The ability to use the curved-arrow or electron-pushing formalism is one of the most vital skills in the organic chemist's repertoire. The ability to use this formalism to visualize and then write the mechanism for a reaction is a powerful tool for practicing organic chemists, particularly synthetic chemists who routinely use their knowledge of mechanistic organic chemistry to break apart a target molecule during retrosynthetic analysis (1). Mechanisms play a key role in predicting the selectivity of a synthetic transformation (2) and in the development of novel reaction methodologies. The most common method for communicating these mechanisms is curved-arrow or electron-pushing drawings. In this formalism, single- or double-headed curved arrows are used to show the flow of electrons from source to sink.1 Practicing organic chemists use this formalism in the ever-changing environment of new molecules and intermediates, which forces them to think about the classic mechanisms of organic chemistry outside of the traditional or simple contexts in which they are first taught.

A variety of prescriptive articles regarding the arrow-pushing formalism have been published (3–12). Sections describing the art of using curved arrows can also be found in most introductory organic textbooks, and several supplements to the traditional textbook have been devoted to this topic (13, 14). While these ‘how-to’ accounts are important pedagogical tools and tell us something about the thought processes of practicing organic chemists, little is known beyond anecdotal evidence about how novices approach the process of solving mechanism problems.

As part of a larger investigation of problem solving in organic synthesis, we studied the way graduate students solved mechanism problems that were far removed from the simple systems in which mechanisms are traditionally presented. One of our goals was to probe the extent to which the students’ experiences with organic chemistry as undergraduates prepared them to solve mechanism problems they are likely to encounter as graduate students or practicing organic chemists.

Methodology

The theoretical framework for this study was phenomenography (15), a research tradition defined as “... the empirical study of the limited number of qualitatively different ways in which various phenomena in, and aspects of, the world around us are experienced, conceptualized, understood, perceived, and apprehended” (16). The phenomenographic perspective focuses on how people experience a given phenomenon, rather than the phenomenon itself. Although people experience a particular phenomenon in different ways, phenomenography presumes that the total number of variations is finite and limited.

Phenomenography can help the subject’s awareness “change from being unreflected to being reflected” (16). Thus, the interview process often makes explicit what was previously implicit, enabling the researcher to elucidate underlying thought processes and then interpret them, thereby giving a voice to the participants. Phenomenography was an appropriate theoretical perspective for this study because we assumed that our participants might not approach the problem-solving tasks in the same way, but they would do so in a limited number of ways that we could describe and interpret.

The participants in this study were recruited from a first-semester graduate-level organic chemistry course at a large, state-supported, research-oriented university. The catalog entry for the course reads: Advanced Organic Chemistry: Modern Structural Organic Chemistry, Including Introduction to Molecular Orbital Theory and Reaction Mechanisms. The course covers current theories of structure and reactivity and uses those ideas to describe mechanisms of organic reactions. Enrollment is primarily intended for first-year graduate students in the organic division of the Department of Chemistry, although students from other divisions or even other departments often take this course, as well.

Fourteen graduate students, who represented a quarter of the total course population, were recruited on a voluntary basis. One of the students had an M.S. in Chemistry and one was a fourth-year student majoring in analytical chemistry; the others were recent graduates of B.S. programs. The students in the sample population were working toward Ph.D. degrees in a variety of divisions, including: analytical (2), biochemistry (3), inorganic (2), organic (5), and medicinal chemistry (2). The two medicinal chemistry students came from research groups involved in organic synthesis and are therefore essentially “organic” graduate students. The sample population for the study closely resembled the total population of the course.

The participants were interviewed as they used the curved-arrow or electron-pushing convention to predict the mechanisms of reactions that would transform an indicated starting material into a specified target molecule. All interviews were conducted using the think-aloud protocol (17). The problems were two- to four-step variants of traditional reactions, such as $\text{S}_{\text{n}}1$ and $\text{S}_{\text{n}}2$ substitution, shown in Figure 1. The first part of question 1, the addition of bromine to cyclohexene, was a reaction that these students were likely to have seen in their sophomore-level organic chemistry class. It was therefore used as a warm-up problem so that the participants could get used to the interview process. The answers to questions 2, 3, 4, 6, and 9 can be found in traditional organic chemistry textbooks. Answers to questions 1, 5, 7, and 8 can be found in Figures 2, 3, 4, and 5, respectively.
Figure 1. The interview questions.

Figure 2. Answer to question 1. Gray arrows show the alternate path to produce the stereoisomer.
Because content knowledge is a confounding variable in research on problem solving in chemistry (18), the following resources were made available for use during the problem-solving interviews: Advanced Organic Chemistry: Parts A and B by Carey and Sundberg (19); Advanced Organic Chemistry by March (20), and a set of molecular models. The participants were also told that the interviewer would answer any content-specific questions that did not reveal the solution to one of the problems. Not surprisingly, only the most successful problem-solvers used any of these resources.

The primary source of data were interviews that were audio-taped and then transcribed. Key observations in the form of field notes written during the interviews or immediately after the interview provided a second source of data. The participants’ written solutions represented a third source of data. All three sources of data—interview transcripts, field notes, and written solutions—were carefully and repeatedly examined. The data were coded to generate emergent themes, which were further subdivided into categories based on the characteristics of the data (21). The final conclusions were discussed with the professor who taught the course as a validity check, to ensure that the researchers’ interpretations of the data were consistent with his experiences with the students.

Figure 3. Answer to question 5.

Figure 4. Answer to question 7.

Figure 5. Answer to question 8.
Results and Discussion

If asked to distill the results of this study to a single sentence, we might respond: *The curved arrows used in the electron-pushing formalism held no physical meaning for the graduate students involved in this study.* Like the arrows drawn when equations are first used to represent simple chemical reactions, they were nothing more than a vehicle for getting from the reactants to the products. Using a distinction from previous work (22), these arrows are not “symbols” because they did not symbolize anything in the students’ minds. The students did not understand that the function of this formalism is to explain the “how” and the “why” of a reaction. The vast majority of their comments during the problem-solving process focused on entities such as the starting materials, intermediates, and products rather than on the physical processes involved in the transformation of starting materials into products.

Patterns that emerged during the analysis are summarized below. Direct quotes from the problem-solving interviews are given to support our claims. All participants are identified by pseudonyms; comments by the interviewer are indicated by an “I.” Italics have been added for emphasis.

**“It Gets Me to the Product”**

Because the arrows bore no physical meaning, the most common justification the participants used for any given step in the problem-solving process was: “It gets me to the product.” Jen provides useful insight into arrow-pushing as a way of “playing around”:

I hope this is right. It seems right to me. *It’s basically just playing around.* It’s the hardest part I think when you’re doing these things because I’m so intent on getting from reactant to product and if I see that something is not working I’ll try and force it to work instead of just letting my mind go and play with what you have.

Like Jen, the other students found it very easy to force a solution because the curved arrows had no physical meaning. Consider the following dialogue, for example, that occurred when Hubert referred to one of the reference books:

I: If you don’t mind me asking, what are you looking up?
Hubert: Well I was hopefully going to try to find something on metal halides. And if that doesn’t work, I’m going to start looking for formation of esters. If that doesn’t work, I’m going to read the section on Grignard reagents and force the Grignard mechanism to fit.

When asked about her general strategy of mechanistic problem-solving, Marion noted:

Um, well I just try to force it to work. That way I can get it to work. I don’t know if it’s always right or not.

As a result of their “it-gets-me-to-the-product” orientation, the students had a tendency to propose nonsensical steps in which they formed unlikely intermediates. In showing the demethylation of anisole to phenol with BBr₃, for example, all of the participants generated the highly unstable phenyl cation intermediate shown in Figure 6.

Another example of the “it gets me to the product” phenomenon is shown in Figure 7. Most of the participants in this study protonated the ester oxygen in both questions that dealt with ester saponification reactions. Protonation at the carbonyl oxygen, however, would have been expected in both cases because of the additional stabilization of the resulting cation. This behavior may stem from the participants’ method of analyzing the reactivities of a molecule. In these saponification reactions, the students frequently talked about the ester as if it were a carbonyl attached to an ether, rather than as a single unit that would have a characteristic reactivity.

A third example of the “it gets me to the product” phenomenon is shown in Figure 8. After numbering the corresponding carbon atoms in the starting material and target molecule, from 1 to 7, Homer tried to use the electrons from the vinyl group in some form of nucleophilic attack to open the cyclobutane ring. In all, 12 of the 14 participants tried to do the same thing, using the vinyl group electrons to attack the four-membered ring. This pathway is particularly egregious since it would require these electrons to break apart a relatively unactivated carbon–carbon bond.

Homer’s response in Figure 8 illustrates another result of the participants’ approach to these problems. Because they focused upon only those steps that would generate some aspect of the product, the participants were unlikely to take

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Figure 6. Marion’s response to question 9.

Figure 7. Horace’s response to question 3.

Figure 8. Homer’s response to question 5. This problem was based on a classic synthesis of estrone (23).
the necessary steps used to prepare for another, often key, step. In this example, the electrocyclic ring opening to set up the Diels–Alder would be considered a preparatory step. Because of their product-based strategy, the participants did not consider this step because it would not immediately be useful to generate product. Although Jen initially thought of the Diels–Alder reaction to make the final product, her strategy guided her away from that path:

Jen: Oh, I’m numbering the carbons, trying to figure out which ones correspond from starting material to product and you figure out how they moved. [Long pause.] You know what, I don’t think it’s Diels–Alder, because I don’t see a diene that I want to play with.

Another example of this phenomenon can be found in Marcus’ attempt to solve question 2, in which the hydroxy group is deprotonated so that it can be used as a base in the subsequent step. Although he correctly recognized the deprotonation of the alcohol he did not pursue that avenue further:

Marcus: Well, I’m thinking is yeah, O.K. that makes sense, I’m going to deprotonate it. But then what’s that going to do? It’s going to give the t-butanol and then, um. Then I don’t know, it’s going to reprotonate or something. That’s not, but that’s not. What I’m saying is that’s not getting me towards a product.

This failure to consider preparatory steps would be especially detrimental in solving problems that contain retro-condensation or cycloaddition steps. The students’ tendency to focus on only those steps that bring them closer to the product also played an important role in the ester saponification problems, where leaving groups must be generated as a prelude to bond-breaking.

Another aspect of the “it gets me to the product” philosophy was the participants’ use of a fairly naive mapping strategy in which the starting materials and target molecules were essentially static. This strategy turned out to be especially problematic in the ester saponification problems. Consider the comments of Jen, for example:

Yeah, you know to me it was like well, if I label this oxygen 1 and this oxygen 2, then when I looked at the product I automatically labeled this oxygen 1 and oxygen 2 like they couldn’t move. And that’s silly. Because, it’s because of the way the molecule is, I could easily flip that in space. You know what I’m talking about?

As noted by Bodner and Domin (22), one of the key differences between novices and experts in organic problem-solving is that molecules that are dynamic in the minds of experts remain static in the minds of novices.

**Connect the Dots Strategy**

The students’ tendency to focus on doing anything that gets them to the product led them to rely on essentially a “connect-the-dots” strategy, in which they used curved arrows as a conduit between intermediates in the pursuit of the target molecule. This was seen most often in the warm-up problem, where the participants first drew the bromonium ion and then drew the arrows between the olefin and bromine molecule. Consider the following answer to the question: “What do you think was the hardest part to solving this problem?”

Marcus: Drawing the actual mechanism—the arrows, the curved arrows. Those are the hardest part. ‘Cause even though I may know, I know what’s going on. Like I know the bromine’s, you’re going to get this bridged intermediate and then you’re going to have a back, like backside attack from the other bromine. I’m kind of confused on how exactly the arrows are going, whether it’s going like this or that double bond’s actually attacking and that kind of thing.

The students’ inability to determine the first intermediate—that is, their cue to which dots to connect—was one reason why participants often found it hard to even start a problem. Another aspect of the connect-the-dots strategy involved the participants tendency to identify a reaction type, such as elimination, and then use the curved arrows to go to the next step in the reaction, as illustrated by the following quotes from Charles and Hubert:

Charles: Um, well to form a double bond here means you have two hydrogens there. You have one hydrogen there, here you have one, one. O.K. so you’re removing a hydrogen, so subtract a hydrogen, hydrogen and a bromine comes out. So HBr is eliminated in the reaction. Now you got to figure out what causes that to come out.

Hubert: I knew I had to get rid of a hydrogen, through an elimination reaction to form this double bond. I knew bromine was a good leaving group so I had to find a way to, you know, to abstract that hydrogen.

Marcus shares his rationale behind his correct response to a problem as follows:

Well I guess maybe, just knowing that it’s going to be a [4+2], knowing … that … it’s going to give me a six-membered ring with the double bond here and just kind of, I don’t know. I mean knowing that the [4+2] addition is going to give me a cyclohexene and that’s what I needed to make. ‘Cause this is a cyclohexene derivative, that maybe would go back into the aromatic ring. I don’t know.

**Conclusion**

The participants in this study were the kind of students others would classify as “good.” They were bright, conscientious, and working hard to master the elements of organic chemistry. They also were students who did well in terms of the grades they received in this course.

There was a disconnect, however, between the way they approached the problems in this study and the approach expected by their instructor. For example, almost all of the participants readily produced the accepted sequence of steps for the warm-up problem. When asked to explain each step, however, it became clear that the participants had simply reproduced a memorized sequence of events. Rather than solving chemical problems, they were essentially playing with puzzles.

The literature on conceptual problem solving has suggested that students can often produce correct answers to mathematical calculations in general chemistry courses without understanding the concepts on which their solutions are based (24–26). This study demonstrated that organic chemistry students can produce correct answers to mechanism tasks without having an understanding of the chemical concepts
behind their responses. In both contexts we need to find a way to help good problem-solvers develop into good chemists. Within the context of organic mechanisms, this means helping the students recognize that there are concepts and principles that lie behind each step in the mechanisms they propose that need to be more clearly comprehended.

One could argue that this task can be most easily accomplished by having students justify each step of the mechanisms they draw, thereby helping them recognize that the majority of organic mechanisms are permutations and combinations of the paradigmatic steps of acid–base chemistry and S_N1, S_N2, E1, and E2 mechanisms. However, two things need to happen before this can occur. First, students need to be more explicitly aware that arrow-pushing serves an explicatory function. The results of this study suggest that many students who have completed the sophomore course in organic chemistry and gone on to graduate work in chemistry are not aware that the function of the mechanisms they draw with the fundamental principles of chemistry. This gap occurred because students were not aware that the function of the mechanisms they proposed were to explain the process the reactant(s) underwent to generate the product. A better understanding of the purpose of mechanisms in organic chemistry would be a step toward helping students shift their focus from determining lower-energy intermediates or conformations when proposing mechanisms to seeking lower-energy reaction pathways.

Second, even students who might be aware of the need to connect the curved arrows with chemical concepts cannot achieve this goal because their knowledge of the principles of organic chemistry is not at an operational stage where they can apply it to problem solving. For example, the participants in this study could readily define the concepts of Brønsted bases and nucleophiles but were often hard pressed when asked to differentiate between the two while solving a problem so that they could apply these concepts to proposing an appropriate mechanism for the reactions in this study.

We are not questioning the utility of the theoretical definitions of these concepts introduced in class; we are advocating the inclusion in our courses of explicit insight into how that theory is incorporated into problem solving. Aspects of this phenomenon are captured in the following quotes from participants in this study:

Hubert: They write textbooks for people that already know chemistry. ... So since the textbooks aren’t very useful, I generally don’t, don’t even bother with them. That’s my problem all through doing chemistry is the textbooks. They use this specialist language to be more correct, but then in the process of being correct they make themselves much less useful.

Charles: That’s the thing about organic chemistry too, I wish the teachers would, would emphasize the visual aspects of what’s actually going on to help you understand. Let your eyes see it. ‘Cause I mean, uh, when I go in to classes, just all I see is bonds move here and there.

The results of this study are consistent with both authors’ experiences with graduate-level courses in organic synthesis—separated in time by almost 30 years—that did an excellent job of discussing organic reactions but spent virtually no time discussing how organic reactions are put together when one is faced with the task of solving a synthetic problem.

One example of a definition that would be more operational is that bases target protons, which are small, whereas nucleophiles target larger atoms such as carbon. Another example might involve noting that anions derived from atoms from the first or second row of the periodic table may exhibit basic and nucleophilic behavior, whereas anions derived from third row and larger atoms will typically only exhibit nucleophilic behavior.

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Notes

1. Single-barbed arrows denote the movement of a single electron, double-barbed arrows indicate a pair of electrons.

Literature Cited