prior to the introduction of the CAN methodology and establishes a reasonable and stable baseline assumption for how the students perform in the absence of the student tutorial CAN mechanisms. These data are from first-semester organic chemistry, where only a portion of the course contained reaction mechanisms, and from second-semester organic chemistry, where no CAI mechanisms were made available. The mechanisms were graded by a single person using a rubric to assign credit for the mechanism (Table 1). Within this rubric, 30% partial credit (1.5 points out of a total 5 points) was given for correctly identifying the product of the reaction without any of the underlying curved-arrows or mechanistic reasoning. Half credit (2.5 points out of a total 5 points) might be given for identification of the first reactive intermediate(s) with proper "curved-arrows", while 75–80% credit might be given for all reactive intermediates without proper "curved-arrows". Discretion was used by the grader for levels of correctness that might be intermediate to these limiting conditions.

In an attempt to identify our experimental methodology in a qualitative environment, several methods of instruction were utilized. First, instruction of the mechanism during the traditional lecture is performed for each new reaction. The students were informed that complete curved-arrow electron-pushing mechanisms must be written on the exams. In addition the traditional laboratory experiments, for which applicable mechanisms could be drawn, were given as laboratory quiz questions and graded by the teaching assistants responsible for their laboratory instruction. Significant is the fact that no practice capabilities concerning reaction mechanisms were provided via CAI techniques for the drawing of mechanisms. Only questions concerning the correct final product of the reaction were asked, leaving students to learn their "own" methods for obtaining the final product of the reaction.

The results of student performance in these "pre-treatment" studies[1] were disappointing. Despite presenting every mechanism in lecture and reminders that the drawing of organic reaction mechanisms would be included on the exams, the cumulative average of the class after grading these mechanisms was only ca. 30%, that is, the same score as they would have obtained for only getting the correct product of the reaction. Clearly, the students were not learning the mechanisms, at least not in the way that practicing organic chemists would understand. This does not mean that no one learned the mechanisms. It only means that the group average tended towards what they had practiced using the WE_LEARN CAI techniques to predict the products of the reaction. These data are reflected in Exams 2 and 3 of Fall 2005,as shown in Table 2, where no CAN mechanistic strategy had been used.

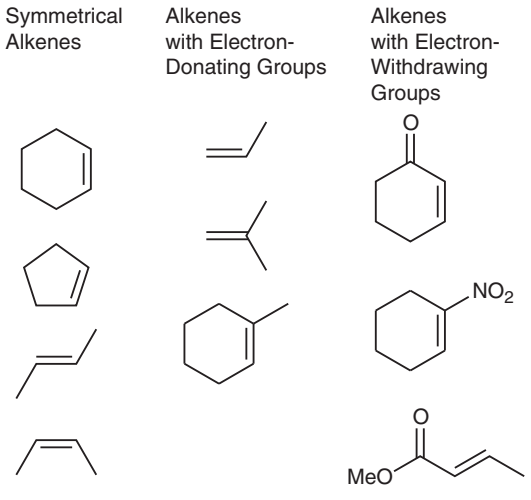


Figure 4. Example for database construction.

Table 1. Control Rubric for Grading Reaction Mechanisms

Points	Characteristic
1.5	Correct final product, without any hint of, or even incorrect "curved arrows"
2.5	Correct intermediates drawn without "curved arrows"
2	First intermediate drawn with correct "curved arrows" but incorrect pathway following the first intermediate
–1	Minor mistakes in "curved arrows" (e.g., one or two out of the total number of arrows going in the wrong direction)
–2	More than two mistakes in arrow direction
–0.5	Missing a "curved arrow"

Note: Each mechanism is worth a total of 5 points.

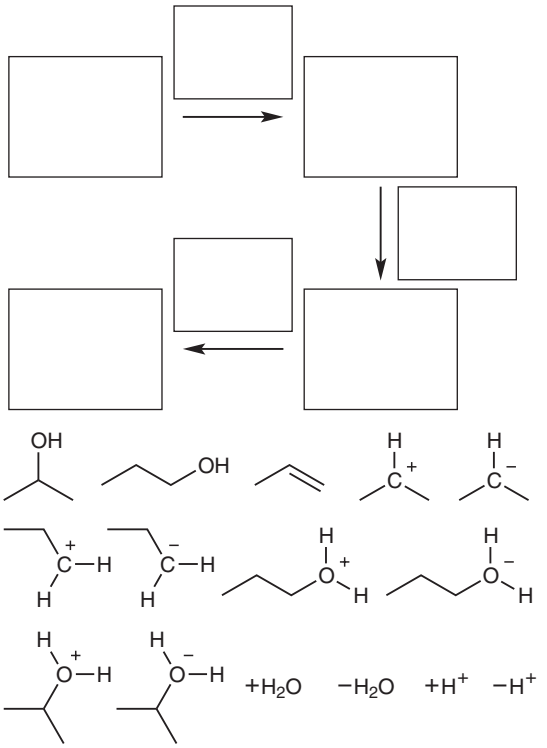


Figure 5. Click-and-drag strategy for drawing a CAN mechanisms for the hydration of propene.

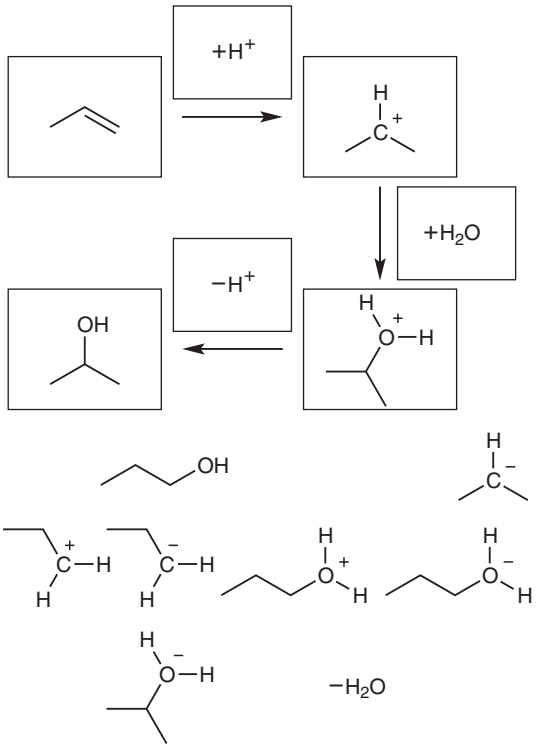


Figure 6. Correct answer for the question posed in Figure 5.

Implementation and Testing of the CAN Strategy

Preliminary evidence that the CAN strategy could be used to enhance students' ability to draw mechanisms was obtained for Exam 1 of the Fall 2005 semester. Two alternative, but similar, techniques were used to provide testing and preliminary data for CAI techniques. In the first technique, a reaction scheme without relevant chemical structures was generated and the students were required to click on the structures and drag them to their proper places in the overall scheme. This strategy is reminiscent of the Erdik *(9)* fill-in-the-blank puzzles. A sufficient number of distracting structures were given to ensure that the students needed to pay attention to the relevant issues (e.g., charge, resonance). An example of this strategy as applied to propene hydration is shown in Figure 5 and a correct answer to this question is shown in Figure 6.

With this type of CAN strategy for teaching and learning mechanisms, CAI techniques could easily be used to count the number of correctly placed structures compared to the number of incorrectly placed structures. More importantly, it allowed students to practice some form of drawing mechanisms, where previously only the traditional classroom techniques were available. Although student response to this technique was positive-to-enthusiastic, this technique was soon abandoned, because of the computer-based requirements for the reactive intermediates (i.e., large number of structures to draw, size issues that prevented having all pictures on the computer screen simultaneously, and the inability of the software to randomize the order of presentation of the possible answer choices).

The alternative CAN strategy for teaching and learning organic reaction mechanisms has been shown in Figures 2 and 3. A sufficient number of questions could be easily generated to assess the feasibility of the CAN approach in a CAI format. The preliminary results are shown in Table 2 for Exam 1 of the Fall 2005 semester, where this strategy was first implemented. Note that the performance of students in drawing mechanisms on paper was dramatically improved from our previous levels of ca. 30% to ca. 55%.

Table 2. Average Mechanistic Exam Scores

Semester	Exam Type	Exam 1		Exam 2		Exam 3	
		N[a]	Score (%)	*N*	Score (%)	*N*	Score (%)
				Pre-Treatment			
Fall 2005	Paper	—	—	159	33	150	27
				Post-Treatment			
Fall 2005	Paper	163	54[b]	—	—	—	—
Fall 2006	Paper	73	61	66	42	62	50
	Computer	106	74	94	62	94	62
Fall 2006	Paper	35	61	26	66	13	70
	Computer	194	73	192	69	195	68

[a]Number of students. [b]Contains preliminary testing data.

These positive results from the first exam caused us to continue the CAN methodology and to develop the required CAN mechanism materials for Exams 2 and 3 of the 2006 calendar year. The necessity for waiting an additional year relates to the large number of reactions, intermediate structures, and so forth that must be generated to implement this strategy. The single variable being changed from the Fall 2005 semester to the Fall 2006 semester was in the testing methodology. Students were given the option of drawing two complete electron-pushing reaction mechanisms *with* curved arrows (labeled here as the paper version of the exam) or completing five structures of the CAN-type strategy that ask for the next reactive intermediate along the reaction coordinate.

Two trends seem to be apparent in the data. First, the paper-exam results show a clear improvement in exam scores for being able to draw mechanisms, raising from our pre-treatment levels of ca. 30% to levels as high as 70%, which is close to the overall exam average. We conclude that providing students with CAN mechanisms in a way that they can practice providing the correct structure, gives enhanced results in drawing mechanisms with curved arrows. This seems to be true, regardless of the student population taking the exam.

The second trend apparent from the data is the increased willingness of the students to take the computer version of the exam, compared to taking the paper version of the exam. The reasons for the numbers of students taking the computer exam, compared to taking the paper exam, are unclear. The data in Table 2 indicate either similar exam scores between the two methods to slightly enhanced performance on the computer exam. Whatever the reason, we conclude that the methods give approximately equivalent measures of student capability. Reasons for the enhanced number of students taking the exam by computer will be the subject of another report from these labs.

Summary

We have proposed the curved arrow neglect (CAN) method for drawing structures as a way to provide a CAI method for teaching and learning organic reaction mechanisms. Application of this method shows enhanced capabilities for students to draw reaction mechanisms, even with the inclusion of curved arrows. This CAN method for describing reaction mechanisms can be used in any CAI package currently available or to be developed. It requires only proper incorporation of the individual chemical structures of the CAN mechanism into an appropriate learning format (e.g., flash cards, CAI technique).

Note

1. Pre-treatment is represented in "quotes" here, because this is not a true pre-treatment. A true pre-treatment would be prior to any instructional methodology.

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Supplement

Examples of the methodology