

Heuristic chemistry—a qualitative study on teaching domain-specific strategies for the six-electron case

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We investigate the efficiency of domain-specific heuristic strategies in mastering and predicting pericyclic six-electron rearrangements. Based on recent research findings on these types of reactions a new concept has been developed that should help students identify and describe six-electron rearrangements more readily in complex molecules. The goal of this qualitative study with chemistry majors is to understand the way students cope with this new concept depending on their prior knowledge, and to reveal the merits and limitations of this approach. The results suggest that the use of domain-specific heuristic strategies provides the students with process-orientated thinking skills to identify six-electron rearrangements and to determine as well as predict reaction mechanisms and outcomes. The explicit emphasis on recurrent patterns and structure–property relationship fosters the conceptual thinking of the learner.

Introduction

Knowledge in organic chemistry increases constantly and new facts are often packed into curricula in an unreflected fashion, rarely abandoning older or revising existing concepts (De Vos *et al.*, 2002). The content of the total chemistry curriculum has thus over time turned into a series of knowledge packages that often are disconnected. The traditional memorization and retrieval-learning and the missing emphasis on similarities and comparabilities of molecular structures and reactions, often not recognized by the learner, prevent them from constructing effective (interconnected) and sustainable (long-term) chemical knowledge.

As organic chemistry is more structure-laden than other disciplines (Habracken, 1996; Hoffmann and Laszlo, 1991) an appropriate concept emphasizing structure–property relationships could help students cope with the amount of structural information and support the reasoning processes in the discipline (Stösser *et al.*, 2009, 2010). Understanding and successfully mastering organic processes combines the recognition of structural patterns, the assignment of properties or reactivities and the manipulation of various structural representations (Kozma, 2003; Kozma and Russell, 1997; Stieff, 2007; Stieff and Raje, 2008). Successful organic chemistry practitioners are able to understand the depiction of structures, to derive properties and reactivities from functional groups, and have

the skills to transform structure presentations (Bhattacharyya, 2006; Bodner and Herron, 2002; Carter *et al.*, 1987; Pribyl and Bodner, 1987). In marked contrast, students enrolled in organic chemistry courses have various difficulties with the “meaning-making” process of structural representations. They show an overall poor performance in completing mechanisms and solving problems, and surface-level understanding of concepts and theories (Anderson and Bodner, 2008; Bhattacharyya and Bodner, 2005; Bodner and Domin, 2000; Ferguson and Bodner, 2008; Kraft *et al.*, 2010; Strickland *et al.*, 2010). Many display unconnected and surface-orientated algorithmic knowledge (Fischer *et al.*, 2005; Tiemann, 1999). Research on reasoning difference between experts and novices has also shown that experts display domain-general and domain-specific heuristics while problem-solving or decision-making (Bhattacharyya, 2008; Chi *et al.*, 1988; Stieff and Raje, 2008). Ongoing research also shows that students make use of intuitive heuristic reasoning, *i.e.*, implicit strategies while ranking or classifying substances (Maeyer and Talanquer, 2010; McClary and Talanquer, 2011).

However, the explicit development of domain-specific heuristics and their use for improving the understanding and problem-solving in organic chemistry has not yet been explored. Therefore we propose a novel top-down approach for teaching organic chemistry that is based on the idea of domain-specific heuristic reasoning. Our approach follows a pragmatic approach in combining prevalent concepts and new research findings with the aim to develop straightforward strategies that easily guide the decision process in a domain-specific context.

In our research, we focus primarily on thermal pericyclic reactions because of their high value in organic synthesis for the formation of new C–C bonds, their predictable stereochemistry, and the biradical forming cyclizations such as the

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Bergman- and Myers-Saito-type reactions (Nagata *et al.*, 1989). The structural diversity of pericyclic reactions, *e.g.*, hydrocarbon or heteroatom derivatives, is considerable and the identification of rearrangement reactions as well as the description of outcomes are often very difficult for students. Appropriate strategies with a simplifying and summarizing function have been derived from new research findings that should reinforce fast estimation and prediction of reaction outcomes.

The simplicity and predictive power of this six-electron concept developed for this type of reactions has led us to investigate its possible role in teaching and learning (Graulich *et al.*, 2010b).

Background and outline of the study

The present work is based on our recent findings on six-electron rearrangements to identify principles that can help simplify and accelerate the ways to predict reactions and rationalize mechanisms for the six-electron case. The theoretical work on six-electron rearrangements dates back to the last century; they have been studied and discussed abundantly, both experimentally and computationally (Borden *et al.*, 1988; Graulich, 2011; Houk *et al.*, 1995; Viola *et al.*, 1981; Wiest *et al.*, 1997). A few systematic approaches aiming at reaction and synthesis planning by computers were engaged in a full-range classification of these types of reactions (Hendrickson, 1974; Herges, 1990; Ponc and Strnad, 1992). These approaches are in contrast to our own objectives and were primarily not meant to improve teaching and learning.

In textbooks, pericyclic reactions are generally classified as cycloaddition, electrocyclic, sigmatropic and cheletropic reactions, as well as group transfer reactions. Additionally some of the observed stereochemistry as well as the degree of concertedness of these reactions can be rationalized by the Woodward–Hoffmann rules (Woodward and Hoffmann, 1969).

However, in 2004, computational studies on six-electron rearrangements revealed that not only known concerted six-electron rearrangements, *e.g.*, Diels–Alder, Cope, Claisen, or electrocyclic rearrangements (*cf.* Type 1 in Fig. 1) but also biradical forming reactions (*cf.* Type 2 and 3 in Fig. 1) display comparable transition structures and activation energies. The findings revealed a continuum from concerted reactions with cyclic transition states toward biradical forming six-electron reactions that proceed *via* intermediates. The general heuristic strategy deduced from these results was that “a non-concerted reaction takes place when biradical intermediates are stabilized either by allyl or aromatic resonance” (Schreiner *et al.*, 2004).

This rationale comprises known rearrangements, for instance, concerted reactions, Cope and Diels–Alder reactions, but also biradical forming reactions, like the well-known Bergman and the Myers-Saito reaction. As the latter do not fit into the prevalent concept of pericyclic reactions, they have largely been ignored in traditional organic chemistry textbooks (Clayden *et al.*, 2005).

Beside this reactivity heuristics that had been formulated for the six-electron case a structural heuristic can be deduced that fosters the topological recognition of this family of reactions. The minimal structural unit of all six-electron rearrangements

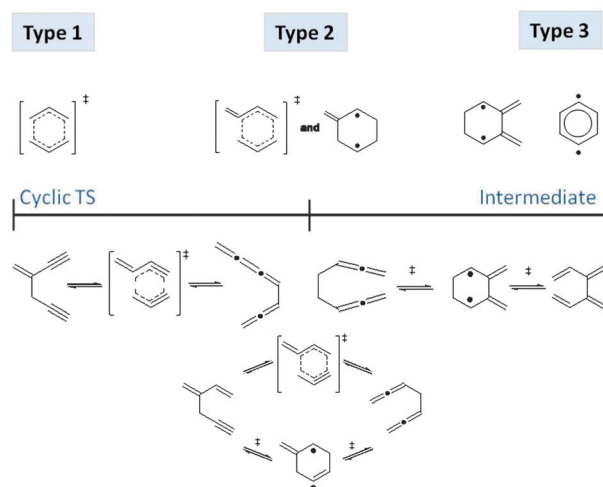


Fig. 1 Three types of six-electron rearrangements.

can be reduced to the 1,5-hexadiene unit, bearing a double bond between C¹–C², C⁵–C⁶ and a single bond between C³–C⁴ (Graulich *et al.*, 2010b).

This minimal unit can easily be identified in complex molecules by counting the atoms of the involved bonds, from C¹ to C⁶ (*cf.* Fig. 2). Based on this structural feature the unsaturation of the bond can be increased in these positions building up higher (unsaturated) congeners, like enediyne or allenic structures that are also able to undergo six-electron rearrangements (*cf.* examples in Fig. 1). Various research findings in this area evoked a new perception of six-electron rearrangements, initiated the prediction of yet-to-be synthesized structures (Bui and Schreiner, 2006; Kawatkar and Schreiner, 2002; Schreiner and Bui, 2006), and the question arises whether this concept can be adapted to teaching and learning.

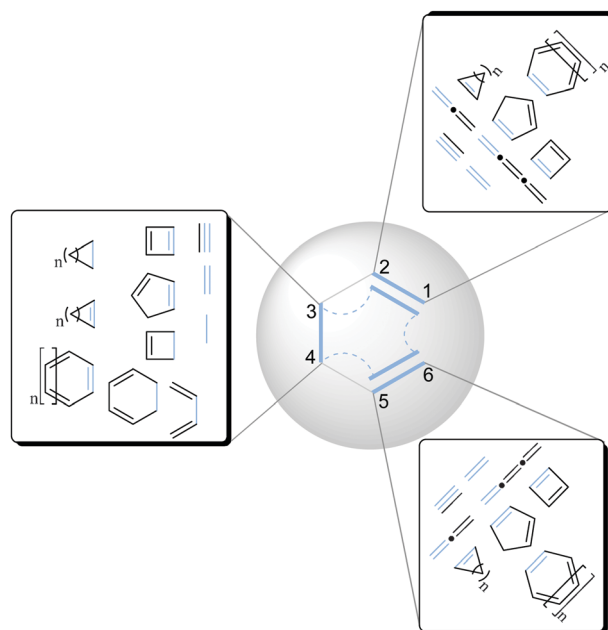


Fig. 2 Structural unit of six-electron rearrangements (Graulich *et al.*, 2010b).

As the inherent function of heuristics is not to take all available information into account, but only to use the information that is necessary to make appropriate decisions or assumptions (Gigerenzer and Todd, 1999), we have, for the sake of simplicity, neglected mechanistic details, stereochemical outcomes, molecular orbital considerations, or reaction conditions of six-electron rearrangements. We do not suggest to omit these details completely in teaching; we only propose organizing principles that should help understand and predict six-electron rearrangements.

Domain-specific strategies for the six-electron case

The heuristic concept for six-electron rearrangements can be divided into two parts. One is the content knowledge, which had been presented above, and the second is the procedural dimension that consists of different steps of information processing. Based on our concept we developed principle-based strategies that would guide the decision-making process in learning and teaching these types of reactions. The process can be divided into four distinct steps or questions; where to start the search for information, *i.e.*, how to identify a possible six-electron rearrangement, how to draw transition states (TS) and/or biradicals (BR), how to estimate a putative pathway, and how to determine the outcome. The identification of a possible six-electron rearrangement can be done through a counting strategy that helps find the structural unit of these reactions. Explicit strategies how to draw easily both structures (TS and BR) have also been developed and the estimation whether a radical is stabilized had already been part of the curriculum and is only refreshed during the interviews. The following steps have been defined:

- Identify the rearrangement by counting and ascertain if you have double bonds between C¹–C², C⁵–C⁶ and a single bond between C³–C⁴ and mark the bonds that contain the six-electron in the starting material (*cf.* Fig. 2).
 - Draw two hexagonal structures of the remaining bonds.
 - Add a dashed cycle to one of these two structures and you obtain the TS.
 - Draw the BR by closing the other structure at both sides and place two radicals in *para* position.
 - Decide if the radicals are stabilized by allyl or aromatic resonance and decide which pathway is favored (*cf.* Fig. 1).
 - Draw the product.

To illustrate these steps, we chose the cognitive apprenticeship approach (Brown *et al.*, 1989; Stewart and Lagowski, 2003) that transmits simultaneously the content knowledge and the heuristic strategies. Following the four stage model (scaffolding, modeling, mentoring, and coaching), from an observing to an autonomous stage of the learner, the process of thinking can be modeled and the reasoning process of the participant assessed.

Methodology

A qualitative research design is the most appropriate method for our research purpose, because it enables us to capture student thinking and to understand the entire process, rather than to measure the effects of discrete variables. The dynamics of individual constructions are better analyzed with process-based investigations. This qualitative design allows us to reveal

new paths of investigation or hints for improvement of the designed learning strategies.

The present study is situated within the research paradigm of Pragmatic Constructivism. This research focus tries to understand how people experience, interpret, and perceive a phenomenon or a presented content and construct knowledge and meaning from these experiences. Each individual will perform the construction differently, depending on his or her pre-existing knowledge, learning style and personality traits (Duit, 1995). The aim is to elucidate the different possible conceptions and thought processes and to interpret them. We assume that the participants of our study do not experience the new concept and the corresponding strategies in the same manner, but in limited ways that we can describe and interpret. The all-embracing question of our research is whether the heuristic approach for understanding the six-electron case helps students describe and predict reaction outcomes of six-electron rearrangements. Based on the theoretical considerations addressed above, our research is guided by three research questions:

- Are the students able to deduce the structural element from classical rearrangement reactions by inquiry?
- How does prior knowledge influence their decision-making and their use of the presented strategies?
- How does the new approach affect the decision making process and students' abilities in formulating and predicting rearrangement reactions?

Data collection and instruments

The six participants of this study were undergraduate chemistry majors in their last year of their bachelor chemistry studies recruited from the last semester organic chemistry course at the Justus-Liebig University. They were enrolled in all three organic chemistry courses that were taught by the professors of organic chemistry of the department. These three courses cover modern organic chemistry topics, reaction mechanisms, molecular orbital theory, retro-synthesis, catalysis as well as topics related to the content of this study, *e.g.*, pericyclic reactions, cycloadditions and transition state theory. The study design is shown in Fig. 3.

A prior knowledge test (PKT) had been designed and validated together with current faculty members, to assess different abilities and their level of prior knowledge. It covered the application of general concepts, like aromaticity, *i.e.*, Hückel's rule, the designation of aromatic or non-aromatic molecules, and simple electron counting exercises. Further classical six-electron reactions, where the formulation of the products of cycloadditions, sigmatropic, and 1,3-dipolar reactions should be filled in. Thirdly, process-orientated exercises to assess their ability in formulation transition states of rearrangement reactions have been included. These exercises had been taken from the lecture courses and from an organic chemistry textbook (Clayden *et al.*, 2005). All 20 students of the course had passed the prior knowledge test. Based on their score in the prior knowledge test, six students were selected, three students with a low and three students with a high score in the test. The prior knowledge test only serves as a preselection of the sample and has not been included in the main analysis. Three female and three male students participated in the study, to guarantee gender balance.

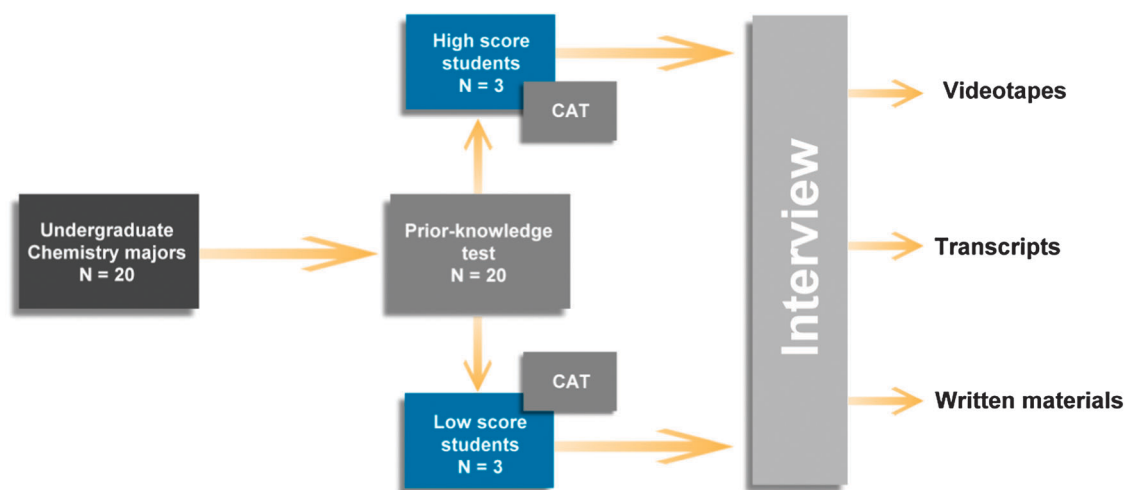


Fig. 3 Study Design (CAT = cognitive ability test).

These students completed a standardized cognitive ability test (Heller and Perleth, 2000) (CAT), to ascertain their non-verbal cognitive competence.

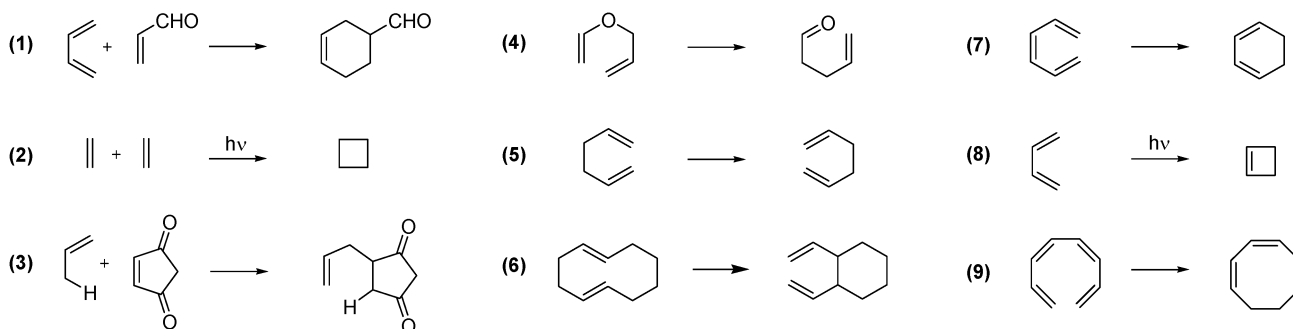
The interviews consisted of a semi-structured face-to-face interview (45–60 min) between one participant and the interviewer. Before starting the interview, the interviewer introduced herself, explained the method of “think-aloud” protocols. In the first section common pericyclic reactions have been presented, *e.g.*, Diels–Alder (1), Claisen rearrangement (4) and Cope rearrangement (5, 6) (Scheme 1) and general questions about their knowledge on the topic have been evoked to refresh their minds and to collect information about their abilities to describe pericyclic reactions verbally and their knowledge on prominent reactions of this type (5 min). In the second section the participants were asked to pay attention to the number of the involved electrons and structural similarities of presented pericyclic reactions and to describe a common structural feature of these reactions (5–10 min).

The minimal structural unit of those six-electron rearrangement reactions, being the 1,5-hexadiene unit (Fig. 2), has been explicitly emphasized afterwards, and the heuristic counting strategy—how to identify this structural element in complex structures—had been explained. The students were then asked to decide which reactions of a selection of eight molecules, which were not presented in the lecture, would undergo a pericyclic reaction (*cf.* Fig. 4) (10 min).

They were told to choose their own way of identifying possible rearrangements. In the third part the three types of six-electron reactions have been introduced (concerted reactions, biradical forming reactions and competing pathways) and how to estimate possible pathways has been explained (Fig. 1) (25 min). Consequently the different steps of dealing with a six-electron rearrangement reaction—identifying, drawing of TS and BR, estimation of stability and reaction outcome—have been demonstrated following the cognitive apprenticeship approach (Brown *et al.*, 1989) with various exercises differing in complexity. In the first modeling part the interviewer verbalized explicitly how to draw transition states and biradicaloid structures and how to decide which pathway would be favored. In the scaffolding and coaching part the supporting system comprising hints, assistance and feedback was gradually removed. The students worked more and more independently on the exercises that comprised traditional pericyclic and more complex structures. Finally, they were asked which strategy had been the most useful for them and were invited to ask questions, to add comments on the subjects, and to give their personal opinion (5 min).

Data analysis

The results of the cognitive ability test CAT showed no large difference within the sample and only slight differences between females and males (Table 1).



Scheme 1 Rearrangement reactions shown at the beginning of the interview.

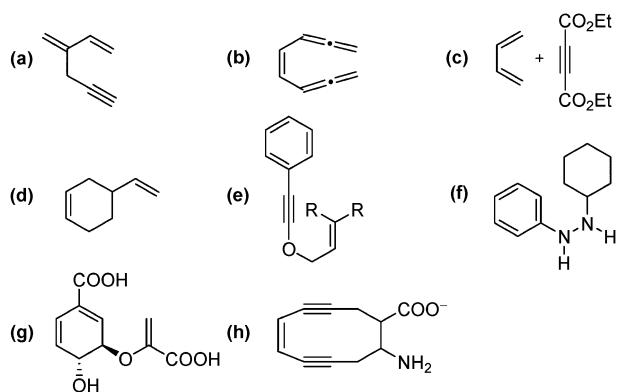


Fig. 4 Exercise for identifying possible rearrangements.

As the scores do not differ much, the conclusions that will be drawn about the visuospatial competence and the ability to handle rearrangement reactions are primarily based on the field notes and hints that appeared during the interviews. We designate Justus, Heike, and Doris as high achievers and Richard, Marie, and Paul as low achievers. The interviews have been videotaped and transcribed. After each interview the interviewer took field notes for each participant. The written work of the student was collected and analyzed along with the transcription of the videotape. The verbal data and drawings from the interviews were analyzed following our initial research questions. The data analysis involved the qualitative coding software MAXQDA (MAXQDA, Software für qualitative Datenanalyse, 1989–2010), to use structured codings of emergent themes and categories, following theoretically the qualitative content analysis approach (Mayring, 2008). This allowed us to define emergent trends and topics during the analysis of the data. We generated categories by analyzing common statements, drawings of the participants and major trends relevant to the research questions. We focus on the one hand on the use of the strategies, be it in an elaborate or algorithmic way, and on the relation between their performance during the interview and their prior knowledge, in order to make assumption on possible teaching implications. We observed a relation to their prior knowledge in both aspects. Compared to previous research investigating reasoning types (Bhattacharyya and Bodner, 2005; Kraft *et al.*, 2010), we could identify two types of reasoning, *i.e.*, model- and case-based reasoning. The high achiever of the sample showed the first type of reasoning and the low achievers could be categorized as case-based reasoners, as they often stuck on surface features.

The reader should bear in mind that all numerical comparisons in this study do not imply statistical significance. Therefore, the

Table 1 Sample

	Pseudonym	Gender	PKT (45)	CAT	OC grade ^a
High achiever	Justus	m	40	92%	1.0
	Heike	f	29	84%	1.7
	Doris	f	24	78%	1.3
Low achiever	Paul	m	23	88%	2.3
	Richard	m	19	92%	2.3
	Marie	f	17	78%	2.0

PKT = prior knowledge test/CAT = cognitive ability test/OC = organic chemistry. ^a German grade: 1 very good–6 insufficient.

results from the comparison between high and low achievers cannot be taken as universally valid and display only the findings within the framework of this study.

We ascertain our research hypothesis with quotes from the transcripts that were translated with respect to the meaning and word choice of the participants. The quotes from each participant were assigned with a chosen pseudonym to protect their anonymity.

Results and discussion

One of the main research questions in our study was to determine how the students' ability to master the concept and the use of the corresponding strategies depends on their pre-existing knowledge. Are the students able to deduce the structural element from classical rearrangement reactions by inquiry and does this depend on their prior knowledge?

During the interviews the weaker students often showed tacit knowledge. The initial questions which of the depicted reactions in Scheme 1 are familiar to the students have been answered by reproducing name reactions, such as the Diels–Alder, Claisen, or Cope reactions. Marie's response shows the phenomena of name dropping:

Q1 Marie: "This (1) should be a Diels... äh a [2+2] cycloaddition. No, this (2) is a photochemically allowed and thermodynamically forbidden reaction... Yes this (1) is a classical Diels–Alder reaction. This reaction (3), I don't know. It may be that it is a rearrangement (...) this (4) is definitely a rearrangement—I think Claisen. This (5) is a Cope reaction. This (6) is also a rearrangement, but I don't know the name."

It seems easy to reproduce the name when simple recognizable systems (1,5-hexadiene) are presented but this knowledge cannot be transferred to slightly different starting compounds (cyclodeca-1,5-diene) that undergo the same reaction. Mainly Marie, but also other low achievers, demonstrated this surface feature orientated reasoning during the interview.

In order to determine students' capability to deduce an underlying structural unit of these rearrangement reactions, the participants were asked to compare the reactions and the bonds that are involved in the rearrangements. The observed trend showed that the high achievers were more likely able to explain and to abstract the structural similarities of six-electron rearrangements (*cf.* Q2).

Q2 Justus: "In principle, there are always two double bonds in Z-configuration and another that is directed in opposition to them."

Justus' response suggests a model-based reasoning, as he describes the structural similarities of the depicted six-electron rearrangements in a general way. Marie and Richard, in contrast, were not able to deduce satisfying explanations, their answers show case-based reasoning, as they only focus on one aspect of the reaction or recall familiar reaction patterns (Kraft *et al.*, 2010).

Q3 Marie: "The electron pair of one double bond migrates. So, one electron pair of the double bond is closing the ring or generates a single bond."

Q4 Richard: "There are always two, how is it called... a diene and a dienophile, if I describe it like that. I believe that the

easiest way to see it is here the Diels-Alder reaction. In the Diels-Alder reaction in the diene, we have both bonds in one molecule and it generates a cycle.”

We cannot exclude that the two latter students do not have a distinct idea for this type of reaction, the question could have cued them to make these puzzling assumptions. The conclusion we draw is that their achievement and the degree of intensity with which they make use of the offered strategies is related to their level of prior knowledge and thus influences their ability to abstract the structural unit (Fig. 2) of various six-electron rearrangements.

Due to the limited time during the interviews, the 1,5-hexadiene unit (Fig. 2) has been shown to the participant after their own suggestions, to have a common basis for the following steps. All participants stated that they recognize the structural unit in the presented reactions (Fig. 4). In the next step, students were asked to decide which molecules of a selection are able to undergo six-electron rearrangements. We observed that high achievers had fewer problems with this task and low achievers made considerably more use of the explained counting strategy. With the extension of distinct content knowledge the use of own mental models in reasoning increases. Therefore we tried not to enforce the use of the counting strategy, but emphasized instead their free choice. Both groups were nevertheless able to successfully estimate possible rearrangements of the molecules and determined molecules that do not rearrange (Fig. 4, structure f). The following figure shows details of Marie's, Doris', Justus', and Richard's written work. High achievers (Fig. 5, Doris and Justus) used the counting strategy only when the molecule showed a different geometry from the 1,5-hexadiene unit and classified the other molecules by circling the involved bond or by drawing arrows. This behavior suggests, with regard to Justus' above suggestion for the structural element, that high achievers are more likely to have an idea of this kind of reactions that help them quickly order these molecules. All high achievers showed this reasoning strategy, e.g., Doris used the traditional electron pushing formalism to see whether a rearrangement is possible. Justus also identified the possible electrocyclic ring-opening reaction of cyclohexadiene (lower left corner).

Marie in contrast had the most difficulties in this task. She strictly followed the counting strategy and classified a Diels-Alder reaction as a non-rearrangement reaction. This was opposite to her knowledge and she also realized this conflict.

Q5 Marie: “In this case there is a double bond between 1 and 2, a single bond between 3 and 4, but a single bond between 5 and 6. I would say that this does not work... But intuitively I would say that this is in fact a Diels-Alder reaction.”

I.: “Can you count in another way?”

Marie: “Simply by ignoring the residues and counting 5 and 6 in this way.”

I.: “Does this help?”

Marie: “Yes, now it works.”

Marie showed a clear algorithmic application of the strategies, and immediately started to count somewhere. With some prompting to search for the structural unit, she began to use the strategy appropriately to make her decisions. This conflict shows clearly the difference between an algorithmic and the

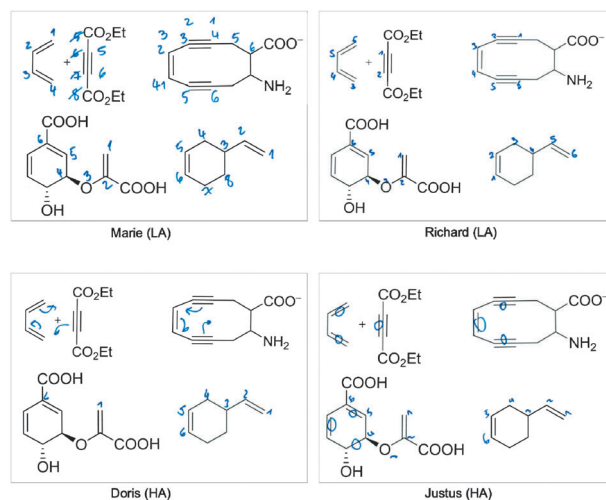


Fig. 5 Written examples from Marie, Richard, Doris, and Justus (LA = Low achiever, HA = High achiever).

heuristic idea behind the six-electron concept. The presented strategy to identify rearrangement reactions cannot simply be applied as an algorithm, always giving the right solution regardless of the substrate, but it is rather a heuristic strategy that does not always work, but indicates possible solutions. For an effective learning of this concept it is important to address explicitly this way of reasoning in teaching.

Throughout the interview and based on the written materials, one can assume that the extent to which the students make use of the counting strategy can be associated to the extent of sophistication of their mental idea of rearrangement reactions. Summarizing this research question, the results suggest that the counting strategy helps both groups of students. Low achievers were able to cope with rearrangement reactions and for high achievers this strategy helps them tackle more difficult reactions, where the geometry of the 1,5-hexadiene unit is not directly obvious. The explicit training to recognize six-electron rearrangements in teaching can foster the development of a putative mental model for low achievers. These results suggest that the use of simple strategies helps focus the reasoning process. Students were able to focus on the reactive part of the molecules and to ignore residues or distracting functional groups. This fastens the decision-making process.

The second question we investigated in this study was how the new approach affects the decision-making process and a student's ability in formulating and predicting rearrangement reactions.

Having identified a molecule that undergoes a rearrangement reaction, the next step is to determine the reaction mechanism and to formulate the product. As the concept for the six-electron case also includes important biradical reactions, a strategy to decide between transition state and biradical is needed to classify possible reactions. This process had been divided into different steps that were taught through the four stages of the cognitive apprenticeship approach. The interviewer started to explicate his reasoning while solving rearrangement reactions; how to transfer the substrate into the transition state and the biradical, estimation of the stability and drawing the outcome. In the next steps the participants did exercises on their own, with increasing complexity and gradual

removal of the interviewer's support. The following figure shows drawings that Justus and Heike did in the last, autonomous phase of the cognitive apprenticeship.

They drew both structures, estimated the stability of the biradical and formulated the final product considering the presence of cyclohexadiene (CHD), as a hydrogen donor. With the presented strategy they were able to determine the reaction pathway and to draw the final product. Heike's statement shows that she realized the relevance to differentiate between both mechanistic pathways.

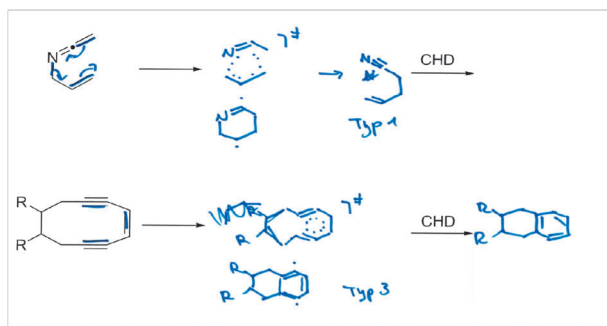
Q6 Heike: "So this works. Even if I'm very slow at such things, I understand... I know why I should apply this."

The following quotation from Justus shows how he pursues his decision-making process: visualization of possible intermediates, estimation of stability, and formulation of the reaction outcome. In his quotes he especially mentions the Bergman reaction (*cf.* Fig. 6, second example).

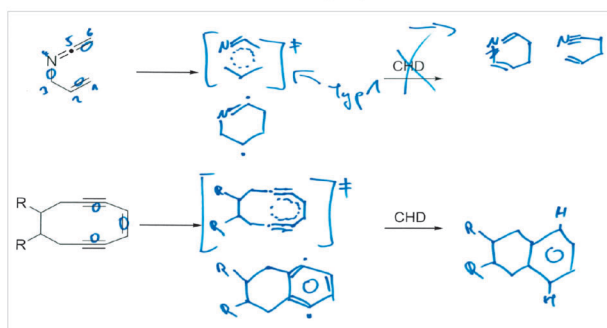
Q7 Justus: (first reaction, he encircles the bonds and draws the arrows) "Ok. This means this and this bond would be formed. If I draw it without bonds, it would be like this—this is the transition state. The radical would look like this. Exactly! And this is not stabilized, this means it would proceed via this way (he points to the transition state)... What results is... this. No! Hold on a second. This is certainly wrong. It is like that. I have to move all three electron pairs. Okay yes."

I: "You can proceed to the next exercise if you have finished."

Justus: (second reaction) "Yes. This, this and this (he encircles the bonds) Now the transition state (he draws the transition state and the biradical). Here (he points to the biradical) we have aromaticity and for this reason it would react with CHD and one obtains this product. I see, that is clear, this is the educt from the Bergman cyclization. It works. Ok."



Heike (HA)



Justus (HA)

Fig. 6 Drawings of intermediates and outcomes from Heike and Justus.

The following quotation from Marie shows a different way of describing the reasoning. She did not make use of chemical terms (*cf.* Fig. 7).

Q8 Marie: "Hm, ok yes. Then it is this, this and this (she highlights the bonds) and not this. And this is what remains (she draws the transition state). So I close the ring, here and here (she draws the biradical). So I have one stabilized and this not, so it is type 2."

Although Marie seemed to be the most unreflective rule learner of the sample and the only person of the interviewees that often fall back to algorithmic thinking and even neglect other chemical principles, she realized the purpose of these strategies as she stated at the end of the interview:

Q9 Marie: "That something completely different can result if it proceeds through the cyclic transition state or through the biradical... this has become pretty clear to me."

The following quotation **Q10** from Paul, regarding the same reaction, shows comparable reasoning. Even though the low achievers have demonstrated difficulties in describing their own reasoning steps, they were able to identify the resonance stabilization of the biradical and to determine the supposed pathway.

Q10 Paul: "So, these bonds are involved (he highlights the bonds). Then we have this one (he draws the transition state). The other structure should be closed, yes... or? This looks good... because this (points to the radical) would interact with this double bond. This would be type 2, because this (points to the above radical) is too far of being stabilized."

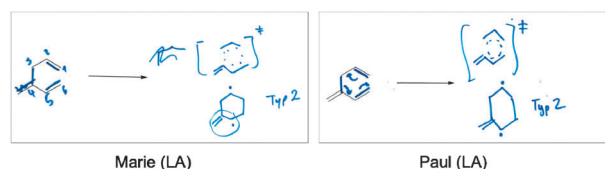
At the end of the interview, the students had time to give their personal opinion and to reflect on the issue. All students interviewed felt rather comfortable with the strategies. To conclude with the discussion section, two opinions from Heike and Paul.

Q11 Heike: "I think that I would look at the next rearrangement with different eyes."

Q12 Paul: "I wonder why such fundamental things are not explained at the beginning of the course. That one can do so simple things, like counting or the radicals. This opens new perspectives."

Some remarks in dealing with structural representations

One emerging trend that had been observed and that had not been explicitly addressed in the study was the influence of the high visuospatial demand of rearrangement reactions on the students' ability to draw structural presentations. Although we did not explicitly address the interaction of representational competence and reasoning in our research, the following findings that emerged during the study could initiate future research topics.



Marie (LA)

Paul (LA)

Fig. 7 Drawings from Marie and Paul.

Research has shown that successful reasoning in chemistry is related to visuospatial competence and the cognitive ability to manipulate structural information, to move electrons or change bonds (Bodner and McMillen, 1986; Carter *et al.*, 1987; Coleman and Gotch, 1998; Gilbert, 2005; Pribyl and Bodner, 1987).

The students showed various problems while drawing transition states or intermediates. Some ill-proportioned and lopsided or non-symmetric variations were observed. Two different aspects emerged during the interview: (a) The inability to transfer linear structures, *e.g.*, allenes or alkynes to hexagonal transition structures or problems with cyclic systems and (b) the generation of methyl groups or deletion of groups of atoms. These problems often hindered the reasoning process. We observed that low achievers tend to separate completely the highlighted six electrons from the rest of the molecule. So they lost focus on the involved atoms and just drew something with the remaining bonds and atoms. The low achievers easily tend to give up when they are faced with problems and do not take ownership of the exercises.

Q13 Marie: “*Shall I just put the bond somewhere or should this give a ring?*”

This becomes evident in Marie’s question while she was drawing the biradical for one of the exercises where she had problems with. Consider further Marie’s problems with the cyclic Bergman starting material (*cf.* Fig. 8, 1st example).

Marie was not able to see both cycles. This inability to distinguish between the two cycles was an insurmountable barrier for her finishing this problem.

Q14 Marie: (She starts to draw the transition structure) “*This is not a real cyclic transition structure.*”

I: “*The six electrons that you omitted are missing.*”

Marie: (She draws the dashed cycle) “*But still... I’m confused because it is a closed system, because until now I always had... it was always an open in the transitions state.*”

During the interview Marie often sticks on surface features of the molecules. She was not able to make transformations across different representational forms and was only able to use the heuristic strategies when the presented exercise was clear and without any visual distraction (residues or angles). In the second exercise she integrated the residues in the cycle and generated a seven-membered ring. Her behavior is consistent with the research findings that some students are “unable to see” beyond the representation” (Kozma, 2003; Kozma and

Russell, 1997; Stieff, 2007; Strickland *et al.*, 2010). Novices often do not attribute function to the structural representation and stick on a basic surface level. This causes problems when implicit information should be deduced from a molecular structure. Exercises without distracting features are not challenging, but additional structural features, like residues or differing angles, changed the performance.

Paul had fewer problems. One strategy that he used to cope with the complexity of the structures is the abbreviations of residues to focus only on the important part of the structure (*cf.* Fig. 9, 1st example). This approach has been observed in the drawing of some high achievers and also Paul showed this behavior somewhat.

Some students had especially problems to draw the transition structure for the rearrangement of 1,2,3-heptatriene-6-yne. The drawing of the hexagonal transition structure from the linear structure of the branches had only been solved straight away by Doris. Justus drew a linear transition structure, but this also did not interfere his further reasoning to estimate the pathway and the product. These findings support the notion that the high achievers tend to have a distinct mental idea and are able to abstract meaning, even from lopsided drawings. Although he stated that he had difficulties with molecules that were too linear to transform it to a hexagonal transition state.

Q15 Justus: “*I find it more difficult to see, if there are triple bonds... To see, how they get to the six-membered ring, is complicated. Unless it is slightly bent (he points to the Bergman educt). It is difficult when it is too linear.*”

Richard, for instance, needed some promptings to get on the right way (*cf.* Fig. 10).

Q16 I: “*Count the electrons, if you are not sure which electrons are involved.*”

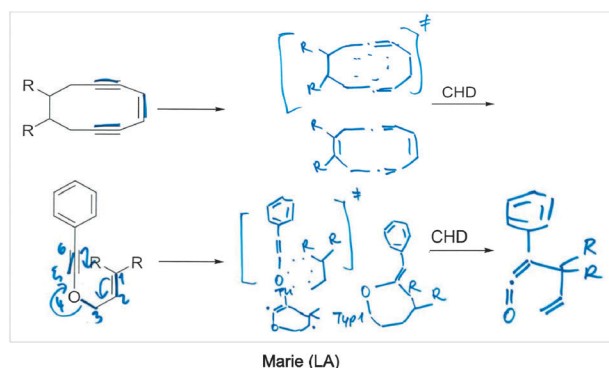


Fig. 8 Drawings of intermediates from Marie.

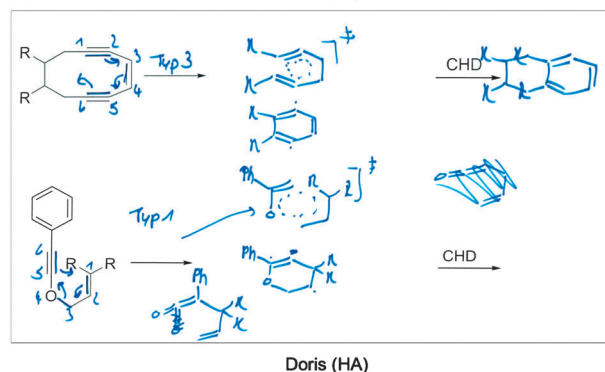
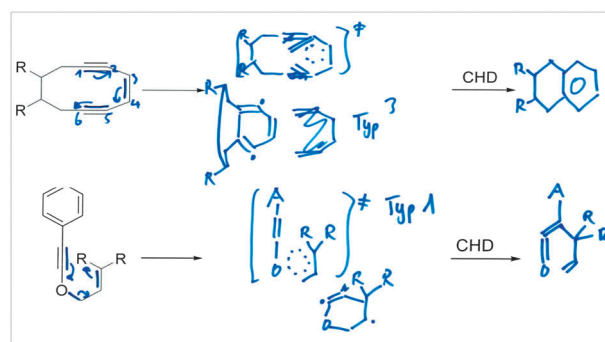


Fig. 9 Drawings of intermediates from Paul and Doris.

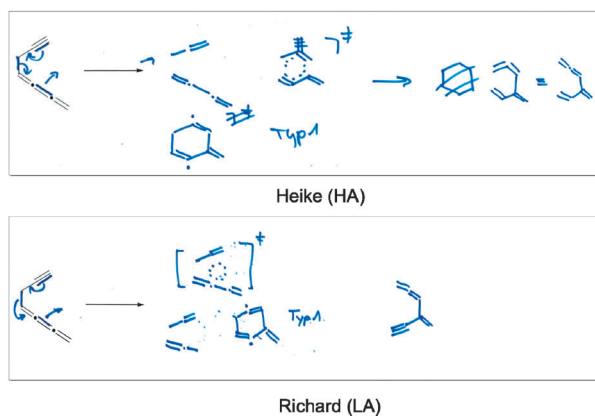


Fig. 10 Drawings from Heike and Richard.

Richard: "This should look like this, or? (he highlights the bonds) Ok, let's draw it like that (he draws the transition structure). I should draw this again to close the ring."

I: "You can draw it again, if you want."

Richard: "Like That?"

I: "Now you have your six-membered ring."

Richard: "It would look like this. Is this right... Yes. Electrons arranged here and two in para position and one can see that this should be type 1, because they are not stabilized."

Heike struggled as she generated an "external" double bond (cf. Fig. 10).

Q17 Heike: "Here, one, two, three, I draw what remains... Hm where is my ring... Ok, let's try this (she draws an angled version). Is this right? Something is missing. One, two, three, four, five... something is missing... I lost my carbon."

I: "Your carbon that you lost is now here." (I. points to the external double bond)

Heike: "So, I should have drawn this like that." (she corrects her transition structure).

I: "So, you have automatically your ring."

Heike: "Exactly. This is type 1... Nothing stabilized. It would proceed via this way."

The problems with this kind of structure are not surprising as these functional groups usually do not appear in regular exercises in courses or textbooks and require developed representational competence. However, it was interesting to see the different ways students dealt with the drawings; some had no problems in drawing or started independently to draw again an angled version of the transition structure while others needed more promptings, and others reasoned successfully with their lopsided drawings.

General discussion and implication for teaching at the university level

We have shown that teaching of domain-specific strategies for the six-electron case is possible and that students may gain a more holistic view on rearrangement reactions. The development of the structural unit of these reactions can easily be done in a course and it is a good anchor for relating other reactions, e.g., pyrolysis, retro-ene, and many other reactions that involve the rearrangement of six electrons. The ability to identify patterns in complex molecules and to make predictions about

possible reactions is a core skill in organic chemistry. Furthermore, the strategies to draw and estimate reaction pathways can be trained in class and recalled whenever six-electron rearrangements reappear in the curriculum.

The development of distinct representational competence of chemistry students is a challenge. As it appears in the study especially these types of reactions are challenging the visuo-spatial ability of students. This aspect should be explicitly taken into account when approaching this concept in teaching. As it has not yet been clearly determined which factors mainly influence representational competence, particularly while drawing rearrangement reactions, we cannot give an appropriate answer to this problem (Harle and Towns, 2010).

Regarding appropriate methods of teaching domain-specific heuristics, we have chosen the cognitive apprenticeship approach to combine an expert-like modeling of the reasoning process with an active participation of the students. This helps students quickly understand reasoning steps while solving problems and foster the development of own mental models. Therefore it might be constructive to actively encouraged students to deal with chemical transformations; drawing transition structures from substrates and transferring starting materials into final products. The ability to handle various rearrangement as well as many other processes, can be trained with this concept. Students should be engaged in using explicitly structure–reactivity relationships as a guide for their reflection on meaning and decision making, as it is one of the most powerful problem solving tools in organic chemistry. This potential is important for future chemists and affords explicit instruction, primarily through hands-on activities and discussing interpretations of structures and their meaning.

Conclusions

We investigated the effect of describing and predicting six-electron rearrangements through teaching domain-specific heuristics. The results of our study showed that explicit training of strategies and the detailed illustration of reasoning steps may help students improve their reasoning skills. A difference in performance and adaptation of the offered strategies depends on their level of prior knowledge in this specific domain. A consolidated view indicates that the heuristic perspective reduces the cognitive demand of this reaction type and allows students, both low and high achievers, to develop a visual concept of this type of transformation and to suggest mechanistic pathways and reaction outcomes of concerted and stepwise rearrangements.

Stepwise proceeding rearrangements, involving biradical intermediates play an important role in medicinal chemistry and in the advancement of anti-cancer drugs, but these have been largely ignored in teaching. The heuristic concept is thus not only an improvement for teaching concerted six-electron reactions but also includes biradical forming reactions, e.g., the Bergman and the Myers-Saito reactions.

In general the students' attitudes toward using heuristic strategies were quite positive. They felt that using these allowed them to handle complex reactions, but also to develop skills that would be valuable to them in the future. The six-electron rearrangement concept turned out to be not only a powerful way to connect structural representations with chemical

meaning and to develop process-thinking skills but also an epistemological issue of how we might perceive and understand chemistry from a more simplified perspective.

Heuristics are not meant to be universally valid rules; they are pragmatic and economic strategies and should thus be taught with an emphasis on their application. We believe that the most compelling aspect of this approach is the possibility to work directly with the students, to provide them with hands-on-strategies, and to discuss with them the merits and drawbacks of heuristic thinking in chemistry.

The reported study is part of a larger project that aims at a complete revision of organic chemistry transformations, under a heuristic perspective. Beside the six-electron concept, also addition and elimination reactions have been scrutinized in order to develop a simplified and comprehensive concept (Graulich *et al.*, 2010a, 2011).

Notes and references

- Anderson T. L. and Bodner G. M., (2008), What can we do about 'Parker'? A case study of a good student who didn't 'get' organic chemistry, *Chem. Educ. Res. Pract.*, **9**, 93–101.
- Bhattacharyya G., (2006), Practitioner development in organic chemistry: how graduate students conceptualize organic acids, *Chem. Educ. Res. Pract.*, **7**, 240–247.
- Bhattacharyya G., (2008), Who am I? What am I doing here? Professional identity and the epistemic development of organic chemists, *Chem. Educ. Res. Pract.*, **9**, 84–92.
- Bhattacharyya G. and Bodner G. M., (2005), "It Gets Me to the Product": How Students Propose Organic Mechanisms, *J. Chem. Educ.*, **82**, 1402–1407.
- Bodner G. M. and Domin D. S., (2000), Mental Models: The role of representations in problem-solving in chemistry, *Univ. Chem. Educ.*, **4**, 24–30.
- Bodner G. M. and Herron J. D., (2002), Problem-solving in chemistry, in J. K. Gilbert, O. De Jong, R. Justi, D. F. Treagust and J. H. Van Driel (ed.), *Chemical education: towards research-based practise* (pp. 235–266), Dordrecht: Kluwer.
- Bodner G. M. and McMillen T. L. B., (1986), Cognitive restructuring as an early stage in problem solving, *J. Res. Sci. Teach.*, **23**, 727–737.
- Borden W. T., Loncharich R. J. and Houk K. N., (1988), Synchronicity in Multibond Reactions, *Ann. Rev. Phys. Chem.*, **39**, 213–236.
- Brown J. S., Collins A. and Duguid P., (1989), Situated Cognition and the Culture of Learning, *Educational Researcher*, **18**, 32–42.
- Bui B. H. and Schreiner P. R., (2006), Thermal Rearrangements of Heteroatom-Bridged Diallylenes, *Eur. J. Org. Chem.*, 4187–4192.
- Carter C. S., Larussa M. A. and Bodner G. M., (1987), A study of two measures of spatial ability as predictors of success in different levels of general chemistry, *J. Res. Sci. Teach.*, **24**, 645–657.
- Chi M., Farr M. and Glaser R., (1988), *The Nature of Expertise*, Hillsdale, NJ: Lawrence Erlbaum Associates.
- Clayden J., Greeves N., Warren S. and Wothers P., (2005), *Organic Chemistry*, New York: Oxford University Press.
- Coleman S. L. and Gotch A. J., (1998), Spatial Perception Skills of Chemistry Students, *J. Chem. Educ.*, **75**, 206–null.
- De Vos W., Bulte A. and Pilot A., (2002), Chemistry Curriculum for General Education: Analysis and Elements of a Design, in J. K. Gilbert, O. De Jong, R. Justi, D. F. Treagust and J. H. Van Driel (ed.), *Chemical Education: Towards Research-based Practise* (pp. 101–124), Dordrecht: Kluwer Academic Publishers.
- Duit R., (1995), Zur Rolle der konstruktivistischen Sichtweise in den naturwissenschaftlichen Lehr- und Lernforschung, *Zeitschrift für Pädagogik*, **41**, 905–923.
- Ferguson R. and Bodner G. M., (2008), Making sense of the arrow pushing formalism among chemistry majors enrolled in organic chemistry, *Chem. Educ. Res. Pract.*, **9**, 102–113.
- Fischer H., Klemm K., Leutner D., Sumfleth E., Tiemann R. and Wirth J., (2005), Framework for Empirical Research on Science Teaching and Learning, *J. Sci. Teacher Educ.*, **16**, 309–349.
- Gigerenzer G. and Todd P. M., (1999), *Simple heuristics that make us smart*, Oxford: Oxford University Press.
- Gilbert J. K., (2005), Visualization: A metacognitive skill in science and science education, in J. K. Gilbert (ed.), *Visualization in science education* (pp. 1–27), Dordrecht: Springer.
- Graulich N., (2011), The Cope rearrangement—the first born of a great family, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, **1**, 172–190.
- Graulich N., Hopf H. and Schreiner P. R., (2010a), Heuristic Chemistry—Addition Reactions, *Chem. Eur. J.*, **17**, 30–40.
- Graulich N., Hopf H. and Schreiner P. R., (2010b), Heuristic Thinking makes a Chemist smart, *Chem. Soc. Rev.*, **39**, 1503–1512.
- Graulich N., Hopf H. and Schreiner P. R., (2011), Heuristic Chemistry—Elimination reactions, *Chem. Asian J.*, **6**, 3180–3188.
- Habraken C. L., (1996), Perceptions of chemistry: Why is the common perception of chemistry, the most visual of sciences, so distorted? *J. Sci. Educ. Tech.*, **5**, 193–201.
- Harle M. and Towns M., (2010), A Review of Spatial Ability Literature, Its Connection to Chemistry, and Implications for Instruction, *J. Chem. Educ.*, **88**, 351–360.
- Heller K. A. and Perleth C., (2000), *Kognitiver Fähigkeitstest für 4.-12. Revision (KFT 4-12+R)*, Göttingen: Hogrefe.
- Hendrickson J. B., (1974), The Variety of Thermal Pericyclic Reactions, *Angew. Chem., Int. Ed.*, **13**, 47–76.
- Herges R., (1990), Reaction Planning: Prediction of New Organic Reactions, *J. Chem. Inf. Comput. Sci.*, **30**, 377–383.
- Hoffmann R. and Laszlo P., (1991), Representation in Chemistry, *Angew. Chem. Int. Ed. Engl.*, **30**, 1–16.
- Houk K. N., Gonzalez J. and Li Y., (1995), Pericyclic Reaction Transition-States—Passions and Punctilios, 1935–1995, *Acc. Chem. Res.*, **28**, 81–90.
- Kawatkar S. P. and Schreiner P. R., (2002), Cycloaromatization of 1,4-Pentadiynes: A Viable Possibility? *Org. Lett.*, **4**, 3643–3646.
- Kozma R., (2003), The material Features of multiple representations and their cognitive and social affordance for science and understanding, *Learn. Instr.*, **13**, 205–226.
- Kozma R. B. and Russell J., (1997), Multimedia and understanding: Expert and novice responses to different representations of chemical phenomena, *J. Res. Sci. Teach.*, **34**, 949–968.
- Kraft A., Strickland A. M. and Bhattacharyya G., (2010), Reasonable reasoning: multi-variate problem-solving in organic chemistry, *Chem. Educ. Res. Pract.*, **11**, 281–292.
- Maeyer J. and Talanquer V., (2010), The role of intuitive heuristics in students' thinking: Ranking chemical substances, *Science Education*, **94**, 963–984.
- MAXQDA, Software für qualitative Datenanalyse, (1989–2010), Berlin-Marburg-Amöneburg, Germany: VERBI Software. Consult. Sozialforschung GmbH.
- Mayring P., (2008), *Qualitative Inhaltsanalyse* (10 edn). Weinheim, Basel: Beltz Verlag.
- McClary L. and Talanquer V., (2011), Heuristic Reasoning in Chemistry: Making decisions about acid strength, *Int. J. Sci. Educ.*, **33**, 1433–1454.
- Nagata R., Yamanaka H., Okazaki E. and Saito I., (1989), Biradical Formation from Acyclic Conjugated Enyne-Allene System related to Neocarzinostatin and Esperamicin-Calicheamicin, *Tetrahedron Lett.*, **30**, 4995–4998.
- Ponec R. and Strnad M., (1992), Similarity Ideas in the Theory of Pericyclic Reactivity, *J. Chem. Inf. Comput. Sci.*, **32**, 693–699.
- Pribyl J. R. and Bodner G. M., (1987), Spatial ability and its role in organic chemistry: A study of four organic courses, *J. Res. Sci. Teach.*, **24**, 229–240.
- Schreiner P. R. and Bui B. H., (2006), Moore Cyclizations: Rearrangements of 3-Heteroatom-pent-1-en-4-yn-1-ones—A Computational Search for New Reactions, *Eur. J. Org. Chem.*, 1162–1165.
- Schreiner P. R., Navarro-Vásquez A. and Prall M., (2004), Cope Reaction Families: To Be or Not to Be a Biradical, *Org. Lett.*, **6**, 2981–2984.
- Stewart K. K. and Lagowski J. J., (2003), Cognitive Apprenticeship Theory and Graduate Chemistry Education, *J. Chem. Educ.*, **80**, 1362.
- Stieff M., (2007), Mental rotation and diagrammatic reasoning in science, *Learn. Instr.*, **17**, 219–234.
- Stieff M. and Raje S., (2008), *Expertise & spatial reasoning in advanced scientific problem solving*, Paper presented at the Proceedings of the 8th International Conference of the Learning Sciences.

- Stösser R., Ulbrich S. L. and Tiemann R., (2009), Von der Struktur zur Eigenschaft—Phänomenologische Aspekte der chemischen Bindung zur Veranschaulichung von Basiskonzepten, *Der mathematische und naturwissenschaftliche Unterricht MNU*, **62**, 498–504.
- Stösser R., Ulbrich S. L. and Tiemann R., (2010), Von der phänomenologischen Eigenschaft zur Struktur—Ausgewählte Bindungsphänomene zur Umsetzung der Bildungsstandards, *Der mathematische und naturwissenschaftliche Unterricht MNU*, **63**, 498–504.
- Strickland A. M., Kraft A. and Bhattacharyya G., (2010), What happens when representations fail to represent? Graduate students' mental models of organic chemistry diagrams, *Chem. Educ. Res. Pract.*, **11**, 293–301.
- Tiemann R., (1999), *Analyse individueller Wissensstrukturen im Kontext Chemie mit Hilfe eines neuen Mapping Verfahrens* (vol. 31), Münster: LIT.
- Viola A., Collins J. J. and Filipp N., (1981), Intramolecular Pericyclic Reactions of Acetylenic Compounds, *Tetrahedron*, **37**, 3765–3811.
- Wiest O., Montiel D. C. and Houk K. N., (1997), Quantum Mechanical Methods and the Interpretation and Prediction of Pericyclic Reaction Mechanisms, *J. Phys. Chem. A*, **101**, 8378–8388.
- Woodward R. B. and Hoffmann R., (1969), The Conservation of Orbital Symmetry, *Angew. Chem., Int. Ed.*, **8**, 781–932.