Making sense of the arrow-pushing formalism among chemistry majors enrolled in organic chemistry

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This paper reports results of a qualitative study of sixteen students enrolled in a second year organic chemistry course for chemistry and chemical engineering majors. The focus of the study was student use of the arrow-pushing formalism that plays a central role in both the teaching and practice of organic chemistry. The goal of the study was to probe how students made sense of the arrow-pushing formalism by examining their responses to seven organic chemistry problems that required the use of this formalism. This paper discusses common barriers to students' understanding of the arrow-pushing formalism, the concepts and ideas students apply when they use this formalism to solve mechanism problems, and implications of the observation that they used this formalism in a meaningless, mechanical manner.

Keywords: Organic chemistry, mechanisms of reactions, problem solving, sense-making, arrow-pushing formalism, constructivism

Introduction

There is a fundamental change in the thought process required to master the material students encounter when they move from the introductory general chemistry course to the second year course on organic chemistry. General chemistry takes a product-oriented view of chemical reactions, focusing on two moments in time. The materials that would be present at the moment the reaction starts are placed on one side of a single or double arrow and the substances that would exist when the reaction either comes to equilibrium or the limiting reagent is consumed are listed on the other side of the arrow. Organic chemistry requires that students adopt a process-oriented view of the reaction, in which they must envision a continuous flow along the mechanistic pathway that transforms the reactants into the products of the reaction. The movement of electrons that plays a vital role in this continuous process is also indicated with an arrow, but now the arrow is curved. These curved arrows can have a single barb on the head to denote the movement of a single electron, or a double barb to indicate a pair of electrons (Bhattacharyya and Bodner, 2005).

A variety of names are used to describe this formalism, including 'curved arrow', 'electron pushing', and 'arrow pushing.' Regardless of the name, the function of this formalism remains the same, as we have noted elsewhere (Ferguson and Bodner, in press). It is a *"symbolic device for keeping track of electron pairs in chemical reactions"* (Loudon, 1995, p. 89). Curved arrows represent the movement of electrons from an electron-rich 'source' to an electron-deficient 'sink' in a rigorous manner, as covalent bonds are formed and broken (Scudder, 1992; Loudon and Stowell, 1995; Grossman, 2003). Furthermore, curved arrows represent much more than a convention designed to help students when they first encounter the relatively simple reactions examined in the first organic chemistry course. This formalism is used routinely, either explicitly or implicitly, when practicing organic chemists discuss complex organic reactions in real-world situations.

The arrow-pushing formalism allows a chemist to explain reactions at the level of the flow of electrons, to understand new or previously unseen reactions, and to deconstruct the reaction into steps. In the strictest sense, arrow pushing serves as a form of electron bookkeeping. But it can do more than just keep track of electrons. In the hands of a practicing organic chemist, it can be used to explain or describe other physical manifestations, including why a reaction does (or does not) take place; why it takes place at a certain site and not at other reactive centers; and why attack occurs on one side or plane of a molecule and not on the other. Arrow pushing begins simply enough, with the examples encountered in the introductory organic chemistry course, but it is ultimately a very complex and indispensable tool for the organic chemist (Bhattacharyya and Bodner, 2005).

Some have questioned our use of the term *arrow-pushing formalism* to describe the use of curved arrows to represent details of the mechanisms of organic reactions. They have said, "*we don't push arrows, we push electrons*." The authors have

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deliberately chosen to use the term *arrow-pushing formalism* because we believe there is a fundamental difference between the way students and practicing organic chemists use curved arrows. We believe that organic chemists do, in fact, use curved arrows to 'push electrons'. Our work indicates, however, that many students are not 'pushing electrons'; they are, in fact, pushing arrows.

In the traditional undergraduate organic chemistry course the arrow-pushing formalism is first taught explicitly and then, as more reactions become known and the semester progresses, it becomes an implicit component of the course. In order for students to be able to draw a correct arrow-pushing mechanism, they must simultaneously keep in the mind an array of chemical principles, many complex and abstract theories, and numerous facts. They must be able to look at the problem from different perspectives, selectively apply specific chemical and physical concepts, and correctly draw the starting material, all intermediates, and the final product of the reaction while maintaining the strict conventions of the arrow-pushing formalism.

The primary goal of the study upon which this paper was based was a better understanding of how students enrolled in a two-semester second year organic chemistry course for chemistry and chemical engineering majors make sense of the arrow-pushing formalism. The study also tried to identify barriers that stood in the way of sense-making by looking at the processes students use to solve mechanism problems that involve the arrow-pushing formalism, to see whether students apply what they are taught within the context of the arrow-pushing formalism, and to probe what students believe they are supposed to be doing when solving these problems.

Theoretical framework

The constructivist theory of knowledge (Bodner, 1986) provided the theoretical framework for this study. The constructivist theory, or constructivism as it is also known, describes "*how people incorporate new knowledge and learning into existing knowledge and then make sense of that knowledge*" (Ferguson, 2007, p. 20). The personal constructivist model proposed by Kelley assumes that *"individuals construct knowledge for themselves through construing the repetition of events, and that knowledge is individual and adaptive rather than objective"* (Geelan, 1997, p. 17). Bodner *et al*., (2001) summarized Kelly's personal constructivism as follows, *"Kelly argues that we each create our own ways of seeing the world; the world does not create them for us. Each of us builds our own constructs, tries them on for size, and eventually revises them"* (p.15). Because of the focus on how individuals build and eventually refine personal constructs, Kelly's model of personal constructivism provided a useful theoretical framework that allowed us to focus on how the participants in this study made sense of a very specific construct within the field of organic chemistry, the arrow-pushing formalism.

Methodology

The most appropriate methodology for investigating a research question that deals with sense-making was one based on qualitative techniques (Denzin, 1994; Denzin and Lincoln, 1994). The approach known as grounded theory (Strauss and Corbin, 1994, 1998) was chosen because the goal of the research study was to describe what students did, rather than test one or more hypotheses. Grounded theory allowed the analysis of the problem-solving processes of the undergraduate students to be first coded, then organized, and finally described. Purposeful sampling (Patton, 1990) was used to obtain volunteers for this study who would potentially provide the greatest amount of information. We chose undergraduate chemistry majors as the population on which to focus because they represented a section of the organic chemistry student population who were most likely to be motivated to learn and master the arrow-pushing formalism. Sixteen college students majoring in chemistry at a large Midwest University enlisted as volunteer-participants. The volunteer population was equally divided in terms of gender, with 8 males and 8 females. The participants all came from a second-semester organic laboratory course for chemistry majors that was taken at the same time as the second semester of the organic chemistry lecture course for chemistry and chemical engineering majors.

The participants volunteered to explain their thought processes while solving problems associated with writing the mechanisms to the seven organic reactions shown in Figure 1. The problem-solving interviews were conducted with the sixteen participants, one at a time, in a small conference room. The traditional 'think-aloud protocol' (Larkin and Rainard, 1984) was used during the hour-long interviews. During the interviews, the first author (RF) watched, listened, and observed the volunteers. He also conversed with the volunteers, asked them questions, and when necessary, provided hints. Pseudonyms by which the participants will be referred were created for each of the sixteen students interviewed.

The interviews occurred toward the end of the spring semester, when the maximum amount of lecture and laboratory material had been presented in the two-semester course. Each interview started with an explanation of the nature of the study, a description of the think-aloud protocol, and a discussion of what we expected the students to do during the interview. The researcher audiotaped and videotaped each interview with concurrent note-taking. Videotaping was used to record the action of a very visual process

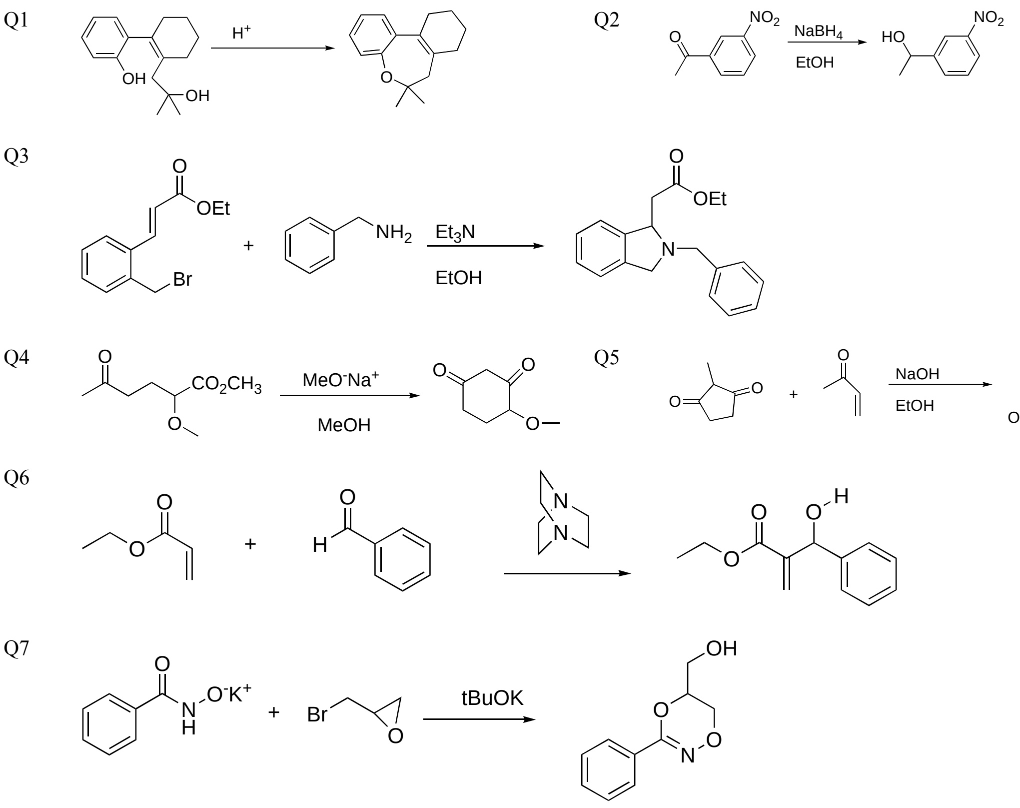

Fig. 1 Mechanism problems given to the participants.

— the drawing of the structures of molecules and the writing of a reaction mechanism — and recorded changes the students made in their drawings during that process. The videotape allowed the researcher to listen, ask questions, and make observations. The audiotape was used as a basis for transcripts of what was said during the interviews. The combination of video and audiotape allowed the interviewer to note, during the process of transcription of the interviews, whether a particular statement was uttered before, during, or after something was written on the mechanism worksheet.

The organic chemistry problems selected for the interviews were organized on the basis of our perception of increasing difficulty for second year students. To provide a benchmark for analysis of the data obtained from the students, four organic chemistry professors were interviewed to obtain their perspective on the problems. The professors agreed that, in general: the problems embodied typical reactions seen in a second year organic course; they represented a broad survey of the common reactions of organic chemistry; and the problems became successively more difficult in the order in which they were given. All the reactions used for the interviews contained mechanisms that involved the flow of electron pairs via acid/base, nucleophile/electrophile, or oxidation/reduction reactions. Reaction mechanisms that would involve radicals, single-electron transfer reactions, pericyclic reactions, and/or intramolecular rearrangements were deliberately excluded from the problem set.

The data available for analysis existed in four forms: audiotapes, videotapes, worksheets, and field notes. The first stage in the analysis involved transcribing the audiotapes. The content of the videotapes was then used to augment the transcripts. This stage involved watching the videotapes while annotating a copy of the transcript of each interview. This approach to augmenting the transcripts was useful for several reasons. First, participants frequently used pronouns such as ‘this’ and ‘that’ to describe their mechanism or employed other vague terms, such as ‘here’ and ‘there’. The videotapes provided the information needed to resolve any confusion about the way in which these terms were used. Videotape augmentation of the transcripts also enabled us to resolve confusion about many of the inaudible sections on the audiotape. Occasionally, the review of the videotape also allowed us to rectify phrases and words that had been incorrectly transcribed, and therefore ensured greater fidelity of the final transcript.

In our analysis, we avoided the temptation to list common errors with the arrow-pushing formalism that have been generally acknowledged by experienced instructors and textbook authors. Scudder (1992), for example, devoted an entire section of his book to common errors students make with the arrow-pushing formalism. In particular, he warned the reader against creating intermediates with multiple charges, electron flow starting with a proton, and mixed media errors because "*…the pitfalls of using arrows are so numerous that something needs to be said*" (p. 127). Grossman (2003) highlighted the difficulty in drawing a reasonable mechanism by listing twenty-five 'common error alerts' in the first chapter of his book on writing reasonable mechanisms for organic reactions. Because the errors identified by Scudder and Grossman are already familiar to current instructors, we resisted recording student mistakes, and instead, employed a naturalistic approach (Denzin and Lincoln, 1994) with the intent of describing "… *phenomena in terms of the meaning people bring to them*" (p. 2). This allowed our research to focus on our goal of understanding the process by which students used curved arrows from their perspective.

Once the interviews had been described, a grounded theory approach was used to search for themes that might emerge from the data (Strauss, 1987; Strauss and Corbin, 1994, 1998). Data analysis involved using qualitative coding software (Dupuis, 2000); organizing codes using concept maps and matrices; writing narratives of each participant's interview; and then structuring coded quotes around emergent categories and themes. The last stage in the data analysis involved member checking, in which the results of our analysis was discussed with the participants, to corroborate our ideas about the participants' sense-making process, and to verify or validate the emergent themes.

What are the barriers to sense-making and where do they occur?

Four different categories emerged from our data that were related to barriers that interfered with students' making sense of what they were doing when they employed the arrow-pushing formalism. Sometimes these barriers were nothing more than a 'bump' along the road to a correct mechanism for the reaction, hindering progress toward a solution. At other times they acted as a dead-end, halting all progress. The four codes that were related to the idea of barriers toward a solution were labeled *inability to recall*, *inability to apply or understand*, *poorly understood content*, and *non-content-specific barriers*. The first three of these codes shared a common characteristic, they were barriers to successful performance that resulted from a reliance on factual knowledge that either had been or could have been memorized, rather than a strong conceptual understanding of the material.

The first category, *inability to recall*, was used to describe segments of the transcript in which the participants relied on memory for an answer, as opposed to predicting the answer on the basis of a conceptual understanding, and their memory failed them. Consider Jim's description of the $NaBH_4$ reduction, for example. Jim confessed that, *"I just can't remember what ethanol does. I know that it comes in at the end of the reaction."* Jim knew that ethanol was more than just the solvent for this reaction, but he could not remember the role that it played in the reaction. He only remembered that ethanol reacted during the later part of the mechanism.

As he worked on this mechanism, he drew resonance structures for the carbonyl and spent several minutes on the resonance interactions between the NO_2 group and the aromatic ring. At this point he seemed to confuse question #2 with an electrophilic aromatic substitution reaction, mentioning electron-withdrawing and electron-donating groups. He eventually returned to the carbonyl, correctly using the hydride to reduce the carbonyl — a step that now made sense to him — and then exclaimed, "*I'm thinking I remember it now*." He then tried to invoke a hydroboration mechanism, and his inability to recall specific content took him off the correct path. Only after the interviewer asked him about the function of ethanol, did Jim reconsider the wisdom of the hydroboration route. For several minutes he was not willing to abandon hydroboration, but he eventually deprotonated the EtOH and presented a reasonable mechanism for the reaction.

Barb faced a similar situation with question #2, when she remarked, *"OK, I am not remembering how this reaction works. Like, it seems easy to have this [ambiguously points to either a proton or hydride] go here [carbon of carbonyl]. It has to do with the ethanol but I can't remember."* Barb recognized the reaction, drew the carbonyl as R_2C-O without keeping track of charges, and then drew a pentavalent borane (H_4BNa). After a period in which she remained stuck because she wanted to use $NaBH_4$ to protonate the oxygen of the carbonyl, she eventually remembered the reaction between borohydride and a carbonyl. It seemed as if she was using a 'source to sink' approach, in which the hydride attacked the carbon of the carbonyl, but she could not string the steps of the reaction together. Several times, she commented that she couldn't remember the steps of the reaction and it was clear that her inability to recall memorized information was a barrier to success. Like Jim, Barb eventually produced a plausible mechanism for the reaction. Furthermore, both Barb and Jim seemed to recognize electron donors and electrons acceptors, even if they did this in a somewhat ambiguous fashion. Yet, throughout their work they relied on memory rather than the application of a conceptual understanding, which means that the inability to recall information was an important barrier on the way to answering this mechanism problem.

The *inability to recall* barrier influenced the work of other students, such as Ryan and Andy, for whom it

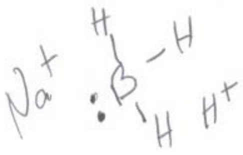

Fig. 2 Jill's structure for $NaBH_4$

acted as a dead-end. They recognized the reagent, $NaBH_4$, and it triggered an emotional response. They remembered that they did not like reactions in which this reagent was involved, and chose not to answer this question. Because of their inability to recall information about $NaBH_4$, they independently employed the same strategy when they encountered the $NaBH_4$ reduction reaction: skip it!

The second barrier, the *inability to apply or understand*, was used to code situations in which the student either misapplied information they recalled from memory or did not understand the information that was remembered. Jill's work on the $NaBH_4$ reduction reaction provides an example of the inability to apply or understand information. She correctly understood the trivalent nature of a borane, but could not apply this information. Jill said, "*I know boron is three bonds, I think. And, but, to bond with sodium, it would need to be minus. It would have to be extra proton that makes me think that it would be plus.*" She correctly predicted the number of bonds for a neutral boron atom, and deduced that the borohydride ion would be negatively charged, but then created the structure shown in Figure 2. She did not recognize that a trivalent boron atom would be a Lewis acid or that a hydride ion would correspond to a hydrogen atom with a pair of electrons. Most significantly, she did not balance her charges.

The inability to apply or understand information interfered with students successfully distinguishing between similar intermediates, similar reactions, and similar reagents, which resulted in the participants often becoming confused. Some of the participants confused the acid-hydrolysis reaction in question #1 with an electrophilic aromatic substitution (EAS) reaction, for example. When Naomi drew the structure of the intermediate in this mechanism and noted the existence of a phenyl cation, she associated it with the carbocation intermediate in the EAS reaction. She did not seem to understand the special conditions and reagents required for EAS reactions, nor the difference between a phenyl cation and the carbocation intermediate.

Beth, Elizabeth, Jackie, Naomi, Ryan and Jill all provided an example of confusing reactions that looked similar on the surface when they used the alkene in question #3 to attack the protonated nitrogen atom. Jill demonstrated this confusion when she said, *"When you have four bonds to nitrogen, it is positively charged. So, if this [a hydrogen] leaves as H^+, these electrons stay. So this [alkene] would be bonded to on there [nitrogen] and then the hydrogen would go away."* As can be seen in Figure 3, Jill tried to use the alkene to attack a saturated nitrogen the way an alkene might abstract a proton in a reaction with HBr.

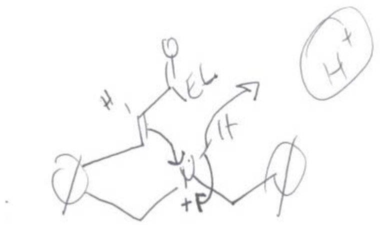

Fig. 3 Jill's drawing of the attack on an ammonium nitrogen by an alkene

Students were also confused by reaction names that sounded similar. Edward, as well as several others, exhibited confusion between hydroboration and borohydride reduction. This is not surprising because the names of the reactions are similar and the starting materials, at first glance, look similar. On two separate occasions, Edward tried to form a B–C–OH linkage. He repeatedly wanted the boron (either as BH_3 or the BH_4^- ion) to attack the carbon of the carbonyl. But he never made it much farther than BH_4^- dissociating into BH_3 and an H^- ion.

A third category of barriers to success could be labeled *poorly understood content*. It differs from the second category because it did not involve content that had been memorized and then poorly applied or understood. It sometimes involved application of general chemistry topics, such as acid-base and oxidation-reduction, and at other times involved topics that been encountered in the organic chemistry course, such as aromaticity. A subcategory emerged within the category of poorly understood content that was coded as *energetics*, which was a one-word description of the misuse of a variety of concepts including kinetics, equilibrium, and driving force. Jackie provided an interesting example of this category while writing the mechanism for Question #3, when she said: "*So, let's see what we can do ... well, bromine sometimes, it just leaves 'cause it wants to. So, we'll draw that out and we'll say that bromine leaves."* Rather than relate the dissociation of a leaving group to an organic chemistry concept, she invoked a mystical version of 'free will'.

Having a poor understanding of acids and bases acted as a barrier for the undergraduate students. Because so many of the reactions students encounter in an introductory organic chemistry course involve acids and bases, it is important for undergraduate students to understand these concepts well. Acids by definition either donate protons or accept lone pairs; bases either accept protons or share lone pairs. Although the definitions of acids and bases seem simple, identification of a substance as an acid or base is not. After nearly four semesters of college-level chemistry, the participants in this study struggled to identify acids or bases involved in the reactions in Figure 1, which resoundingly qualified *poorly understood content* as a barrier to success. Scott and Ryan provide good examples of this phenomenon.

While working on Question #3, Scott noted, *"I suppose if you had this bromine anion [Br^-] out here it could take, it could be willing to pull the hydrogen off the nitrogen ... The electrons could go into the nitrogen that the bromine is pulling off."* While Scott did use an anion to abstract a proton, he used the bromide ion to deprotonate the $R_2NH_2^+$ ion in spite of the fact that it is a very weak base.

While working on question #5, Ryan was unable to distinguish between a base and a nucleophile.

> *"It is going to be a nucleophile now, absorb with a proton. It's going to attract it toward it, and I am just looking in the other part of the reagent for a strong proton source because there are no protons on it to pull over and it really wouldn't make a whole heck of a lot of sense to pull a proton over from the methyl group."*

Two noteworthy barriers emerged from Ryan's vignette. First, Ryan knew that pulling a proton off of a methyl group was not likely, which implied he understood something about the strength of a C—H bond and the relatively poor ability of hydrocarbons to act as Brønsted acids. Yet, for Ryan, the concept of a nucleophile was poorly differentiated from that of a base. Ryan's poor understanding of the content knowledge that would enable him to discriminate between a reactant acting as an base and the same reactant acting as a nucleophile hindered his progress with the mechanism. Ryan's transcript also provided a key phrase illustrating the difficulty students often had identifying acids and bases in reaction mechanisms. He was searching for a strong proton source and therefore wanted to find a weakly attached proton. Unfortunately for Ryan, all the protons looked the same and he missed the most acidic hydrogen. The barrier facing Ryan revolved around his inability to evaluate the relative acidic strength of the hydrogen atoms on the molecule. Without a conceptual understanding of the concept of pK_a, Ryan lacked the means to overcome this acid/base obstacle.

Ryan's was not the only participant to ignore pK_a's in his work. The concept of pK_a never surfaced in any of the interviews even though this topic was explicitly taught, the textbook dedicated several pages to the topic, and it was continually reviewed in lectures. Without exception, the participants did not identify, think about, or employ any acid/base principles based on pK_a in their work on the questions in this study.

The concept of oxidation/reduction reactions is another fundamental principle from the general chemistry course that should be a familiar concept for a second year chemistry major. It is therefore interesting to examine the ways in which the participants in this study handled the second question, which involved a typical organic-chemistry redox reaction in which $NaBH_4$ is used to reduce a carbonyl. Most of the participants recognized the question as one that involved reduction. That does not mean that they had a good understanding of what that term meant. During the interview, whenever one of the participants uttered the word *reduction* while discussing this reaction, they were asked: What does that word mean to you? Consider Barb's answer: "*A reducing agent is going to take electrons, accept electrons? No, it's going to reduce the species ... [pause] ... OK, a reducing agent reduces this [the carbon]. So, it's going to take away a pair of electrons, I mean ... I just confused myself."* Barb's use of terms such as *reduction* or *reducing agent* might be considered an example of what Vygotsky (1986) called a *verbalism*, "*... a parrot-like repetition of words ..., simulating a knowledge of the corresponding concepts but actually covering up a vacuum."* Vygotsky argued that verbalisms occur when scientific concepts are excessively abstract and detached from reality.

Barb knew the word *reduction*, correctly associated it with something in which $NaBH_4$ would be involved, and used it appropriately in a sentence. Yet, when pressed to explain what it meant, she could not relate 'reduction' to either the mechanistic details of the reaction, a chemical definition of the term, or the experiment she had performed in her laboratory course that utilized this compound as a reducing agent. Like so many others in this study, her content knowledge could only be described as poorly understood.

Other participants exhibited a similar lack of a clear understanding of the concept of redox reactions. Consider Ryan's description of the function of sodium methoxide in the mechanism for question #4.

> Interviewer*: OK, MeONa is sodium methoxide. Do you have any idea ... how it might act in a solution?*
> Ryan*: Isn't [it] a strong base?*
> Interviewer*: Very good. Very strong base. So, the definition of a very strong base is what?*
> Ryan*: It's gotta; it generally has an extra pair of electrons.*
> Interviewer*: And what might it do to another molecule? Like ... a high school/gen. chem. definition of a base?*
> Ryan*: Oxidize a molecule.*

As might be expected, Ryan's inability to distinguish between the role the methoxide ion would play in acid/base versus redox reactions was an insurmountable barrier to his finishing the problem. His weak understanding of how the concepts of oxidation/reduction would apply to organic reactions also showed up in his reluctance to try to answer question #2, which involved a $NaBH_4$ reaction.

The fourth category, which was coded as *non-content related barriers*, was created to include barriers that involved the spatial reasoning abilities of the students. As might be expected, this barrier arose when students could not 'see' the connection between a reactant drawn in a linear conformation and the subsequent cyclical product. Alex described his problem with question #4 as follows: *"This [the starting material], we'll just have to switch ... hmm, I don't know. I am at a loss ... It [the product] just doesn't seem right because they [the starting material and the product] are different."*

Although Alex recognized that the final product was very different from the starting product, he continually tried to draw out the chain and close the ring. Yet, he could not bring the two ends of the chain together to form a six-membered ring. It did not make sense to him that the straight chain given in the problem would cyclize. Alex's lack of spatial reasoning ability therefore prevented him from solving this mechanism problem. All the participants who struggled with spatial reasoning did so when solving either question #4 or question #5.

More than 20 years ago, Bodner and McMillan (1986) argued that spatial reasoning abilities are related to *"... a learner's ability to disembed information from a visual field and restructure it."* Although barriers related to spatial reasoning abilities were limited to only certain participants, they played an important role in preventing these students from solving problems that required a significant transition between the structure of the starting material and product of the reaction.

What concepts and ideas do the students apply?

Another aspect of our study of sense-making within the context of the arrow-pushing formalism involved probing the concepts and ideas the students applied while using it. Our results suggested that the participants adhered to the constructs of the formalism as best they could. In many ways, they did the things they were taught to do, applying the rules.

Loudon and Stowell (1995) clearly delineated six rules for arrow-pushing. They defined a curved arrow as "*always drawn with its tail at the source of electrons and its head at the destination"* (p.37). Our participants often correctly applied this rule, drawing the arrow from high- to low-electron-density, from negative charge to neutral or positive charges, and from neutral to positive charges. In general, the students pushed the arrows they drew in the correct direction, and seemed to understand the formalism behind using curved arrows.

The participants in this study often recognized the key features of the reaction, contemplated the properties of the starting material or product, and tried to use the fundamental concepts or principles of chemistry. The principles invoked during the problem-solving interviews were diverse and often included ideas such as basicity, nucleophilicity, electronegativity, and stability. In light of other work described in this issue of the journal, it is not surprising that they invoked a wide range of rules to govern their actions. Consider Naomi's response to a comment the interviewer made when she called a reagent a conjugate base.

Naomi: *Yeah, yeah, I always have to go through several different steps to get back to remembering what my leaving groups are. A good leaving group is a strong base, which means that it will be a weaker acid. And then I just ... I just know it leaves. Ha. It will pop off, not a big deal.*

Elizabeth provided a good example of the students' understanding of the convention that curved arrows should be drawn from the "source" to the "sink."

Elizabeth: *Oh, I just saw, that maybe since that [$NaBH_4$] has an excess of negative charge that might be a good candidate for donating, donating its excess electronic charge. And then I would have to invent a mechanism as to how it would break off. Maybe it just naturally would. [draws] ... I guess that would be my answer.* [attacks the C=O with a H^- ion from $NaBH_4$].

Erika invoked the concept of basicity when the interviewer probed how she would figure out whether a proton is acidic.

Erika: *If the conjugate base is stabilized by resonance, so this [carbonyl] would be I think because it had these electrons in it.*

Naomi invoked the concept of nucleophilicity while working on question #4.

Naomi: *Well, a lot of times when I see a salt like this [MeONa], I think of this, oxide, as like an attacking group. A lot of times it will come up on a ketone or an aldehyde and come up from the bottom and attack them.*

Scott used electronegativity to analyze the chemistry of a carbonyl group.

Scott: *And compared to carbon, oxygen is more electronegative, so, ... uhm ... moving these electrons to oxygen and away from carbon is a little bit easier than doing that [in] the other direction and taking them from oxygen and putting them on carbon.*

The concept of stability was invoked by Steve, as follows:

Steve: *The way that I think of it is, you don't want to make any one atom too unhappy. And so if it can distribute its misery around to the other side, then it works out a little better, and makes for better chemistry.*

Although the students invoked the common concepts or principles of organic chemistry while describing their problem-solving efforts, a careful

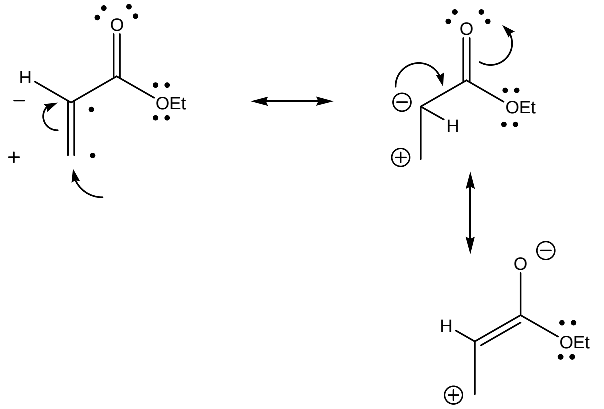

Fig. 4 A reconstruction using ChemDraw of Jim's use of resonance structures

analysis of their responses suggested that the students' conceptual understanding of these principles might best be described as a broad, but superficial. They were familiar, but not overly familiar, with many of the concepts of organic chemistry.

Two unexpected applications were encountered in our analysis of the student responses to the mechanism problems in Figure 1, a mapping process and a heavy reliance on resonance structures. We use the term *mapping* to describe a careful matching, on an atom-by-atom basis, of features of the starting material to the structure of the product. Erika explained how this mapping process worked when she stated, "*Well, the first thing that I think of is what I need to lose and what I need to get rid of. You know, to form this [product], and what has to become connected, eventually.*" Mapping, as part of the arrow-pushing formalism, was not explicitly described in either the textbook or lectures associated with the course, and yet every participant did this. Every one of the undergraduates, and even the professors with whom the problems were discussed, described how they compared the starting material and the product to understand the differences between these molecules. Although the process of mapping was universal, the extent to which it was used varied among the participants. Furthermore, some only vocalized the mapping process, whereas others explicitly labeled the carbons to physically link atoms in the starting material and product.

The idea of resonance was frequently applied. In some cases it played such a fundamental role in the problem-solving process it seemed to be used as a driving force toward the solution. For others, it was appropriately applied to help the participant understand the mechanism. For most participants, it was only invoked for one step in the reaction. Consider Jill's approach to the reaction that used $NaBH_4$ as a reducing agent. She explained her work by noting, "*But, I am trying to think how I would draw this out [carbonyl], the two ions. Because I know that this [C=O] is also gonna form this [$^+$C-O$^-$].*" For Jill, resonance structures were another form of atom mapping.

Jim used resonance structures in question #3 as the basis of his mechanistic pathway, as shown in Figure 4, while deciding whether the double bond attacked the nitrogen or the nitrogen attacked the double bond. He noted, "*the electrons here [nitrogen] were to attack at this carbon [the β-carbon] because you can draw the carbon as a negative charge on one end and a positive charge on the other end.*" Once Jim saw that the β-carbon had a positive charge in one of his resonance structures and that the carbonyl helped separate the charges, he knew the answer to his question about the site of attack and the direction in which the curved arrow would flow.

The meaninglessness of the arrow-pushing formalism

On the surface, there was a resemblance between what the students drew on paper as they worked on these mechanism problems and what a practicing organic chemist would draw. In spite of this resemblance, there was little, if any, connection between what the students did and what chemists think about when they visualize a chemical reaction. For many of the students, the process of drawing curved arrows was purely mechanical; it had little (if any) intrinsic meaning. Like the graduate students in a previous study (Bhattacharyya and Bodner, 2005), the curved arrows had a pragmatic or utilitarian function; they got the student to an answer to an academic exercise.

The mechanical aspect of the curved arrow symbolism resulted in an interesting aspect of the mystical being incorporated into answers provided by Natalie, Andy, Barb, Beth, and Jill. Consider Natalie, for example, who twice confessed to being an electron goddess. At one point in the interview she admitted, "*They called me 'electron goddess' on one exam because I moved electrons to wherever I wanted to.*" Barb captured the essence of the meaninglessness of the arrow-pushing formalism for so many students in the following interchange with the interviewer.

Barb: *And, I can push the electrons around.*

Interviewer: *Now what does that mean? Just pushing them around?*

Barb: *Kind of putting them where I want so I can get, so I can get the charges to ... Well, not putting them where I want but ... yes I am.*

Barb reluctantly admitted that she was putting the electrons where she needed them so she could get the charges to balance by just "*push[ing] the electrons around*".

The participants viewed arrow-pushing as an academic exercise, producing a mechanism on paper because they were asked to do this. One of the professors, on the other hand, remarked how mechanisms, by design, removed the supernatural factor of organic chemistry. With great zeal, this professor talked about how mechanisms could be used to show that organic chemistry was not ‘magic’. For the undergraduates, who sometimes forced the electron flow to proceed in whatever direction they wished, arrow-pushing was nothing more than a form of mental calisthenics. It was as meaningless as solving algebraic calculations from a math book, with no direct connections to the world in which they lived, or even to the laboratory from which the participants were recruited.

No one encapsulated the meaninglessness of the arrow-pushing formalism better than Andy. When asked about his test strategy while working on problems that he could not answer, Andy explained:

> *…[I] knew when I was going to get a zero on a question but I had to try, you know. So, I just ran with it. I had to call it the Andy reaction. It gets [you to] whatever product you want but you may not get any points on a test.*

Andy created his own named-reaction as a test-taking strategy for answering mechanisms that did not make sense. Motivated by pure desperation, the Andy reaction represented an effort to gain points on an exam where none should exist.

Summary, assertions and implications

The participants in this study made sense of the arrow-pushing formalism in a complicated and complex manner. From a pragmatic point of view, they understood what they were supposed to do; they used curved arrows to transform a starting material into a product. While doing this, they demonstrated an academic understanding of organic chemistry that was both broad and shallow. They knew some of the fundamental rules and applied them sparingly, but they had a relatively poor understanding of the concepts, theories, and rules that were relevant to the reactions on which they worked. While solving specific mechanism questions, they either did not remember the necessary concepts and rules, or only remembered part of this information. Material that they correctly remembered was often misapplied because the concept was not understood or because the relevant concept was confused with a competing idea. This confusion forced the students to rely on rote memory and recall. The arrow-pushing formalism that was designed as a powerful construct for explaining the mechanism of organic reactions, and for predicting the products of new reactions, was reduced to ‘just pushing arrows’.

Because they lacked a firm grasp on the fundamental concepts they were expected to master, the undergraduate students approached the arrow-pushing formalism as a meaningless exercise. This was clearly indicated in the interviews, in which the participants were remarkably candid. At least half of them explicitly commented that producing a mechanism lacked meaning for them; that it was a form of mental gymnastics. These participants exuded a feeling of disconnect between the reaction as it occurred in the laboratory and the paper exercise of drawing arrows depicting this reaction.

The participants knew that they could provide a ‘route’ that connected the starting materials to the product. They did this by either coupling content knowledge with adept problem solving or by drawing arrows to make the mechanism look real, to make it look feasible, or to make it look acceptable to their instructor. But they only articulated a rationale for the reaction occasionally. The important foundational aspects of energetics, pK_a, stability, and reactivity were frequently absent during the problem-solving process.

Participants who were the most likely to struggle with writing reasonable mechanisms for a reaction had a strong tendency to invoke the ‘mystical’ as a key link in the problem-solving process. In spite of de-mystification philosophies held by the faculty who taught the second year organic courses, several students ironically described themselves as if they were ‘electron goddesses’, capable of moving the electrons a will. These students invoked the mystical as a resource for extricating themselves from a dead-end that resulted from either confusion or a weak knowledge base. This was allowable, from their perspective, for several reasons. First, the tasks before them were academic exercises that had no connection to the world of a practicing chemist. Second, they had a tendency to focus on the ‘how’ involved in discovering a route between the starting material and the product with little emphasis on a rational discussion of ‘why’. Third, they had significant difficulty transferring fundamental principles mastered during the first-year general chemistry course to the second-year organic chemistry course. Finally, their poor understanding of why a reaction occurred the way it did often led to confusion about competing principles. This led them to rely on recall, rules, and ‘tricks’ or magic to overcome a dead-end in their problem-solving efforts.

Conclusions

To help remedy the meaninglessness that characterizes the curved-arrow, arrow-pushing formalism in the minds of many students, we advocate two changes in the way the organic course is taught. First, repeatedly focus class time on an explicit recognition of the themes and core concepts that run through organic chemistry, so that students do not concentrate exclusively on the minute detail of specific functional groups and specific transformations. Second, significantly increase the frequency with which connections are made between the symbolic world with which chemistry is communicated and both the atomic scale on which reactions occur and the macroscopic world of the laboratory. This second intervention is important because students are not making the appropriate connections between the symbolic world and either the particulate scale on which collisions between molecules occur that lead to chemical reactions, or the manipulations they encounter in the laboratory course associated with the organic chemistry experience.

The first suggestion would require a careful rethinking of the number of rules, facts, and details that are taught so that time is available in class to emphasize general themes and concepts. Consider the comments offered by one of the organic instructors with whom we discussed the questions used in this study.

> *There are three classes of curved-arrow situations. And we are not talking about the free radical ones. Thing number one is there is Lewis acid/base associations. There is Lewis acid/base dissociations and one's the reverse of the other. Each of them requires one arrow. Then there's electron-pair displacement reactions. The S_N2 is an example of that. That requires two or more arrows and a subclass of that is the Brønsted acid/base reactions. You need to know rough pKa values so you can assess whether they are favorable or not.*

Another organic professor offered a similar comment on the basic themes of the introductory organic course.

> *When I teach organic chemistry I basically tell them that there are less than a dozen fundamental processes in organic chemistry and if you know those and you know the periodic table and its relationships?, you can either infer or predict anything else in organic chemistry. It's a little known secret.*

Interestingly enough, the students recognized that they would benefit from a discussion of basic themes, rather than the details of reactions to which they were exposed that can be learned by reading the textbook. Elizabeth confessed, "*I guess ... that's one thing that I always had a hard time with in organic was trying to think along in general, like that. It always seems very specific.*" Elizabeth was not alone, her peers offered similar remarks. For example, Ryan stated:

> *One of the few things that we got out of [first semester Organic Chemistry lecture] is that they beat the crap into our heads was S_N2 reactions. Here are the four or five main things that S_N2 reactions happen and here's what they are. Throughout lecture and classes more people can recognize, 'hey, that's an S_N2-type reaction.' So, at least I have a place to know, or at least I have a general idea of how the mechanism is supposed to work out. It would be more beneficial if there were more guidelines than just 'memorize the Diels-Alder'.*

It would be a mistake to think of Ryan's comment about having to memorize the Diels-Alder reaction as just the typical complaint of a student who didn't understand organic chemistry or didn't want to memorize factual material. It would be easy to make this mistake because Ryan did, after all, create some of the most incorrect answers to the mechanisms we encountered in the study. Yet, Erika, who nearly flawlessly answered the questions and represented the opposite end of the understanding spectrum, articulated a similar emphasis. She declared:

> *I try not to ... memorize everything but I think that it would be really helpful to have ... a set of rules ... I just need an overall general view of like good leaving groups and ... what happens when you have acid and when you have a base and like more of the general stuff.*

Erika, like Ryan and Elizabeth, was looking for a set of core guiding principles she could apply across the field, rather than a laundry list of rules and named-reactions for which organic chemistry is famous.

We found it significant that none of the participants called for a 'watering down' of the content. They asked, instead, for the guiding principles or recurring themes to be brought to the forefront while they were in class. They wanted these core concepts to be made explicit. After nearly a full year of instruction, the students in this study left the class with the image that organic chemistry was a course based on a large number of unrelated reactions. This was interesting because it reminds us, once again, of a phrase we cited more than twenty years, in a paper on the constructivist theory of knowledge: *Teaching and learning are not synonymous; we can teach, and teach well, without have the students learn* (Bodner, 1986). In spite of repeated attempts by both the instructor teaching the class and the efforts of the author of the textbook used in the class to emphasize general themes and guiding principles, these general themes and guiding principles are lost in the detail of seemingly unrelated reactions.

Our work also suggests that it is important for instructors to review periodically some of the fundamental properties of molecules that would allow students to distinguish between situations in which a reactant acts as a nucleophile rather than as a base, or situations in which a reactant acts as an oxidizing or reducing agent rather than as an acid or base. These issues are frequently discussed at the beginning of the first semester, and the instructor then approaches the course as if they were understood rather than as if they needed to be constantly reinforced within the context of new reactions and new functional groups.

Our interviews indicated that students lack a clear distinction between the concepts of base and nucleophile even at the end of the second semester. When Barb was asked to define a reducing agent while working on question #2, which involved a $NaBH_4$ reduction, she responded *"I just confused myself."* Ryan and Andy responded to the same issue by giving up trying to solve question #2. When they encountered question #4, which involved a Dieckmann condensation that required students to use sodium methoxide as a base, many of them could only use it as a nucleophile. Of the eight participants who started and completed the Dieckmann condensation, six initially used the methoxide as a nucleophile. Only after receiving explicit hints about the alkaline character of the methoxide ion did they use it as a base.

The students in this study were not alone in encountering problems distinguishing between a base and a nucleophile. The second author struggled with this distinction throughout his introduction to organic chemistry more than 40 years ago only to recognize that organic chemists were using a different language to describe the distinction between Brønsted bases and Lewis bases from that he had encountered the previous year. Another factor that contributed to his confusion was the difference between the way general chemistry and organic chemistry treat the concepts of Brønsted versus Lewis bases. General chemistry courses focus on the effect of acids or bases on the pH of an aqueous solution. In organic chemistry, very few reactions occur in water, and the focus is on the relative strength of the acid and base as described by the appropriate acid-dissociation constant or $pK_{a.}$

The concept of pK_a is introduced in the typical organic chemistry course, but it needs to be reinforced until it becomes a theme that connects reactions that appear to the student to be unrelated. Students often believe that only important information or ideas are written on the chalkboard. Conversely, information that does not appear on the blackboard can be viewed as unimportant. When reaction mechanisms are written in terms of symbols that identify the nuclei of the atoms in a reaction, students are likely to ignore the location of nonbonding electrons that play a determining role in the reaction when they try to write mechanisms of their own. When the pK_a of acidic protons is left off the blackboard, students walk away with the impression that pK_a's do not play an integral part in determining the mechanism of the reactions they encounter.

By identifying common themes that recur throughout the course, such as the distinction between a base and a nucleophile, an understanding of fundamental concepts of this nature will grow. The development of this conceptual understanding would be reinforced by including it as a routine component of assessment, and interweaving pK_a's, for example, in the regular exams or quizzes.

Yet shifting the focus of the content of the course is not enough. The goal of the second recommendation is a transformation of the symbols with which reaction mechanisms are written so that they become more meaningful. It involves increasing the frequency with which explicit connections are made between the arrow-pushing formalism (the symbolic world) and the students' experience in the laboratory (the macroscopic world). Instructors could require an explanation of the mechanism for reactions performed in the laboratory. This could be achieved by requiring that these mechanisms be explained in the reports students are required to submit, but that would entail reading the responses generated by as many as 200 students running the same reaction. A more viable alternative would involve requiring students to write the mechanism during the laboratory, while a reaction is being run. The laboratory instructors could then move from student to student and ask each individual to verbally explain the mechanism in their laboratory notebook. Alternatively, an instructor can exploit the ubiquity of the internet by having students post and evaluate each other's responses.

The other 'something' needed to facilitate the development of a conceptual understanding might require converting the lecture hall into an active learning center, in which instructors implement group activities and cooperative learning under a variety of conditions and to differing degrees of commitment. Straight lectures, lectures with preprinted notes, punitive quizzes, and the presentation of the molecules as static objects contribute to misconception and misunderstanding. Infusing cooperative learning at the very least produces positive results when compared to traditional lectures and presents ample opportunity for problem solving (Paulson, 1999; Tien *et al.*, 2002). Bodner *et al.* (2001) provided a theoretical backing for active learning when they stated: "*Each of us builds our own constructs, tries them on for size, and eventually revises them*" (p.15). Implementing active learning allows for the learner to evaluate and refine their personal constructs.

References

Bhattacharyya G. and Bodner G., (2005), "It gets me to the product": how students propose organic mechanisms, *J. Chem. Educ.*, **82**, 1402-07.

Bodner G. M., (1986), Constructivism: a theory of knowledge, *J. Chem. Ed*uc., **63**, 873-878.

Bodner G. M. and McMillan T. B. L., (1986), Cognitive restructuring as an early stage in problem solving, *J. Res. Sci. Teach.*, **23**, 727-37.

Bodner G. M., Klobuchar M., and Geelan D., (2001), The many forms of constructivism. *J. Chem. Educ.* **78**, 1107. [Online] Available: http://jchemed.chem.wisc.edu/Journal/Issues/2001/Aug.

Denzin N. K., (1994), The art and politics of interpretation,. In N. K. Denzin and Y. S. Lincoln (Eds.) *Handbook of Qualitative Research*, Sage Publications, Thousand Oaks, CA, 500-515.

Denzin N. K. and Lincoln Y. S., (1994), Introduction: entering the field of qualitative research. In N. K. Denzin, and Y. S. Lincoln (Eds.) *Handbook of Qualitative Research,* Sage Publications, Thousand Oaks, CA, 2-17.

Dupuis P., (1999), HyperResearch (Version 2.0) [Computer Software]. Thousand Oaks, CA: Scolari, Sage Publications Software.

Ferguson R. L., (2007), Constructivism as a research lens, In G. M. Bodner, and M. Orgill, (Eds)**,** *Theoretical Frameworks for*

Research in Chemistry/Science Education (pp. 27- 47). Upper Saddle River, NJ: Pearson/Prentice Hall.

Ferguson R. L. and Bodner G. M., (in press). Misconceptions held by chemistry majors while taking organic chemistry, *J. Chem. Educ.*,

Geelan D. R., (1997), Epistemological anarchy and the many forms of constructivism, *Sci. Educ.*, **6**, 15-28.

Grossman R. B., (2003), The art of writing reasonable organic reaction mechanisms, Springer-Verlag. New York, NY

Larkin J.H. and Rainard B., (1984), A research methodology for studying how people think, *J. Res. Sci. Teach.*, **21**, 235 – 254.

Loudon G. M., (1995), *Organic chemistry*, (3rd ed.), The Benjamin/Cummings Publishing Company, Inc Menlo Park, CA.

Loudon G. M. and Stowell J. G., (1995), *Study guide and solutions manual, Volume 1 to accompany organic chemistry*, (3rd ed.), The Benjamin/Cummings Publishing Company, Inc., Menlo Park, CA.

Patton M. Q., (1990), *Qualitative evaluation and research methods,* (2nd ed.), Sage Publications, Inc., Newbury Park, CA.

Paulson D. R., (1999), Active learning and cooperative learning in the organic chemistry lecture class, *J. Chem. Educ*, **76**, 1136-1140.

Scudder P. H., (1992), *Electron flow in organic chemistry*, John Wiley and Sons, Inc., New York, NY.

Scudder P. H., (1997), Database vs. expert system teaching paradigms: using organic reaction mechanisms to teach chemical intuition, *J. Chem. Educ*, **74**, 777-781.

Strauss A. and Corbin J., (1994). Grounded theory methodology: an overview. In N. K. Denzin, and Y. S. Lincoln (Eds.) *Handbook of qualitative research*, Sage Publications, Thousand Oaks, CA, pp.273-285.

Strauss A. and Corbin J., (1998), *Basics of qualitative research: techniques and procedures for developing grounded theory*, Sage Publications, Thousand Oaks, CA.

Tien L. T., Roth V. and Kampmeier J. A., (2002), Implementation of a peer-led learning instructional approach in an undergraduate organic chemistry course*, J. Res. Sci. Educ.,* **39**, 606-632.

Vygotsky L., (1986), *Thought and language,* The MIT Press, Cambridge, MA.