

**APPLICATIONS OF THE TOPIC-SPECIFIC PEDAGOGICAL CONTENT
KNOWLEDGE MODEL FOR TEACHING ELECTROPHILIC
AROMATIC SUBSTITUTION IN ORGANIC CHEMISTRY**

by

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*To the Murderinos,
SSDGM*

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GLOSSARY

Activating Group: An electron-donating group that increases the reactivity of an aromatic ring toward electrophilic aromatic substitution (McMurry, 2004).

Anchoring Concept: Any concept associated with organic chemistry appearing in one of the four levels of the Anchoring Concepts Content Map of organic chemistry, produced by the American Chemical Society Examinations Institute.

Arrow Pushing: a term used to define the process of using arrows to conceptually move electrons in order to describe the mechanistic steps involved in the transition of starting materials to products (Levy, 2008).

Deactivating Group: An electron-withdrawing substituent that decreases the reactivity of an aromatic ring toward electrophilic aromatic substitution (McMurry, 2004).

Directing Substituent: The nature of the substituent already present on an aromatic ring influences the position of the second substituent (McMurry, 2004).

Electrophile: An “electron-lover,” or substance that accepts an electron pair from a nucleophile in a polar-bond forming reaction (McMurry, 2004).

Electrophilic Aromatic Substitution: A reaction in which an electrophile reacts with an aromatic ring and substitutes for one of the ring hydrogens (McMurry, 2004).

Electrostatic Potential Map: Image showcasing the electrostatic potential energies on the isosurface of a molecule. Electron-deficient regions are defined by the color blue, electron-rich are red, and neutral positions are green (Mahaffy et al., 2015).

General Knowledge Domains: As defined in the TS-PCK model, the three general knowledge domains that teacher’s use to inform their TS-PCK are knowledge of students, subject matter knowledge, and pedagogical knowledge (Davidowitz & Rollnick, 2011).

Lewis Structure: Molecular structure in which the valence electrons are shown as dots so placed between the bonded atoms that one pair of dots represents two electrons or one covalent (single) bond (McNaught & Wilkinson, 2017).

Misconception: Any concept that differs from the commonly accepted scientific understanding of the term (Nakhleh, 1992).

Nomenclature: When referencing the positions of substituents on desired molecules in which the full name has been verbalized, ortho, para, and meta will be shortened to the first letter and italicized (e.g. meta-nitrotoluene will become *m*-nitrotoluene).

Nucleophile: A “nucleus-lover,” or species that donates an electron pair to an electrophile in a polar bond-forming reaction (McMurry, 2004).

Pedagogical Content Knowledge: the union of subject matter knowledge and the understanding of instruction (Shulman, 1986).

Reactant: A substance that is consumed in the course of a chemical reaction. It is sometimes known, especially in the older literature, as a reagent, but this term is better used in a more specialized sense as a test (Nic, Jirat, & Kosata, 2017).

Substituent: An atom (group) that replaces one or more hydrogen atoms attached to a parent structure or characteristic group except for hydrogen atoms attached to a chalcogen atom (McNaught & Wilkinson, 2017).

Resonance: The donation or withdrawal of electrons through orbital overlap with neighboring π bonds (McMurry, 2004).

Topic Specific PCK: The specific PCK components of (i) Learner's Prior Knowledge, (ii) Curriculum Saliency, (iii) Topic Easiness/Difficulties, (iv) Representations, and (v) Conceptual Teaching Strategies are heavily considered, resulting in knowledge that is specific to the topics being taught (Mavhunga & Rollnick, 2011, 2013).

Understanding: Application of concepts and foundational knowledge to reason through novel problems (Holme, Luxford, & Brandriet, 2015)

LIST OF ABBREVIATIONS

ACCM: Anchoring Concepts Content Map

CK: Content Knowledge

EPF: Electron-Pushing Formalism

EPM: Electrostatic Potential Map

GKD: General Knowledge Domain

KoS: Knowledge of Students

PCK: Pedagogical Content Knowledge

PK: Pedagogical Knowledge

SMK: Subject Matter Knowledge

TS-PCK: Topic-Specific Pedagogical Content Knowledge

ABSTRACT

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Title: Applications of the Topic-Specific Pedagogical Content Knowledge Model for Teaching Electrophilic Aromatic Substitution in Organic Chemistry

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Students studying organic chemistry often have difficulty applying prior knowledge from general chemistry in their thinking about organic reaction mechanisms. In the United States, electrophilic aromatic substitution (EAS) mechanisms can be taught towards the end in a second-semester course of organic chemistry, providing students with almost two-semesters' worth of experience with organic chemistry reactions before solving problems on synthesis of substituted aromatic compounds.

Little research has been done on how, or if, instructors consider their students' prior knowledge or understanding of these concepts in EAS in their teaching activities. The purpose of this study was to describe how students reason through EAS synthesis problems and to identify concepts or gaps in understanding that inhibit students from successfully solving these types of problems. Participants were interviewed using a think-aloud protocol in which they were asked to describe the reactants and mechanisms necessary to synthesize di- and tri-substituted benzenes using EAS. The interviews were transcribed and analyzed using a qualitative inquiry approach and the data interpreted in terms of the ACS Examinations Institute's Anchoring Concepts Content Maps for general and organic chemistry.

The findings from this study indicated that while the students correctly applied their knowledge of substituent effects to solve these types of problems, they relied on rote-memorization

of these effects, resulting in inflexibility when applying them to novel situations. Additionally, students exhibited gaps in understanding of fundamental concepts in resonance theory and Lewis structures, differentiating and utilizing Friedel-Crafts reactions, and recognizing when to use oxidation/reduction reactions in their syntheses.

Another component of this study focused on instructors of organic chemistry from a range of institutions in the United States. The purpose of this study was to describe how organic chemistry instructors perceived their students' reasoning about these types of problems, and to describe the characteristics of each instructor's topic-specific pedagogical content knowledge (TS-PCK) and the three general knowledge domains (GKDs) instructors draw upon to inform their TS-PCK. These knowledge domains are knowledge of students, subject matter knowledge, and pedagogical knowledge. These participants were remotely-interviewed using a think-aloud protocol in which they were asked to describe their classroom practices and teaching strategies when teaching EAS, and to describe how they would synthesize the same aromatic compounds as their students (a selection of which were interviewed in the previous study). Participants were asked to consider how their students would approach the syntheses and to specify what parts of the syntheses their students would find challenging, and why. The interviews were transcribed and analyzed using a qualitative inquiry approach.

The findings from this study indicated that the instructors were aware of their students' tendencies to use rote-memorization without understanding in the course, but there was still a misalignment between how instructors' perceived their students' reasoning through EAS synthesis problems and the reasoning the students actually used. The instructors believed that their students would only rely on the directing effects of substituents in their reasoning, but the students demonstrated they were aware of the activating and deactivating effects too. Additionally,

instructors believed their students would not be hindered by an understanding of resonance or Lewis structures in their syntheses.

Finally, there are some recommendations for addressing the students' propensity for rote-memorization by providing a visual way to represent directing and activating/deactivating effects of substituents using electrostatic potential maps. There are also suggestions for further studies building on this work.

CHAPTER 1. INTRODUCTION

1.1 Rationale

In the United States, organic chemistry is a sophomore-level college course that follows two semesters of general chemistry in which basic definitions and chemical concepts are covered (Holme, Luxford, & Murphy, 2015). Undergraduate students enrolled in organic chemistry need to apply this fundamental knowledge to deeply understand the structures and reactivities of organic compounds. Not unreasonably, many instructors of upper-level chemistry courses assume that students enter more advanced courses with a reasonable conceptual understanding of the foundational concepts (Holme, Luxford, & Brandriet, 2015), and build upon them to present more complicated theories/concepts. However, if a student's prior learning in general chemistry is superficial, there is a high likelihood this will be reflected in the student's performance in organic chemistry (Seery, 2009). An inadequate understanding of fundamental concepts, such as electronegativity, and skills, such as the ability to draw accurate Lewis structures, can impede students from understanding more advanced concepts, or appropriately applying these concepts in new contexts (Nakhleh, 1992), like drawing reasonable reaction mechanisms. In organic chemistry, this problem is revealed most clearly when trying to solve synthesis problems requiring application of multiple concepts and skills.

Most students enroll in organic chemistry with the assumption that the least-effort learning strategy of surface-level memorization of reactants, reagents, reactions, preferred products, and mechanisms will be successful, and that a deep understanding will not be necessary and will not be assessed (Anderson & Bodner, 2008; Pursell, 2009; Zurer, 2001). One of the reasons students use rote memorization without understanding as a learning heuristic has been attributed to the heavy content load in most organic chemistry courses (Anderson & Bodner, 2008; Grove & Bretz,

2012). Indeed, many students have continued with their academic chemistry careers having passed organic chemistry with this strategy, never seeing the field's logical consistency and predictive power. Bhattacharyya and Bodner (2005) asked graduate students enrolled in an advanced-level organic chemistry course to predict reaction mechanisms to transform a given starting material into a given product. These graduate students were able to successfully reproduce mechanistic problems with a "memorized sequence of events" (Bhattacharyya & Bodner, 2005, p. 1406), but did not display an understanding of the underlying chemical concepts. Similar results were obtained with fourth-year undergraduate students when asked to identify the correct reaction mechanism, in which students chose to evaluate the stability of the intermediates rather than evaluate if the proposed curved-arrows would indeed lead to the intermediates shown (Rushton, Hardy, Gwaltney, & Lewis, 2008a). This indicates how students have successfully passed their introductory courses without developing the deep understanding of the concepts needed to fully engage in advanced courses.

To study this problem in detail an advanced-level topic in organic chemistry was chosen to study how students and instructors deal with this issue. Electrophilic aromatic substitution (EAS) has been identified as an anchoring concept by the ACS Examinations Institute in the Anchoring Concepts Content Map (ACCM) for organic chemistry (Raker, Holme, & Murphy, 2013). The ACCM was designed to list the essential content in an undergraduate chemistry curriculum (Holme & Murphy, 2012). The map is comprised of four levels: the top two levels span across, and are applied to, the entirety of undergraduate chemistry; levels 3 and 4 are specific to the sub-discipline of chemistry (i.e. organic chemistry). An example of this hierarchy of concepts and skills relevant to EAS can be seen in Figure 1.1. In this dissertation, an anchoring concept is defined as any concept that appears in any of the four levels of the organic chemistry ACCM. Other anchoring

concepts involved in EAS are substituent effects, aromaticity, Friedel-Crafts alkylation and Friedel-Crafts acylation reactions, and reduction of aromatic nitro groups (Raker et al., 2013).

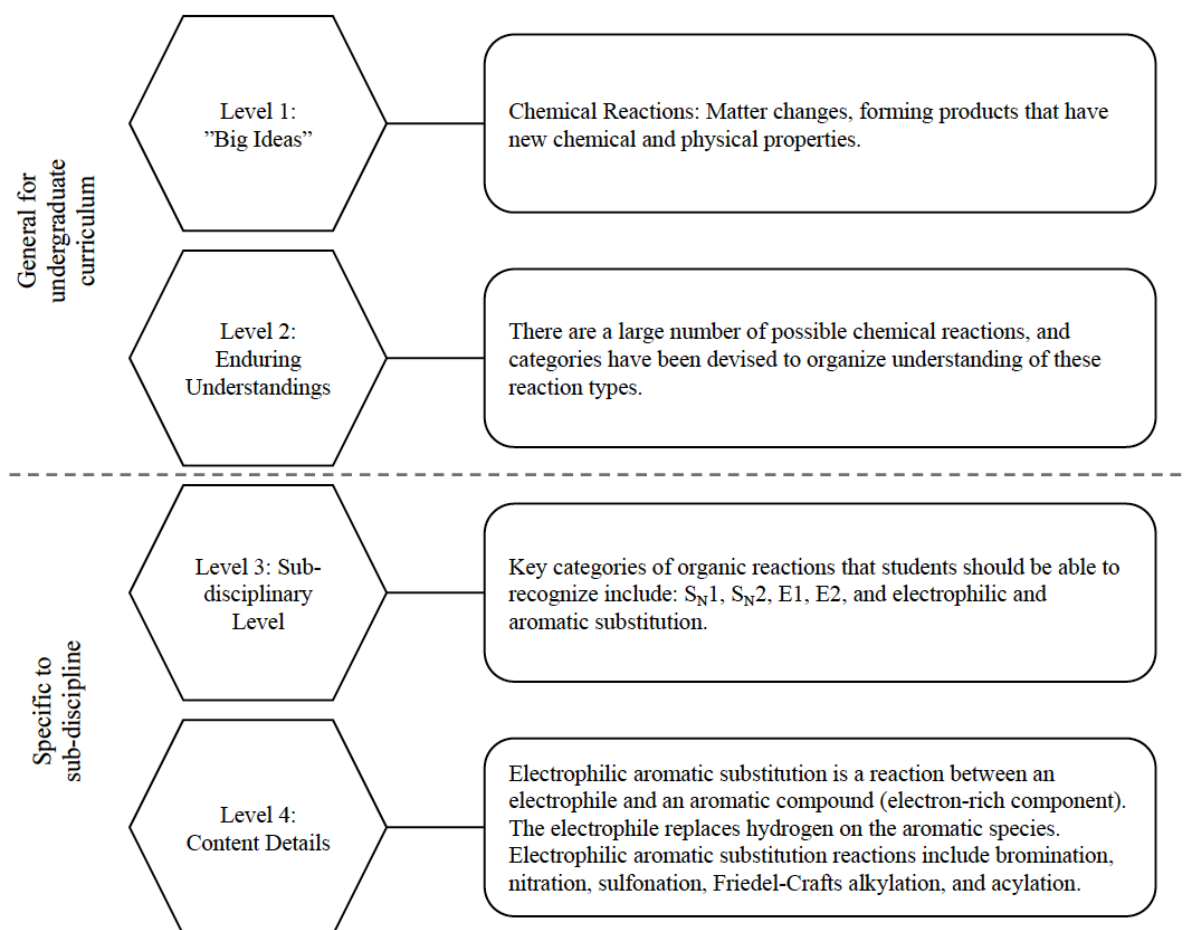


Figure 1.1 An example of the ACS Examinations Institute in the Anchoring Concepts Content Map (ACCM) for organic chemistry relating to electrophilic aromatic substitution (Raker, Holme, & Murphy, 2013).

The concepts, skills and synthetic strategies involved in EAS are important. They are widely used for synthesis of key compounds in the industrial, pharmaceutical, and agriculture industries (Smith & El-Hiti, 2011). In addition, investigating the depth of student understanding of this important topic also provides information on their prior knowledge of the underlying concepts required.

The approaches used by students in synthesis problems in which more than one step are required are worthy of study to provide insight into how these can be scaffolded by instructors.

Students need to meet the significant cognitive demand in synthesis problems by identifying the types of reactions required to transform a starting molecule to a final product, recalling the appropriate reagents and reaction conditions, and sometimes reasoning through the order of reactions to result in the desired product in good yield. Without adequate understanding and chunking of information this cognitive demand can result in working memory overload (Johnstone, 1991).

Chemistry instructors impact their students' education with their decisions on what students should learn, and how that material is delivered through their teaching practices; therefore, it is important to investigate student learning from both the student's perspective as well as the instructor's perspective. The instructor needs to understand the content thoroughly and also take into account the prior knowledge and cognitive demands of the topic. Pedagogical content knowledge (PCK) is the overlap between content knowledge (CK) and pedagogical knowledge (PK), which allows the transformation of subject matter to support student learning (Shulman, 1986, 1987). An instructor's PCK influences their knowledge of their students' understanding of chemistry topics. For this transformation to be successful, instructors not only need to comprehend the subject matter (CK), but create learning activities and demonstrations (PK) relevant to that subject matter (PCK) (Shulman, 1987). PCK is a crucial component of an instructor's practical knowledge since it is developed through an integrative process embedded in classroom practice (Seung, Bryan, & Haugan, 2012; Verloop, van Driel, & de Vos, 1998). For this dissertation, topic-specific pedagogical content knowledge (TS-PCK) was used as a theoretical framework to evaluate each instructor's PCK, and is described in Section 2.5.2.3.

Most studies in the chemical education literature describe student understanding of specific topics within the context of organic chemistry - such as the use of Lewis structures (Cooper, Grove,

& Underwood, 2010; Cooper, Underwood, & Hilley, 2012), the types of chemical bonding (Henderleiter, Smart, Anderson, & Elian, 2001), the nature and relative reactivity of nucleophiles and electrophiles (Anzovino & Bretz, 2016), and the reactivity of functional groups (Akkuzu & Uyulgan, 2016). However, little research has been published on how, or if, instructors consider their students' understanding of these concepts in designing their teaching activities. Instructors use three general knowledge domains to inform their PCK: knowledge of students (which includes their knowledge of students' prior learning, motivations, and learning difficulties specific to a topic), subject matter knowledge, and pedagogical knowledge (Mavhunga & Rollnick, 2013).

In the United States, large introductory science courses are generally taught by faculty in large lecture classes, with teaching assistants acting as tutors or laboratory demonstrators for facilitating student learning in smaller groups. This produces a disconnect in the student-teacher relationship and communication that does not occur with smaller classes. Additionally, the instructors of these large lecture courses will often use multiple-choice assessments for evaluating student's learning, for practical, not pedagogical reasons. Instructors can often mistakenly correlate student performance on these assessments with conceptual understanding of the material (Pickering, 1990; Sawrey, 1990). Therefore, instructors need other measures to assess student learning in their classroom.

1.2 Statement of Purpose

The purpose of this study was to describe how organic chemistry students reason through EAS synthesis problems, and identify concepts or gaps in understanding that impede students from successfully solving these types of problems. To accomplish this, students enrolled in organic chemistry were asked to answer questions about concepts required in EAS and then to solve several synthesis problems using EAS.

Another goal of this study was to describe how organic chemistry instructors perceive their students' reasoning about these types of problems. To accomplish this, instructors from universities in the United States were interviewed and asked to solve the same EAS synthesis problems as their students, from their student's perspectives, to anticipate the difficulties and challenges that may arise in the process of solving a synthesis problem. Additionally, this study investigated the relationship between an organic chemistry instructor's TS-PCK and the three general knowledge domains instructors draw upon to inform their TS-PCK.

1.3 Significance

This study is significant for several reasons: 1) organic chemistry instructors will learn how students reason through EAS synthesis problems, the relationship between the three GKDs that are used to inform their TS-PCK with respect to EAS, and recommendations for promoting a deep understanding of the concepts involved in EAS using molecular visualization, rather than just using rote-memorization, 2) the findings indicate that pedagogical changes are needed to help students learn EAS, and organic chemistry in general, deeply rather than superficially, and 3) the findings add to the existing literature on students' alternative conceptions and cognitive challenges in organic chemistry.

This study reveals the impact of specific teaching practices on student understanding of EAS. At Purdue University, EAS is a topic that is taught in the latter part of the second semester, meaning students should have almost four semesters of chemistry courses before studying this topic. Success with EAS problems can be hindered by a students' weak understanding of the concepts involved, and by incorrectly remembering the reactants necessary in a reaction. Many organic chemistry instructors are aware that students enrolled in their class have a weak understanding of general chemistry topics, and that their students will all be approaching organic

chemistry problems in diverse ways (Duis, 2011). These instructors may adjust their instructional strategies for these differences by using different modes of instruction or providing multiple representations in the classroom. However, there are also numerous instructors who assume their instructional strategies are accounting for these differences, without investigating the final outcome of what their students are actually learning. Comparing student reasoning of these topics with how the teachers perceive this understanding may be informative for teacher self-evaluation of the impact of their instructional strategies on student understanding of EAS synthesis problems.

Most of the instruction of this topic is spent on showing how different reactants convert a starting material into the desired product with the appropriate stereochemistry and in good yield. Exam questions in organic chemistry ask students to identify the necessary reactants for a given reaction, or to produce a reaction scheme that uses several reactants in sequence to get from starting reactant A to final product B. Many of the reactants used in organic chemistry have been introduced in general chemistry courses, but it is not until organic chemistry that the reactants are applied to transform a starting material through mechanistic reasoning. For example, the molecule of water is introduced in first semester general chemistry when discussing polarity. In organic chemistry, water can be used as a base, acid, or solvent in a reaction. By investigating how students are selecting and using reactants in EAS synthesis problems, instructors may be able to reevaluate their teaching practices to persuade students to understand when they are appropriate, and not just use rote-memorization.

There are many factors that can affect student learning of chemistry, including how the material is presented, the learning activities involved, and the students' prior knowledge. Although instructors cannot change what information a student possesses when they are enrolled in their course, they can be more reflective about their own teaching practices with the numerous

instructional strategies for teaching sophomore organic chemistry that have been validated through rigorous research studies. This study aims to highlight what concepts in the EAS unit are most challenging for students to learn, and which teaching practices could facilitate a more conceptual understanding of the material.

1.4 Research Questions

The research questions guiding this study are:

1. How do organic chemistry students reason through EAS synthesis problems?
2. Which misunderstandings or gaps in understanding emerge when students are asked to describe their syntheses of compounds using EAS?
3. How do organic chemistry instructors perceive student reasoning in EAS synthesis problems?
4. What are the differences between an instructor's perception of their students' reasoning and the reasoning they actually use?
5. How are the three general knowledge domains (knowledge of students, subject matter knowledge, and pedagogical knowledge) of topic-specific pedagogical content knowledge reflected in organic chemistry instructors with respect to EAS?

1.5 Assumptions

The following assumptions were made during this study:

1. A constructivist research paradigm was used with the assumption that "reality is socially constructed and the goal of social scientists is to understand what meanings people give to that reality" (Engel & Schutt, 2009, p. 56).

2. The instructors interviewed were representative of organic chemistry instructors in the United States.
3. The instructor explanations and responses were accurate representations of their experiences and thinking at the time of the interviews.
4. The student explanations and responses were accurate representations of their experiences and thinking at the time of the interviews.
5. Not all cognitive information is received in think-aloud interviews. An assumption was made that the information participants gave was a sufficient representation of their thinking.

1.6 Limitations

This study was conducted with the following limitations:

1. Only eleven students volunteered for this study, limiting the possibility of data saturation.
2. The eleven students were recruited from one course at Purdue University. The participants in this study may not be representative of any other population other than students enrolled in this course at this university.
3. Instructor participants may have been primed by the questionnaire before the one-on-one interviews, giving them time to conduct their own research into student understandings in organic chemistry.
4. Interviews with seven of the eight instructors occurred in the Fall semester, leaving an approximate seven- month gap in time from when they would have last covered the material.
5. Remote interviewing with faculty resulted in brief interruptions in audio and video recordings. Interviews were transcribed to the best of the researcher's ability.

1.7 Overview of Chapters

The literature background in Chapter 2 will review research on student understanding in organic chemistry, including student approaches to learning organic chemistry and alternative conceptions. In addition, the history of PCK, common models of PCK, and the PCK demonstrated by experienced chemistry instructors will be described. The methodologies of the student and instructor components of this study will be discussed in Chapter 3. The results and discussion will be presented in three chapters: Chapter 4 – students' understanding of EAS synthesis problems, Chapter 5 - instructors' perceptions of student understanding of EAS synthesis problems, and Chapter 6 - TS-PCK of organic chemistry instructors. Chapter 7 will describe the conclusions and implications that can be drawn from the findings of this study, with some recommendations for addressing some of the issues revealed.

CHAPTER 2. LITERATURE BACKGROUND

2.1 Overview

When investigating student understanding of a topic, it is important to include how students are approaching novel problems, their reasoning behind those approaches, and the environment in which they are learning. Included in the environment is the instructor of the course – the teaching strategies they implement and how they perceive their students' understanding based on those strategies. This literature review will focus on two major areas: student understanding of organic chemistry and PCK, including a history of the model and the current literature on the PCK of experienced chemistry teachers.

2.2 Student Approaches to Learning Organic Chemistry

Most students enroll in organic chemistry with the mind-set that the most successful learning strategy in the class will be surface-level memorization of reactants, reagents, reactions, preferred products, and mechanisms (Anderson & Bodner, 2008; Pursell, 2009; Zurer, 2001). Anderson and Bodner (2008) proposed that the complexity and heavy content load in most organic chemistry courses force students to superficially apply memorized rules without developing an understanding as to *why* the rules exist and when and where they can be applied appropriately. Pursell (2009) agrees that the rapid pace and complexity of material in the course prompts students to memorize rules, but adds that the callout boxes in textbooks showing consolidated material indicate content to memorize. Furthermore, Grove and Bretz (2010, 2012) proposed that as the organic chemistry curriculum progresses, it becomes less straightforward and relevant for the students, particularly when there appears to be more than one correct answer or multiple correct mechanistic pathways to a product.

2.3 Student Understanding in Organic Chemistry

Student understanding of topics in organic chemistry has been studied extensively over the last few decades – from student challenges with specific topics taught throughout the course like mechanistic reasoning to identifying student learning difficulties and alternative conceptions in specific concepts. Studies have shown that students taking this sophomore-level course struggle with topics encountered in general chemistry, which could negatively impact their performance (Seery, 2009). Specific general chemistry concepts encountered in organic chemistry that students struggle with include Lewis structures (Cooper et al., 2010, 2012), and acid/base concepts (Cartrette & Mayo, 2011; Cruz-Ramírez de Arellano & Towns, 2014).

Lewis structures are used as a model to symbolically visualize what is occurring at the molecular level – lone pairs, bonded electrons, and resonance where applicable. In organic chemistry, students are expected to be able to construct acceptable Lewis structures, and from these structures reasonably predict the reactivity of substances and their chemical and physical properties (Cooper et al., 2010, 2012; Tiettmeyer et al., 2017). Cooper et al. (2010) asked undergraduate students (freshman to senior-years), graduate students, and faculty members to draw valid Lewis structures from various chemical formulas. They found that the way the chemical formula of methanol was presented (CH_4O versus CH_3OH) greatly affected their performance, suggesting that students were relying on the memorized rules to drawing Lewis structures, rather than understanding the application of these rules (Cooper et al., 2010). Tiettmeyer et al. (2017) suggest the cognitive load that comes with drawing Lewis structures makes the task daunting to the students. Both researchers suggest that instructors should limit their instruction to common elements and second-row elements for introductory students (Cooper et al., 2010; Tiettmeyer et al., 2017). Additionally, continuous practice throughout the course could help students develop

competence with the process of drawing Lewis structures before they get to organic chemistry (Cooper et al., 2010).

There have been numerous studies where researchers investigated student understanding of topics in organic chemistry. Their findings showed that students had an incomplete understanding of general chemistry topics and that this negatively impacted their performance of the organic chemistry tasks. The significance of lone pairs in Lewis structures played a role in students' abilities to solve nucleophile/electrophile problems and questions about aromaticity. Anzovino and Bretz (2016) found that students depended on the structural features (lone pairs) of a molecule to identify a nucleophile, but were unable to provide a defining characteristic of an electrophile. Ealy and Hermanson (2006) found that students were unable to identify when a lone pair was part of a pi system for aromaticity. Additionally, students also had difficulty in identifying the number of valence electrons an element possessed (Ealy & Hermanson, 2006).

Poor understanding of acid and base concepts affected students abilities to identify electrophiles and nucleophiles, as well as complete alkyl halide reaction problems (Anzovino & Bretz, 2016; Cartrette & Mayo, 2011; Cruz-Ramírez de Arellano & Towns, 2014). Cartrette and Mayo (2011) found that students relied on the Brønsted-Lowry definition of acids and bases; therefore they were unable to connect Lewis acid-base theory to help identify electrophiles and nucleophiles. Additionally, students incorrectly ranked molecules on acid strength that were capable of Brønsted-Lowry and Lewis acid behavior (Cartrette & Mayo, 2011). Anzovino and Bretz (2016) found similar results when evaluating student conceptions of electrophiles and nucleophiles. In reactions that involved a hydroxide ion, most students labeled it as a nucleophile, even though the given products showed a proton transfer taking place (Anzovino & Bretz, 2016). In other problems where students were asked to provide the reaction products, students did not

consider the hydroxide would act as a Brønsted-Lowry base and accept a proton (Anzovino & Bretz, 2016). Cruz-Ramírez de Arellano and Towns (2014) found that students had difficulty identifying if methanol would act as a base or a nucleophile in a given alkyl halide reaction. Furthermore, students that identified methanol as a weak base, did so by rote memorization of a chart that had been provided in class and could not elaborate further on their reasoning (Cruz-Ramírez de Arellano & Towns, 2014).

The use of mechanistic thinking to predict reaction products is challenging for students in organic chemistry. Not only are students trying to explain how reactants are converted to major and minor products, but they are also trying to use the electron-pushing formalism (EPF) or curved-arrow approach as a heuristic tool in their explanation. Although this approach holds meaning to experts as a way to predict realistic intermediates and products through the movement of electrons (Bhattacharyya, 2013), students tend to use EPF as an afterthought rationalization of a product (Anderson & Bodner, 2008; Bhattacharyya & Bodner, 2005; Grove, Cooper, & Rush, 2012). Additionally, senior-level and graduate students have been observed to use curved-arrows after predicting intermediates in a mechanism (Bhattacharyya & Bodner, 2005; Rushton, Hardy, Gwaltney, & Lewis, 2008b). Throughout a student's progression in learning chemistry, this powerful explanatory tool poses a difficult challenge even for advanced students.

2.4 Alternative Conceptions in Organic Chemistry

As described in section 2.3, it is common to have students entering organic chemistry with an incomplete understanding of the fundamental knowledge and skills necessary to be successful in the course. There is extensive literature on alternative conceptions specific to undergraduate chemistry. As defined by Nakhleh (1992), an alternative conception, sometimes referred to as a misconception, refers to, “any concept that differs from the commonly accepted definition” (p.

191). The literature also describes the alternative conceptions held by upper-level students, graduate students, and teachers (Bodner, 1991; Rushton et al., 2008b; Şendur, 2012).

Some examples of alternative conceptions held by students studying organic chemistry include: (1) atoms bordering nitrogen and oxygen in the periodic table are the only atoms that can participate in hydrogen bonding, (2) molecules that can form hydrogen bonds to other molecules can induce a hydrocarbon to hydrogen bond with it, (3) acidic strength is determined by the functional groups that are present within the molecule, (4) addition reactions can only occur if a molecule contains a π bond, (5) covalent bonds are broken when the molecule changes from liquid to gas, and (6) the stability of final products is more important than the mechanism that led to the products (Henderleiter et al., 2001; McClary & Bretz, 2012; Rushton et al., 2008b; Şendur, 2012; Taagepera & Noori, 2000). Students with alternative conceptions may find understanding future concepts that contradict them more challenging. Detecting the same alternative conceptions held by more advanced students and teachers indicates their persistence and resistance to change through instruction (Bodner, 1991).

2.5 Pedagogical Content Knowledge

Shulman (1986, 1987) developed the concept of PCK and described it as the union of subject matter (content) knowledge and knowledge of pedagogy. PCK incorporates how an instructor uses their pedagogical knowledge and subject matter knowledge concurrently to support student learning (Shulman, 1986, 1987). PCK is comprised of beneficial forms or representations of the concepts, useful analogies, examples and diagrams, and knowing what makes learning certain concepts easy or difficult (Maries & Singh, 2013; Shulman, 1986). Not only do instructors need to have a strong understanding of the material they teach, but it is important that they are also

able to present the same information in novel ways to increase student understanding (Shulman, 1987).

2.5.1 Conceptualizations of PCK

Although Shulman set the foundation for the core of PCK, his definition and model of PCK have been expanded upon and reconceptualized by many scholars over the years. A summary of the components that scholars have included in their models of PCK from 1987-2006 are listed in Table 2.1. A discussion about the scholar's reasoning to their additions to the PCK model follows below.

Table 2.1 Components of the PCK model included by past scholars [adapted from Park and Oliver (2008)]

Scholars	Knowledge of								
	Student Understanding	Instructional Strategies and Representations	Curriculum	Assessment	Purposes for Teaching a Subject Matter	Media	Subject Matter	Context	Pedagogy
Shulman (1987)	X	X							
Tamir (1988)	X	X	X	X					
Smith and Neale (1989)	X	X			X				
Grossman (1990)	X	X	X		X				
Marks (1990)	X	X				X			
Geddis et al. (1993)	X	X	X						
Cochran et al. (1993)	X						X	X	X
Fernandez-Balboa and Stiehl (1995)	X	X			X		X	X	
Magnusson et al. (1999)	X	X	X	X	X				
Hashweh (2005)	X	X	X	X	X		X	X	X
Loughran et al. (2006)	X	X			X		X	X	X

Tamir (1988) added knowledge of curriculum and assessment to the model. Since there is an infinite amount of material that can be taught in a course, it is the responsibility of the teacher to have, “organized and arranged [the material] into systematic programs of instruction” (Tamir, 1988, p. 106). After interviewing 10 primary science teachers that had completed a four-week summer program on teaching science in primary school, Smith and Neale, (1989) found it important to include the teachers’ beliefs about the purpose of teaching a specific topic in PCK. The researchers found that a teacher’s beliefs affected the development of the science lessons they implemented in their classroom. Grossman (1990) combined the ideas of Tamir (1988) and Smith and Neale (1989) to include a teacher’s beliefs about the purpose of teaching specific subject matter and knowledge of the curriculum on top of Shulman’s (1987) knowledge of student understanding and instructional strategies and representations. Media for instruction, which includes the textbook and other classroom materials, was added when Marks (1990) conceptualized his definition of PCK after interviewing eight fifth-grade mathematics teachers. Some of the teachers had discussed examples in textbooks that could confuse their students and impact their learning. For example, a problem asking about the fraction of balls that were yellow out of a group of different sized balls and colors. It seemed unnecessary to include other superficial differences that would distract their students from the question. Similar to Tamir (1988), Geddis et al., (1993) saw the importance of an instructor’s knowledge of curricular saliency when describing two student teachers’ PCK covering atomic theory in the secondary classroom. Teachers who consider the curricular saliency of a topic can more easily “deal with the tension between *covering the curriculum* and *teaching for understanding*” (Geddis et al., 1993, p. 589).

The definition of PCK was broadened even further to explicitly include knowledge of subject matter, context, and pedagogy with student understanding. Pedagogical content *knowing*

was modified based on a constructivist view and became defined as “a teacher’s integrated understanding of four components of pedagogy, subject matter content, student characteristics, and the environmental context of learning” (Cochran, DeRuiter, & King, 1993, p. 266). Cochran et al. (1993) argue the word *knowledge* to being too static for the constructivist view, thus changing the word to *knowing*.

Fernandez-Balboa and Stiehl (1995) studied ten college professors and categorized their PCK into five components: (i) knowledge about the subject matter, (ii) knowledge about the students, (iii) knowledge about instructional strategies, (iv) knowledge about teaching strategies, and (v) knowledge about one’s teaching purposes. Magnusson, Krajcik, and Borko (1999) singled out assessment as its own component of PCK. Their research was specific to science teaching; therefore, the categories were defined by the learning of science. These included the beliefs teachers had about science teaching, knowledge of the curriculum, student understanding of science topics, assessment, and knowledge of science teaching strategies (Magnusson et al., 1999). Hashweh's (2005) model included all of the previously described components except for knowledge of assessment. While Loughran, Berry, and Mulhall (2006) have made one of the more recent conceptualizations of PCK, they highlight the importance of gathering enough evidence so that the reader can identify the situation and make meaning from it.

2.5.2 Modern Models of PCK

Today, researchers that use PCK either choose the model that is most appropriate for their research questions or they conceptualize their own by intertwining the ideas posed by previous researchers. Individuals conceptualize PCK differently, but the core of the definitions are cohesive; PCK comes from an individual’s experience of blending subject matter knowledge with pedagogical knowledge and is constantly developed in individuals through personal reflections

(Fernandez-Balboa & Stiehl, 1995; Grossman, 1990; Magnusson et al., 1999; Shulman, 1986; Verloop, Van Driel, & De Voos, 1998). It has been reported that PCK has the greatest impact on teachers' practice and student learning after researchers investigated the development of PCK in teachers through workshops and certification programs (Clermont, Krajcik, & Borko, 1993; Grossman, 1990; Park & Oliver, 2008).

In 2012, researchers from various countries devoted to investigating and defining PCK met at a summit to collaborate and discuss the constructs and developments of PCK (Berry, Friedrichsen, & Loughran, 2015). This section will discuss three of the most recent models of PCK that were presented and developed at the summit: teacher-professional knowledge and skill, the pentagon model, and topic-specific PCK.

2.5.2.1 Teacher Professional Knowledge and Skill

Gess-Newsome (2015) refined and presented her model of PCK at this summit, seen in Figure 2.1. This model, titled *teacher professional knowledge & skill* (TPK&S), places PCK within a teacher's professional knowledge.

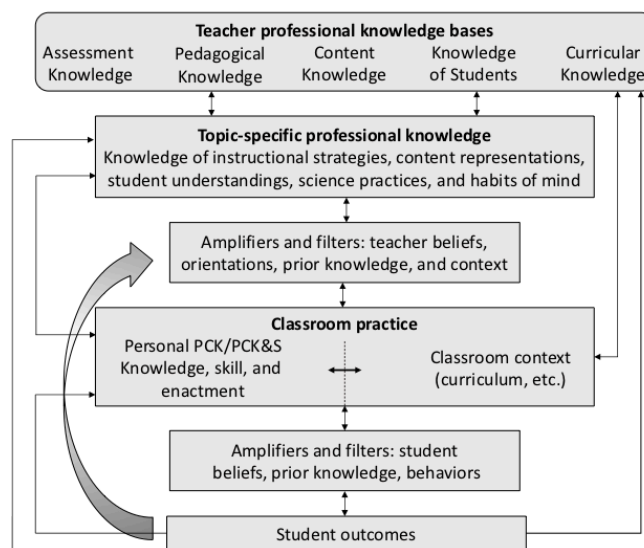


Figure 2.1 Teacher Professional Knowledge and Skill; model of PCK conceptualized by Gess-Newsome (2015).

Within this model, PCK defines the “knowledge base used in planning for and the delivery of topic-specific instruction in a very specific classroom context, *and* as a skill when involved in the act of teaching” (Gess-Newsome, 2015, p. 30). The latter definition is an important distinction of this model; not only does it function to assess what a teacher knows, but also what they are able to do. Both classroom practice and student outcomes are taken into account when assessing a teacher’s TPK&S. Furthermore, content for teaching occurs at a topic level rather than subject level (i.e. *intramolecular forces* rather than *chemistry*).

2.5.2.2 Pentagon Model of PCK

The pentagon model shown in Figure 2.2, was conceptualized following a thorough literature review of constructs of PCK (Park & Chen, 2012; Park & Oliver, 2008b, 2008a). This model was heavily influenced by the work of Tamir (1988), Grossman (1990), and Magnusson et al. (1999).

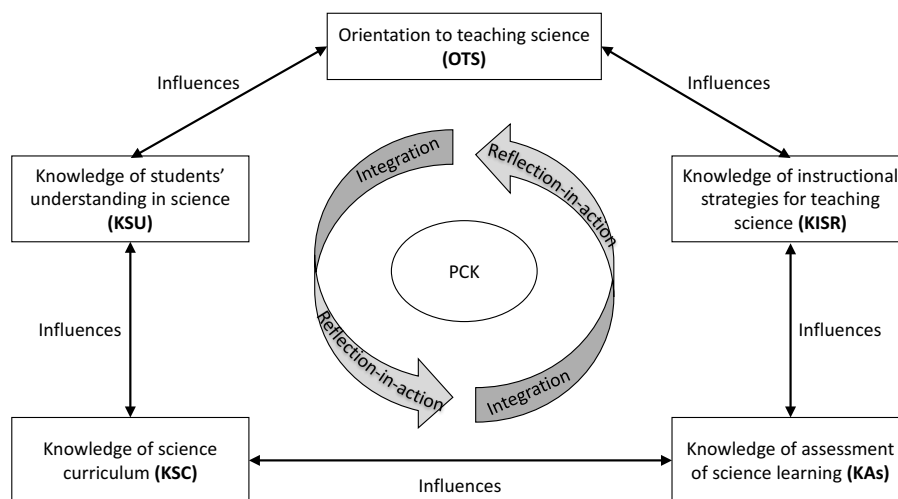


Figure 2.2 Modified pentagon model of PCK (Park & Chen 2012; Park & Oliver, 2008b).

The pentagon model (Park & Oliver, 2008a) is comprised of five parts: *orientation of teaching science* (OTS), *knowledge of instructional strategies for teaching science* (KISR), *knowledge of assessment of science learning* (KAs), *knowledge of science curriculum* (KSC), and

knowledge of students' understanding and the purposes of learning science, as well as teaching decisions made by the instructor (KSU). KISR refers to the topic- or subject-specific pedagogical strategies implemented in the classroom. This component could include representations or activities. Various approaches used for assessment in science learning is covered in the KAs. KSC is the adjustment of curriculum materials to teaching for understanding. Finally, KSU includes the instructors' knowledge of student misconceptions, learning difficulties, and motivation. These five parts are constantly being revised by instructors to develop their PCK as they reflect on different strategies they have implemented.

2.5.2.3 Topic-Specific PCK

Mavhunga and Rollnick (2011) conceptualized a model of PCK that specifically considers the transformation of knowledge dependent on the subject matter, referred to as topic-specific PCK, Figure 2.3. In other words, the TS- PCK of an individual for EAS reactions will be different than for NMR analysis.

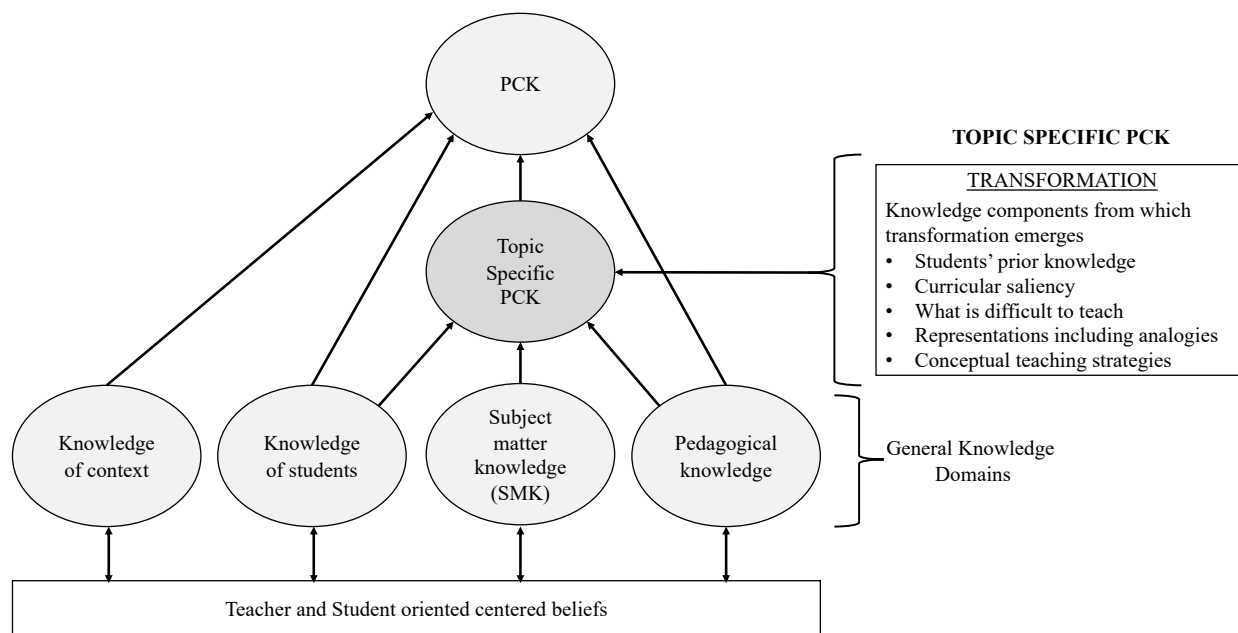


Figure 2.3 Topic-specific PCK conceptualized by Mavhunga and Rollnick (2011).

The TS-PCK model includes five components that are dependent on specific content. The five components encompassed in this model are: (1) the students' prior knowledge, (2) curricular saliency, (3) what makes a topic difficult or easy, (4) the representations, including analogies, and (5) the conceptual teaching strategies (Mavhunga & Rollnick, 2013). The consideration of the five components transforms an instructors' specific subject matter knowledge (SMK) into transformed specific subject matter knowledge (SMK'). TS-PCK is grounded on the idea that "comprehended ideas must be transformed in some manner if they are to be taught," (Shulman, 1987, p. 16).

2.6 PCK in Chemistry

Current research on PCK in the chemistry literature falls into two main categories: those that describe PCK in expert or experienced teachers (Davidowitz & Potgieter, 2016; Drechsler & van Driel, 2008; Kilinc & Aydin, 2013; Padilla & Garritz, 2015; Padilla & van Driel, 2011; Park & Oliver, 2008b), and those that examine developing PCK in pre-service and novice teachers (Adadan & Oner, 2014; De Jong, van Driel, & Verloop, 2005; Geddis et al., 1993; Gee, Boberg, & Gabel, 1996; Mavhunga & Rollnick, 2011; van Driel, De Jong, & Verloop, 2002; van Driel, Verloop, & de Vos, 1998), including graduate teaching assistants (Barlow, Gardner, Boyd, Caukin, & Rutledge, 2015; Bond-Robinson, 2005; Maries & Singh, 2013; Seung, 2013). This review will focus on PCK studies specific to experienced instructors teaching chemistry since one of the goals of this study is to describe the PCK in organic chemistry instructors.

2.6.1 PCK in Experienced Chemistry Teachers

PCK is a necessity for effective science teaching at all grade levels. In a study that examined high school teachers' PCK for the concepts of heat transfer, energy and temperature, three components of PCK were investigated: (1) alternative frameworks, (2) student understanding,

and (3) pedagogical strategies (Magnusson, Borko, Krajcik, & Layman, 1992). Results showed that the students of teachers who had alternative conceptions displayed little improvement, or a decrease in content knowledge, over the unit (Magnusson et al., 1992). Alternatively, students that displayed the most improvement over the unit had teachers with substantial PCK (Magnusson et al., 1992).

Drechsler and van Driel (2008) used PCK to categorize nine high school teachers that were enrolled in a teacher training course specific to acid-base models. The teachers were categorized into two groups based on their approaches to teaching acids and bases, summarized in Table 2.2.

Table 2.2 Results of how teachers approach their lessons about acid/base chemistry concepts

Category	
Student- and Model-Oriented	Teacher- and Micro/Macro-level Oriented
Reflect on students' difficulties when planning lessons	Focused on how stimulating a lesson would be for themselves when planning lessons
Refined explanations to make them clearer to the students	Media and news influenced lessons
Concentrated teaching to the concept of acid/base models	Identified simpler demonstrations and calculations
Students' preconceptions caused mistakes	Taught acids and bases through macroscopic or microscopic levels

Although teachers believed the course was informative about the models of acids and bases, some thought it would have been more helpful to include ways that these teachers could apply what they had learned directly to their classroom. This suggests that more than one teacher training course should be provided to allow teachers to become comfortable with the material and ways to apply their knowledge to new lesson plans (Drechsler & van Driel, 2008).

Further studies investigate the relationship between the PCK components and their influence on each other. Park and Oliver (2008) completed a case study of three experienced high

school teachers. To fully assess teachers' PCK and the relationship between the components of PCK using the pentagon model described earlier, the authors collected multiple sources of data including classroom observations, semi-structured interviews and teachers' written reflections (Park & Oliver, 2008b). Findings indicate that the five components of the pentagon model influence each other and are constantly being molded through the teachers' acquisition of knowledge and reflecting on their teaching (Park & Oliver, 2008). Additionally, the teachers that had a better understanding of their students' alternative conceptions were more advanced in their lesson planning, classroom instruction, and assessment (Park & Oliver, 2008).

Davidowitz and Potgieter (2016) investigated the relationship between a teachers' content knowledge of organic chemistry and their TS-PCK. Grade 12 teachers completed two exams that the researchers had developed to test their content knowledge and PCK. Although there was a strong correlation between one's content knowledge and TS-PCK, some outliers were seen with teachers having high content knowledge with low TS-PCK (Davidowitz & Potgieter, 2016). This was attributed to the teachers having limited teaching experience and professional development.

There are limited studies where researchers have investigated the PCK of college chemistry professors. Two studies have investigated the PCK of quantum chemistry professors and how the beliefs of university professors influence their practice (Padilla & Garritz, 2015; Padilla & van Driel, 2011). Magnusson's (1999) PCK model was used for the study of quantum chemistry professors, specifically the components of orientations towards teaching science: process (introducing students to how scientists think), academic rigor (challenging students with difficult problems and activities), didactics (presenting information through lectures, discussions and directed questions), conceptual change (pressing students for their views about the world and considering alternate conceptions), and activity-driven (hands-on activities). While the PCK of

each teacher varied, it was apparent that the teachers agreed on their views of what was and was not important for teaching quantum chemistry. They had similar orientations towards teaching, highlighting didactics and academic rigor as important for success in the course (Padilla & van Driel, 2011).

Padilla and Garritz (2015) examined the effects of teacher beliefs with their practice. They interviewed ten professors in various STEM fields including chemistry and chemical engineering. Findings indicated that the professors' beliefs greatly impacted their teaching and that they were more inclined to meet their perceived University's need of covering content rather than facilitating student understanding (Padilla & Garritz, 2015). Most professors felt that their success as a teacher stemmed from being a content expert rather than having pedagogical knowledge (Padilla & Garritz, 2015). Furthermore, all but one participant saw their teaching as an important part of their university role in addition to their research commitments, and therefore put in the effort to create a good learning environment for their students (Padilla and Garritz, 2015).

2.7 Summary and Conclusions

The literature shows that many students entering a sophomore-level organic chemistry course have not mastered the fundamental topics that were covered in general chemistry. This can cause them to struggle with new concepts taught in organic chemistry. Topics described above include student difficulties with Lewis structures, acid/base concepts, functional groups, and hydrogen bonding. Students struggling with these concepts may have developed alternative conceptions that make the learning of new material more challenging.

An overview of the models of PCK and its importance in teaching were described. While little research has focused on the PCK of college chemistry professors, studies of K-12 chemistry

teachers have shown that PCK is continuously developed through reflection on their teaching practices and considering the knowledge that students bring to their classroom.

This study aims to describe student understanding of EAS reaction synthesis problems by identifying (1) how students reason through synthesis problems using EAS and (2) the apparent gaps in understanding from their synthesis. This study will also describe how organic chemistry instructors perceive their students' understanding of EAS synthesis problems and evaluate their TS-PCK. This study addresses the gap in the literature by comparing instructors' perceptions of student understanding of EAS synthesis problems to the reasoning students are using when solving these types of problems. Additionally, this study will add to the TS-PCK literature by evaluating the TS-PCK of organic chemistry instructors on the topic of EAS.

CHAPTER 3. METHODOLOGY

3.1 Research Design

This research study had three goals: 1) to describe how organic chemistry students reason through EAS reaction synthesis problems, 2) to describe how organic chemistry instructors perceive their students' reasoning while solving these EAS synthesis problems, and 3) to explore the relationship between the three general knowledge domains an organic chemistry instructor draws upon to inform their TS-PCK: knowledge of students, subject matter knowledge, and pedagogical knowledge. A qualitative research approach was chosen because the research questions aim to answer "hows" and "whys" (Patton, 2015), rather than "how many". Qualitative methods have also been used by previous researchers to study organic chemistry students' understanding of alkyl halide reactions (Cruz-Ramirez de Arellano, 2013), their understanding of the arrow-pushing formalism (Bhattacharyya & Bodner, 2005; Bodé & Flynn, 2016; Ferguson, 2003; Grove et al., 2012), teachers' existing PCK with novel subject matter (Wischow, 2010), and faculty approaches to teaching undergraduate physical chemistry courses (Mack, 2015). The purpose of this study is to build a detailed picture of student reasoning while solving EAS problems, and the perceptions that organic chemistry instructors have of their students' reasoning about EAS synthesis problems.

3.2 Theoretical Frameworks

The following section will describe PCK and phenomenography; the two theoretical frameworks used to inform this study with the investigation of students' understanding of EAS reaction synthesis problems; instructors' perceptions of their students' understanding, and the

relationship of the three general knowledge domains an instructor draws upon to inform their TS-PCK with respect to EAS synthesis problems.

3.2.1 Pedagogical Content Knowledge

PCK was one of the theoretical frameworks that guided this study. As described in Section 2.5, PCK is the composition of useful forms of representations of the concepts, useful analogies, examples and diagrams, and knowing what makes learning certain concepts easy or difficult (Maries & Singh, 2013; Shulman, 1986). Several models of PCK were described in Sections 2.5.1 and 2.5.2.

I began this study using the modified pentagon model (Park & Chen, 2012; Park & Oliver, 2008) discussed in Section 2.5.2.2, comprised of the five components of PCK: orientation to teaching science, knowledge of instructional strategies for teaching science, knowledge of assessment of science learning, knowledge of science curriculum, and knowledge of students' understanding in science. This model was developed to highlight the interactions between the parts of PCK based on the foundational work by Tamir (1988), Grossman (1990), and Magnusson et al. (1999). This PCK framework represents a model that suggests that merely knowing science content is not sufficient for effectively teaching science; rather the transformation of science content knowledge into effective teaching requires teachers to also possess knowledge about the learners, curriculum, instructional strategies, and assessment (Seung et al., 2012).

After my initial data analysis, I found that the TS-PCK model (Mavhunga & Rollnick, 2013) was a better framework for processing the data due to the specificity of exploring student understanding of EAS reaction synthesis problems and the connection between the emergent codes. The TS-PCK model, discussed in Section 2.5.2.3 and depicted in Figure 2.3, was chosen to complement and inform the analysis for this study.

This model includes five components that are dependent on specific content. In other words, the TS-PCK of an individual for EAS reactions will be different than for NMR analysis. The five components encompassed in this model are: (1) the students' prior knowledge, (2) curricular saliency, (3) what makes a topic difficult or easy, (4) the representations, including analogies, and (5) the conceptual teaching strategies (Mavhunga & Rollnick, 2013). The consideration of the five components transforms an instructors' specific subject matter knowledge (SMK) into transformed specific subject matter knowledge (SMK'). TS-PCK is grounded on the idea that "comprehended ideas must be transformed in some manner if they are to be taught," (Shulman, 1987, p. 16). Additionally, teachers rely on three general knowledge domains to inform their TS-PCK: knowledge of students, subject matter knowledge, and pedagogical knowledge (Rollnick, Bennett, Rhemtula, Dharsey, & Ndlovu, 2008). In this study, an instructor's PCK is evaluated with topic of EAS, making TS-PCK an appropriate theoretical framework.

3.2.2 Phenomenography

Phenomenographic studies allow researchers to "orient [themselves] towards people's ideas or experiences of the world," (Marton, 1981) in relation to answering questions about learning. Experiences with a phenomenon will be unique between individuals, therefore a single experience cannot constitute a phenomenon (Orgill, 2007). Rather, it is the collection of these experiences that comprise a phenomenon (Marton, 1981). Different individuals can have varying perceptions of how they feel they experienced a phenomenon. Phenomenographers gain a better understanding of a phenomenon by studying the similarities and differences between the perceptions of the individuals. These concepts of phenomenography have directed the methodological decisions of this study.

Students in organic chemistry experience problem solving often throughout the course. This can occur in lectures, on homework, and on assessments. One's perception of an experience is influenced by the person, the environment, and their own interpretations (Orgill, 2007). These factors lead students to have different experiences with the same phenomenon. In this study, problem-solving with EAS reactions is the phenomenon.

This study also explores organic chemistry instructors' experiences in teaching the unit of EAS in a sophomore-level organic chemistry class and the interactions these instructors have with their students. Instructors can construct varying knowledge and beliefs about teaching organic chemistry that are influenced by their background and current experiences. This study sought to collect these experiences and examine the commonalities and differences amongst them to construct an understanding of how organic chemistry instructors approach their teaching of EAS reactions in organic chemistry.

3.3 Methodological Framework

One of the goals of this study is to describe how organic chemistry students reason through EAS synthesis problems. This goal stems from trying to answer a descriptive research question. A descriptive research question is one that aims at identifying all the ways in which a phenomenon can appear (Elliott & Timulak, 2005). Therefore, qualitative research methods are most appropriate and include the analysis of document artifacts and semi-structured interviews. For this study, a semi-structured interview was used to gain insight into what problem-solving methods organic chemistry students were using to solve EAS reaction problems. Following the interviews, the work that students generated during the interview was analyzed alongside the transcripts to assist in developing a more complete understanding of how students were reasoning through these problems.

Interviews can also be used as a qualitative method to study TS-PCK. To study the variability in organic chemistry instructors' TS-PCK, I set out to interview a diverse group of organic chemistry instructors from a range of institution types (community-college through research-intensive universities) with varying levels of teaching experience and background. The goals of the interviews were to allow me to gain insight into instructors' views on instructional decisions made in the classroom and how they were interpreting their students developing an understanding of a topic. Instructors also generated reaction schemes that were analyzed alongside the interview transcripts that contributed to making a more complete representation of how these instructors interpreted their students' understanding of EAS reaction problems.

3.4 Participants and Setting

Two populations were investigated in this study:

- 1) undergraduate students enrolled in organic chemistry, and
- 2) organic chemistry instructors.

The student population consisted of undergraduate students enrolled in the Organic Chemistry II course for chemistry majors at Purdue University during the Spring 2017 and Spring 2018 semesters. All students had the same instructor teaching the course. A purposeful homogeneous sampling approach was used. The goal of homogeneous sampling (Patton, 2015) is to thoroughly describe a particular subgroup. In the Spring 2017 course, six participants were recruited through personal visitations to the lecture, with permission from the instructor. In Spring 2018, five participants were recruited using the same techniques. All participants were compensated with a \$20 gift certificate. All participants were in their second year of study. Participants were interviewed within one month following the completion of the EAS unit in the

Spring 2017 and Spring 2018 semesters. This study was IRB approved January 2017 (Appendix A).

The second population consisted of college organic chemistry instructors from a range of institutions in the United States. A convenience sampling approach was taken (Patton, 2015). An email was distributed through the CER listserv (Chemical Education Xchange, 2016) asking for organic chemistry instructor volunteers to contact the researcher if interested. An online questionnaire (Appendix B) was adapted from Duis (2011) and sent to 25 instructors through Purdue Qualtrics. The purpose of the questionnaire was to screen for instructors that taught EAS to the extent of covering mono-substitution, di-substitution, activation/deactivation, and directing effects of substituents. The questions adapted from Duis (2011) included demographic/background information and perspectives of student learning in organic chemistry. This study was IRB approved in April 2016 (Appendix C).

EAS is generally taught in the second semester, and questions in the interview protocol would require them to solve tri-substituted benzenes. If participants met these criteria, they were asked if they would be willing to participate in a one-on-one interview with the researcher. Eight of the twenty-five instructors participated in an interview, and their demographics can be seen in Table 3.1.

Student's grades or class ranking were not used as a pre-requisite for participation. Additionally, differences in ethnicities or gender for students and instructors were not used. To protect their identity, all participants were given pseudonyms. In this dissertation, all participants were given male or gender-neutral pseudonyms and male pronouns were used when referencing a participant. This is not indicative of the gender of the participant.

Table 3.1 Demographic data of instructor participants.

Participants (pseudonym)	Institution Type ^a	Working Title ^b	Years Teaching Experience ^c	Class Size ^d
Dr. Berkowitz	Highest Research Activity	Senior Lecturer	10+	300
Dr. Gacy	Highest Research Activity	Chemistry Laboratory Coordinator	2-5	40
Dr. Gaskins	Higher Research Activity	Associate Professor	10+	120
Dr. Raider	Higher Research Activity	Lecturer	2-5	15
Dr. Manson	Master's Colleges and Universities	Assistant Professor	0-2	20
Dr. Kemper	Baccalaureate Colleges	Associate Professor	5-10	10
Dr. Bundy	Baccalaureate Colleges	Assistant Professor	2-5	20
Mr. Ramirez	Associate's College	Chemistry Faculty	5-10	20

^aBased on the Carnegie Classification of Institutions of Higher Education (<http://carnegieclassifications.iu.edu>)

^bBased on titles listed on department websites at time of data collection

^cBased on information declared through the online questionnaire

^dBased on information declared during the interview

3.5 Data Collection

Data collected from the participants included interviews, video and audio recordings, transcripts, digitalized copies of work produced during the interviews, field notes, and memos. This section describes how each of the data sources were collected and the methodological decisions used in this study.

3.5.1 Pilot Study

The first phase of data collection involved conducting a pilot study with three graduate students affiliated with the division of organic chemistry and one organic chemistry instructor. The focus of the pilot study was to gauge the appropriateness of the interview protocol, as well as make sure that undergraduate participants would be familiar with the reactants necessary to solve the EAS synthesis questions. This was assessed by having the graduate students and instructor participate in individual interviews mimicking how the students and would be participating in the study. Participants completed all of their problem solving using a *LiveScribe* pen and dot-patterned paper to simultaneously record what the participant was writing and saying. This technology has been shown to be useful when exploring student understanding of a topic that is dependent on drawing diagrams or other representations (Linenberger & Bretz, 2012). Four warm-up questions were added to the beginning of the protocol to allow the participants to get comfortable with the interviewer. Furthermore, the last question of Duffy's protocol (synthesis of 1,3,5-tribromobenzene) was eliminated as it was identified as being too difficult by the instructor and graduate students. Additionally, it was discovered that if a participant used the *LiveScribe* pen as a pointer when explaining items written on the page, the system had no way to signal what was being referenced. A *GoPro* video camera was set up above the *LiveScribe* notebook to capture any references the participant may have made during the interview.

3.5.2 Student Interviews

To begin, each participant was given a brief overview of the project and signed a waiver of consent (Appendix D). Participants solved problems using a *LiveScribe* pen and dot-patterned paper as done in the pilot study. A *GoPro* video camera was oriented above the dot-patterned notebook to capture any references the participant may have made during the interview. Participants were instructed on how to use the *LiveScribe* pen, and the purpose for the GoPro camera was described. Participants were also asked to express their thoughts as verbally as possible during the interview.

The interview protocol was adapted from Duffy (2006), a dissertation project that investigated student understanding of aromaticity and electrophilic aromatic substitution reaction problems. The length of the interviews lasted between 30-60 minutes. The interviews were transcribed by the researcher immediately after the interview at an average rate of eight minutes of transcription per minute of interview.

Based on the pilot study, four warm-up questions were added at the beginning of the protocol to allow the participants to get comfortable with the researcher. Questions 5-10 were designed to prime students to start thinking about the concepts necessary to solve EAS reaction problems. Questions 11-15 were the five EAS questions posed to the students. Any follow-up questions were at the discretion of the researcher and used to clarify responses for further elaboration of their train of thought. The student interview questions in the protocol follow:

Warm-up questions

1. Tell me about your experiences so far in organic chemistry.
2. What are your career aspirations after graduation?
3. What are your motivations for taking this class?

4. Tell me about your past experiences with chemistry. (High school chemistry, freshman-level courses)

EAS questions

5. Explain whether phenols, anilines, alkylbenzenes, phenyl ethers, and phenoxides are activating or deactivating.
6. Order the above substituents (in molecules in question 5) in order of increasing activating strength. Explain why you chose this order.
7. What are the directing effects of the above molecules? How do you know this?
8. Using phenol as an example, show me why the substituent is ortho and para directing.
9. Are all ortho and para directing substituents activators or deactivators? Explain why you think this.
10. Are meta directing substituents activating or deactivating? Why?
11. How would you synthesize *p*-chloroaniline? (provide structure if necessary.)

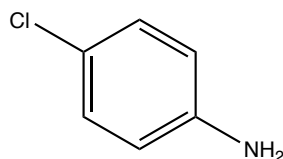


Figure 3.1 Molecular structure of *p*-chloroaniline provided to students if necessary.

12. How would you synthesize *m*-nitrotoluene? (provide structure if necessary.)

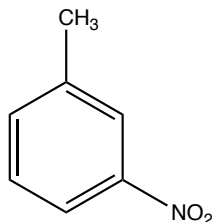


Figure 3.2 Molecular structure of *m*-nitrotoluene provided to students if necessary.

13. How would you synthesize *m*-hexylbenzenesulfonic acid? (provide structure if necessary.)

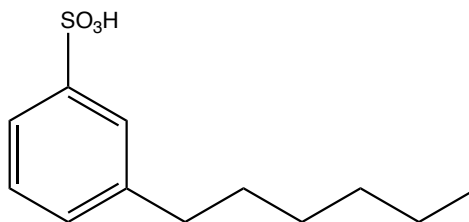


Figure 3.3 Molecular structure of *m*-hexylbenzenesulfonic acid provided to students if necessary.

14. How would you synthesize 1,2-dichloro-4-nitrobenzene? (provide structure if necessary.)

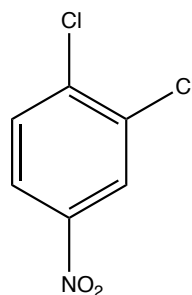


Figure 3.4 Molecular structure of 1,2-dichloro-4-nitrobenzene provided to students if necessary.

15. How would you synthesize 4-chloro-2-nitroaniline? (provide structure if necessary.)

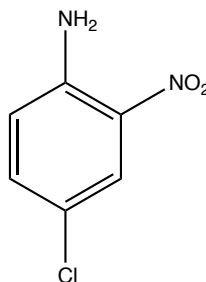


Figure 3.5 Molecular structure of 4-chloro-2-nitroaniline provided to students if necessary.

Questions 11-13 refer to di-substituted benzenes that would be familiar to the students and probe understanding of the substituent effects and reagents needed to synthesize the desired products. For the synthesis of *p*-chloroaniline, students would need to remember that the amino substituent is synthesized through the reduction of nitrobenzene. Additionally, they would need to compare the deactivation of a chloro group to the activating amino group since both groups are ortho and para directing. For the synthesis of *m*-nitrotoluene, students would need to consider the

limitation of Friedel-Crafts reactions not reacting with nitrobenzene, and would need to get the substituents meta to each other. For the synthesis of *m*-hexylbenzenesulfonic acid, students would need to consider the carbocation rearrangement that would occur with the addition of the hexyl chain with Friedel-Crafts alkylation. Friedel-Crafts acylation conditions should be used, and students would need to compare the levels of deactivation between a sulfonic acid group and a ketone since both groups will be meta directing. Questions 14 and 15 would be novel to the students, adding the more complex task of synthesizing tri-substituted benzenes and further deliberations of the substituent effects. However, all of the reagents used in previous answers would be applicable for use in solving these questions. For the synthesis of 1,2-dichloro-4-nitrobenzene, students had to consider the fact that all of the substituents are deactivating. Additionally, several products could be formed with the addition of two chloro groups since chloro groups are ortho and para directing. For the synthesis of 4-chloro-2-nitroaniline, students would need to consider the reduction of one nitro group and evaluate the appropriate step in the synthesis to do so. Additionally, two of the substituents, nitro and chloro groups, are deactivating and two of the substituents, chloro and amino groups, are ortho and para directing.

3.5.3 Instructor Interviews

All interviews with instructors were conducted and recorded using Skype or Google Hangouts. Prior to the interview, participants were sent the waiver of consent (Appendix E), in which they signed and returned to the researcher before the interview. To begin the interview, each participant was given a brief overview of the project and verbal consent to continue the interview.

The order of questions shown below was followed in all interviews in accordance with a semi-structured interview protocol, but follow-up questions depended on their questionnaire responses or clarifications to responses made during the interview. The length of the interviews

ranged from 30-75 minutes. The interviews were transcribed by the researcher immediately concluding the interview at an average rate of eight minutes of transcription per minute of interview.

Seven warm-up questions were asked at the beginning of the protocol to establish a comfortable relationship between the researcher and the participant. Additionally, this initial exchange allowed the participant to settle into the interview and allow the researcher to gain insights into their teaching practices and obtain information about their institution and organic chemistry course. The purpose of the priming questions (questions 8-10) was to lead the participants to the topic of EAS and gain insight into how they were instructing their students on the main concepts associated with EAS. The EAS problems (questions 11-15) were the same synthesis questions that were posed to the student participants. Instructors were directed to solve these problems as an expert. Following those responses, instructors were asked to solve the problems from the viewpoint of their students, considering where students would struggle and what steps of the synthesis would be challenging for their students and specify concepts that would impede their students at successfully solving these problems. Since the interviews with instructors occurred through a teleconferencing application, instructors were asked to solve the problems using pen and paper at their desk. When participants described their syntheses, they held up their work to the camera. Following the interviews, instructors scanned any work that was generated during the interview, and the scans were emailed to the researcher. The questions posed in the interview protocol are listed below

Instructor-Interview Protocol:

Warm-up questions

1. Tell me a little bit about yourself.

2. Have you had experience teaching other college chemistry courses, besides organic chemistry?
3. Do you use an online homework system?
4. Are there teaching assistants to help with the course? (If yes, ask what their responsibilities are.)
5. How big would you say the course is during the Spring semester for the second-semester organic course?
6. Describe a typical lecture in your class.
7. Tell me about the layout of your exams. (scantron/free response ratio, length of time, etc.)
8. What is the process for grading exams?

Priming questions

9. Here is the structure of aspirin. What information do you think students glean from this structure? For example, would they recognize electrophilic/ nucleophilic centers, mention the electron distribution in the molecule, or its molecular shape)

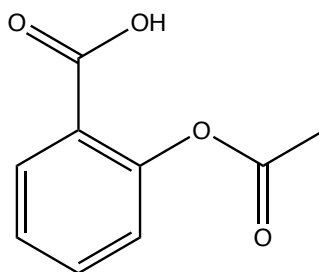


Figure 3.6 Structure of aspirin provided to instructors during the interview.

10. Explain how you perceive your students' thinking about substituents that are activating/deactivating. How do you teach concepts related to activation/deactivation?

11. How do you perceive your students keeping track of which substituents direct incoming substituents to specific positions on the ring? Is this reflective of how you teach the concepts?

EAS questions

12. How would you synthesize *p*-chloroaniline? How would your students be approaching this problem? What difficulties do you expect your students to encounter with this problem? (Probe for evidence to support their claim.)
13. How would you synthesize *m*-nitrotoluene? How would your students be approaching this problem? What difficulties do you expect your students to encounter with this problem? (Probe for evidence to support their claim.)
14. How would you synthesize *m*-hexylbenzenesulfonic acid? How would your students be approaching this problem? What difficulties do you expect your students to encounter with this problem? (Probe for evidence to support their claim.)
15. How would you synthesize 1,2-dichloro-4-nitrobenzene? How would your students be approaching this problem? What difficulties do you expect your students to encounter with this problem? (Probe for evidence to support their claim.)
16. How would you synthesize 4-chloro-2-nitroaniline? How would your students be approaching this problem? What difficulties do you expect your students to encounter with this problem? (Probe for evidence to support their claim.)

3.5.4 Field Notes and Memos

Field notes were taken throughout the interview to capture observable aspects of human behavior (Patton, 2015). Field notes were taken in the moment, and anything the researcher deemed worth noting was recorded (Mulhall, 2003; Patton, 2015). This included quotes from

participants, the observer's feelings and reflections of the experience, and insights and interpretations to what the researcher was observing (Patton, 2015). Participants' behaviors while they were solving the interview questions were recorded by the researcher, as well as statements the participants might have said that the researcher wanted to follow-up on during the interview.

Immediately following the interview, the researcher wrote a memo reflecting on the experience. Memoing is an effective tool in qualitative research that includes writing commentary and reflects on some portion of the data for deeper analysis (Birks, Chapman, & Francis, 2008; Denzin & Lincoln, 2011). In qualitative research, the perspective of the researcher has a significant influence on the context of the study (Birks et al., 2008; Patton, 2015). Included in the memos for this study were notes about any ideas that had emerged from the participant, how the researcher was feeling, and how that may have affected the interview process, as well as a holistic reflection on the interview.

3.6 Data Analysis

All the interviews were transcribed by the researcher. Screenshots of *LiveScribe* images were inserted into the transcripts of student participants at the appropriate timeframes. Additionally, digital images of work generated by instructor participants were inserted into the appropriate timeframes of those transcripts. Completed transcripts were imported into NVivo 12 software for data management and analysis. With NVivo 12, the researcher can code portions of each transcript and organize the codes into categories and themes. The software also calculates inter-rater agreement by comparing transcripts coded by two individuals.

The transcripts and memos were printed and the researcher met with a member of the research group to collaboratively code a portion of the transcripts using *in vivo* coding. *In vivo* coding prioritizes the participants' voice in the data analysis (Saldaña, 2016). This preliminary

review of the data allowed the collaborators to mark the transcripts with words or phrases that could be used later in the data analysis for analytical consideration (Saldaña, 2016). After discussion between the collaborators, a consensus was reached on views of the emergent codes, definitions of the codes, as well as their interpretation. Following agreement, the researcher independently coded the remainder of the transcripts. Additionally, a thematic analysis was conducted using the ACS Examinations Institute's Anchoring Concepts Content Map (ACCM) for general and organic chemistry (Fereday & Muir-Cochrane, 2006; Holme, Luxford, & Murphy, 2015; Raker et al., 2013). A descriptive case study approach was used for the analysis of three instructor interview transcripts to describe how each of the three general knowledge domains related to an instructors' TS-PCK (Baxter & Jack, 2008; Yin, 2003). Multiple data sources were used to enhance data credibility (Baxter & Jack, 2008; Patton, 2015), including interview transcripts, responses to the online questionnaire (Appendix A), syntheses generated by the instructors, observations made by the interviewer, and video recordings of the interviews.

After the researcher had completed coding at least one instructor and one student transcript, two graduate students independently coded these transcripts using the codes and definitions developed by the researcher and collaborators. The initial codes and definitions were modified or combined for clarity until an acceptable agreement (above 80%) was reached. After two rounds, the agreement was 71%. After discussion with the collaborators and an expert in organic chemistry, the code for *misappropriated knowledge* was removed from the calculation. This decision was determined by the necessary organic chemistry knowledge needed to appropriately use this code that the two graduate students did not possess. After removal of this code, the agreement was above 80%. To get a more accurate inter-rater agreement of *misappropriated knowledge*, two other graduate students with a background in organic chemistry each individually coded two transcripts.

Inter-rater agreement of *misappropriated knowledge* was above 80% and no further analysis was done for inter-rater agreement.

3.7 Trustworthiness

The four criteria for trustworthiness: credibility, confirmability, transferability, and dependability (Lincoln & Guba, 1985) were considered in the research design and data analysis. Credibility was addressed by the adoption of appropriate research methods for composing the research questions, collecting data from instructors from a variety of institution types and years' experience, and use of reflective commentary and memos. Transferability refers to how generalizable the results are (Shenton, 2004), and was addressed with an in-depth literature search to gain background insights. Confirmability refers to the researcher's ability to conduct the study in an objective manner (Shenton, 2004). Interview protocols were based on those in the peer-reviewed literature, with triangulation of data from interview transcripts, memos, and student-generated work, or digitalized scans of instructors' work. Dependability was achieved through a meticulous description of the research methods of the study for repeatability of the study findings.

3.8 Limitations

This study describes how eleven organic chemistry students understand and reason through EAS synthesis problems. These students were enrolled in the same organic chemistry II course with the same instructor. Greater generalizability of the findings would be achieved by studying students in organic chemistry courses taught by a sample of the instructors who participated in this study. Multiple sources of data were used in this study; however, the data was collected in a limited time frame by one individual.

Instructor interviews were conducted online using Skype or Google Hangouts. Technical difficulties did occur during some of the interviews with brief interruptions, frozen or blurred images, and audio interruptions. One interview was recorded on Skype without sound, but audio of the interview was recorded by simultaneously projecting a phone call on speaker with an audio recorder. The researcher transcribed the interviews immediately following each interview in an attempt to capture the significant points made in context. Although only eight instructors participated in this study, their demographics show a diverse range of institution types and years' teaching experience.

Students may only have participated in the study to receive the modest compensation offered. Therefore, the compensation student participants received may have limited the study. It is possible that the data given by the participants were at a superficial level, without deeper thought, since they were not being graded on their responses to questions.

3.9 Role and Background of the Researcher

I had several responsibilities as the researcher facilitating this study. These responsibilities included organizing and conducting all the online and face-to-face interviews with the participants, setting up the recording equipment, conducting interviews protocols, transcribing, and coding the interviews, and analyzing the data. My background includes a Bachelor of Science degree in chemistry from the University of Northern Arizona. Following, I completed a Master of Science degree in organic chemistry at the University of Oregon and was subsequently employed as an analytical chemist at a biotech company.

As an undergraduate student, I was a laboratory teaching assistant for general and organic chemistry laboratories. For three years, I was the supplemental instructor for the organic chemistry

sequence. These responsibilities gave me my first insights into how students attempt to understand the concepts in organic chemistry and where students encounter difficulties within the course.

As an undergraduate and graduate student, I have taken six graduate-level courses in organic chemistry. Together with my industrial experience, I have a broad understanding of organic chemistry in both academic and industrial settings. I have also worked as a graduate teaching assistant for the lecture and laboratory of general chemistry courses, and have been a lecture coordinator for general chemistry. These experiences have given me insights into the difficulties that students have in these fundamental courses and motivated me to understand how they are applying their knowledge from these courses in organic chemistry.

The experiences with undergraduate general and organic chemistry curricula will have inevitably generated some bias in what I believe students understand coming out of general chemistry, and where that knowledge becomes applicable in organic chemistry. As a supplemental instructor, I constantly saw students who were interested solely in passing the exams, relying on memorization, and not motivated to learn the fundamentals. Observing numerous chemistry instructors in my academic career has exposed me to a variety of teaching practices. I made a conscious effort to remain neutral by basing all deductions on the data collected, and not express my own opinions in all interviews with students and instructors. Before each interview with student participants, I let them know that I was only interested in their thought process, and would not be looking for correctness in their responses, nor would I correct them during the interview. During interviews with instructors, I spoke with a friendly conversational style so they would feel comfortable describing their experiences honestly in teaching organic chemistry and solving EAS synthesis problems on the spot. Following each interview, I wrote a memo summarizing any field

notes that were taken during the interview, and reflections of the responses that student and instructor participants may have given.

CHAPTER 4. RESULTS AND DISCUSSION – STUDENT REASONING IN SOLVING EAS SYNTHESIS PROBLEMS

This chapter will describe how organic chemistry students reasoned through synthesis problems using EAS and the gaps in understanding that were apparent while they were solving these problems. The full list of codes and their definitions can be found in Appendix E.

4.1 Student Approaches to Solving Synthesis Problems Using EAS

This section will evaluate how organic chemistry students approached the synthesis problems using EAS. The major themes that emerged from the data analysis can be classified under the headings – substituent effects, the acknowledgment of multiple products, and memorization.

4.1.1 Substituent Effects

Substituent effects in aromatic compounds include the directing effects as well as whether the substituent activates or deactivates the benzene ring. While all participants used the directing effects of substituents when synthesizing the desired molecules, several participants also considered the activation/deactivation properties of the substituents. The example below shows Blake highlighting the activation/deactivation properties when synthesizing *p*-chloroaniline and 4-chloro-2-nitroaniline from benzene.

Well, 'cause chlorine, the chloro substituent would be, would not, would be more deactivating than amino. So if you put the chloro on first, you would have to have much more vigorous conditions to put the amine on. 'Cause the chloro would deactivate the ring. So best to put the ... Best to create aniline first and then chlorinate it.

Later, Blake discussed how he would synthesize 4-chloro-2-nitroaniline from benzene:

We somehow have to make one of the chlorines to be meta and chlorine while it is deactivating, it is ortho, para directing, so the only way would be to ... The only way to ensure that meta product would be added is to have the nitro step before, at

least one of the chlorination's. I'm not sure if it would work if you nitrated it at first. I think, 'cause NO_2 is such a strong meta director, that I don't know that you'd be able to create ... If you'd be able to attach any pair of substituents after you nitrate it. So, probably best to do one chlorination, then nitration, then the other chlorination.

Casey also used the activation/deactivation properties of substituents when he reasoned through the synthesis of 4-chloro-2-nitroaniline from benzene:

Since [chlorine] is more activating, yes, Cl is more activating, I believe. Okay, since this is 1, 2-, let's add one more to our found condition, which is NH_3 . I don't know how to make NH_3 into NH_2^+ , but let's assume we can, using that and heat, because heat always works. What I would do is, with a benzene... [nitration] happens last. Yes, so the addition of the NO_2 . So now which one? Okay, [amino substituent] is more activating because we did not discuss [chlorine] in the previous two pages because [chlorine] is supposed to be deactivating, but it's actually activating because of a special property that I don't know. What we do is we do the third condition first and form this substituent. Then, after that, we do the [chlorination] to form the para which is pretty intuitive since NH_2 is activating therefore ortho, para directing. Then when we add [nitration] condition here, NO_2 forms there because this one is more activating, so therefore the NO_2 would follow to the NH_2 's command even more than the Cl. Therefore it would form the ortho group here.

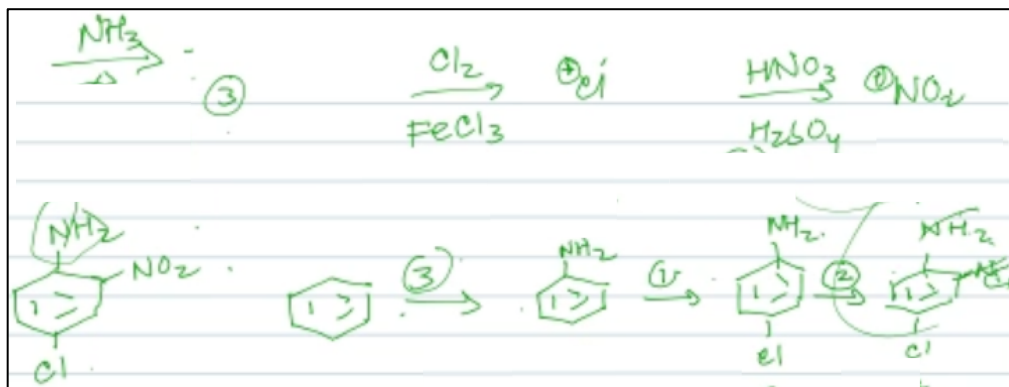


Figure 4.1 Work generated by Casey during the synthesis of 4-chloro-2-nitroaniline from benzene.

Although he incorrectly identified chlorine as a substituent that activates the ring, he relied on both substituent effects of each of the substituents to complete his synthesis. Additionally, he used his answers from previous problems to help him with the synthesis of 4-chloro-2-nitroaniline from benzene and recalled that chlorine's activation had not been discussed in any of the previous synthesis problems.

Substituent effects are identified as an anchoring concept in organic chemistry (Raker et al., 2013). Blake and Casey indicated that in order to solve EAS synthesis problems, considerations of both the directing effects of substituents as well as the activation/deactivation properties must be made. It is significant that Blake and Casey considered these effects even when synthesizing a tri-substituted benzene, and that the complexity of the molecule did not hinder their considerations of one of the substituent effects.

4.1.2 Acknowledging Multiple Products

Many students acknowledged the likelihood that more than one product could be formed in a given reaction during a synthesis. In other words, when adding another substituent onto a benzene that had an ortho and para directing substituent already present, students would state that both products would be formed. In addition to recognizing the formation of a mixture of products in a reaction, some students provided laboratory solutions to isolate the desired products. Peyton described ortho and para products forming, and in his mechanism, Figure 4.2, he has drawn both of the products. He highlighted the target molecule with the box.

Then, if you react the aniline with iron chloride and chlorine gas, then you'll get ortho and para products. It goes by the same electrophilic elimination mechanism. You can probably run a column to isolate this compound.

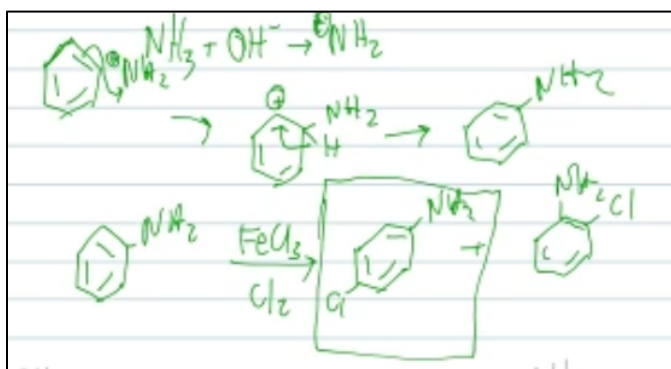


Figure 4.2 Work generated by Peyton for the synthesis of *p*-chloroaniline from benzene.

Peyton's explanation showed the formation of both the ortho and para products. Figure 4.2 showed the two products that would form and the para product is highlighted in the box. Peyton further suggested these products could be separated by using a column to isolate each compound., transferring skills that were taught in the laboratory for separating mixtures of compounds.

Mason also highlighted the formation of multiple products and stated that the nitro substituent could be added at multiple active sites of the benzene. Additionally, he suggested using a column system to purify and obtain the desired product.

Now we add the NO_2 . Whether or not we like it ... NO_2 can be placed everywhere in this case. There will be [1,2-dichloro-4-nitrobenzene] product. TLC, column, purify the one you want, which is [1,2-dichloro-4-nitrobenzene].

Kayden described the formation of multiple products in each step of the reaction scheme. In Figure 4.3, he indicated that multiple products would be formed in each step of the reaction. In addition, he verbally acknowledged that a mixture of products would be formed.

And then I don't think it really matters which one we add first, but if we add the nitro first, for instance ... we'll get two products. And then react those with the Cl_2 , FeCl_3 . And we'll get maybe a mixture of products. So if you add to the first one, it'll want to be meta to the nitro and either ortho, para to the amine. So that would put it here, where we want it, and also ... also here. And then the second one would give ... the nitro group would put meta, and I'll put that ortho so I get a third product.

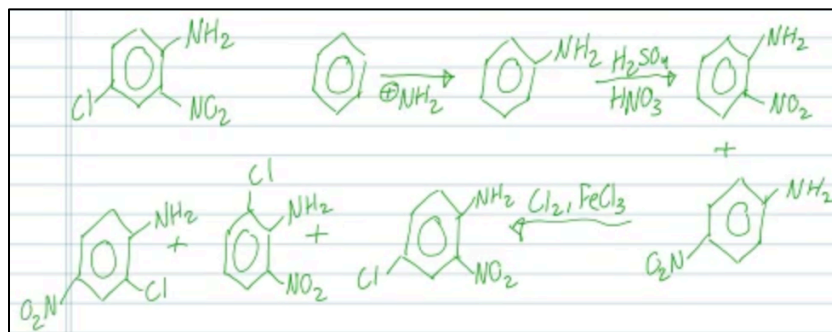


Figure 4.3 Work generated by Kayden for the synthesis of 4-chloro-2-nitroaniline from benzene.

4.1.3 Memorization

Several students stated that they had memorized the tables the instructor had provided in the lecture which listed the substituent effects. This notion was supported when students were able to correctly identify the directing effects of substituents but were unable to produce an answer when asked to show how the substituent directed the incoming electrophile to the designated position(s). Below, Jamison had correctly labeled the hydroxy group in phenol as an ortho and para director; however, he was unable to show why the hydroxy substituent directed the electrophile to those positions, Figure 4.4:

I kind of have a vague idea. Give me one second on that. I'm realizing I don't know as much about this as I thought I did. Yeah. Try that again. Oh, my god. I need to study this. I've got no clue.

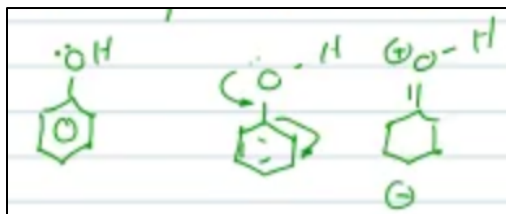


Figure 4.4 Work generated by Jamison when he attempted to show how the hydroxy substituent in phenol was an ortho and para director.

When asked to identify what the most difficult part about synthesizing substituted aromatics using EAS, Mason was quick to admit to difficulties in memorizing the concepts in the unit: “It was not that I forgot some of them. I had trouble memorizing the reagents and how substituents are substituted first before others.”

One task required participants to label the substituents in phenol, aniline, alkylbenzene, phenyl ether, and phenoxide as activating or deactivating. The five substituents are all activators, and once identified, participants were asked to rank them in terms of activating strength. Peyton correctly labeled four of the five substituents as activating (the substituent in phenoxide was

identified as deactivating). When asked to justify the order of activation strength they had chosen, Peyton began his reasoning on the basis of just memorization.

I think it's mostly from memorization, but I know the amine has a lone pair that can donate, and then the oxygen also has a lone pair, but it's more electronegative than the amine.

It is interesting that Peyton's first reasoning was from memorization of the order of activating strengths; however, he then considered the lone pairs on the substituents. Although oxygen is more electronegative than nitrogen, three of the five substituents had an oxygen atom present, yet the substituent in phenoxide was labeled as a deactivating substituent.

4.1.4 Discussion on Student Approaches to Solving EAS Synthesis Problems

There were several problem-solving strategies students implemented when solving synthesis problems using EAS. Directing effects and activating/deactivating properties are the two main concepts associated with EAS. Blake and Casey relied on both of these substituent effects in their syntheses using EAS. It is significant that they were using these concepts when solving for molecules that were di- and tri-substituted, indicating that the cognitive demand of more complex molecules did not deter them from considering the activation/deactivation properties of substituents.

Identifying the major product of an EAS reaction is not in the ACCM for organic chemistry; however, the ability to predict major products or yields of a reaction and their importance are (Raker et al., 2013). While participants did not identify which of the products would be the major product of the selected reactions, acknowledging that multiple products would be formed suggests that they were aware that they would not obtain a 100% yield of the desired product. Additionally, providing reaction schemes that result in multiple products and provided ways to isolate the desired product shows a transfer of knowledge from techniques used in the laboratory to lecture material.

As Pursell (2009) described students' tendencies to memorize information in callout boxes of textbooks, students in this study showed their attempts at memorizing the tables of substituent effects provided by the instructor. Cruz and Towns (2014), saw students incorrectly applying memorized rules in alkyl halide reactions, without a deeper understanding of *why* the rules exist. Jamison was able to label the hydroxy substituent as an ortho, para director, but was unable to provide any mechanistic reason as to *why* it had these directing effects. Mason and Peyton admitted their reasoning, or lack thereof, was affected by just relying on memorizing the concepts associated with EAS. Results in this study align with previous studies that students implement surface-level memorization of topics as a learning strategy (Anderson & Bodner, 2008; Pursell, 2009; Zurer, 2001).

4.2 Misappropriated Knowledge

Misappropriated knowledge is defined as a logical and false belief that a known piece of knowledge influences another piece of information. This includes alternative conceptions of chemistry topics, gaps in understanding of general chemistry topics, necessary concepts needed to successfully solve EAS synthesis problems, and a lack of reference to concepts specifically taught in the course.

4.2.1 Friedel-Crafts Reactions

Two of the synthesis problems contained alkyl substituents, a methyl- and 1-hexyl. Only four of the eleven students were able to remember the reactions and reagents required to add these substituents to an aromatic ring. The Friedel-Crafts alkylation and acylation reactions will not occur if the benzene ring is deactivated. Additionally, alkylation reactions are prone to carbocation rearrangements (McMurry, 2004). Participants did not consider either of these concepts when

synthesizing an alkylated benzene, as seen in the following quotes from Peyton and Mason, and Casey.

To get this hexyl group, I would need to do a Friedel-Crafts acylation followed by a Wolff-Kishner reduction, because if I did a Friedel-Crafts alkylation, the positive charge could rearrange part, move somewhere else to a carbocation rearrangement. Or no, that might not be necessary, because it's just a linear molecule. Yeah, I'm thinking there won't be any rearrangement, so I would just do an alkylation.

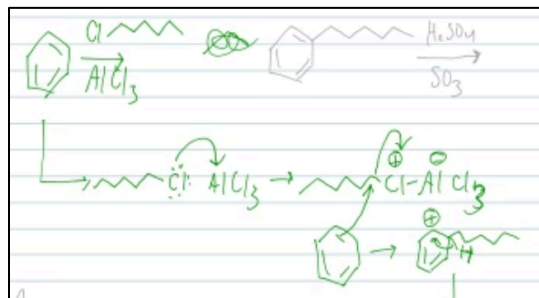


Figure 4.5 Work generated by Peyton during the synthesis of hexylbenzene from benzene.

It is interesting to note that Peyton was originally correct in his reasoning for why Friedel-Crafts acylation would be required to add the hexyl chain onto the benzene ring – Friedel-Crafts alkylation would lead to a carbocation rearrangement for the most stable carbocation. However, Peyton changed his response after incorrectly predicting that a carbocation rearrangement would not occur with a linear molecule. Furthermore, Peyton initially stated that a carbocation would form, but after examining his mechanism, Figure 4.5, he actually showed a substitution mechanism without forming a carbocation intermediate. Mason also used Friedel-Crafts alkylation when he synthesized *m*-hexylbenzenesulfonic acid from benzene without considering the carbocation rearrangement. Following his synthesis, the researcher asked why he had chosen alkylation instead of acylation, in which he replied:

Would it be a problem? That's the part that you produce an electrophile. That's what I remember to make an electrophile.

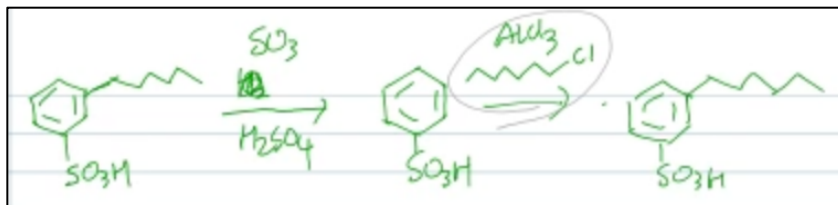


Figure 4.6 Work generated by Mason during the synthesis of *m*-hexylbenzenesulfonic acid from benzene.

Casey described his synthesis of *m*-nitrotoluene from benzene:

Then after that, now it's a harder way on making like a CH-, like a methyl carbocation because it is very hideously unstable. We can do that though by using CH_3Cl , I believe. This would form the, using the same steps as above, the meta-nitrotoluene.

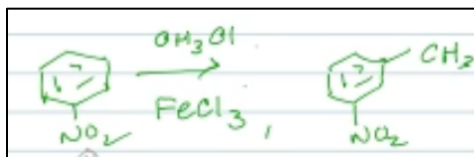


Figure 4.7 A reaction step in Casey's synthesis of *m*-nitrotoluene from nitrobenzene.

Casey was correct in stating that the methyl carbocation would be very unstable, but he did not consider that Friedel-Crafts reactions would not occur on a deactivated benzene. For the synthesis of *m*-hexylbenzenesulfonic acid from benzene, Casey and Jamison drew alternative representations of the hexyl substituent by drawing "C₆." Casey explained:

Ok, the hexyl is basically a methyl, so hexyl, C₆ over there. With the sulfonic acid, it's -OSO₃H. That is the sulfonic acid group, that is a meta director. What we do is we fume benzene, in this case, with that first, so H_2SO_4 , in heat. That's just easy in this case... Using the same thing that we use the C₆, the hexyl Cl, this hexyl, obviously Cl₃.

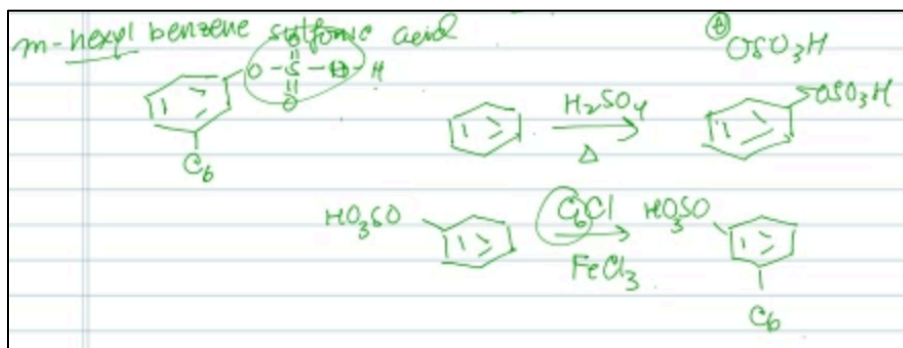


Figure 4.8 Casey's work generated during the synthesis of *m*-hexylbenzenesulfonic acid from benzene.

Jamison also used "C6" to represent the hexyl substituent:

I'm assuming the sulfonic acid's a meta director. It looks like a nitro group...and I know that the alkyl chain's definitely an ortho, para so I just know that would've worked....gonna go with that.

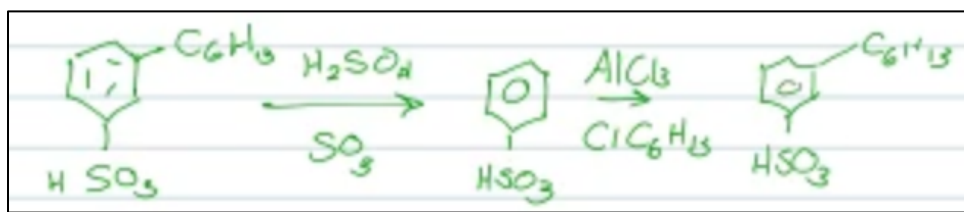


Figure 4.9 Jamison's work generated during the synthesis of *m*-hexylbenzenesulfonic acid from benzene.

By drawing the hexyl substituent as C_6 , Casey and Jamison did not recognize that a carbocation rearrangement would occur, and therefore, only considered Friedel-Crafts alkylation.

Below, Taylor and Morgan had difficulty forming an electrophilic carbocation when they could not remember Friedel-Crafts alkylation or acylation.

I need ... put ... okay, let's do ... the only thing I can think of it is like ethanol. That is definitely not what I'm going to use. God, I want to think it's like something like, I'm going to use a halogen to like ... I just think that's so wrong, though. You know what, let's just do it. Let's just ... put a CH group on there. That's a CH. That did not work. I'm drawing a blank.

Morgan had difficulty forming an electrophilic carbocation when he could not remember Friedel-Crafts alkylation or acylation.

We need some sort of something that'll give us CH_3 in there. I can't remember something that would give a CH_3 . I know it would have to be something like that

... sort of. It would just essentially be a source of it, not just CH_3^+ . I can't remember if it'd be like a lithium cuprate or something. I can't remember. It'd just basically be a source of this.

Both students knew they needed a reagent that would supply a methyl substituent but were unable to remember the reactions that had previously been covered in the course. Their inability to apply prior knowledge in this new context hindered them from successfully solving the synthesis problems in which an alkyl substituent was required.

4.2.2 Reduction of Aromatic Nitrobenzene

Nearly all students in this study (10 out of 11) were unable to remember the reagent required to reduce an aromatic nitro substituent to an amino group in aniline. Alternative incorrect routes provided by participants included using hydroxide with ammonia to create an amino cation (NH_2^+), using heat and ammonia to create an amino cation, or using nucleophilic addition of amide (NH_2^-). Several students tried to reason through various mechanisms to form an NH_2^+ cation before ultimately conceding that they did not know the reagents to do so. The work below shows several students' attempts at forming aniline from benzene. Casey stated, "I don't know how to make NH_3 into NH_2^+ , but let's assume we can, using that and heat because heat always works." Then Alex states:

Okay, so amine. Trying to think. You got NH_2 . Trying to think how it forms an electrophile. NH_3 ... Maybe. This is how I'm gonna do it ... So I'm gonna say that something like H_2O takes ... let's see, there's one negative charge. I'm trying to think ... so maybe if it's ... I don't know. Usually, we don't see that, but it forms N with a positive charge. Actually, I know where it happens. Okay, so it grabs an H from ... and that gets its positive charge, and then this ... oh no, that wouldn't work. I'm kinda stuck.

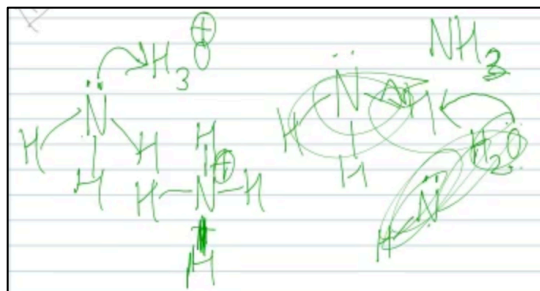


Figure 4.10 Alex's attempt to use EPF to reason through the generation of an NH_2^+ electrophile.

Emery attempted to do try the synthesis with an “electrophilic hydrogen” on ammonia, and then nucleophilic attack of the amide to the carbocation:

Would the reagent to ... Would you be able to use an NH_3 compound, and the use that to attack with electrophilic ... Yeah, I'm pretty sure it won't work, because I'm thinking I know what it's gonna form, but ... yeah.

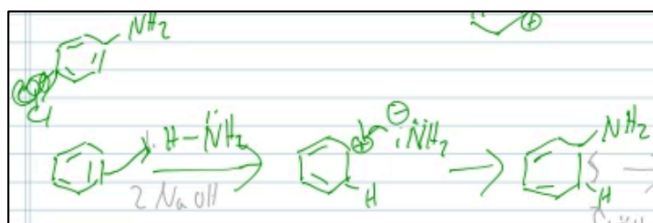


Figure 4.11 Work generated by Emery showing the synthesis of aniline from benzene.

Mason considered the reagents necessary to form aniline, “Would it be NH_3 maybe? I can do kind of the same thing here. Well ... I don't think you do that ...” Below, Figure 4.12, he showed benzene attaching to an amide reactant. However, there would not be an empty orbital to form the new covalent bond. Additionally, the charge on the amide would not be removed, as he indicated in his product.

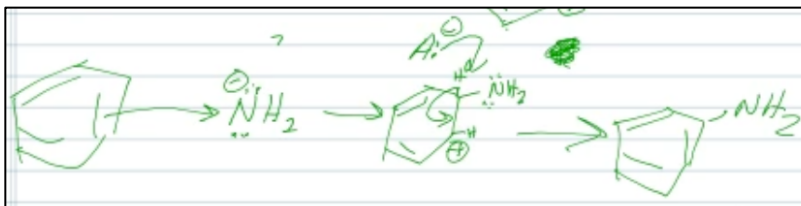


Figure 4.12 Work generated by Mason showing the synthesis of aniline from benzene.

Blake was the only participant to remember the reaction to synthesize an amino substituent from nitrobenzene:

So now we have nitrobenzene and let me redraw that down here. To get from nitrobenzene to aniline, let's see. I actually just learned a mechanism for this. You can reduce it with tin and hydrochloric acid. That takes a really long time, 'cause you have to do a single-electron transfer. Or you could use lithium aluminum hydride as a hydride source. It will add to nitrogen. The oxygens on the nitrogen will be protonated, and I'm skipping a step there, but they'll be protonated to form a leaving group, and then we'll get this positively charged nitrogen. We'll do a similar process for the other oxygen.

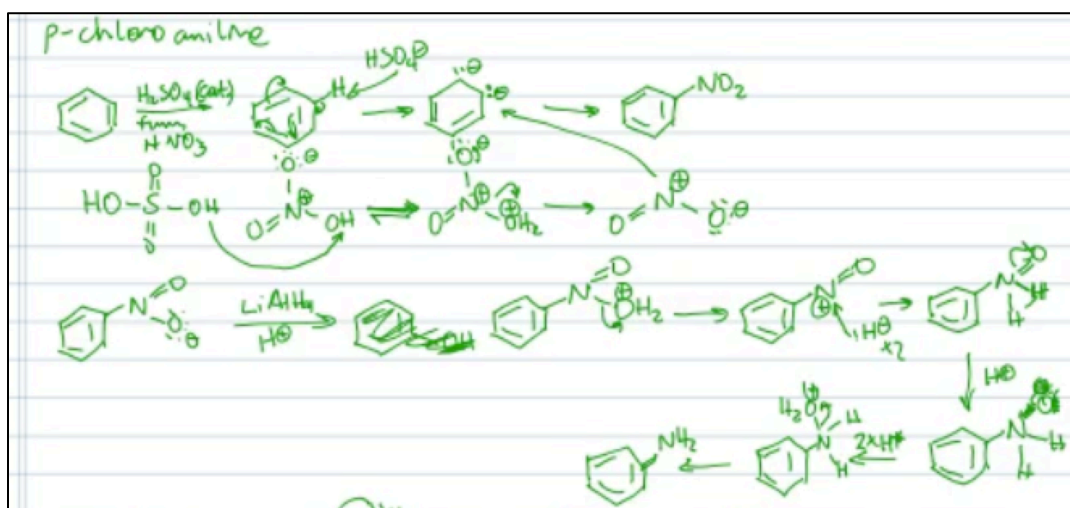


Figure 4.13 Blake's synthesis of *p*-chloroaniline showing the reduction of nitrobenzene.

Although Blake was the only student to remember the reduction of nitrobenzene to synthesize aniline, his proposed mechanism contained a few errors. Blake had forgotten to draw the formal charge on the nitro group, meaning there would be a 2^+ charge on the nitrogen after the removal of water in the second step of his synthesis. Furthermore, he was unable to show the addition of the lone pair of electrons that would be present on the nitrogen of the amino substituent. Several mechanisms have been proposed for the reduction of nitrobenzene (Gelder, Jackson, & Lok, 2005).

Further analysis of Blake's mechanisms for the synthesis of *p*-chloroaniline indicates a misunderstanding of the mechanisms of EAS reactions. Rather than the electrons in benzene

forming a new bond to an electrophile, Blake showed the deprotonation of benzene with a hydrogen sulfate ion. His use of arrows was incorrectly drawn when he showed the addition of the nitro group with the arrow pointing at the lone pair from the positively charged nitrogen.

4.2.3 Resonance

When solving the five EAS synthesis problems, most participants (10 out of 11) would begin by drawing the target molecule before attempting a synthetic route. In the example below, Emery began his synthesis by drawing the target molecule of 4-chloro-2-nitroaniline, Figure 4.13. When he finished the synthesis, the double bonds had been drawn in a different location in the benzene ring.

I drew this wrong. Okay. From that ... And so the final structure would be ... Should be that. Cl ... did I draw it right? No. Okay, and then when used in the Cl as an ortho, para. It'll form ... I'm also noticing how I'm doing this. I'm very sure the benzene ring, electron double-bonds can move around pretty freely, so I would assume I would have to use either some sort ... I'm not sure exactly how I would go about moving those, like purposely or anything.

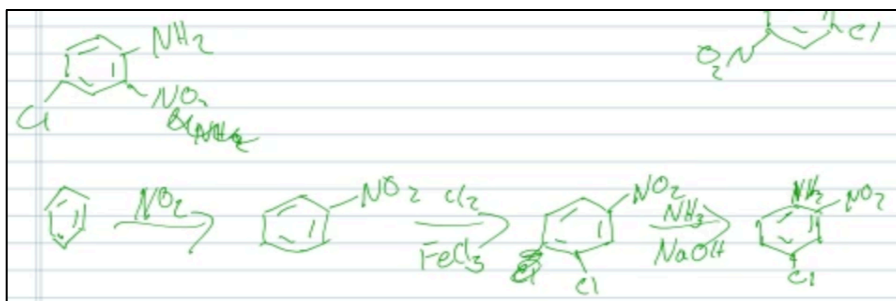


Figure 4.14 Emery's synthesis of 4-chloro-2-nitroaniline from benzene.

The concept of resonance and resonance structures are identified in both the general and organic chemistry ACCM (Holme, Luxford, & Murphy, 2015; Raker et al., 2013). Although Emery correctly stated that the double bonds in the benzene can “move around freely,” he ultimately believed his answer to be incorrect because on paper, the double bonds of his final product did not match the double bonds in the original depiction of the target molecule. However,

the definition of resonance structures states that the only difference is “the absolute location of electrons” (Raker et al., 2013, pg. 3).

4.2.4 Lewis Structures

One of the steps in answering synthesis problems was to show the generation of the electrophile in each case and to provide the mechanism in which the substituent bonds to the benzene. One participant, Kayden, correctly drew $\text{-SO}_3\text{H}$ as the sulfonic acid substituent but was unable to show the mechanism for the sulfonation of benzene. Although Kayden correctly identified the reagents sulfuric acid and sulfur trioxide to sulfonate benzene, he was unable to provide the mechanism. To support the possibility of drawing a mechanism, Kayden was asked to begin by drawing the Lewis structure of either sulfuric acid or sulfur trioxide. He began by trying to draw the Lewis structure of sulfur trioxide: “I know it has three oxygens, but I believe sulfur only has five valence electrons. And that makes it over the eight ...” When he began to show difficulty in drawing the Lewis structure for sulfur trioxide, the interviewer suggested he then try to draw the Lewis structure for sulfuric acid.

Also don't really know how that one looks. I don't really know how the three oxygens ... the additional oxygens are connected to this. Yeah, I'm not entirely sure how this happens.

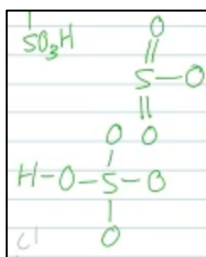


Figure 4.15 Kayden's skeletal structures when attempting to draw the Lewis structures of sulfur trioxide and sulfuric acid.

The ability to draw and use Lewis structures is identified in both the general and organic chemistry ACCM (Holme, Luxford, & Murphy, 2015; Raker et al., 2013). Even though Kayden provided the correct reagents to synthesize benzenesulfonic acid, his inability to draw a reasonable Lewis structure of the molecules hindered him from providing a mechanism for the reaction.

4.2.5 Language Using the Electron-Pushing Formalism

The ability to visualize molecules, show how they react, and use curved arrow notation to depict the movement of electrons are all identified in the organic chemistry ACCM (Raker et al., 2013). Cations and carbocations are formed when electrons are removed from an atom (Holme, Luxford, & Murphy, 2015). When asked to show why the hydroxy substituent in phenol is an ortho and para director, Casey and Emery used the following language to describe the resonance structures of phenol, respectively:

When we do the resonance of this all we move [the carbocation] there. The carbocation would move to this place over here. Because of this, this electron can be donated here. Therefore the charge, sorry, the charge moves to the oxygen. Since oxygen is the more electronegative compound, or molecule, atom, it would be more stable that way. Because of that property, it would then do para. Same thing with ortho, if we had this example, Cl. The OH is here. The carbocation is directly there. It's the same thing as this. Therefore with the movement of the positive charge, sort of, the carbocation to the oxygen, that would be ... That would make the whole resonance structure more stable.

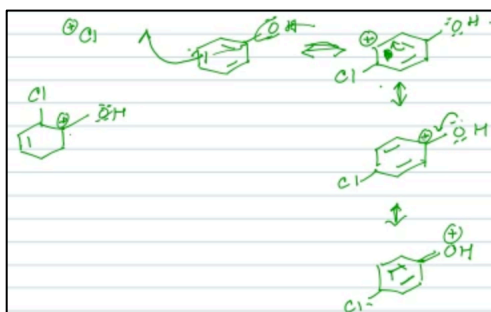


Figure 4.16 Casey's work showing his application of resonance structures to reason through why the hydroxy substituent in phenol is ortho and para directing.

So... Okay. I remember it something to do with the [oxygen] being able to take on the charge ... So I'm trying to remember exactly the details. So the positive charge can move along quite easily there. also the other option would be for to do something along these lines. You see how ... This one however I know it can't do that. Yeah I do have this right, right? Yeah. The reason being, when the charge moves around. Is this still ... Okay I get you. So say the charge moves like this, you'll have this, and a positive here. But then you move this to say the thing might me here, the positive's gonna on here, which means the [oxygen] can never take that positive charge. And so it has ...resonance effect. And of this one, again it'll work like [oxygen]. When you move it around it can be moved from here to here, and from here on to the [oxygen].

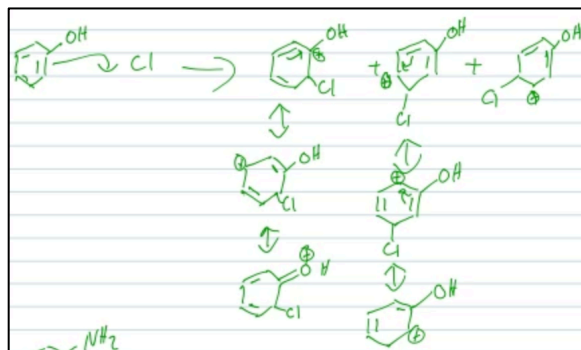


Figure 4.17 Emery's application of resonance structures to reason through why the hydroxy substituent in phenol is ortho and para directing.

Casey and Emery both described the positive charge moving around the benzene, rather than the positive charge being formed due to the removal of electrons.

When considering Friedel-Crafts alkylation versus Friedel-Crafts acylation, Peyton described the carbocation rearrangement as though it was the positive charge moving. Peyton stated, "...because if I did a Friedel-Crafts alkylation, the positive charge could rearrange part, move somewhere else to a carbocation rearrangement."

4.2.6 Discussion of Gaps in Understanding with EAS Synthesis Problems

There were several concepts that students had difficulty with when synthesizing problems using EAS. Friedel-Crafts reactions, reduction of aromatic nitrobenzene, Lewis structures, and resonance posed a challenge for some of the students. Only four of the eleven students could

remember the reagents necessary to produce a carbon electrophile/Friedel-Crafts reactions. One of the limitations of Friedel-Crafts reactions is that they will not occur on nitrobenzene due to the deactivation of the benzene ring. Three of the four students (Casey, Mason, and Jamison) used Friedel-Crafts alkylation on nitrobenzene for the synthesis of *m*-nitrotoluene. Although Peyton used Friedel-Crafts alkylation to methylate benzene, he incorrectly identified the methyl substituent as a meta director. In his synthesis, he nitrated toluene to produce *m*-nitrotoluene. However, *o*-nitrotoluene and *p*-nitrotoluene would be the products of that reaction.

Another concept associated with Friedel-Crafts alkylation reactions is the likelihood of a carbocation rearrangement during the reaction to the most stable carbocation. Mason and Peyton both used Friedel-Crafts alkylation for the addition of the hexyl substituent in *m*-hexylbenzenesulfonic acid. Casey and Jamison both used shorthand to draw the hexyl substituent as “C₆,” shown in Figures 4.8 and 4.9. This shorthand may have prevented them from recognizing that a carbocation rearrangement would occur and that the most likely product would have been 3-(1,2-dimethylbutyl)benzenesulfonic acid. The other seven students could not remember the reagents necessary to alkylate a benzene. Responses varied from providing the appropriate carbocation as a reactant (CH₃⁺ or C₆H₁₃⁺), using neutral carbon chains, or nucleophilic carbons.

Reduction of an aromatic nitro group is an anchoring concept in organic chemistry (Raker et al., 2013). However, only one participant was able to remember the reagents to correctly reduce nitrobenzene to aniline. As seen with Casey and Alex, several students focused on the topic of EAS and believed that in order to obtain aniline, you would need to create an electrophile. Emery and Mason focused on using a nucleophilic amide as a reagent to obtain aniline. Emery's synthesis, Figure 4.8, showed an “electrophilic hydrogen” forming a sigma bond to the benzene ring followed by a nucleophilic addition of amide to the benzonium intermediate. Mason's synthesis, Figure 4.9,

showed an amide ion forming a sigma bond to the benzene ring with two electrons from the benzene forming the bond. Additionally, the second step shows a neutral amide substituent even with the additional electron from the new sigma bond. Although Blake was able to recall the reaction and reagents that reduced nitrobenzene, his mechanism contained several flaws and indicated a misunderstanding of the general mechanism of EAS reaction.

Researchers have investigated the difficulty that students have with drawing reasonable Lewis structures (Cooper et al., 2010, 2012; Tiettmeyer et al., 2017). These studies have focused on undergraduate students, graduate students, and instructors (Cooper et al., 2010). It is not surprising that Kayden was challenged by the task of providing a Lewis structure for sulfur trioxide and sulfuric acid, two molecules that he should have been familiar with from lecture. However, it is worrisome that these students had almost completed the organic chemistry sequence with the inability to draw a valid Lewis structure.

Casey, Emery, and Peyton all described the reactions as the positive charge moving around, rather than the carbocation being formed from the absence of electrons. With the EPF convention, the movement of electrons is shown with the single- or double-headed arrows. Charges are created from the addition or absence of electrons, and EPF is not used to describe the movement of these charges.

CHAPTER 5. RESULTS AND DISCUSSION – INSTRUCTOR PERCEPTIONS OF STUDENT REASONING DURING EAS SYNTHESSES

The following chapter describes what organic chemistry instructors believe about how their students reason through synthesis problems using EAS and the challenges they expect their students to encounter. Appendix F contains the full list of emergent themes from the coded transcripts. The major themes in this study associated with organic chemistry instructor's perceptions with student reasoning of EAS synthesis problems were memorization, substituent effects, multiple products, and prior knowledge expectations and will be discussed in depth in this chapter. Reference Table 3.1 for instructor's demographic data.

5.1 Memorization

As discussed in Section 2.2, students use of memorization as a learning strategy in organic chemistry has been well documented in the literature. Instructors teaching organic chemistry are well aware of students' tendencies and preferences for using this technique to succeed in their course. Dr. Gacy noted that from the beginning of the course students are “taught to use flashcards for memorizing the reagents and what reagents do.” He further added:

They say “Should I memorize this?” And I'll say, “no, you should do it this way,” but they've already started to memorize and it's already started to work for them in a lot of cases.

Since students had begun to memorize concepts in organic chemistry, and it was a successful learning strategy, they were not going to change how they were approaching the learning of new concepts. Dr. Gaskins commented on students' reluctance to understand the flow of electrons and the meaning of mechanism arrows, in preference to memorizing the sequence of events instead:

I think students just see synthesis as just this abstract pile of stuff they need to memorize. They don't seem to see the importance of it and they certainly miss all

the logic to it. And I spend a lot of time, I think, trying to give them ways to not have to memorize, ways to rationalize things. I was never a memorizer myself. I only happened to have things memorized because I had to look them up so many times, you know. And I kind of expect students to be that way too...And mechanisms they also - I've noticed in recent years – they see mechanisms as something that get memorized as well. They have become more and more reluctant to understanding what a curved arrow means, and what the reactivity of certain atoms, certain functional groups would be. They think they need to look at a mechanism, memorize every detail of where the arrows need to be, need to go, which direction they're pointing, rather than learn a system. So yea, so the kind of unifying idea there is they won't learn a system. They'd rather memorize, you know, a million unrelated items than learn a couple of systems that do all of that for them.

He further added that “they’re just coming out of high school with a memorization focused way of learning and it’s very hard for us to train them out of it.” Dr. Gaskins has seen that students try to memorize everything associated with organic chemistry, from reagents to the curved-arrows in a mechanism, even when he has actively tried to give students other strategies to enhance their learning. Students use of this learning strategy in organic chemistry has been well documented in the literature (Anderson & Bodner, 2008; Cruz-Ramírez de Arellano & Towns, 2014; Grove & Bretz, 2012, 2010; Pursell, 2009; Zurer, 2001), so it is not surprising that participants in this study have noticed their students trying to memorize a lot of the concepts introduced in the course.

When instructors were asked how students learn the concepts associated with EAS, they agreed that it was mostly by memorization. Dr. Gacy described his students’ approach to identifying substituents as activating or deactivating from a memorization angle. Dr. Bundy described his students memorizing the table of substituent effects that was provided in the textbook. When Dr. Gacy described how his students identified a substituent as activating or deactivating, he stated:

They identify the group as activating or deactivating basically from a memorization angle instead of applying the electron pushing process, which is how I'd like them to do it.

Dr. Bundy also noted that the textbook that is used in his course provides students with charts containing the substituent effects:

And so I know like our book has a table of electron-withdrawing/electron-donating, ortho, para directors or meta directors, and some students will just memorize that chart.

Dr. Gaskins pointed out that EAS is a topic that students tended to memorize:

I feel like this is a unit that students just, they just memorize and they get lost in it because they don't spend the time to learn the concepts and electron demand and things like that that makes it so simple.

Pursell (2009) pointed out students' tendencies to memorize information in textbooks that are provided in callout boxes. Both Dr. Gacy and Dr. Bundy described their students' attempts at trying to memorize the substituent effects from the tables that are provided in the textbook. Instructors were aware of the processes and skills that can make learning organic chemistry easier than just memorizing the concepts but were unaware of how to break that habit in their students. Most students use the learning strategies that lead to the most successful outcome, and if memorizing the concepts and mechanisms has been effective in the past, they are reluctant to change it. For the topic of EAS, instructors admitted their students try to memorize the information provided in the textbooks of the substituent effects.

As discussed in Section 4.1.3, student participants in this study relied on memorizing the substituent effects to solve synthesis problems using EAS rather than developing an understanding of these effects. This was seen when students were able to identify a substituent as ortho and para directing, but unable to provide mechanistic reasoning as to *why* the substituent had that effect. Instructors in this study were aware that students enter organic chemistry expecting it to be a class where everything gets memorized, and EAS is a topic that lends itself to this learning strategy. EAS is a topic usually taught in the second semester, where students have already been successful using memorization with previous topics.

5.2 Substituent Effects

When instructors considered student approaches to solving EAS synthesis problems, many commented that students focused only on the directing effects of the substituents, and ignored their activation/deactivation effect. Dr. Raider noted that if a student was asked to synthesize *m*-nitrotoluene from benzene that they would focus on the order in which the substituents needed to be added to get the desired product:

They're trying to figure out what order, so they're probably doing order first because we would practice order of doing these syntheses in lecture. So they could quickly think, 'Okay, which one is meta directing? Which one is ortho, para directing?'

Dr. Raider described his students' focus on order as their focus on directing effects. For the synthesis of 4-chloro-2-nitroaniline from benzene, he described his students only considering the directing effects of each of the substituents rather than considering the activation/deactivation properties of the substituents:

You've got the nitro ortho and then, you've got to get the amine. Then, you've got the nitro meta to the chloro group. I think that they would just jump in, do it, and get an answer. I think, probably, the electron withdrawing and electron donating power of each group; they would probably lay that aside and go with meta or the para directing and do their plan that way.

Dr. Raider also noted that questions requiring students to consider both substituent effects may be too complex for students and that he would test these concepts in separate questions:

I could go into a separate problem and have them draw energy diagrams to look at activation/deactivation that way. If I'm simply looking for ordering in this problem, then it would just simply be about order and how to get to the right product. Then, a separate question, I would probably bring the activation/deactivation out. I think that's too much for them at the same time.

Mr. Ramirez discussed his students' approaches to synthesizing 1,2-dichloro-4-nitrobenzene from benzene as also only focusing on the directing effects of the substituents:

Again, recognizing where the substituents go so it's still what the pieces are. They need to do it twice, it's just a question of the order in which you do it. And which

is more likely to form. When referencing the directors, I don't call them ortho, para, I call them para, ortho to help emphasize the para position is more active.

On how students approached the synthesis of *p*-chloroaniline from benzene, Dr. Bundy believed that students' reasoning would be similar to his own, and focused solely on the directing effects of the substituents:

I'd hope the same way. I mean, I always try to get them to recognize if something's an ortho, para director or meta director. And then once they do that, obviously recognize what is ortho, what's in those positions and do they complicate each other. Then is there a way to, you know, add one of the groups so that the next group goes in to the spot that you want. Maybe you have to manipulate that to get to the final product. In this case it didn't necessarily matter too much if you thought about adding the nitro group first then recognizing that it's not going to put the next group in the ortho, para positions. You'd have to make sure that that is an ortho, para director before you try to add the other groups.

Dr. Bundy did not mention the activation or deactivation properties of the substituents but rather focused on identifying the positions on the benzene that would match the desired product and relied on the directing effects of substituents to do so. Dr. Bundy did not consider the activation/deactivation effects during his synthesis and believed his students would be approaching the problem the same way.

Dr. Gacy suggested his students' strategies to solving EAS synthesis problems would be similar to his own, namely that solving EAS synthesis problems is similar to playing with Lego® pieces and attaching the pieces together rather than considering the electronics involved:

This is like a particular EAS thing, like, just like Legos, like plugging the group on right? Like you kind of don't think about the hydrogen that left and you don't think about the exact mechanism ... I think they mostly think about it like I'm just plugging in a group at that position and whatever's on there already helps direct that group to a specific position.

He later added, "aromatic substitution falls into the same mental process of 'I'm just bolting groups on to the aromatic ring.' " Just as children play with Lego® pieces by attaching them together, students approach EAS as attaching substituents to the benzene ring.

Instructors believe it is the inherent requirement of solving EAS synthesis problems (and aromatic substitution in general) to be synthesizing products that have substituents in the correct locations, leading students to disregard the electronic effects of those substituents. This could be attributed to the ease with which a student can memorize a chart of directing effects and know where that location is on a benzene ring, rather than developing a deeper understanding for what it means for a benzene ring to be activated or deactivated.

Instructors also believed that their students only use the directing effects when synthesizing molecules using EAS because thinking about activation/deactivation is too complex for students. Dr. Raider would test these concepts in separate questions and would not expect his students to be thinking about the activation/deactivation properties of the substituents. Agreeing with Dr. Raider, Dr. Gacy suggested that students approach EAS problems as just “bolting on the groups.” Therefore, if a student knows a substituent will direct to the desired position, then that is solely what they will focus on. However, as discussed in Section 4.1.1, students did apply both substituent effects when describing their synthetic routes in these types of reactions. This was observed when synthesizing di-substituted and tri-substituted products. Even with the more complex tri-substituted products, students were considering the activation/deactivation properties of substituents.

5.3 Multiple Products

Instructors were in agreement that their students would not discuss reaction product yields or acknowledge the formation of multiple products in a reaction. Rather, students would focus only on the intermediate products required to form the desired products. When asked if his students would be considering the yields of an ortho, para directing substituent, Dr. Kemper stated bluntly,

“I think they’re not going to consider it.” When Dr. Gacy was asked how his students would approach the synthesis of 1,2-dichloro-4-nitrobenzene from benzene, he stated:

If you hit this with a ton of chlorine, you might get the 1,2-dichloro, but you’re throwing away the major product, which they might not consider.

Dr. Bundy also commented on his students not recognizing the formation of multiple products if his students were asked to synthesize 1,2-dichloro-4-nitrobenzene from benzene:

If you add the first chlorine and then you go to add the second chlorine, you’ll get some at the ortho position, but there’ll probably be more in the para position. So I don’t know if they recognize that fact.

He continued further by discussing why he believes students do not recognize or acknowledge the formation of multiple products in a reaction:

I think the hardest thing is that students don’t have enough experiences in realizing that you want to minimize the amount of biproducts and possible other products. Students don’t necessarily worry so much about that unless they’re in the lab and it makes a difference. So I think that would be what the biggest hang up would be. If you added both chlorines first, then you’re going to have a lot more biproducts that you’re going to have to deal with, so that would probably be the biggest mistake that they would do. I think a lot of that comes from just not being experienced about, I mean, it’s very hard to impress upon students that if this was costing them money, then you would try to find the most efficient route.

Dr. Bundy believed that if students had more laboratory experience in which there were consequences associated with producing multiple products in significant yield in a reaction, then students would become more adept at identifying all possible products that could be formed in a reaction. However, synthesis on paper has no direct consequence for ignoring the production of side products.

As discussed in Section 4.1.2, students did acknowledge when more than one product could be formed in a reaction, contradicting the beliefs of their instructors. Furthermore, some students also provided laboratory separation techniques that would isolate the desired product, showing a transfer of knowledge of skills acquired in the laboratory and applying them to new contexts. While

instructors were correct in believing students would not provide product composition or yield percentages, students were aware that there would be byproducts in a reaction.

5.4 Prior Knowledge Expectations

Prior knowledge expectations are defined as knowledge students are assumed to have from previous chemistry instruction. Described below are four chemistry topics that instructors believed would influence students' abilities to solve synthesis problems using EAS and that they expected students to know. These include Friedel-Crafts acylation and alkylation reactions, reduction of aromatic nitrobenzene, Lewis structures, and resonance.

5.4.1 Friedel-Crafts Reactions

Friedel-Crafts reactions were discussed most frequently when synthesizing products using EAS. Six of the eight instructors mentioned Friedel-Crafts reactions and the difficulties students could have with these reactions. Additionally, instructors talked about the differences in the emphasis a textbook can place on concepts associated with Friedel-Crafts reactions. For example, the concept that nitrobenzene is deactivated enough that Friedel-Crafts reaction conditions will not react with nitrobenzene. Dr. Gaskins bluntly stated that his "students would not, most of the time, remember that they couldn't do Friedel-Crafts with the nitro group there" when trying to synthesize *m*-nitrotoluene from benzene. For the same synthesis problem, Dr. Gacy agreed that students would attempt to alkylate nitrobenzene to get the desired product:

I think a lot of students would try the Friedel-Crafts alkylation of the nitrobenzene. Which has like one of these things where it would probably get you the product but it would also get you the dialkylated, probably, to some extent, and it would just be really hard to do all around because the NO₂ group is strongly deactivating.

Dr. Gacy appeared to contradict himself by stating that multiple additions could occur since alkylation does not stop at just one addition. However, he admitted the challenge of trying to add

anything on to nitrobenzene. His students would not recognize the multiple alkylation products that would occur in a Friedel-Crafts alkylation reaction, nor would they consider the deactivation of nitrobenzene, just as he did not. Although, Dr. Gacy did not mention that the limitation of Friedel-Crafts reactions is that they will not occur with nitrobenzene. Dr. Manson discussed the multiple additions that occur with Friedel-Crafts alkylation reactions, and how challenging that recognition would be for his students:

I think with my students, they would attempt to put a CH_3 group on the benzene ring right away. There wouldn't be any good way to do that. I teach them that alkylation doesn't stop at one product. That, I think, would be a challenge for them. So many of them will just write 'alkylation reaction' and then when they realize that alkylation would not give them [the desired product] because it's an activating group and it's an ortho, para director. I think that many of them will quit there.

He also stated that students would attempt to alkylate nitrobenzene, even though he explicitly told them of the difficulty in trying to do so:

They would put the nitro group on first and then try to alkylate the ring. Technically, it should give them the meta product, but the nitro group is deactivating. I tell them that once you have the nitro group there, it's very hard to put more substituents on there.

Dr. Kemper also agreed that most students would alkylate nitrobenzene:

They would nitrate first and then alkylate it. Not really being concerned about the level of deactivation. We know it's deactivating, but does that mean it's going to kill it or not? I don't know. And I don't emphasize that 'cause frankly, I don't think it's important.

Dr. Berkowitz talked about the different levels of emphasis that were placed on how deactivated a nitrobenzene is. Dr. Berkowitz taught an organic chemistry course for Life Science majors, and stated that students at that level would be given credit for alkylating nitrobenzene simply because it would follow the directing effects of the substituents:

Nitrate and then Friedel-Crafts. What I know that doesn't work, that they won't know, is that you can't do Friedel-Crafts on nitrobenzene. It's just too deactivated. If I said to my students, 'do this synthesis,' I would give them 100 percent credit

for this. Because at the [Life Science's majors] level, that's perfect in terms of directing effects.

Dr. Berkowitz recognized his own emphasis, or lack thereof, on the limitations of Friedel-Crafts reactions. Therefore, he would score his students based on the concepts they were taught, which was partially dictated by the student population in his course. Dr. Bundy agreed that with the level of his students, he would also give credit for alkylating a nitrobenzene. Furthermore, he talked about the different degrees of emphasis in textbooks on how deactivated a nitrobenzene is when describing how he would approach the synthesis of *m*-nitrotoluene from benzene:

I concern myself with the fact that nitro is a deactivating group, right? But that's depending on the reaction conditions. A lot of times the books will say that it's so deactivating that they won't let anything else react. And in certain circumstances books will and some circumstances they won't. So as far as my student level, I would allow them to get to that point where they understand that a nitro group can add one complimentary group, but not multiple, or depending what it is...I would add the nitro group first and then add the methyl group, so that would be HNO_3 , H_2SO_4 and then CH_3Cl , aluminum trichloride.

He further explained:

Depending on the emphasis, one might think that you can't add anything after you have a nitro group on there. And like I said, I think for us, we would say maybe one thing is ok, but you try to add multiple things or you if have multiple nitro groups it's definitely not going to happen.

Similarly to Dr. Gacy, Dr. Bundy did not recognize that Friedel-Crafts reactions would not occur on a nitrobenzene. Therefore, his students would receive credit if that was how they approached the synthesis of *m*-nitrotoluene from benzene.

Dr. Berkowitz also discussed the carbocation rearrangement that would occur if Friedel-Crafts alkylation was used to add a hexyl chain to benzene in order to synthesize *m*-hexylbenzenesulfonic acid from benzene. Additionally, he thought his students should be familiar with this concept:

They might actually try to do Friedel-Crafts alkylation with n-hexylchloride, so it's probably going to rearrange. and that's something they should know. I do talk about that.

The difficulty of alkylating nitrobenzene and carbocation rearrangements in Friedel-Crafts reactions were discussed by most of the instructors. As discussed in Section 4.2.1, Friedel-Crafts reactions did pose a challenge for students, as only four out of the eleven students were able to recall the reactions and their respective reagents. Out of those four, three of them described the alkylation of nitrobenzene without considering how deactivated nitrobenzene would be, yet they were explicitly instructed about Friedel-Crafts reactions not working on nitrobenzene. The other student who was able to recall the correct reagents, incorrectly nitrated toluene to synthesize *m*-nitrotoluene. This would actually yield *o*-nitrotoluene and *p*-nitrotoluene. Additionally, all four participants did not mention the need to stop the reaction after one alkylation. Although instructors had taught concepts about Friedel-Crafts reactions and their limitations, they were aware that specific concepts may be forgotten by the students while they are solving these problems. The level of emphasis of how deactivated a nitrobenzene varies between textbooks and professors. However, a specific limitation of Friedel-Crafts reactions is that they will not occur on nitrobenzene. Instructors would allocate credit if students applied this incorrect concept, and some instructors seemed to have forgotten the limitation.

Dr. Berkowitz believed correctly that students would forget the rearrangement that occurs with Friedel-Crafts alkylation reactions. All four students that were able to recall the reagents, used Friedel-Crafts alkylation to synthesize hexylbenzene from benzene. None of the instructors mentioned the difficulty that students may have in remembering these types of reactions when synthesizing products using EAS. Out of the seven students that could not recall Friedel-Crafts reactions or their respective reagents, only three of them stated that they would need to generate a carbocation. The other four students used neutral carbon chains (3) or anionic carbon sources (1).

5.4.2 Reduction of Nitrobenzene

Several instructors discussed the reduction of nitrobenzene and how combining multiple types of reactions in one synthesis problem could be asking too much from their students. Dr. Gaskins noted that his students may not be aware of the difference between a nitro and an amino substituent and would stop at nitrobenzene with the assumption they had synthesized the correct molecule:

I think a number of students would actually make the nitro group and stop there and not even think that they hadn't put the right functional group on.

Rather than incorrectly identifying nitrobenzene as aniline, Dr. Gacy stated that his students would use the nitration reagents to add the amino substituent to benzene to synthesize aniline:

Some of them might forget that the reducing agent step is necessary so they might try to use the nitration reagents to just throw the NH_2 group on directly.

While Dr. Gacy believed that his students “would recognize that you can't add the NH_2 group directly,” he further added that his students may try to add the amino substituent using other familiar mechanistic pathways like a “nucleophilic aromatic substitution approach, like the very end of the chapter, after they've talked about that.” He described how his students would synthesize *p*-chloroaniline from benzene:

They would try to put the NH_2 group directly on the ring. Which might be possible if you chlorinate [benzene], then maybe use sodium amide but that will be way harder to do.

Dr. Gacy also discussed the difficulty that emerges when students are asked to utilize multiple reaction types to get to the desired product:

One thing to mention about this is you're really bringing in two different reaction types into the synthesis. Naively on the surface you see an aromatic starting material, aromatic product - benzene in the starting material and in the product. Aromatic substitution, nucleophilic and electrophilic, both fall into the same mental process of, ‘I'm just bolting groups on to the aromatic ring.’ Whenever oxidation and reduction come in to play, you add this extra layer of complexity where you know the student has to understand that replacing the carbonyl group with

hydrogens requires a different type of reagent, different type reaction than the electrophilic aromatic substitution. That introduces a lot of complexity and I think a lot of students will try to fit a synthesis into a particular box, just to make it as simple as possible.

When examining how his students would synthesize 4-chloro-2-nitrobenzene from benzene, Dr. Manson similarly discussed the challenge of incorporating oxidation and reduction concepts into the synthesis:

I think what will kind of throw them off a little bit because you have an NH_2 group and an NO_2 group. So both the most oxidized and the most reduced group on the ring at the same time. That suggests they will be put on at different stages of the synthesis and not at the same time. So if you have two nitro groups you cannot selectively reduce one of them into an NH_2 , or if you have two NH_2 groups you cannot selectively oxidize one of them to an NO_2 group. So that would be a challenge for them.

Dr. Bundy stated that if his students were aware that a reduction step was necessary, they may not reduce nitrobenzene at the right time in the synthesis:

For some reason they don't always think about reducing the nitro group at the right time. I think they kind of have a challenge with that sometimes so that might be one problem that they might run into.

Incorporating oxidation and reduction reactions into synthesis problems incorporates another layer of complexity that instructors are aware may pose a challenge for their students. Additionally, instructors believe their students may not be aware that this extra step is necessary when trying to synthesize an amino substituent. As discussed in Section 4.2.2, the most difficult challenge that students had when synthesizing products using EAS was the reduction of nitrobenzene to form aniline. While none of the participants stopped their syntheses at nitrobenzene with the assumption they had made the correct product, as suggested by Dr. Gaskin, all but one student struggled with this problem. Additionally, none of the students used the nitration reagents to make aniline, but all of them had difficulty remembering exactly what reagents would be required to do so. Dr. Gacy and Dr. Manson discussed the complexity that arises when incorporating different types of

reactions into one synthesis, and Dr. Gacy further added how students try to categorize the reactions and focus on the topics most recently discussed. This was seen with the student participants who incorrectly tried to synthesize an 'amino electrophile.' These students appeared to have categorized the topic of the study as being based solely on EAS, and therefore all steps in the syntheses would need to have to generate an appropriate electrophile.

5.4.3 Lewis Structures

Only one instructor, Dr. Bundy, discussed the importance of Lewis structures and how drawing and interpreting a Lewis structure would help in conceptualizing substituents as activating or deactivating:

By looking at the one substituent already on the [benzene], being able to look at that substituent and describe how that could be deactivating or activating based off of its structure. That would mean that they need to know what the Lewis structure of it would be and how it could contribute to resonance or not.

He further added the impact that a poor understanding of Lewis structures would have on other concepts seen in the course:

If you don't know the Lewis structure properly then you can't really see that something has a lone pair of electrons, or a proton to give up. And being able to draw Lewis structure helps you evaluate whether a substituent or a molecule will act as an acid or base or nucleophile/electrophile

He also talked about his incoming students entering organic chemistry and experiencing difficulties when asked to draw a Lewis structure during class:

As far as Lewis structure, I don't know if difficult is the right word, but it's the part that they need to spend more time on, just getting better at. You throw a problem early on in the semester, you throw sulfuric acid at them and then all of a sudden they're confused, and at this point you would hope that they're not...I would hope even in the first three or four lessons that wouldn't be such a daunting task to them.

Unfortunately, Dr. Bundy recognized that his students did not have a complete understanding of how to draw and interpret Lewis structures, and the implications this has for deeply understanding

other concepts in the course. As discussed in Section 4.2.4, the inability to draw a Lewis structure did not affect Kayden's ability to identify if a substituent was activating or deactivating; however, it did impact his ability to provide a mechanistic pathway to generate an electrophile and complete the synthesis. Dr. Bundy specifically identified that the Lewis structure of sulfuric acid confused his students. Kayden was unable to provide the Lewis structure for sulfuric acid, after almost completing the organic chemistry course.

5.4.4 Resonance

While instructors approached a lot of the concepts associated with EAS from a resonance standpoint, only one of them mentioned that students would experience difficulty in understanding what a resonance structure is and the impact that could have on understanding concepts associated with EAS. Dr. Raider relied on resonance structures to convey the meaning of activation and deactivation of a substituted benzene, as well as the directing effects of substituents:

I can kill two birds with one stone. I can look at deactivating/activating and kind of compare that to benzene but then at the same time I can talk about directing as well. That's more of a lecturing efficiency for me because I feel like it's a big topic, and I've got to get it in. I'm out of time so I put it all together in one lecture.

When asked if his students had an understanding of what resonance structures were, he stated, "not when they come into organic." While his students would be able to draw resonance structures towards the end of the course, they would not be able to interpret these structures during the EAS unit to predict percent compositions:

They can write the resonance structures, but they can't see percentage composition of the resonance structures as a way to predict composition.

Furthermore, he had seen that his students rely on the resonance structures of substituted benzenes to predict the directing effects during a synthesis problem on an exam:

They do a lot of extracurricular jotting down, and you can kind of see it when they turn their exams in. They sketch out their resonance structures so that they can see which one's going to go first.

Dr. Bundy hoped that his students would use their understanding of resonance as a tool to visualize how a substituent could be activating or deactivating:

They would definitely want to understand the resonance and how resonance plays a part in this, and the stability of the resonance structures. So I would hope that they would be able to talk about that or understand that. And then, by looking at especially if you have you know, one substituent already on the [benzene], being able to look at that substituent and describe how that could be deactivating or activating based off of its structure.

Dr. Gacy talked about the impact of not understanding resonance and how it would affect his students' abilities to predict whether a substituent was activating or deactivating the benzene:

I try to teach activating and deactivating groups from very generalized perspective by identifying any atom that has a lone pair on it that's directly attached to the ring as being an activating substituent. I try really hard to train students to identify different types of groups as falling into that general pattern. And then you know, this all kind of connects back to resonance as well. I find that if students have never really connected the dots on resonance, they won't know that the lone pair on an activating group is a direct participant in resonance with the aromatic ring.

He also discussed the complexity in identifying deactivating groups because the majority of deactivating groups are, "multi-atom, polarized pi bonds, or a carbonyl, or nitro" and therefore:

You really can't get by without drawing the resonance structure that has the positive carbon or the two plus nitrogen, the nitro or something like that.

In order to be successful at identifying activating and deactivating substituents, Dr. Gacy believed his students need to have an understanding of resonance structures. If students have not grasped a good understanding of this topic, they will struggle with some of the concepts associated with EAS. As discussed in Section 4.2.3, one student concluded that his final answer in his synthesis was incorrect because the benzene ring double bonds did not match the location of the double bonds in the original structure he had drawn before attempting the synthesis.

CHAPTER 6. RESULTS AND DISCUSSION – TOPIC-SPECIFIC PEDAGOGICAL CONTENT KNOWLEDGE OF ORGANIC CHEMISTRY INSTRUCTORS

The following chapter will describe three case studies with instructors associated with the three general knowledge domains (GKD) that influence an instructors' TS-PCK (Davidowitz & Rollnick, 2011; Mavhunga & Rollnick, 2013): knowledge of students (KoS), subject matter knowledge (SMK), and pedagogical knowledge (PK), shown in Figure 6.1. The TS-PCK framework was described in Sections 2.5.2.3 and 3.2.1. There are five components for which knowledge transformation occurs in the TS-PCK model: student's prior knowledge, curricular saliency, what is difficult to teach, representations including analogies, and conceptual teaching strategies (Mavhunga and Rollnick, 2013). Each participant in these case studies is described in detail, but some comments, statements, statistics, and references have been omitted to ensure anonymity of institutions and participants.

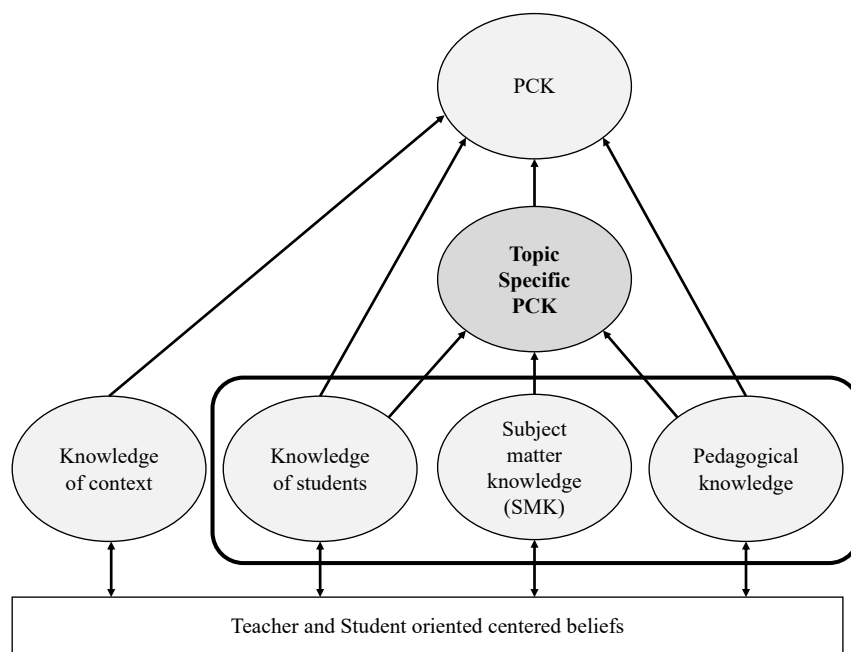


Figure 6.1. Topic-specific pedagogical content knowledge model highlighting the three general knowledge domains instructors use to influence their TS-PCK (Mavhunga and Rollnick, 2013)

The data collected in this study was expansive. As such, the data presented will provide a narrative for the best examples for the GKDs that influence an instructor's TS-PCK from each of the case studies. It should be noted that each of the case study participants exhibited examples of each of the GKDs, but one domain was chosen for each of the cases.

A descriptive case study approach was used for the analysis of three instructor interview transcripts to describe how each of the three GKDs relates to an instructors' TS-PCK (Baxter & Jack, 2008; Yin, 2003). Multiple data sources were used to strengthen the credibility of the findings (Baxter & Jack, 2008; Patton, 2015), including interview transcripts, responses to the online questionnaire (Appendix A), syntheses generated by the instructors, observations made by the interviewer, student population data, and video recordings of the interviews. Every attempt has been made to describe each participant in these case studies. However, some comments, statements, statistics, and references have been omitted to ensure anonymity of institutions and participants. The three cases described below will evaluate how the three general knowledge domains relate to TS-PCK: Dr. Gacy's KoS, Dr. Kemper's SMK, and Dr. Manson's PK.

6.1 Case Study 1: Knowledge of Students – Dr. Gacy

6.1.1 Describing the Participant: Dr. Gacy

Dr. Gacy was the general chemistry laboratory coordinator at an institution with the Carnegie classification of highest research activity. His Ph.D. was in organic chemistry and he had 5-10 years' chemistry teaching experience, including his teaching responsibilities during his graduate career. He had 2-5 years' experience specifically teaching organic chemistry.

Dr. Gacy taught organic chemistry in the summer terms. While EAS is usually taught in the second semester, he reported that he taught it during his first-semester class. There were approximately 40 students enrolled in Dr. Gacy's organic chemistry courses. His exams were

comprised of multiple-choice and free-response questions. Teaching assistants were assigned to the course to support the instructors with grading the exams and hold optional recitation sessions for the students. The ACS final exam was administered as the final exam at the end of the course.

6.1.2 Dr. Gacy's Students

The institution had approximately 25,000 students enrolled, including graduate and undergraduate students. The undergraduate student population was approximately 65% male and 35% female, and the majority were residents of the state the institution resides in. Over 50% of the student population declared their ethnic background as white, approximately 20% reported Asian and over 10% were international. Less than 10% reported African American, Hispanic/Latino or Native American.

The Department of Chemistry and Biochemistry had approximately 400 students that declared their major as chemistry or biochemistry. Demographics data reported by Dr. Gacy about the 400 students in the department indicated that approximately 250 were female and 150 were male. Demographically, around 50% reported their ethnic background as white and 25% Asian. Approximately 10% were international students. Students who declared chemistry, biochemistry, pre-health, biology, biomolecular or chemical engineering as their major would take the same organic chemistry sequence.

The students in Dr. Gacy's organic chemistry course would have had to complete two semesters of general chemistry. EAS and nucleophilic aromatic substitution reactions were the last topics taught in the first semester of his organic chemistry class. Before the topic of EAS, they would have encountered lectures covering structure and bonding, conformations, and stereochemistry, S_N1/S_N2 and E1/E2 reactions, alkene reactions, alkyne reactions, and spectroscopy (IR, and NMR).

Dr. Gacy reported that he believed his students had a challenging time grasping the curved-arrow formalism and drawing reasonable reaction mechanisms. He further elaborated:

Many students feel that there are no limitations on curved arrows, especially as they develop fluency for their meaning in terms of breaking and forming bonds. I would argue something like 85% of students nationally get out of organic II without an understanding that curved arrows must be associated with a reasonable orbital interaction.

He also added that students had a demanding time interpreting and applying the meaning of “acidic-” or “basic-conditions” in mechanisms. He added, “Ideas like ‘carbocations and carbanions cannot exist together’ are often lost on students.” He is suggesting that because students do not fully understand that basic conditions favor anionic interactions, their mechanisms will contain both carbocations and carbanions under either condition.

Dr. Gacy also reported that his students “struggle to mentally rotate and reflect molecules [molecular structures].” He further supported his claim with his own observations:

And kind of the evidence I have to go on is that you can do funky things like draw the same molecule in a different orientation and get a different outcome from a lot of the students.

He believed that students would interpret the same molecule drawn in different orientations as two distinctive molecules because of his students’ inability to properly visualize and rotate molecules on paper.

6.1.3 TS-PCK of Dr. Gacy

During the interview, Dr. Gacy discussed four of the five components of TS-PCK. Prior knowledge topics he believed would affect students’ abilities to solve synthesis problems using EAS included resonance, acid/base concepts, and Friedel-Crafts reactions. He discussed how he approached teaching the substituent effects with atoms that have lone pairs, and how resonance plays an important role in assessing what influence the lone pair has on the molecule:

This kind of connects back to resonance as well. I find often that if students have never really connected the dots on resonance they won't know that the lone pair on an activating group is a direct participant in resonance with the aromatic ring.

When describing how his students would approach the synthesis of 4-chloro-2-nitroaniline from benzene, he talked about his students not recognizing a substituent or reactant as basic or acidic:

A ton of them would just try to nitrate aniline, not realizing that the NH_2 group would get protonated. That frustrates me from an electron-pushing perspective because if they recognized that there was a lone pair on the nitrogen, they would see that that group is somewhat basic and it's gonna get protonated by the strong acid, which is just gonna throw everything off. Just recognizing H_2SO_4 is a strong acid and NH_2 is a decent base on that molecule would fix that.

Recognizing the limitations of Friedel-Crafts reactions were also discussed, including Friedel-Crafts reactions not occurring on a nitrobenzene, and carbocation rearrangements that can occur with Friedel-Crafts alkylations. When he described how his students would approach the synthesis of *m*-nitrotoluene, Dr. Gacy stated:

I think a lot of students would try the Friedel-Crafts alkylation of the nitrobenzene. Which has like one of these things where it would probably get you the product but it would also get you the dialkylated, probably, to some extent. And it would just be really hard to do all around because the NO_2 group is strongly deactivating.

He later added:

In Friedel-Crafts, if you don't know that a carbocation is potentially involved, then you might get tripped up by rearrangements, or something like that. If you don't know that an acylium ion is involved in an acylation, then you might not know that rearrangements aren't an issue.

Dr. Gacy discussed several conceptual teaching strategies and representations that he used to teach concepts associated with EAS. He described his approach to teaching concepts about activation and deactivation:

I try to teach activating and deactivating groups from very generalized perspective of like, you can think of any atom that has a lone pair on it that's directly attached to the [benzene] ring as being an activating substituent. So I'll draw like an X, a generic X atom, with a lone pair on it to represent any activating group and you know, I try really hard to train students to identify different types of groups as falling into that general pattern.

He used the lone pair of a Lewis structure to convey the concept that his students should look for unbonded electrons on an adjacent atom to the benzene ring to identify an activating substituent.

He further elaborated on how he wanted students to rely on these visual cues:

I hope that they start to recognize these visual cues. That's why I try to hammer home the generic, like what you're looking for is a polarized pi bond directly connected to the ring, which means two atoms double or triple bond, difference in electronegativity, that kind of thing. I think there's a lot of superficiality that goes on where like, activating groups tend to be heteroatoms directly connected to the ring. They tend to have single bonds directly connected to the ring. But they're not connecting that to the electron density, so they're doing a very good job of making it look like they understand the electronic implications of the groups when they're really just doing visual mapping, right? It's like identifying an impressionist painting just by noticing that it's blurry, right?

Dr. Gacy mentioned the complexity and difficulty in adding multiple reaction types to a synthesis, and how that played a role in the students that approach EAS as, “just bolting groups on to the aromatic ring.” He continued:

Whenever oxidation and reduction come in to play, you add this extra layer of complexity where you know the student has to understand that replacing the carbonyl group with hydrogens requires a different type of reagent, different type of reaction than the electrophilic aromatic substitution. That introduces a lot of complexity. I think a lot of students will try to fit a synthesis into a particular box, just to make it as simple as possible.

He elaborated further:

We want our syntheses to be as simple as possible, ideally. But sometimes bringing in a different reaction type actually makes the synthesis either more effective or in some cases, simpler itself. So I think that that actually complicates things a lot. Any synthesis that requires oxidation or reduction in addition to these reactions is gonna throw some people off.

Dr. Gacy discussed the difficulty in specifically having oxidation and reduction reactions in the same synthesis that require EAS. Nitrobenzene was synthesized using EAS, but asking students to then reduce nitrobenzene to get aniline becomes too complex for some students.

6.2 Case Study 2: Subject Matter Knowledge – Dr. Kemper

6.2.1 Describing the Participant: Dr. Kemper

Dr. Kemper was an associate professor at an institution with a Carnegie classification of small baccalaureate college. He obtained his Ph.D. in physical chemistry from a private university with the Carnegie classification of highest research activity. He taught both physical chemistry and organic chemistry courses at his institution. At the time of the interview, he had 5-10 years' experience teaching organic chemistry. There were approximately 10 students enrolled in the second-semester organic chemistry course.

6.2.2 Subject Matter Knowledge - Dr. Kemper

To evaluate Dr. Kemper's SMK of EAS, this section will discuss how he reasoned through five synthesis problems using EAS and which mistakes in understanding emerged from his syntheses. For clarity, his synthetic schemes have been redrawn using a chemical structure drawing software. Actual images of his work can be found in Appendix H.

6.2.2.1 Synthesis of *p*-chloroaniline

For the synthesis of *p*-chloroaniline, Dr. Kemper used three steps, Figure 6.2. The first step showed the nitration of benzene, followed by reduction of nitrobenzene to form aniline, and then chlorination of aniline to produce *p*-chloroaniline.

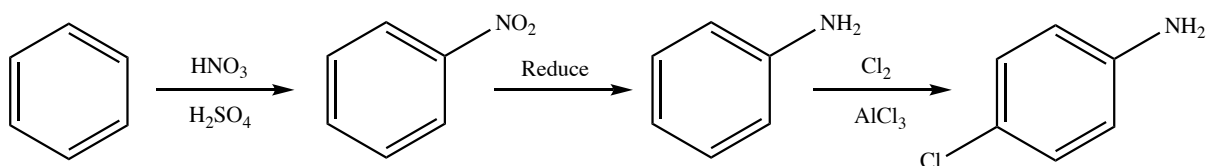


Figure 6.2. Dr. Kemper's synthesis of *p*-chloroaniline.

Synthetically, *p*-chloroaniline is produced by chlorinating benzene, followed by nitration, and then reducing *p*-chloronitrobenzene to *p*-chloroaniline (Booth, 2012). This is due to the over

chlorination that can occur from the chlorination of aniline (Booth, 2012). However, Dr. Kemper's response would be consistent with the substituent effects. Reducing nitrobenzene to aniline makes the substituent ortho, para directing. Although there would be a mixture of *o*-chloroaniline and *p*-chloroaniline, Dr. Kemper did not mention this.

6.2.2.2 Synthesis of *m*-nitrotoluene

For the synthesis of *m*-nitrotoluene from benzene, Dr. Kemper provided two mechanistic pathways, because he was unsure "which one was correct," and added, "I don't know how deactivating a deactivator is." Before he began his synthesis, he drew out the molecule he was trying to synthesize and then crossed it out to begin with benzene. With the directing effects only, both syntheses would produce *m*-nitrotoluene. In the first route, Figure 6.3, Dr. Kemper acylated benzene, followed by nitration, and then reduced the carbonyl to a methyl substituent. When he explained his mechanistic pathway, he stated:

If nitro is too deactivating, I'm gonna write here, "suppose NO₂ is infinitively deactivating," for path 1 (Figure 6.3). If that's true, then I'm going to take benzene and acylate it first with Friedel-Crafts acylation. Then I'm going to nitrate it. And then I'm going to reduce it, and I'm not sure if I can. I have to look this up. I'm not sure if I can reduce preferentially.

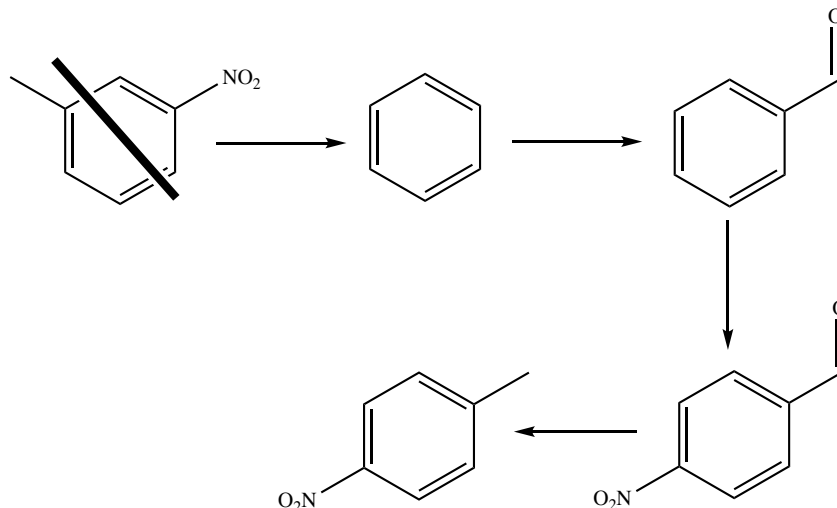


Figure 6.3. One of Dr. Kemper's syntheses of *m*-nitrotoluene.

It would be synthetically difficult to preferentially reduce one of the substituents over another. He would need to provide specific reactants and provide reasoning as to why the aldehyde would be reduced rather than the nitro substituent. It is also interesting that he originally drew the target molecule for *m*-nitrotoluene, but when he wrote out the rest of the mechanism, the structures were drawn with para substitution.

The second pathway that he provided, Figure 6.4, showed the nitration of benzene as the first step, followed by Friedel-Crafts alkylation. He explained his synthesis:

Then the other way is I would nitrate it first and I wouldn't have to reduce it. Then I would alkylate it with a Friedel-Crafts alkylation.

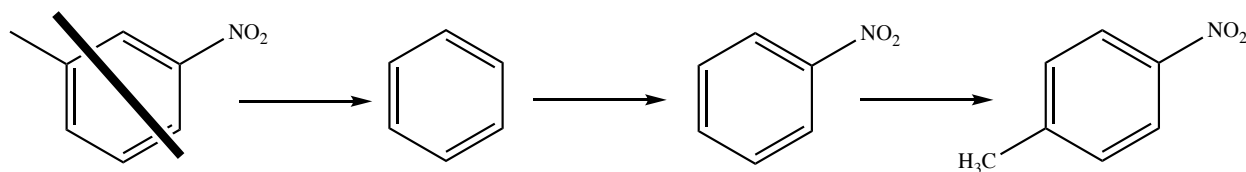


Figure 6.4. The second synthesis of *m*-nitrotoluene by Dr. Kemper.

As discussed in Chapters 4 and 5, a limitation of Friedel-Crafts reactions is that they will not occur on a nitrobenzene due to its deactivation. Again, after drawing *m*-nitrotoluene, he drew the final product with para substitution.

6.2.2.3 Synthesis of *m*-hexylbenzenesulfonic acid

When asked to synthesize *m*-hexylbenzenesulfonic acid from benzene, Dr. Kemper began by joking, “one, two, three, four, how many carbons in a...in a...I’m joking,” appearing to attempt to make light of his shortcomings in the previous synthesis. He then resumed the task by drawing *m*-hexylbenzenesulfonic acid, and talked aloud, “one, two, three, four, five, six, seven, eight, nine, ten...hexyl.” Participants were informed that the interviewer would be taking notes throughout the interview, and therefore may not always be looking at the screen. After Dr. Kemper continued his joke about the number of carbons in a hexyl chain, he tentatively looked at the camera, appearing

to look for a response from the interviewer, before continuing. “I’ve got bad news for you. I don’t know if the sulfonyl group is activating or deactivating.” For his synthesis, Figure 6.5, he acylated benzene, followed by sulfonation, and then reduced the ketone off of the hexyl chain. After he finished his synthesis, he realized he had drawn the para product instead of the *m*-product, so he crossed off the substituent and re-drew the product of *m*-hexylbenzenesulfonic acid. He explained his synthesis:

So if it’s deactivating, then that’s what I’m going to do. I don’t know if it ranks higher or lower than an acyl group. If it ranks lower, let’s assume for now ‘cause it’s got all those oxygens on it that it’s ranked lower than an acyl group. I’m gonna acylate it first, and then sulfonate it.

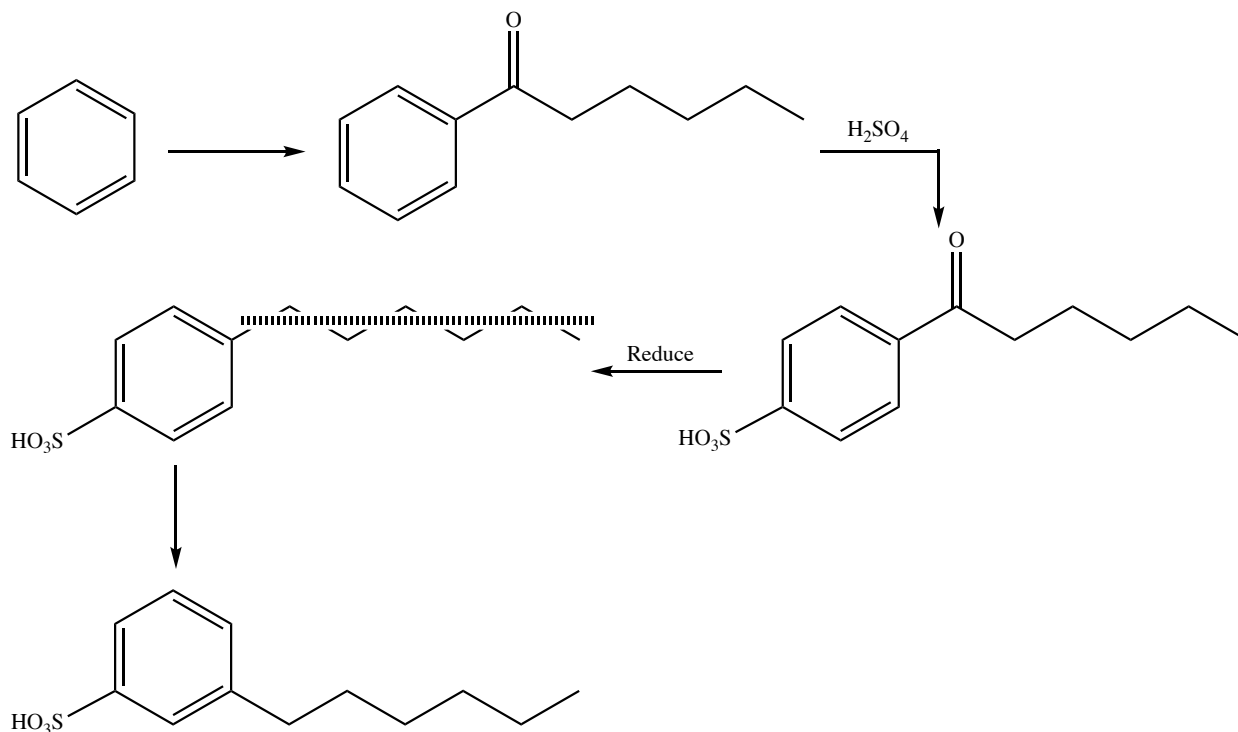


Figure 6.5. Dr. Kemper’s synthesis of *m*-hexylbenzenesulfonic acid from benzene.

Dr. Kemper’s synthesis was correct as it is consistent with the substituent effects. The ketone is a deactivating meta director, meaning the sulfonic acid would be at the meta position. His reasoning about the deactivating strength of a sulfonic acid substituent was also correct;

sulfonic acid was a stronger deactivator than a ketone due to the number of oxygens. Although he did not specify which reducing agents he would use, the reagents would need to be ones that would only reduce the ketone, and would not reduce the sulfonic acid substituent to a thiol.

6.2.2.4 Synthesis of 1,2-dichloro-4-nitrobenzene

For the synthesis of 1,2-dichloro-4-nitrobenzene from benzene, Dr. Kemper again proposed two mechanistic pathways. In the first mechanistic pathway, Figure 6.6, Dr. Kemper discussed yield:

Yield is another thing that I just give so very little thought to. I'm not giving thought to yield, because I think if you were going to chlorinate this thing twice, it would be just as likely to go para as ortho. So my yield is more likely to go para than ortho just because of the sterics. I'm going to chlorinate this thing twice, and I'll put them in the ortho position, and then I'll nitrate it.

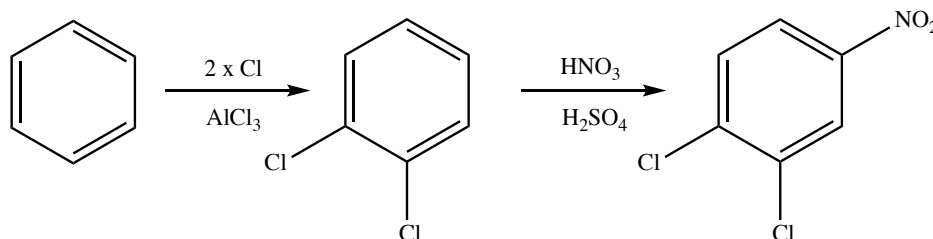


Figure 6.6. One of Dr. Kemper's syntheses of 1,2-dichloro-4-nitrobenzene.

He reconsidered this pathway and proposed another one, Figure 6.7. In this pathway, the same steps to produce *p*-chloroaniline seen in the first synthesis were drawn. From *p*-chloroaniline, the amino substituent was oxidized to form a nitro substituent, followed by another chlorination. He further added:

I got a bad feeling about this one because there's a whole class of reactions that I just don't think about until I'm ready to teach it. I'm going to write another solution on here. I don't think it's a good one because it's too many steps.

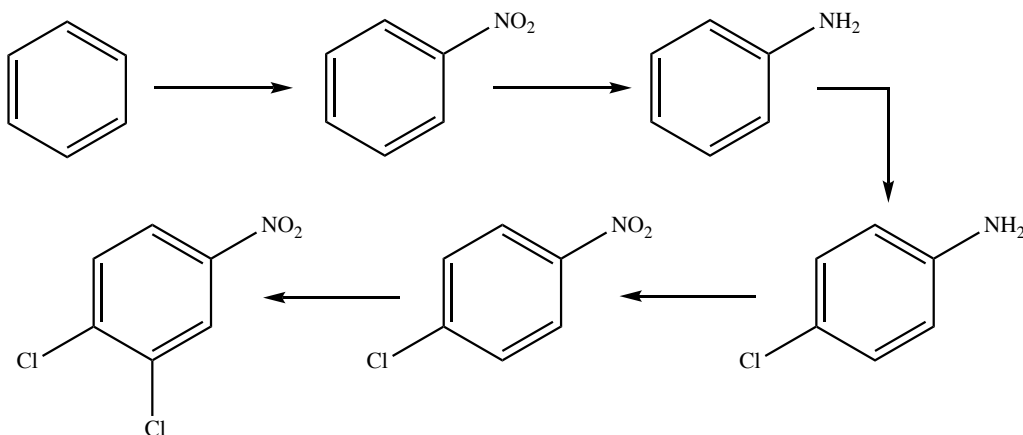


Figure 6.7. Another synthesis of 1,2-dichloro-4-nitrobenzene proposed by Dr. Kemper.

Synthetically, 1,2-dichloro-4-nitrobenzene is synthesized by chlorinating 4-chloronitrobenzene (Booth, 2012), meaning the last steps of his synthesis were correct. However, Dr. Kemper would run into the same issues from the first problem; it would be hard to stop the reaction after only one addition of chlorine on aniline.

6.2.2.5 Synthesis of 4-chloro-2-nitroaniline

For the synthesis of 4-chloro-2-nitroaniline from benzene, Dr. Kemper appeared to be more confident when he described his synthesis:

I would say that I would first of all nitrate, then reduce, then chlorinate. And then nitrate again. Yeah, I feel better about this one.

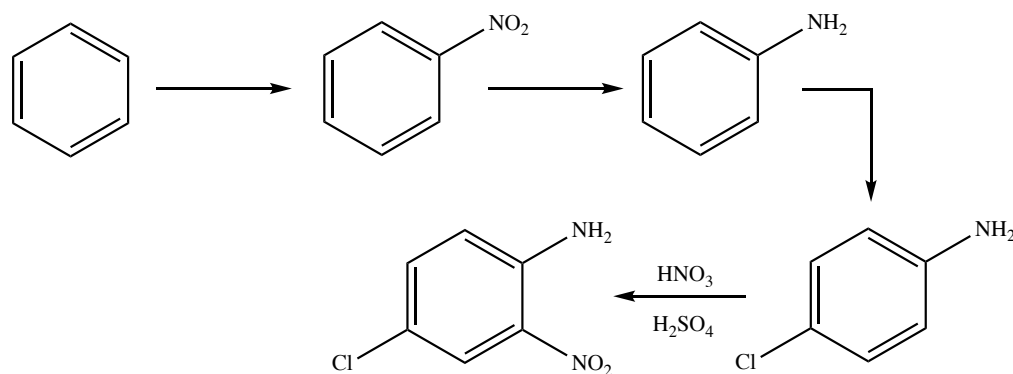


Figure 6.8. Dr. Kemper's synthesis of 4-chloro-2-nitroaniline from benzene.

Dr. Kemper reduced the nitro substituent to aniline, an ortho, para director. Although he did not mention that addition of the chlorine would occur at both of these sites, chlorine was bonded to the para position. Again, Dr. Kemper did not mention that based on the directing effects, the next substitution by a nitro group could bond to the 2- or 3- position. The chloro group and the amino group are both ortho, para directors. Although the activating strength of the amino group would favor the nitro group's addition at the 2-position, Dr. Kemper did not mention this during the synthesis.

6.2.3 TS-PCK of Dr. Kemper

Dr. Kemper briefly described some of the components of TS-PCK throughout the interview. One of the first points at the beginning of the synthesis problems that he made was about his Ph.D. being in physical chemistry and how that impacted his knowledge of organic chemistry. He made this comment when he described his synthesis of *p*-chloroaniline from benzene and was thinking aloud about the directing effects of chlorine and amino substituents:

And by the way, I'm not one hundred percent sure that I'm-, my Ph.D. is in P Chem. So I teach organic because I like it, not because I'm one hundred percent sure that's the right answer.

When asked to describe how his students would approach the synthesis of *m*-nitrotoluene from benzene, he stated:

I think my guess is that they nitrate first and then alkylate it, like my second method. Not really being concerned about the level of deactivation. We know it's deactivating, but does that mean it's going to kill it? I don't know. And that's the reason I have to take the blame for that, because I don't emphasize that. I don't think it's really important.

Dr. Kemper expressed his opinion that teaching the strengths of activators and deactivators as not being important concepts associated with EAS. He also defended his

shortcomings by declaring that his Ph.D. was not in organic chemistry and that he was teaching the course because he enjoyed it.

When Dr. Kemper explained how students would approach the synthesis of *p*-chloroaniline from benzene, he described the difficulty that students who memorized concepts in the course had with seeing the overall reaction and preemptive ability to break the overall reaction into individual steps.

In order to get aniline from [benzene], you have to have some foresight and you've got to know that you've got to go through [the reduction of nitrobenzene] that you've got to nitrate it first. One thing is, I think, a lack of foresight is the biggest problem. The lack of being able to rise up above the forest and look down and see what's going on, or rise up above the maze and get an understanding of the fact you know that you start in one position, you go to another place, and how are you going to get there, instead of seeing every individual reaction as the right answer. I would say the biggest problem is just students' inability to recognize that in order to get to Michigan we have to drive north.

When Dr. Kemper described his approaches to teaching activation/deactivation and the directing effects, he appeared uneasy with the question and asked that both questions be repeated or reworded, and asked, "Could you be more specific with the question?" or "Would you ask the question again?" The representations he used included mechanisms, resonance, and the Hammond postulate:

I teach it by showing the mechanisms of the activated complex. I emphasize the mechanisms very much at the beginning. I actually don't ask them to memorize a table. I don't give them the table, so they do ultimately have to know it. But we do it by [mechanisms] and the Hammond postulate which shows you where what groups are electron donating. I emphasize resonance and induction and emphasize how you might expect an oxygen or a nitrogen atom to be electron withdrawing, which it is via induction, but the resonance is so important here that it turns out to be an electron donator. So, you've got resonance and induction that are working against each other or in balance. I mean, I'd say they're in balance and the resonance wins in this case.

6.3 Case Study 3: Pedagogical Knowledge – Dr. Manson

6.3.1 Describing the Participant: Dr. Manson

Dr. Manson had a Ph.D. in chemical education and was an assistant professor with at most 2 years' experience teaching organic chemistry. He reported that his institution was Hispanic serving, meaning the institution's student population has more than 25% Hispanic or Latinos. The Carnegie classification of his institution is a Masters College and University with approximately 3000 students. He also reported that the institution has two to five chemistry graduates per year.

Dr. Manson taught an organic chemistry II course. He reported that his students were mostly biology majors, with some chemistry and exercise science majors. His class had approximately 20 students enrolled. His class met five times per week for a 50-minute lecture, in addition to one weekly laboratory class. Four exams were administered during the semester, with a weekly quiz. The quiz consisted only of open-ended questions, while the exams had a mix of multiple-choice and open-ended questions. Although he reported that his institution's chemistry programs were not ACS-approved, the ACS final exam was given at the end of organic chemistry I and organic chemistry II.

6.3.2 Pedagogical Knowledge

Dr. Manson used several modes of instruction to teach organic chemistry. These included lecturing, activities, and clicker questions. Dr. Manson did not elaborate on the details of the activities in his course. When probed about whether he used clicker questions to evaluate student understanding during class time, he talked about using other methods to assess how his students were doing with the material in the class, including taking advantage of a small class size to see how students are approaching activities or review-problems that were posed at the beginning of a new lecture:

When we do activities, I ship around the room and check on what they are doing. In lecture, I often pause and ask them questions. Or sometimes I start my class with “Let’s review what we did last time. Here is the reaction, draw me the products.” And I walk around and the class size allows that and I can see what they’re drawing through their eyes and get some ideas about where they are at.

Dr. Manson incorporated both student-centered and teacher-centered approaches when he taught concepts associated with EAS. The activities and questions he posed at the beginning of lecture would be considered student-centered since he asked students to complete a task while he watched how they solved the problem.

His teacher-center approaches included lecturing and providing students with the tables of information from the textbook on the substituent effects. He reported that he presented the material in lectures and wrote information on the board. He discussed how he gave students the tables from the textbook of the electron-donating and electron-withdrawing substituents:

I use the table from the textbook that tells which of the substituents are electron-donating, which are electron-withdrawing. Then I’ll talk about a mechanism. If I draw a mechanism, I would show why a particular resonance will be favored and the charge. That explains why some substituents are meta directing, some substituents are ortho, para directing. Sometimes, it’s worth exploring all of the possible substitution ways: ortho, meta, and para to see which of them will yield more resonance structures and better resonance structures.

One of the first questions of the interview protocol asked instructors to consider the molecular structure of aspirin (2-acetoxybenzoic acid), which was held up to the camera during the interview. They were asked what information they would hope their students would be able to tell them about this specific molecule. He talked about the example of aspirin, and how he could use that structure to teach his students how to reason through the preference of ortho versus para attack.

To decide between ortho and para, I think the example that you showed me [aspirin] will require them to do that. So I would bring molecular models and show them the big ester and how that rotates and prevents ortho attack.

However, Dr. Manson did not specify whether he allowed students to handle the models, or if they were used solely as a visual aid.

When asked to describe how he taught the substituent effects of activation and deactivation, Dr. Manson described implementing a combination of teacher-centered and student-centered approaches; he provided the list from the textbook to his students, but asked them to draw the mechanisms to apply the given information:

I give them the list of substituents, but they'll go through the mechanism. That's sometimes what I use to explain it.

Dr. Manson relied on several resources and teaching strategies to educate his students on concepts associated with EAS. As he mentioned above, he used the textbook as a resource to provide tables of the substituent effects. He also mentioned bringing in model kits to show how steric effects can direct where another substituent will bond on a benzene molecule. He linked these resources with lectures covering mechanisms and resonance structures to facilitate student understanding of EAS in his course.

6.3.3 TS-PCK of Dr. Manson

Dr. Manson discussed four of the five components of TS-PCK throughout the interview. Prior knowledge that he expected students to have before this unit included concepts with the deactivation of nitrobenzene, Friedel-Crafts reactions, oxidation/reduction reactions, and substituent protecting groups. When he described how his students would approach the synthesis of *p*-chloroaniline from benzene, he described the difficulty in adding a substituent to nitrobenzene:

If students get to the stage where you have nitrobenzene, they should then realize that it's almost impossible to put anything else there.

When he described how his students would approach the synthesis of *m*-nitrotoluene from benzene, he talked about how he specifically taught his students that it is difficult to stop a Friedel-

Crafts alkylation from adding more than one alkyl substituent to the ring and again mentioned that adding anything to a nitrobenzene would be challenging:

I think with my students, they would attempt to put the CH_3 group on the benzene right away. And there wouldn't be any good way to do that because I teach them that alkylation doesn't stop at one product, so to put methyl there they need to use some tricks. So that would be a challenge for them ... Or they would put the nitro group first and then try to alkylate the ring. But well, technically, it should give them the meta product, but the nitro group is deactivating. I tell them that once you have a nitro group there, it's very hard to put more substituents on there.

Dr. Manson also described the difficulty when students are asked to synthesize molecules using multiple reaction types. He described how his students would approach the synthesis of 4-chloro-2-nitroaniline:

I think what will kinda throw them a little bit is that you have an NH_2 group and an NO_2 group, so the most oxidized and the most reduced group on the ring at the same time. So that suggests that they will be put on at different stages of the synthesis, not at the same time. So if you have two nitro groups, you cannot selectively reduce one of them into an NH_2 . Or if you have two NH_2 groups, you cannot selectively oxidize one of them to an NO_2 group. That will be a challenge for them.

Dr. Manson talked about how his students should be able to link the knowledge they acquired in the laboratory and apply it to paper syntheses, specifically when thinking about protecting groups:

We have a lab where we nitrate acetanilide, and then cleave the amide group to get nitroaniline. They know that when you do that reaction in nitric acid, for example, you need to put the acetanilide group. So organic chemistry is about reactions you can do in the laboratory. And sometimes, I think the problem with solving paper chemistry and actually using those reactions in the lab can give them more practical experience.

When he talked about how his students would approach the synthesis of *p*-chloroaniline, his immediate response was, "they would not put any protectional groups" on the substituents.

Dr. Manson critiqued the choice in investigating such a specific topic in organic chemistry that he believed his students understood easily:

I think with electrophilic aromatic substitution, it more or less goes smoothly because it's somewhere in the beginning of the second semester. So they have fresh minds and they're ready to go ... It's kinda surprising that you chose this topic. I think it's isolated a little bit. The whole idea is that most of the stuff before that deals with just carbon chains and branches – more or less aliphatic products. And perhaps some cycles, then aromatics. But the whole idea with aromaticity, electrophilic aromatic substitution is only usually limited to that benzene. So we don't talk about triphenylmethyl ions or cyclopropenyl ions.

He described the limitation or “easiness” of EAS to the fact that benzene is the only aromatic compound used during the topic.

As discussed previously, Dr. Manson implemented several teaching strategies and representations when he discussed how he taught the topic of EAS. These included teacher-centered approaches including lectures covering mechanism and resonance structures. He also provided students with tables of the substituent effects from the textbook and models of molecules to show steric effects of substituents. Additionally, he implemented several student-centered approaches including activities and warm-up questions so he could evaluate student understanding of the material by directly engaging with the students as they completed these tasks.

6.4 Conclusions

These three cases highlighted one of the three general knowledge domains that teachers use to inform their TS-PCK. Dr. Gacy taught EAS in his first semester organic chemistry course and had a strong understanding of the students enrolled in his class, including their demographics and concepts that students find challenging. This included the curved-arrow formalism and acid/base chemistry in relation to mechanisms. Throughout the interview, he described multiple components of TS-PCK. He was aware of the prior knowledge that influenced student's abilities to solve synthesis problems using EAS, including Friedel-Crafts reactions concepts, resonance, and acid/base chemistry. He believed that if students were unaware that Friedel-Crafts reactions

produce a carbocation, then they would not consider any type of rearrangements to the most stable carbocation. Students who had a poor understanding of resonance would not recognize a lone pair contributing to the benzene pi system, making the substituent activating. Furthermore, students who had a weak grasp of acid/base concepts may use reagents that would protonate a basic amino substituent, rather than adding a new substituent to the molecule. He taught EAS through a teacher-center approach, providing students with a general Lewis structure of a substituent with a lone pair on it, and his intention was to provide students with the visual cues to reason about a substituent's effects. He acknowledged that students approached EAS from a puzzle perspective, just "bolting on the groups," with mechanistic reasoning being unnecessary. Dr. Gacy also recognized the level of complexity that is involved if a synthesis required students to consider multiple reaction types.

The five components of TS-PCK were identified following two studies that focused on the influence that SMK has on PCK (Davidowitz & Rollnick, 2011; Rollnick et al., 2008). The studies concluded that SMK played a significant role in an instructors' classroom practice and their presentations of the material. Instructors' with a strong understanding of the subject (strong SMK) were able to implement multiple conceptual teaching strategies and provide different representations to facilitate student understanding (Davidowitz & Rollnick, 2011). Dr. Kemper superficially described some of the components of TS-PCK throughout the interview, without much specificity. He made it clear that his Ph.D. was in physical chemistry, implying he was not necessarily an expert in organic chemistry. He was not confident with some of the syntheses, providing two synthetic pathways, unsure of which one would be right. Although he was aware of carbocation rearrangements occurring in Friedel-Crafts alkylations, shown in his use of Friedel-Crafts acylation in the synthesis of *m*-hexylbenzenesulfonic acid, he was unaware of one of the limitations of these reactions being they cannot occur on a highly deactivated nitrobenzene

(McMurray, 2004). Some of the final products in the synthesis were drawn with the substituents at the wrong positions, and he did not acknowledge that certain reactions would produce a mixture of products. His conceptual teaching strategies and representations consisted of mechanisms, resonance, and the Hammond postulate. He did not discuss specific prior knowledge that he expected his students to need to be successful using EAS in synthesis but expressed his opinion on the strengths of activators and deactivators as not important concepts that students should need.

Dr. Manson used student-centered and teacher-centered approaches when he lectured about concepts associated with EAS. He provided his students with opportunities to reflect on their learning by posing questions at the beginning of class. The small class size allowed him to roam throughout the room to evaluate his students' understanding of the material. He used several resources in combination to facilitate conceptual understanding of the material. He used information from the textbook, molecular models, activities, and clicker questions and reflected on his teaching strategies with the tasks of the interview. He discussed several components of TS-PCK throughout the interview. As previously mentioned, he used different representations of the material. Like Dr. Gacy, he recognized the level of complexity that is involved if a synthesis required students to consider multiple reaction types. He acknowledged that students should be able to utilize the knowledge they acquire in the laboratory as a tool for solving synthesis problems on paper. Dr. Manson believed that EAS is a topic that does not challenge his students, as it only includes benzene as the aromatic compound.

6.5 Limitations

There were a few limitations to this component of the study. These results emerged from the data analysis. Therefore, specific questions tailored to each of the three general knowledge domains were not posed to the instructors. Conclusions about the general knowledge domains and

components of TS-PCK for each of the cases were drawn from the interview transcripts, video recordings/observations, responses from the online questionnaire, and synthesis generated by the instructors. Furthermore, each instructor appeared to teach the unit of EAS at different time points in the semester: Dr. Gacy taught the unit in the first semester of organic, Dr. Kemper taught it in the middle of the second semester, and Dr. Manson taught it at the beginning of the second semester. Therefore, students' prior knowledge expectations would be different for each instructor with respect to organic chemistry concepts.

CHAPTER 7. CONCLUSIONS AND IMPLICATIONS

7.1 Conclusions About Student Understanding of EAS

One of the goals of this study was to describe how organic chemistry students reason through EAS synthesis problems and to identify gaps in understanding that inhibit students from successfully solving these types of problems. Several conclusions regarding student approaches to solving EAS synthesis problems and gaps in understanding are described below from the findings of this study.

One of the most important aspects of synthesizing molecules using EAS is understanding and applying the directing and activating/ deactivating effects of different substituents. While most students were able to identify the directing effects of a substituent, they were unable to provide mechanistic reasoning for *why* a substituent had that effect. This shows that students are relying on memorizing the concepts associated with EAS without deep understanding. Student memorization without understanding in organic chemistry has been well documented (Anderson & Bodner, 2008; Grove & Bretz, 2012, 2010; Pursell, 2009), and the findings from this study are consistent with these studies. It would be beneficial for instructors to include assessment questions in which students need to justify how a substituent activates or deactivates the benzene ring, or why a substituent has the directing effect(s) that it does, rather than simply identifying the substituent effect. Additionally, rather than relying on the symbolic notation to teach the substituent effects, instructors may find it beneficial to implement electrostatic potential maps (EPMs), described below, into their teaching as a visual reference to help students understand the electronic effects that these substituents have on the benzene ring.

Odyssey Molecular Explorer, a computer software program produced by Wavefunction, Inc., can be used as a molecular visualization tool. This software allows students to build molecules

and produce the EPMs on electron density isosurfaces. Examples of how instructors can use these representations to supplement student understanding of the substituent effects can be found in Appendix I. These activities were exported from the *Odyssey Molecular Explorer* software used in conjunction with the *Chemistry: Human Activity, Chemical Reactivity* textbook (Mahaffy et al., 2015). Following the generation of the EPMs, students would be able to rotate the 3-D models in space to see the distribution of electron-poor (blue) and electron-rich (red) regions. Neutral regions are represented by the color green. Charge distributions are represented with differing intensities of the colors described above. This program would allow students to get a “feel” for how the substituents affect the electron density (activation/deactivation) of the aromatic ring with a visual representation. They would be able to compare different activating and deactivating substituents. They would also be able to visualize how different substituents can stabilize the carbocation intermediate by decreasing the accumulation of positive charge in different positions on the ring (directing effects). Comparing the color intensities of the charge distributions may be subjective to the individual. This program also allows students to select specific atoms in an aromatic structure and shows the calculated atomic charge using quantum theory. In this way, the positive (or negative) charge on various carbon atoms could be compared directly. This valuable tool could be used to help students develop a deeper, more intuitive understanding of the substituent effects rather than simply memorizing these effects.

Another important aspect of learning organic chemistry, in general, is being able to apply the knowledge of the outcomes of numerous reactions and their reagents and conditions taught in the course to solving synthesis problems. Students appeared to focus on the topic of the study, EAS, in which an electrophile is usually involved, and failed to remember reactions covered previously, such as redox reactions. For example, only one student out of eleven remembered that

an amino substituent can be produced from the reduction of a nitro substituent. Several students tried to generate the amino electrophile (NH_2^+) with various reagents such as hydroxide and ammonia to react with benzene directly to produce aniline. This is an example of students failing to develop an integrated knowledge of chemical transformations in organic chemistry beyond the topic they are currently learning.

In addition to the challenge of reducing nitrobenzene, students also struggled with remembering the mechanism and reagents of the Friedel-Crafts reactions to add alkyl substituents to benzene. Only four of the eleven students remembered the necessary reagents for these reactions. However, none of the participants chose to use Friedel-Crafts acylation conditions, even though the hexyl substituent in *m*-hexylbenzenesulfonic acid was bonded to benzene at the primary carbon. This suggests that students did not recall that a carbocation rearrangement would occur. Furthermore, the limitations of both Friedel-Crafts alkylation and Friedel-Crafts acylation were difficult for students to remember. It is difficult to stop Friedel-Crafts alkylation after one addition, resulting in polyalkylation of the benzene. Additionally, Friedel-Crafts alkylation and acylation reactions will not occur on a nitrobenzene. Out of the four students that remembered these constraints, three of them described the alkylation of nitrobenzene without considering how deactivated the nitro groups makes the benzene ring. These students had been explicitly instructed about Friedel-Crafts reactions not working on nitrobenzene. The other student who was able to recall the correct reagents, incorrectly nitrated toluene to synthesize *m*-nitrotoluene. This would actually yield *o*-nitrotoluene and *p*-nitrotoluene. Additionally, neither of the four participants mentioned the need to stop the reaction after one alkylation. It may be beneficial to remind students that EAS is just another set of reactions that they can use for synthesis, and that reactions learned

previously can still be useful. When designing synthesis problems instructors should consider the number of steps and types of reactions required to complete a synthesis problem.

Several gaps in student understanding emerged in the data, including difficulties with concepts of Lewis structures and resonance – two topics taught in general chemistry. Students entering organic chemistry with a poor understanding of Lewis structures clearly have difficulty drawing the structures of reagents (e.g., NO_2^+) needed in mechanisms. For example, Kayden was unable to provide a mechanism synthesizing meta-hexylbenzenesulfonic acid from benzene because he could not draw the Lewis structures of sulfuric acid or sulfur trioxide.

Emery did not recognize the equivalence of resonance structures as indicated when he thought his answer to a synthesis problem was incorrect when the double bonds did not match the ones drawn in his original structure. The structures were resonance hybrids, but Emery believed his answer was wrong. Instructors need to be aware that these underdeveloped understandings are still prevalent in students about to complete the course. Cooper et al. (2010) suggested that the ability to see equivalent and non-equivalent resonance structures should be practiced regularly throughout the course to further develop competence with drawing Lewis structures. Instructors could create assessment questions that focus on Lewis structures and resonance structures, especially when teaching EAS since the non-equivalence in energy of certain resonance structures explains the directing effects of substituents.

7.2 Conclusions on Instructor's Perceptions of Student Understanding of EAS

In order to describe how organic chemistry instructors perceived their students' reasoning of EAS synthesis problems, instructors were asked to synthesize molecules using EAS from the perspective of their students. Instructors were asked to predict where students would struggle, what steps in the synthesis would be challenging for their students, and to specify concepts that would

impede their students from successfully solving these types of problems. While there was some overlap with instructor's perceptions of student reasoning and the reasoning students in this study actually demonstrated, there was also some misalignment with their perceptions.

Instructors in this study were well aware that their students used memorization as a learning strategy in their courses but they were unaware of how to demonstrate the need for a deep understanding. Furthermore, some instructors believed that EAS was a topic that can be easily memorized, without needing to understand the factors responsible for substituent effects. It would be beneficial to create assessment questions that require students to justify their reasoning about the substituent effects. These questions could also elicit student's understanding of Lewis structures, mechanistic reasoning, and resonance structures. In addition to creating a variety of assessment questions, instructors may find the implementation of electrostatic potential maps that were described above. Teaching the substituent effect solely through symbolic notation does not give students the opportunity to visualize what the effects are actually doing to the electron cloud around the benzene and substituents.

There were a few gaps in how instructors perceived their student's reasoning through EAS synthesis problems and the reasoning that the students were actually using. Instructors believed that students would only focus on the directing effects of the substituents, and ignore the deactivation and activation effects of those substituents. However, students in this study did consider both substituent effects in their reasoning while solving synthesis problems using EAS. Instructors also did not think their students would acknowledge multiple products forming in a reaction. While instructors believed their students would only focus on the intermediates that led to the desired products, students did verbalize and draw multiple products in their syntheses without being prompted to do so. Dr. Manson was the only instructor who commented on students

needing to be able to connect the knowledge they acquired in the laboratory to paper syntheses. He also stated that laboratory experiments “can give them more practical experience.” Although the students in this study did not use any protection groups on the substituents during their syntheses, they did show a transfer of skills acquired in the laboratory when they discussed separation techniques to isolate a molecule out of a mixture of substances.

The teaching of the subtleties of Friedel-Crafts reactions were discussed extensively with the instructors in this study. Six of the eight instructors mentioned Friedel-Crafts reactions and the difficulties they expected students would have with understanding the synthetic challenges in these reactions. However, none of the instructors mentioned that their students would not even remember what these reactions and necessary reagents were, nor did they predict other routes students would use to add an alkyl substituent to benzene. Only four of the eleven students were able to remember Friedel-Crafts alkylation reactions and the reagents needed in those reactions. The seven other students either could not remember the necessary reagents to produce a carbocation or propose synthetic routes that used neutral carbon chains. Instructors did mention the possibility of their students not remembering that carbocation rearrangements can occur with Friedel-Crafts alkylation. None of the four students that remembered Friedel-Crafts reactions used Friedel-Crafts acylation to prevent a carbocation rearrangement. There appeared to be some confusion with how textbooks and instructors emphasize the deactivating effect of the nitro group in nitrobenzene in Friedel-Crafts reactions. As Dr. Bundy had mentioned, you may be able to add one other substituent to nitrobenzene; however, it is not going to be with Friedel-Crafts reaction conditions. Three of the four students used Friedel-Crafts alkylation to methylate nitrobenzene to synthesize *m*-nitrotoluene, without realizing the reaction would not occur.

Synthesis problems have an inherent cognitive challenge with working memory overload (Johnstone, 1991) as students need to identify the types of reactions required to manipulate the starting molecule to a final product, recall the appropriate reagents, and recall or reason through the mechanism that will complete the transformation. These skills can be developed and the working-memory overload less burdensome through explicit instruction on complex tasks such as synthesis. Rather than approaching each topic as its own entity and then moving on to the next topic, instructors should be incorporating synthesis problems throughout the course that will utilize current and past reaction reagents. This would give students the opportunity to recall reactions previously taught in the course and the application of those reactions in new contexts. Implementing cumulative synthesis problems could help students recall reagents they had learned in the beginning of the course and appropriately use those reagents to for a given transformation.

As discussed previously, students showed gaps in understanding with concepts of Lewis structures and resonance. Only one instructor talked about his students entering organic chemistry with a poor understanding of how to draw Lewis structures, specifically the difficulty his students have with drawing the Lewis structure of sulfuric acid. In this study, Kayden was unable to provide the mechanism due to his inability to draw the Lewis structure of sulfuric acid or sulfur trioxide. Although instructors are not assessing Lewis structure representations through the topic of EAS, the inability to draw Lewis structures of the reagents used during this topic affects students mechanistic reasoning. As described above, continuous practicing opportunities should be provided throughout the course to further develop competence with drawing Lewis structures and the ability to evaluate equivalent and non-equivalent resonance structures.

Only one instructor, Dr. Raider, expressed his concerns with students having difficulty understanding what resonance means, and the ability to apply that knowledge to predict percent

compositions of a mixture of products. Dr. Bundy and Dr. Gacy described how their students would use their understanding of resonance structures to predict the substituent effects. However, students cannot use their understanding of resonance structures and the implicit information that can be obtained from these structures if they have not fully understood the underlying concepts. As discussed previously, Emery did not know how to “move” the electrons on paper so that his two structures would be equivalent with the exact location of the electrons. Although he had mentioned that he knew the double bonds could “move around freely,” he ultimately concluded his answer to be incorrect. It is important for instructors to know that although students have been learning different concepts associated with resonance throughout general chemistry and the first semester of organic chemistry, some students do not have a complete understanding of the term before encountering the EAS topic. It may be beneficial for instructors to incorporate and present the electrostatic potential maps of different substituted benzenes, as this will give students a visual representation of how an activating substituent effects the electron distribution in the benzene ring.

7.3 Conclusions on Topic-Specific Pedagogical Content Knowledge

The last component of this study was to describe how the three general knowledge domains (KoS, SMK, and PK) of TS-PCK were reflected in organic chemistry instructors in their teaching of EAS. A case study approach was used to highlight the characteristics of TS-PCK observed in three organic chemistry instructors, in each case with respect to one of the three general knowledge domains. Several conclusions regarding the characteristics of these components in the TS-PCK model can be drawn from the findings of this study.

Dr. Gacy had a reasonably accurate understanding of the students enrolled in his class, with respect to their demographics and concepts that students would find challenging. Multiple components of TS-PCK were discussed throughout the interview. He was aware of the prior

knowledge that influenced student's abilities to solve synthesis problems using EAS, including concepts associated with Friedel-Crafts reactions, resonance, and acid/base chemistry. Students would need to recall the carbocation rearrangements that can occur with Friedel-Crafts alkylation reactions and that nitrobenzene is too deactivated for Friedel-Crafts reactions to work on. Students would need to have an understanding of resonance structures, and how that affects the directing effects of substituents. Furthermore, students would need to recall the basic nature of an amino substituent, and how that could affect the order of addition of the substituents. He taught EAS through a teacher-centered approach, providing students with a general Lewis structure of a substituent with a lone pair on it, and his intention was to provide students with the visual cues to reason about a substituent's effects. Providing students with the electrostatic potential maps of these molecules could give students another visual representation that they could reference. He acknowledged that students approached EAS from a puzzle perspective, just "bolting on the groups," with mechanistic reasoning being unnecessary. He also recognized the level of complexity that is involved if a synthesis required students to consider multiple reaction types. Dr. Gacy had a strong *knowledge of students*, and components of his TS-PCK were frequently expressed throughout the interview.

The five components of TS-PCK were refined after the conclusion of two studies where researchers investigated the influence that SMK has on PCK (Davidowitz & Rollnick, 2011; Rollnick et al., 2008). Rollnick et al. (2008) concluded that SMK played a significant role in an instructors' classroom practice and their presentations of the material. Instructors with a strong SMK were able to implement multiple conceptual teaching strategies and provide different representations to facilitate student understanding. During the interview with Dr. Kemper, he specifically stated that his Ph.D. was in physical chemistry, implying he was not necessarily an

expert in organic chemistry or with the material. This was seen in his syntheses when he would provide two mechanistic pathways, and admitting to not knowing which one would be correct. Components of TS-PCK were superficially described throughout the interview, without much specificity, concluding that poor subject matter knowledge directly impacted the components of TS-PCK throughout the discussion of the organic chemistry tasks.

Dr. Manson had a thorough understanding of *pedagogical knowledge*. He obtained his Ph.D. in chemical education and he used student-centered and teacher-centered approaches when he lectured about concepts associated with EAS. He provided his students with opportunities to reflect on their learning by posing questions in the beginning of class. The small class size allowed him to roam throughout the room to evaluate his students' understanding of the material. He used several resources in combination to facilitate conceptual understanding of the material. He used the tables of substituent effects from the textbook, physical molecular models, activities, and clicker questions. He did not specify what the details of the activities he implemented were. He also reflected on his teaching strategies with the tasks of the interview. Several components of TS-PCK were discussed throughout the interview. The addition of incorporating EPMs as another representation to convey the substituent effects would further increase his TS-PCK.

The use of TS-PCK as a framework for this study helped to show the relationship between the three general knowledge domains that instructors use to inform their TS-PCK. Dr. Gacy and Dr. Manson showed several characteristics of a thorough understanding of their students and pedagogical knowledge respectively. Throughout the interviews, they were more likely to discuss topics regarding their TS-PCK, including their use of multiple representations, conceptual teaching strategies, and student's prior knowledge. Dr. Kemper admitted and demonstrated his inadequate subject matter knowledge in respect to EAS, and did not discuss many of the components of TS-

PCK throughout the interview. The few components that were mentioned, were done so superficially, without leading to a more in-depth discussion. It can be concluded that the knowledge of the three general knowledge domains influences the appearance of one's TS-PCK.

7.4 Implications for Future Research

This study described how students reasoned through synthesis problems using EAS and revealed gaps in understanding of concepts encountered in general chemistry. Additionally, instructor's perceptions of their students' reasoning through these types of problems was described. The methods of this study could be used to evaluate other topics in organic chemistry from the student and instructor perspectives. Two of the instructors in this study mentioned the topic of EAS to be an easier topic for their students to learn, and that there would be other more interesting topics to investigate student understanding of. Carbonyl chemistry is another topic that can be taught towards the end of the second semester in the United States. Creating synthesis problems around carbonyls and carbonyl derivatives could elucidate further misunderstandings with acid/base chemistry and oxidation/reduction concepts. It may be worth investigating how students reason about the different types of reactions that are most likely to occur with a carbonyl: (1) nucleophilic addition at the carbonyl carbon, (2) whether the lone pair on the oxygen will bond to an electrophile, or (3) an enolate could be formed from the deprotonation on a carbon adjacent to the carbonyl group.

One instructor in this study mentioned that his students are given a reference sheet that lists the reagents that they have learned or will learn during the course. The sheet provides the different reagents over a reaction arrow. Students are allowed to use this during their exams and quizzes. It could be worth investigating how these students are evaluating which reagents are necessary for a

reaction, especially during synthesis problems since they will need to *apply* the reagents mechanistically for the given reactions.

As mentioned previously, the use of electrostatic potential maps could further benefit student understanding of different topics in organic chemistry. Electrostatic potential maps give students a visual map of the electron densities in a molecule, and quantum-calculated atomic charges could be compared. A study could be developed to evaluate student understanding of electrophiles and nucleophiles and the effect that electrostatic potential maps have on their understanding. Giving students a visual representation of the electron-deficient or electron-rich sites of a molecule could help them identify patterns for these descriptions. Additionally, electrostatic potential maps could be used to help students develop a deeper understanding of the meaning of a substituent activating or deactivating the benzene ring, as they would see the changes in electron distribution around the ring.

This study also described the characteristics of the TS-PCK model in organic chemistry instructors, and how the three GKDs influenced those characteristics. The results of this portion of the study emerged from the data. A protocol could be developed to specifically target the five components of TS-PCK and the three GKDs to further define the influence of the GKDs on one's TS-PCK. Furthermore, topics other than EAS could be evaluated for the instructors.

APPENDIX A. IRB APPROVAL FOR STUDENT INTERVIEWS



HUMAN RESEARCH PROTECTION PROGRAM
INSTITUTIONAL REVIEW BOARDS

To:	ROY TASKER BRWN
From:	JEANNIE DICLEMENTI, Chair Social Science IRB
Date:	01/24/2017
Committee Action:	Expedited Approval for Renewal - Category(7)
IRB Approval Date	01/24/2017
IRB Protocol #	1611018419
Renewal Version	
Study Title	Student Understanding in Organic Chemistry
Expiration Date	01/23/2018
Subjects Approved:	30

The above-referenced protocol has been approved by the Purdue IRB. This approval permits the recruitment of subjects up to the number indicated on the application and the conduct of the research as it is approved.

The IRB approved and dated consent, assent, and information form(s) for this protocol are in the Attachments section of this protocol in CoeusLite. Subjects who sign a consent form must be given a signed copy to take home with them. Information forms should not be signed.

Record Keeping: The PI is responsible for keeping all regulated documents, including IRB correspondence such as this letter, approved study documents, and signed consent forms for at least three (3) years following protocol closure for audit purposes. Documents regulated by HIPAA, such as Authorizations, must be maintained for six (6) years. If the PI leaves Purdue during this time, a copy of the regulatory file must be left with a designated records custodian, and the identity of this custodian must be communicated to the IRB.

Change of Institutions: If the PI leaves Purdue, the study must be closed or the PI must be replaced on the study through the Amendment process. If the PI wants to transfer the study to another institution, please contact the IRB to make arrangements for the transfer.

Changes to the approved protocol: A change to any aspect of this protocol must be approved by the IRB before it is implemented, except when necessary to eliminate apparent immediate hazards to the subject. In such situations, the IRB should be notified immediately. To request a change, submit an Amendment to the IRB through CoeusLite.

Continuing Review/Study Closure: No human subject research may be conducted without IRB approval. IRB approval for this study expires on the expiration date set out above. The study must be close or re-reviewed (aka continuing review) and approved by the IRB before the expiration date passes. Both Continuing Review and Closure may be requested through CoeusLite.

Unanticipated Problems/Adverse Events: Unanticipated problems involving risks to subjects or others, serious adverse events, and serious noncompliance with the approved protocol must be reported to the IRB immediately through CoeusLite. All other adverse events and minor protocol deviations should be reported at the time of Continuing Review.

APPENDIX B. ONLINE QUESTIONNAIRE

Qualtrics Questionnaire for Participant Qualification

Q1 How many years have you been teaching organic chemistry?

- ☐ 0-2 years
- ☐ 2-5 years
- ☐ 5-10 years
- ☐ 10+ years

Q2 What area is your Ph.D. in?

- ☐ Organic chemistry
- ☐ Physical chemistry
- ☐ Analytical chemistry
- ☐ Inorganic chemistry
- ☐ Biochemistry
- ☐ Other (Please Specify) _____

Q3 How would you characterize the institution from which you received your doctorate? (small private college, large public university, etc.)

Q4 How would you characterize the institution in which you are currently teaching?

Q5 What types of organic chemistry classes have you taught? (Select all that apply.)

- ☐ Undergraduate
- ☐ Graduate
- ☐ Majors
- ☐ Non-majors
- ☐ Honors

Q6 What type of organic chemistry class have you most recently taught and/or are presently teaching?

- ☐ Undergraduate
- ☐ Graduate
- ☐ Majors
- ☐ Non-majors
- ☐ Honors

Q7 What organic chemistry textbook are you currently using in the courses you teach?

Q8 What topics from general chemistry do you end up reviewing/re-teaching because of student misunderstandings or weak grasp of the topic?

Q9 Which organic chemistry topics seem to be the most difficult for students to grasp?

Q10 What chemistry misconceptions, specifically organic chemistry related, have you encountered?

Q11 Do you cover electrophilic aromatic substitution reactions in your curriculum?

- ☐ Yes
- ☐ No

Q12 Which topics relating to electrophilic aromatic substitution reactions do you cover in this unit?

(Check all that apply.)

- ☐ Mechanisms
- ☐ Mono-substituted aromatics
- ☐ Di-substituted aromatics
- ☐ Tri-substituted aromatics
- ☐ Substituent directing effects
- ☐ Benzene activation/deactivation
- ☐ Other (Please Specify) _____

Q13 Would you be willing to participate in an in-person (or Skype) interview lasting no more than one hour?

- ☐ Yes
- ☐ No

Q14 Preferred method of contact (to set-up interview):

- ☐ Email _____
- ☐ Phone _____
- ☐ Skype _____

APPENDIX C. IRB APPROVAL FOR INSTRUCTOR INTERVIEWS



HUMAN RESEARCH PROTECTION PROGRAM
INSTITUTIONAL REVIEW BOARDS

To:	ROY TASKER BRWN
From:	JEANNIE DICLEMENTI, Chair Social Science IRB
Date:	04/26/2016
Committee Action:	Expedited Approval for Renewal - Category(7)
IRB Approval Date	04/26/2016
IRB Protocol #	1603017341
Renewal Version	
Study Title	Organic Chemistry Faculty Perspectives of Student Misconceptions
Expiration Date	04/25/2017
Subjects Approved:	30

The above-referenced protocol has been approved by the Purdue IRB. This approval permits the recruitment of subjects up to the number indicated on the application and the conduct of the research as it is approved.

The IRB approved and dated consent, assent, and information form(s) for this protocol are in the Attachments section of this protocol in CoeusLite. Subjects who sign a consent form must be given a signed copy to take home with them. Information forms should not be signed.

Record Keeping: The PI is responsible for keeping all regulated documents, including IRB correspondence such as this letter, approved study documents, and signed consent forms for at least three (3) years following protocol closure for audit purposes. Documents regulated by HIPAA, such as Authorizations, must be maintained for six (6) years. If the PI leaves Purdue during this time, a copy of the regulatory file must be left with a designated records custodian, and the identity of this custodian must be communicated to the IRB.

Change of Institutions: If the PI leaves Purdue, the study must be closed or the PI must be replaced on the study through the Amendment process. If the PI wants to transfer the study to another institution, please contact the IRB to make arrangements for the transfer.

Changes to the approved protocol: A change to any aspect of this protocol must be approved by the IRB before it is implemented, except when necessary to eliminate apparent immediate hazards to the subject. In such situations, the IRB should be notified immediately. To request a change, submit an Amendment to the IRB through CoeusLite.

Continuing Review/Study Closure: No human subject research may be conducted without IRB approval. IRB approval for this study expires on the expiration date set out above. The study must be close or re-reviewed (aka continuing review) and approved by the IRB before the expiration date passes. Both Continuing Review and Closure may be requested through CoeusLite.

Unanticipated Problems/Adverse Events: Unanticipated problems involving risks to subjects or others, serious adverse events, and serious noncompliance with the approved protocol must be reported to the IRB immediately through CoeusLite. All other adverse events and minor protocol deviations should be reported at the time of Continuing Review.

APPENDIX D. STUDENT CONSENT FORM

Purdue IRB Protocol #: 1611018419 - Expires: 18-JAN-2019

RESEARCH PARTICIPANT CONSENT FORM

Students' Approach to Solving Electrophilic Aromatic Substitution Reaction Problems

Roy Tasker, PhD
Department of Chemistry
Purdue University

Purpose of Research

The purpose of this project is to identify how students enrolled in CHM 26605 approach solving electrophilic aromatic substitution reaction problems.

Specific Procedures

You will be asked to participate in a semi-structured interview that is estimated to take 45-60 minutes. The interview will be audio recorded.

Risks

All research carries risk. The standard for minimum risk is that which is found in everyday life. Breach of confidentiality is a risk related to this type of research, but safeguards have been put in place to mitigate this risk. These are described in the confidentiality section of the consent form.

Benefits

There are no direct benefits to the subject. However, by participating in this study you may become aware of concepts/topics that you to review before the next exam.

Compensation

Subjects will receive a \$20 gift card to the PMU for participating in this study.

Confidentiality

There is a small risk regarding the confidentiality of your identity. The researcher will take the following steps to minimize this risk:

- 1) Participants will be assigned pseudonyms. These pseudonyms will be used in all presentations and papers that result from this study.
- 2) Only authorized research personnel will have access to data from this project.
- 3) Audio recording will be transcribed. Electronic data will be stored on a password-protected computer at Purdue University and paper data will be stored in a locked room in a locked cabinet at Purdue University.
- 4) The video and audio recordings of interviews will be deleted after a period of 5 years. Electronic and paper interview transcripts will be kept indefinitely and stored

The project's research records may be reviewed by departments at Purdue University responsible for regulatory and research oversight.

Purdue IRB Protocol #: 1611018419 - Expires: 18-JAN-2019

Voluntary Nature of Participation

Your participation in this study is voluntary. You may choose not to participate or, if you agree to participate, you can withdraw your participation at any time without penalty or loss of benefits to which you are otherwise entitled.

Contact Information

If you have questions, comments or concerns about this research project, you can talk to one of the researchers. Please contact Roy Tasker (rtasker@purdue.edu), (765) 496-3055.

If you have questions about your rights while taking part in the study or have concerns about the treatment of research participants, please call the Human Research Protection Program at (765) 494-5942, email (irb@purdue.edu) or write to:

Human Research Protection Program - Purdue University
Ernest C. Young Hall, Room 1032
155 S. Grant St.,
West Lafayette, IN 47907-2114

Documentation of Informed Consent

I have had the opportunity to read this consent form and have the research study explained. I have had the opportunity to ask questions about the research study, and my questions have been answered. I am prepared to participate in the research study described above. I will be offered a copy of this consent form after I sign it.

_____	_____
Participant's Signature	Date

Participant's Name	
_____	_____
Researcher's Signature	Date

APPENDIX E. INSTRUCTOR CONSENT FORM

Purdue IRB Protocol #: 1603017341 - Expires: 03-APR-2019

For IRB Use Only

TEACHER CONSENT FORM

Organic Chemistry Faculty Perspectives on Student Misconceptions
about Electrophilic Aromatic Substitution
Roy Tasker, PhD
Department of Chemistry
Purdue University

Purpose of Research

The purpose of this project is to identify organic chemistry teachers' perspectives on the nature of college-level student misconceptions in organic chemistry in their courses.

Specific Procedures

You will be asked to:

- 1) Complete a survey on your background/demographics and perspectives of teaching organic chemistry in your classroom. The estimated time to complete this survey thoughtfully is 10 minutes.
- 2) Participate in a semi-structured interview that is estimated to take 45-60 minutes. If you are unable to do a face-to-face interview, then a Skype interview will be scheduled at your convenience. The interview will be video and audio recorded.

Risks

All research carries risk. The standard for minimum risk is that which is found in everyday life. Breach of confidentiality is a risk related to this type of research, but safeguards have been put in place to mitigate this risk. These are described in the confidentiality section of the consent form.

Benefits

There are no direct benefits to the subject. However, by identifying your perceptions of student misconceptions, you may be able to reflect on your own involvement in student learning, and identify where students struggle/where their misconceptions arise. This may lead to an increase in your PCK.

Compensation

There is no compensation for participating in this study.

Confidentiality

There is a small risk regarding the confidentiality of your identity. The researcher will take the following steps to minimize this risk:

Purdue IRB Protocol #: 1603017341 - Expires: 03-APR-2019

- 1) Participating teachers will be assigned pseudonyms. These pseudonyms will be used in all presentations and papers that result from this study.
- 2) Only authorized research personnel will have access to data from this project.
- 3) Audio recording will be transcribed. Electronic data will be stored on a password-protected computer at Purdue University and paper data will be stored in a locked room in a locked cabinet at Purdue University.
- 4) The video and audio recordings of interviews will be deleted after a period of 5 years. Electronic and paper interview transcripts will be kept indefinitely and stored in a locked cabinet at Purdue University. The data will not be used for future purposes.

The project's research records may be reviewed by departments at Purdue University responsible for regulatory and research oversight.

Voluntary Nature of Participation

Your participation in this study is voluntary. You may choose not to participate or, if you agree to participate, you can withdraw your participation at any time without penalty or loss of benefits to which you are otherwise entitled.

Contact Information

If you have questions, comments or concerns about this research project, you can talk to one of the researchers. Please contact Roy Tasker (rtasker@purdue.edu), (765) 496-3055.

If you have questions about your rights while taking part in the study or have concerns about the treatment of research participants, please call the Human Research Protection Program at (765) 494-5942, email (irb@purdue.edu) or write to:

Human Research Protection Program - Purdue University
Ernest C. Young Hall, Room 1032
155 S. Grant St.,
West Lafayette, IN 47907-2114

Documentation of Informed Consent

I have had the opportunity to read this consent form and have the research study explained. I have had the opportunity to ask questions about the research study, and my questions have been answered. I am prepared to participate in the research study described above. I will be offered a copy of this consent form after I sign it.

Participant's Signature

Date

Participant's Name

Researcher's Signature

Date

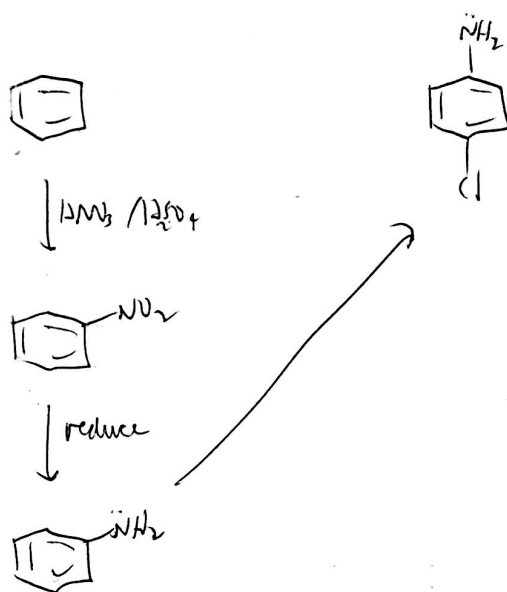
APPENDIX F. STUDENT CODES AND DEFINITIONS

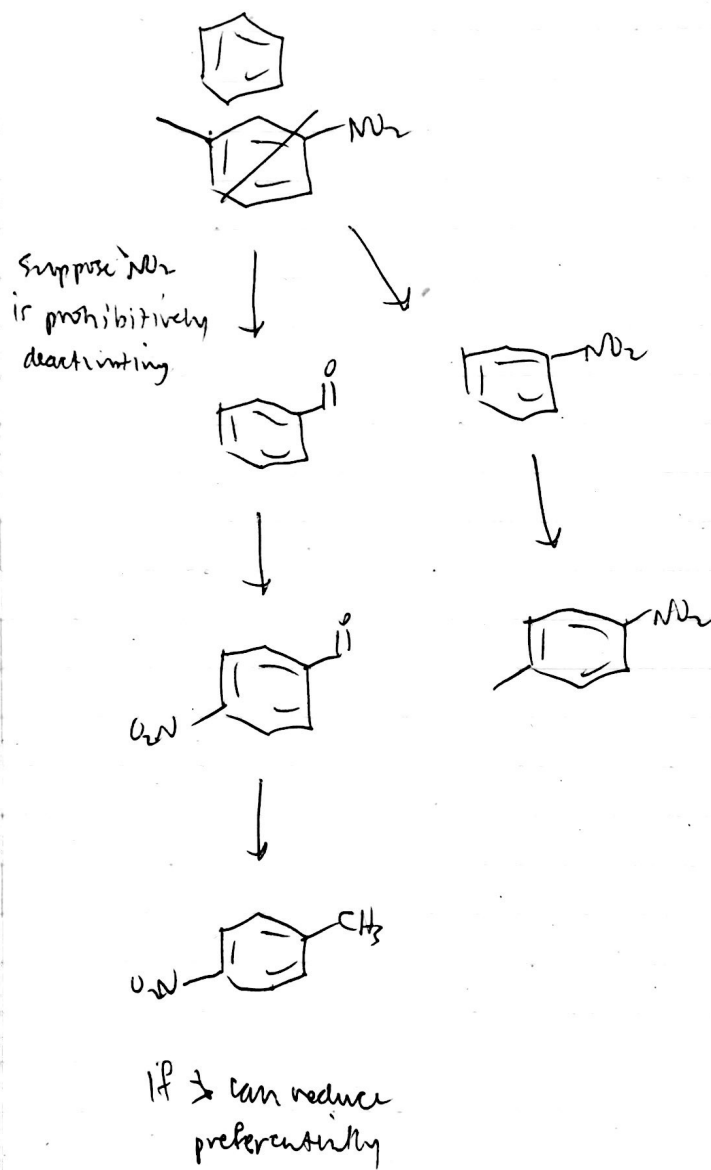
Student Codes	Definition
Equivalents	Participants make a statement about the amount of a substance that reacts with to an arbitrary amount of another substance in a given chemical reaction.
Memorization	Participants make a statement about relying on memorization of topics associated with organic chemistry to solve EAS synthesis problems.
Misappropriated Knowledge	Participants have a logical and false belief that a known piece of knowledge influences another piece of information. This can include alternative conceptions of chemistry topics.
Multiple Products	Participants make a statement acknowledging additional products formed in a reaction or yield probabilities.
Resonance	Participants make a statement about using resonance to acknowledge the formation of multiple products in a reaction.
References Prior Knowledge	Participants make a statement about using prior knowledge to complete EAS synthesis problems.
Substituent Effects	Participants describe the nature of substituents already present on the benzene ring affecting the reactivity of benzene or that they determine the position of a subsequent substituent.

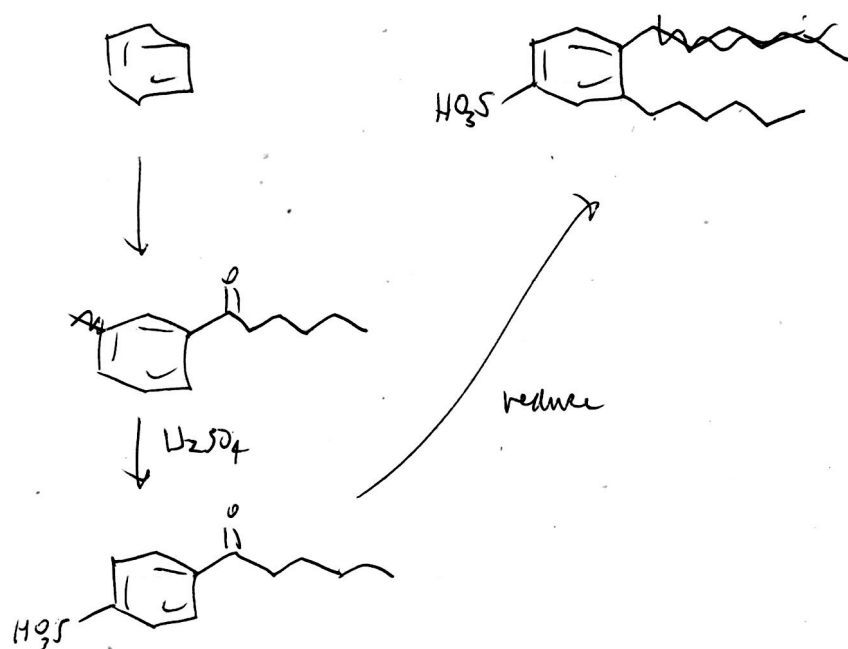
APPENDIX G. INSTRUCTOR CODES AND DEFINITIONS

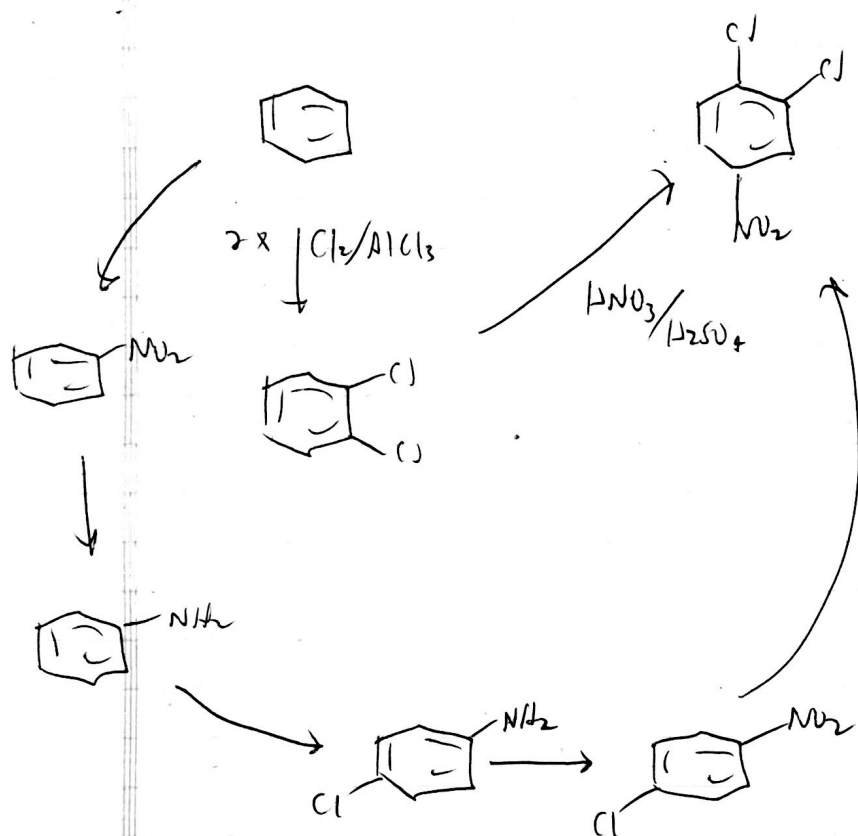
Instructor Codes	Definition
Activation/Deactivation	The participant makes a statement about the nature of substituents already present on the benzene ring can make it more or less reactive than benzene itself.
Directing Effects	The participant makes a statement about the nature of the substituents already present on the benzene ring determines the position of the second substituent.
Equivalents	The participant makes a statement about the amount of a substance that reacts with to an arbitrary amount of another substance in a given chemical reaction.
Illogical Flow	The participant makes a statement about a student using an illogical reaction scheme in order to achieve the desired product.
Memorization	The participant makes a statement about memorization being a component of learning.
Overall Reaction vs. Individual Step	The participant makes a statement about students not considering the overall reaction, but rather each stage individually as a reaction.
Oxidation/Reduction	The participant makes a statement about a type of chemical reaction that involves a transfer of electrons between two species.
Prior Knowledge Expectations	The participant makes a statement about knowledge students are assumed to have from prior chemistry courses.
Multiple Products	Students will not acknowledge additional products formed or yield probabilities of a reaction.

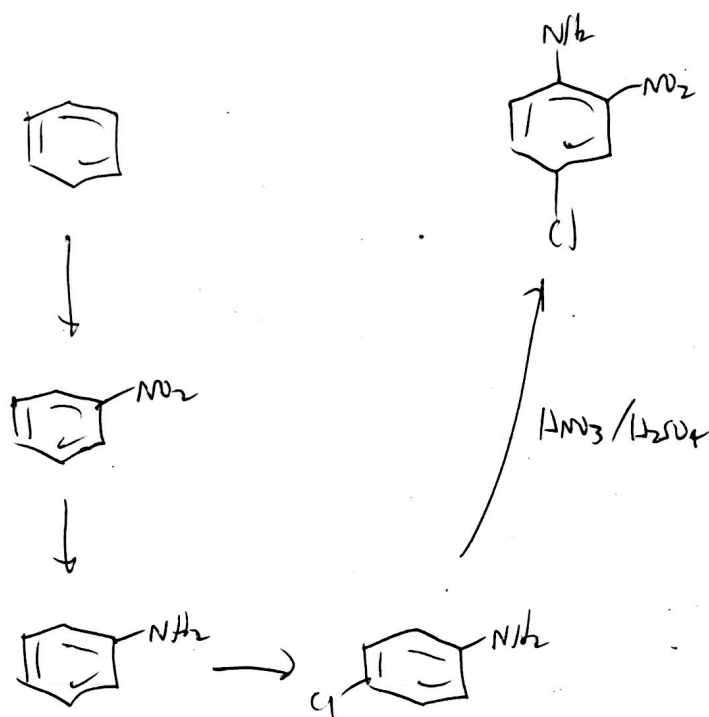
APPENDIX H. IMAGES OF DR. KEMPER'S SYNTHESSES







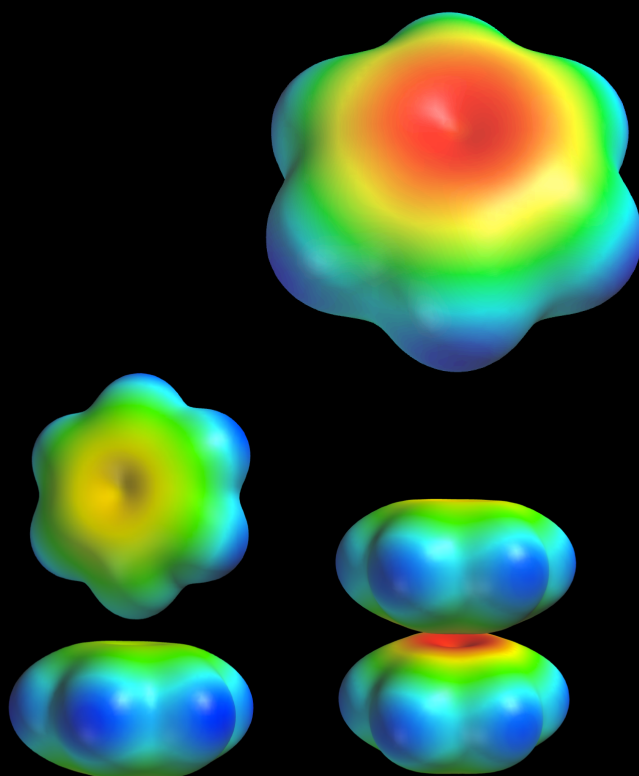




APPENDIX I. ELPLOTS FOR TEACHING AROMATIC SUBSTITUTION

Electrostatic potential map representation for the electron distribution in benzene

The electrostatic potential map shows the electron-rich region (red - yellow) distributed evenly above and below the middle of the plane of the ring, with the electron-deficient regions on the bonded H atoms.

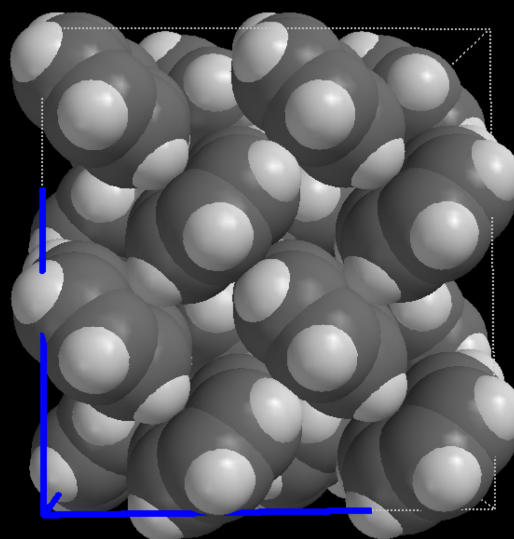


Molecular Modelling

e20.4 Examine the experimental evidence for the delocalized electron density distribution in benzene

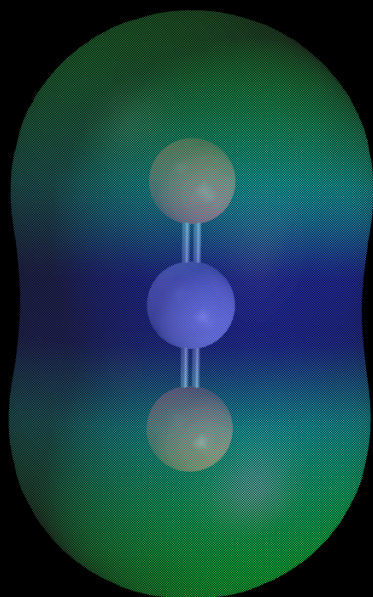
As they are shaped a little like dinner plates, can you predict how benzene molecules stack together in the solid state? Compare your prediction with the actual arrangement determined from the XRD crystal structure.

Here is the answer. The crystal structure is below, showing the alignment of electron-poor C-H regions on one molecule attracted to the electron-rich ring region in an adjacent molecule.



1 nm

Electrostatic potential map representations of the electrophiles show which atom carries the positive charge
 The electrostatic potential map shows the electron-deficient central atom (blue) in the electrophile.



Molecular Modelling

e20.10 Examine the electrostatic potential map of the nitronium ion to identify the electrophilic site

– see p 849 **CHACR International Edition**

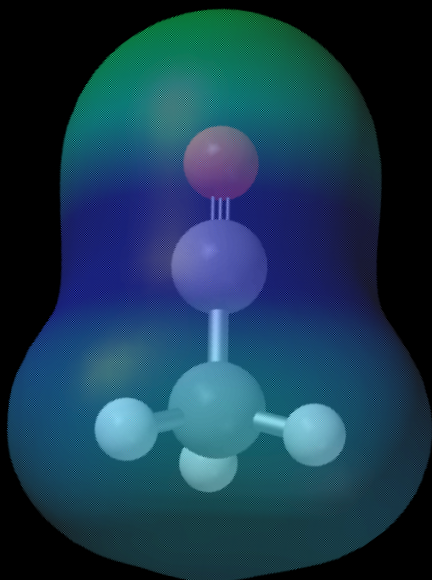
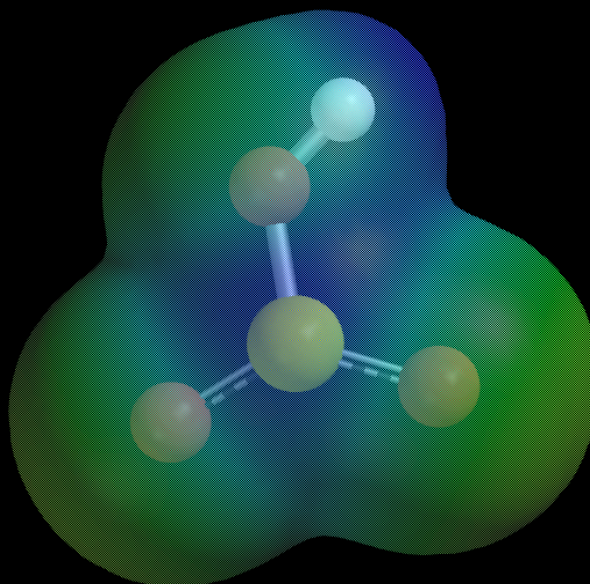
Identify the electron-rich and electron-deficient regions of the ion. Would you expect the nitrogen atom or an oxygen atom in the ion to add to the benzene ring in electrophilic nitration?

Molecular Modelling

e20.11 Examine the electrostatic potential map of the HSO_3^+ ion to identify the electrophilic site

– see p 849 **CHACR International Edition**

Would you expect the sulfur atom, hydrogen atom, or an oxygen atom in the ion to add to the benzene ring in electrophilic sulfonation?



Molecular Modelling (Odyssey)

– see p 852 **CHACR International Edition**

e20.13 Examine the electrostatic potential map of the acyl cation to identify the electrophilic site

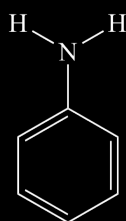
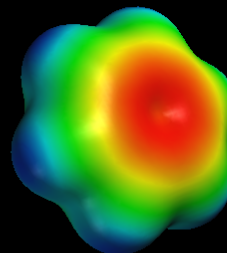
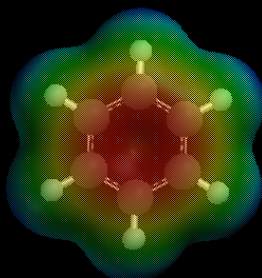
Would you expect the central carbon atom or the oxygen atom in the ion to add to the benzene ring in electrophilic alkylation?

Using elpot maps to indicate the effect of a substituent on the ring – see p 854 CHACR International Edition

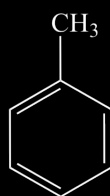
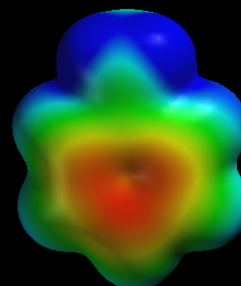
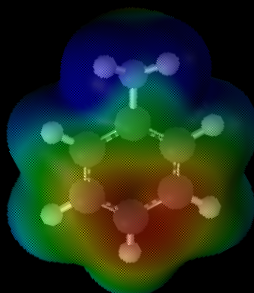
What makes a substituent on an aromatic ring activating or deactivating relative to benzene?



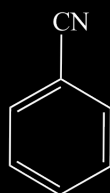
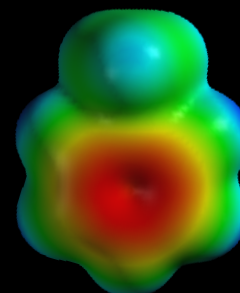
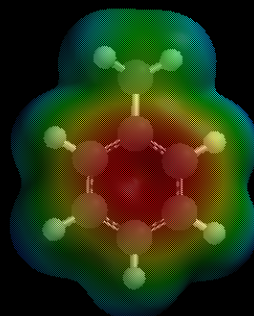
Benzene



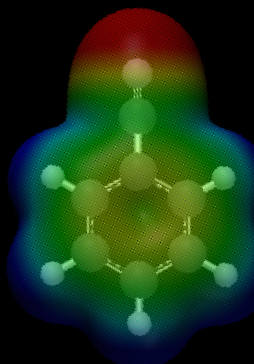
Aniline



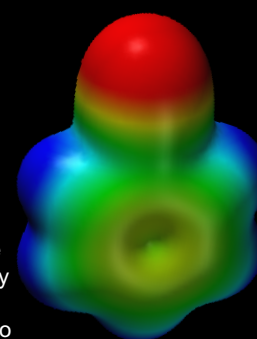
Toluene



Benzonitrile



Electron-withdrawing effect of the cyano group decreases the electron density in the ring, deactivating it to electrophilic substitution



Molecular Modelling (Odyssey)

e20.14 Use electrostatic potential maps to identify the effects of substituents on the electron density in the ring

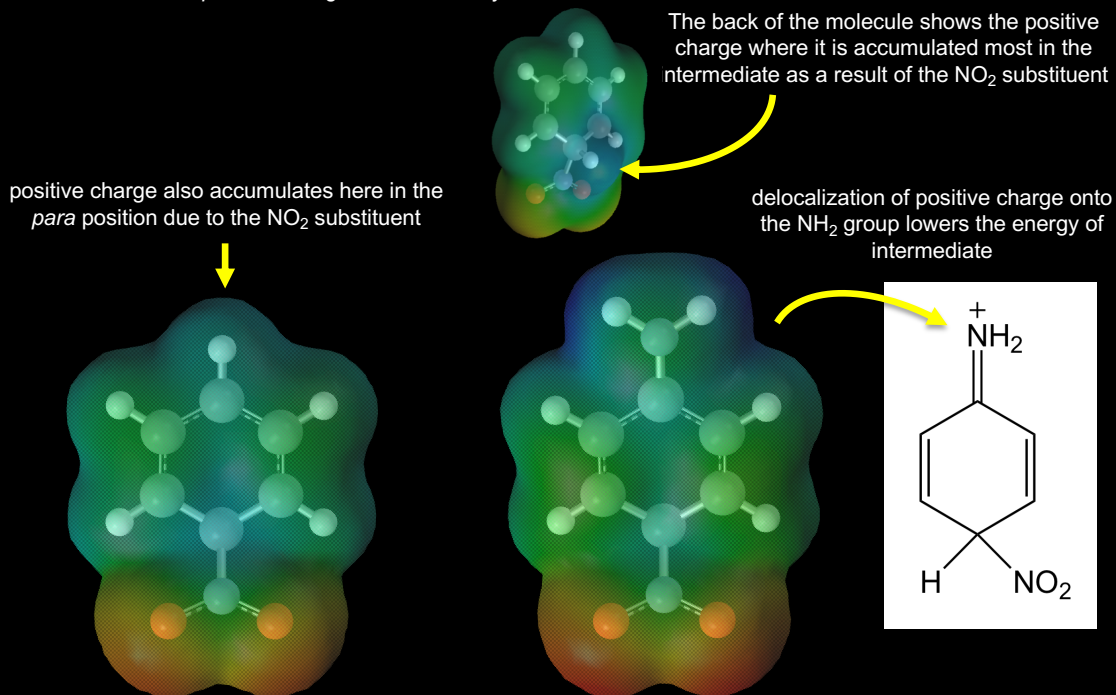
Compare the effect of each substituent on the electron density in the aromatic ring, using benzene as the reference.

Can you predict whether each substituent would activate or deactivate the ring to donate electron density to an electrophile?

Molecular Modelling (Odyssey) – see p 855 CHACR International Edition

e20.15 Examine electrostatic potential maps to see the effect of the -NH_2 substituent on delocalization of the positive charge in the carbocation intermediate produced when the nitro group bonds to the ring

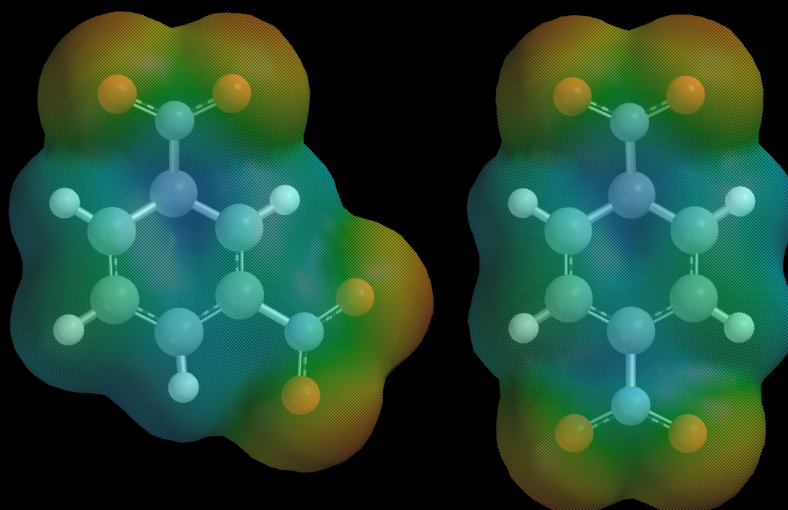
An activating substituent has its greatest effect by decreasing the accumulation of positive charge in the intermediate. In this activity you will start by seeing where this accumulation of charge occurs in the intermediate formed by an incoming NO_2^+ electrophile. Then you can see what happens if an electron-donating, activating substituent (an amino group in this case) is already in that position where the accumulation of positive charge would normally occur.



Molecular Modelling (Odyssey) – see p 856 CHACR International Edition

e20.16 Examine electrostatic potential maps of the intermediates to see how the -NO_2 substituent affects the carbocation intermediate

A deactivating substituent has its greatest effect by increasing the accumulation of positive charge in the intermediate. The electrostatic potential maps of both the *para* and *meta* isomers show significant increase in positive charge in the aromatic ring, consistent with the nitro group being an electron-withdrawing group.



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PUBLICATION

Draft manuscript for publication

Organic Chemistry Students' Understanding of Electrophilic Aromatic Substitution

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Abstract

Students studying organic chemistry often have difficulty applying prior knowledge from general chemistry in their thinking about organic reaction mechanisms. In the United States, electrophilic aromatic substitution (EAS) mechanisms are generally taught towards the end in a second-semester course of organic chemistry, providing students with almost two-semester's worth of experience with organic chemistry reactions before solving problems on synthesis of substituted aromatic compounds. The purpose of this study was to describe how students reason through EAS synthesis problems and to identify concepts or gaps in understanding that inhibit students from successfully solving these types of problems. Participants were interviewed using a think-aloud protocol in which they were asked to describe the reactants and mechanisms necessary to synthesize di- and tri-substituted benzenes using EAS. The interviews were transcribed and analyzed using a qualitative inquiry approach and the data interpreted in terms of the ACS Examinations Institute's anchoring concepts content maps for general and organic chemistry. The findings from this study indicated that while the students correctly used substituent effects to solve these problems, they relied on rote-memorization of these effects, resulting in inflexibility when applying them to novel situations. Additionally, students exhibited gaps in understanding with resonance and Lewis structures, differentiating and utilizing Friedel-Crafts reactions, and when to utilize oxidation/reduction reactions in their syntheses.

Keywords:

Introduction

If a student's prior learning in general chemistry is superficial there is a high likelihood this will be reflected in the student's performance in organic chemistry (Seery, 2009). Furthermore, the heavy content load in most organic chemistry courses tends to provoke students to use rote memorization without understanding as a heuristic for learning. An inadequate understanding of fundamental concepts inhibits students from understanding more advanced concepts, or appropriately applying these concepts in new contexts.(Nakhleh, 1992) This problem is manifested most clearly when trying to solve organic synthesis problems.

Student Approaches to Learning Organic Chemistry

Most students enroll in organic chemistry with the mind-set that the most successful learning strategy in the class will be surface-level memorization of reactants, reagents, reactions, preferred products, and mechanisms (Anderson & Bodner, 2008; Pursell, 2009; Zurer, 2001). Anderson and Bodner proposed that the complexity and heavy content load in most organic chemistry courses force students to superficially apply memorized rules without developing an understanding as to *why* the rules exist and when and where they can be applied appropriately (Anderson & Bodner, 2008). Pursell agrees that the rapid pace and complexity of material in the course prompts students to memorize rules, but adds that the callout boxes in textbooks showing consolidated material indicates content to memorize (Pursell, 2009). Furthermore, Grove and Bretz proposed that as the organic chemistry curriculum progresses, it becomes less straightforward and relevant for the students, particularly when there appears to be more than one correct answer or multiple correct mechanistic pathways to a product (Grove & Bretz, 2012, 2010).

Student Understanding in Organic Chemistry

Student understanding of topics in organic chemistry has been studied extensively over the last few decades – from student challenges with specific topics taught throughout the course like mechanistic reasoning, to identifying student learning difficulties and misconceptions in specific concepts. Students taking this sophomore-level course struggle with general chemistry topics like Lewis structures (Cooper et al., 2010, 2012), and topics usually introduced in the first-semester of an organic chemistry sequence, including functional groups, (Akkuzu & Uyulgan, 2016) electrophiles and nucleophiles (Anzovino & Bretz, 2016), aromaticity (Ealy & Hermanson, 2006), and the electron-pushing formalism (EPF) (Anderson & Bodner, 2008; Bhattacharyya & Bodner, 2005; Ferguson & Bodner, 2008).

Lewis structures are used as a model to symbolically visualize what is occurring at the molecular level – lone pairs, bonded electrons, and resonance where applicable. In organic chemistry, students are expected to be able to construct acceptable Lewis structures, and from these structures reasonably predict the reactivity of substances and their chemical and physical properties (Cooper et al., 2010, 2012). A student's inability to extract the relevant information that can be deduced from a Lewis structure can impact their reasoning about the reactive behavior of functional groups, electrophiles and nucleophiles; the nature of aromaticity; and substituent effects. For example, Anzovino and Bretz showed that students relied on the presence of lone pairs to define nucleophiles, but could not help them identify an electrophile (Anzovino & Bretz, 2016). In another study by Ealy and Hermanson, students showed difficulty in identifying significant lone pairs in a Lewis structure, and identifying if the lone pair could contribute to a pi system for aromaticity (Ealy & Hermanson, 2006).

The use of mechanistic thinking to predict reaction products is challenging for students in organic chemistry. Not only are students trying to explain how reactants are converted to major and minor products, they are also trying to use the electron-pushing formalism (EPF) or curved-arrow approach as a heuristic tool in their explanation. Although this approach holds meaning to experts as a way to predict realistic intermediates and products through the movement of electrons (Bhattacharyya, 2013), students tend to use EPF as an afterthought rationalization of a product (Anderson & Bodner, 2008; Bhattacharyya & Bodner, 2005; Grove et al., 2012). Additionally, senior-level and graduate students have been seen to use curved-arrows after

predicting intermediates in a mechanism (Bhattacharyya & Bodner, 2005; Rushton et al., 2008b). Throughout a student's progression in learning chemistry, this powerful explanatory tool poses a difficult challenge even for more advanced students.

Electrophilic Aromatic Substitution

Electrophilic aromatic substitution (EAS) has been identified as a foundational understanding of an anchoring concept by the ACS Examinations Institute in the Anchoring Concepts Content Map (ACCM) for organic chemistry (Raker et al., 2013). Within EAS, there are several topics that can underlie this unit, including substituent effects, aromaticity, Friedel-Crafts alkylation and Friedel-Crafts acylation reactions, and reduction of aromatic nitro groups (Raker et al., 2013). These topics are also identified in the sub-disciplinary level of the ACCM, which describes the enduring understanding (Holme & Murphy, 2012; Raker et al., 2013). Moreover, EAS is widely used for synthesis in industrial, pharmaceutical, and agriculture industries (Smith & El-Hiti, 2011).

Research Questions

The guiding research questions for this study were:

- *How do organic chemistry students reason through electrophilic aromatic substitution synthesis problems?*
- *Which mistakes or gaps in understanding emerge when students are asked to describe how to synthesize compounds using electrophilic aromatic substitution?*

Methods

Theoretical Framework

The theoretical framework selected for this study is phenomenography. Phenomenographic studies allow researchers to “orient [themselves] towards people's ideas or experiences of the world,” (Marton, 1981) in relation to answering questions about learning. Experiences with a phenomenon will be unique to individuals, therefore a single experience cannot constitute a phenomenon (Orgill, 2007). Rather, it is the collection of these experiences that comprise a phenomenon (Marton, 1981). Different individuals can have varying perceptions of how they feel they experienced a phenomenon. Phenomenographers gain a better understanding of a phenomenon by studying the similarities and differences among the perceptions of the individuals. These concepts of phenomenography have directed the methodological decisions of this study.

Students in organic chemistry experience problem solving often throughout the course. This can occur in lectures, on homework, and on assessments. One's perception of an experience is influenced by the person, the environment, and their own interpretations (Orgill, 2007). These factors lead students to have different experiences with the same phenomenon. In this study, problem solving with EAS reactions is the phenomenon, and we probed the student's perception of their experience in semi-structured interviews.

Participants and Setting

The setting for this study was a large, public, research intensive university in the Midwestern United States of America. The participants were enrolled in the second semester of a sophomore-level organic chemistry course designed for chemistry majors in the Spring of 2017 and the Spring of 2018. The same instructor taught the course in both semesters. Six participants were recruited in Spring 2017, and five participants were recruited in the Spring of 2018. To recruit participants, a purposeful homogenous sampling approach was used. The goal of homogenous sampling (Patton, 2015) is to thoroughly describe a particular subgroup. The subgroup of this study was students enrolled in the second semester of a sophomore-level organic chemistry course designed for chemistry majors. Grades were not a pre-requisite for participation. Participants were a mix of ethnicities and genders; however, differences in responses given by male and female participants were not investigated. All participants were given gender neutral pseudonyms and male pronouns are used when referencing a participant.

Data Collection

The interviews were all conducted by one of the authors of this paper. To begin, each participant was given a brief overview of the study. Participants did all of their problem solving using a *LiveScribe* pen and anoto digital paper to simultaneously record what the participant was writing/drawing and saying. This technology has been shown to be useful when exploring student understanding of a topic that is dependent on drawing diagrams or other representations (Linenberger & Bretz, 2012). A limitation of using the *LiveScribe* system is that if a participant uses the pen as a pointer when discussing items written on the page, the system has no way to identify what is being referenced. To address this limitation, a *GoPro* video camera was set up above the *LiveScribe* notebook to capture any references the participant may have made during the interview.

The interview protocol was adapted from Duffy (2006). The original purpose of her study was to investigate student understanding of aromaticity and electrophilic aromatic substitution reactions, identify students' beliefs about learning organic chemistry, and provide ways to promote more appropriate ways of thinking about aromaticity. The interview protocol was semi-structured and used think-aloud collection methods. The goal of think-aloud research is to elicit inner thoughts or cognitive processes to highlight what's going on in a person's head when they are solving a problem (Patton, 2015). These processes become verbal behavior, and are treated as another form of recordable behavior of the participant (Ericsson & Kintsch, 1995). A limitation of this is that it will only provide us with a snapshot of one's cognitive processes, and is limited by what the participant chooses to verbalize (Ericsson & Kintsch, 1995).

Our research conducted a pilot study with one organic chemistry instructor and two graduate students in the division of organic chemistry that were familiar with the sophomore-level organic chemistry course designed for chemistry majors. The purpose of the pilot study was to gauge the appropriateness of the interview protocol, as well as make sure that undergraduate participants would be familiar with the reagents necessary to solve the EAS synthesis questions. Four warm-up questions were added in the beginning of the protocol to allow the participants to get comfortable with the interviewer. Furthermore, the last question of Duffy's protocol (synthesis of 1,3,5-tribromobenzene) was eliminated as it was identified as being too difficult by the instructor and graduate students. The interview protocol can be seen in the supplemental information. The length of the interviews lasted between 30-60 minutes. The interviews were

transcribed by the researcher immediately after the interview concluded.

Data Analysis

The audio data from the *LiveScribe* pen and the video data from the *GoPro* were formatted and the resulting recording transcribed. Once the transcripts were created, screenshots of *LiveScribe* images were inserted into the transcripts at the appropriate times in the interview. Completed transcripts were imported into *NVivo 12* software for data management and analysis. With *NVivo 12*, the researcher can code portions of each transcript and organize the codes into categories and themes.

To begin coding of the data, the transcripts and memos were printed, and the researcher met with other members of the research group to collaboratively code a portion of the transcripts using in vivo coding. In vivo coding prioritizes the participants' voice in the data analysis by using their own language or phrases as the codes.(Saldaña, 2016) This preliminary review of the data allowed the collaborators to mark the transcripts with words or phrases that could be used later in the data analysis for analytical consideration.(Saldaña, 2016) After discussion, a consensus was reached between the collaborators on their opinions of the emergent codes between the collaborators. Following agreement, the researcher independently coded the remainder of the transcripts. Additionally, a thematic analysis was conducted using the ACS Examinations Institute's Anchoring Concepts Content Map (ACCM) for general and organic chemistry.(Fereday & Muir-Cochrane, 2006; Holme, Luxford, & Murphy, 2015; Raker et al., 2013)

Findings and Discussion

The major themes that emerged from the analysis of student interviews were students' acknowledging the use of memorization as a learning strategy to synthesize molecules using EAS, acknowledging the formation of multiple products when drawing a schematic mechanism, and considerations of substituent effects. Additionally, students showed difficulty in utilizing Friedel-Crafts alkylation versus Friedel-Crafts acylation synthesis routes and the reduction of nitrobenzene. Furthermore, gaps of understanding emerged associated with drawing Lewis structures, language used with EPF, and resonance structures. Each of these themes was compared to the ACS Examinations Institute's organic chemistry anchoring concepts content map (ACCM) and is supported by student quotes and figures below.

Memorization

Several students stated that they had memorized the tables the instructor had provided which listed the substituent effects. This notion was supported when students were able to correctly identify the directing effects of substituents, but were unable to produce an answer when asked to show how the substituent directed the incoming electrophile to the designated positions. Below, Jamison had correctly labeled the OH group in phenol as an ortho and para director; however, he was unable to show why the OH substituent directed the electrophile to those positions, Figure 3. H

Jamison: *"I kind of have a vague idea. Give me one second on that. I'm realizing I don't know as much about this as I thought I did. Yeah. Try that again. Oh, my god. I need to study this. I've got no clue."* (Figure 1)

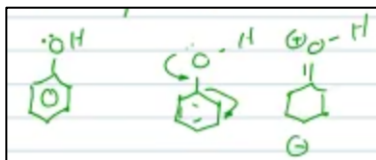


Figure 1. Work generated by Jamison when he attempted to show how the hydroxy substituent in phenol is ortho and para directing.

When asked to identify what the most difficult part about synthesizing substituted aromatics using EAS, Mason was quick to admit to difficulties in memorizing the concepts in the unit.

Mason: *"It was not that I forgot some of them. I had trouble memorizing the reagents and how substituents are substituted first before others."*

One task required participants to label the substituents in phenol, aniline, alkylbenzene, phenyl ether, and phenoxide as activating or deactivating. The five substituents are all activators, and once identified, participants are asked to rank them in terms of activating strength. Peyton correctly labeled four of the five substituents as activating (the substituent in phenoxide was identified as deactivating). When asked to justify the order of activation strength they had chosen, Peyton began his reasoning on the basis of just memorization.

Peyton: *"I think it's mostly from memorization, but I know the amine has a lone pair that can donate, and then the oxygen also has a lone pair, but it's more electronegative than the amine."*

It is interesting that Peyton's first reasoning was from memorization of the order of activating strengths; however, then he considered the lone pairs on the substituents. Although, oxygen is more electronegative than nitrogen, three of the five substituents had an oxygen atom present, yet the substituent in phenoxide was labeled as a deactivating substituent.

Acknowledging Multiple Products

Many students acknowledged the likelihood that more than one product could be formed in a given reaction when completing the syntheses. In other words, when adding another substituent onto a benzene that had an ortho and para directing substituent already present, students would state that both products would be formed. Additionally, some students provided laboratory solutions to isolating the desired products. The quotes below provide examples of students acknowledging the formation of multiple products.

Peyton: *"Then, if you react the aniline with iron chloride and chlorine gas, then you'll get ortho and para products. It goes by the same electrophilic elimination mechanism. You can probably run a column to isolate this compound."* (Figure 2)

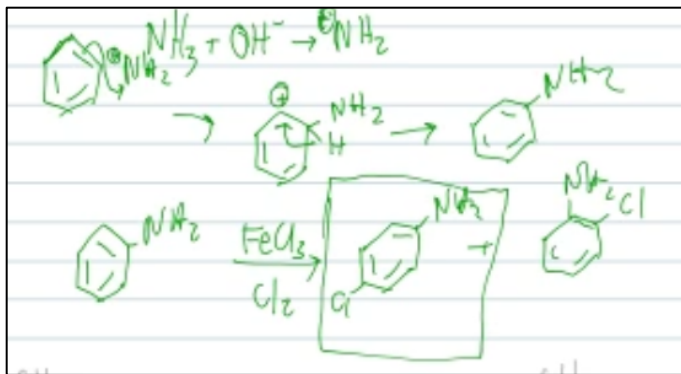


Figure 2. Work generated by Peyton for the synthesis of p-chloroaniline from benzene.

Peyton's explanation shows his acknowledgement for the formation of the ortho and para products. Figure 1 shows the two products that will be formed and the para product is highlighted in the box. Peyton further suggests these products could be separated by using a column to isolate each compound.

Mason: "Now we add the NO_2 . Whether or not we like it ... NO_2 can be placed everywhere in this case. There will be this product. TLC, column, purify the one you want, which is [1,2-dichloro-4-nitrobenzene]."

Mason also highlighted the formation of multiple products by stating that the nitro substituent could be added at multiple sites of the benzene. He also suggests using a column system to purify and obtain the desired product.

Kayden: "And then I don't think it really matters which one we add first, but if we add the nitro first, for instance ... we'll get two products. And then react those with the Cl_2 , FeCl_3 . And we'll get maybe a mixture of products. So if you add to the first one, it'll want to be meta to the nitro and either ortho/para to the amine. So that would put it here, where we want it, and also ... also here. And then the second one would give ... the nitro group would put meta, and I'll put that ortho so I get a third product." (Figure 3)

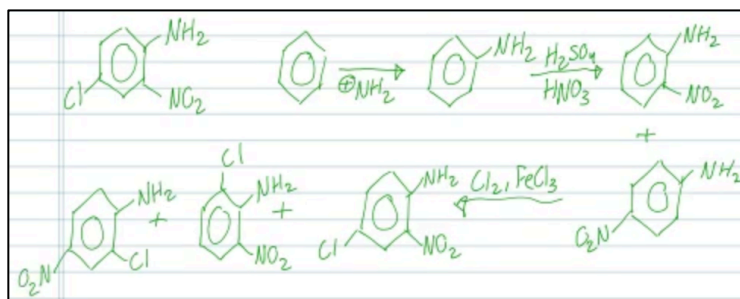


Figure 3. Work generated by Kayden for the synthesis of 4-chloro-2-nitroaniline from benzene.

In Figure 2, Kayden has shown that multiple products will be formed in each step of the reaction. In addition, he has verbally acknowledged that a mixture of products will be formed. While identifying the major product of an EAS reaction is not in the ACCM for organic chemistry; however, the ability to predict major products or yields of a reaction and their importance is (Raker et al., 2013). While participants did not identify which of the products would be the major product of the selected reactions, acknowledging that multiple products would be formed suggests that they were aware that they would not obtain a 100% yield of the

desired product. Additionally, providing reaction schemes that result in the desired product shows a transfer of knowledge from techniques used in the laboratory to lecture material.

Substituent Effects

Substituent effects include the directing effects as well as whether the substituent activates or deactivates the benzene ring. While all participants used the directing effects of substituents when synthesizing the desired molecules, several participants also considered the activation/deactivation properties of the substituents. The example below shows Blake highlighting the activation/deactivation properties when synthesizing *p*-chloroaniline and 4-chloro-2-nitroaniline from benzene.

Blake: *"Well, 'cause chlorine, the chloro substituent would be, would not, would be more deactivating than amino. So if you put the chloro on first, you would have to have much more vigorous conditions to put the amine on 'Cause the chloro would deactivate the ring. So best to put the ... Best to create aniline first and then chlorinate it."*

Later, Blake was discussing how to synthesize 4-chloro-2-nitroaniline from benzene:

Blake: *"We somehow have to make one of the chlorines to be meta and chlorine while it is deactivating, it is ortho, para directing, so the only way would be to ... The only way to ensure that meta product would be added is to have the nitro step before, at least one of the chlorination's. I'm not sure if it would work if you nitrated it at first. I think, 'cause NO₂ is such a strong meta directing, that I don't know that you'd be able to create ... If you'd be able to attach any pair of substituents after you nitrate it. So, probably best to do one chlorination, then nitration, then the other chlorination."*

Substituent effects are identified as an anchoring concept in organic chemistry (Raker et al., 2013). Blake has shown that in order to solve EAS synthesis problems, you must consider both the directing effects of substituents as well as the activation/deactivation properties. It is significant that Blake considers these effects even when synthesizing a tri-substituted benzene, and that the complexity of the molecule does not hinder students at disregarding one of the effects.

Friedel-Crafts Alkylation vs Acylation

Two of the synthesis problems contained alkyl substituents, a methyl- and 1-hexyl. The Friedel-Crafts alkylation and acylation reactions will not occur if the benzene ring is deactivated. Additionally, alkylation reactions are prone to carbocation rearrangements (McMurry, 2004). Participants did not consider either of these concepts when synthesizing an alkylated benzene, as seen in the following quotes from Peyton and Casey.

Peyton: *"To get this hexyl group, I would need to do a Friedel-Crafts acylation followed by a Wolff-Kishner reduction, because if I did a Friedel-Crafts alkylation, the positive charge could rearrange part, move somewhere else to a carbocation rearrangement. Or no, that might not be necessary, because it's just a linear molecule. Yeah, I'm thinking there won't be any rearrangement, so I would just do an alkylation."*(Figure 4)

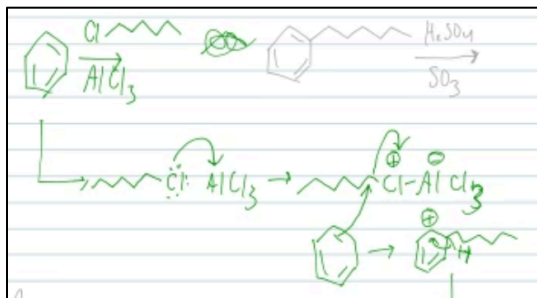


Figure 4. Work generated by Peyton during the synthesis of hexylbenzene from benzene.

It is interesting to note that Peyton was originally correct in his reasoning for why Friedel-Crafts acylation would be required to add the hexyl chain onto the benzene ring – Friedel-Crafts alkylation would lead to a carbocation rearrangement for the most stable carbocation. However, Peyton changed his response after incorrectly considering the linearity of the molecule. Furthermore, Peyton initially stated that a carbocation would form, but after examining his mechanism, Figure 4, he actually showed a substitution mechanism without forming a carbocation intermediate.

Casey: “Then after that, now it’s a harder way on making like a CH^- , like a methyl carbocation because it is very hideously unstable. We can do that though by using CH_3Cl , I believe. This would form the, using the same steps as above, the meta-nitrotoluene.” (Figure 5)

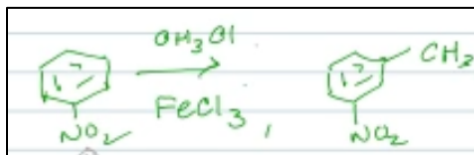


Figure 5. Work generated by Mason during the synthesis of m-hexylbenzenesulfonic acid from benzene.

Casey was correct in stating that the methyl carbocation would be very unstable, but he did not consider that Friedel-Crafts reactions would not occur on a deactivated ring. Below, Taylor and Morgan had difficulty forming an electrophilic carbocation when they could not remember Friedel-Crafts alkylation or acylation.

Taylor: “I need ... put ... okay, let’s do ... the only thing I can think of it is like ethanol. That is definitely not what I’m going to use. God, I want to think it’s like something like, I’m going to use a halogen to like ... I just think that’s so wrong, though. You know what, let’s just do it. Let’s just ... put a CH group on there. That’s a CH . That did not work. I’m drawing a blank.”

Morgan: “We need some sort of something that’ll give us CH_3 in there. I can’t remember something that would give a CH_3 . I know it would have to be something like that ... sort of. It would just essentially be a source of it, not just CH_3^+ . I can’t remember if it’d be like a lithium cuprate or something. I can’t remember. It’d just basically be a source of this.”

Both students knew they needed a reagent that would supply a methyl substituent, but were unable to remember the reactions they had learned previously. Their inability to apply prior knowledge in this new context hindered them at successfully solving the synthesis problems in which an alkyl substituent was required.

Reduction of Nitrobenzene

Nearly all students in this study (10 out of 11) were unable to remember the reagent required to reduce an aromatic nitro substituent to an amino group in aniline. Alternative incorrect routes provided by participants included using hydroxide with ammonia to create an amino cation, using heat and ammonia to create an amino cation, or using nucleophilic addition of amide (NH_2^-). Several students tried to reason through various mechanisms to form an NH_2^+ cation before ultimately conceding that they did not know the reagents to do so. The work below shows several students' attempts at forming aniline from benzene.

Casey: "I don't know how to make NH_3 into NH_2^+ , but let's assume we can, using that and heat because heat always works."

Alex: "Okay, so amine. Trying to think. You got NH_2 . Trying to think how it forms an electrophile. NH_3 ... Maybe. This is how I'm gonna do it ... So I'm gonna say that something like H_2O takes ... let's see, there's one negative charge. I'm trying to think ... so maybe if it's ... I don't know. Usually, we don't see that, but it forms N with a positive charge. Actually, I know where it happens. Okay, so it grabs an H from ... and that gets its positive charge, and then this ... oh no, that wouldn't work. I'm kinda stuck." (Figure 6)

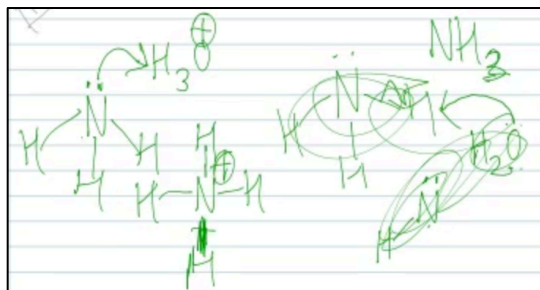


Figure 6. Alex's attempt to use EPF to reason through the generation of an NH_2^+ electrophile.

Emery: "Would the reagent to ... Would you be able to use an NH_3 compound, and the use that to attack with electrophilic ... Yeah, I'm pretty sure it won't work, because I'm thinking I know what it's gonna form, but ... yeah." (Figure 7)

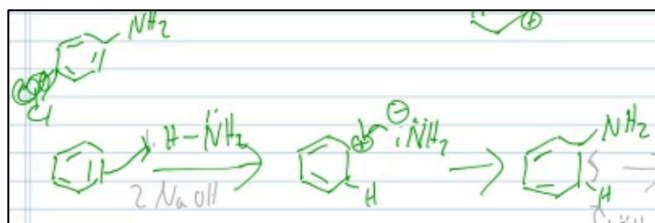


Figure 7. Work generated by Emery showing the synthesis of aniline from benzene.

Mason: "Would it be NH_3 maybe? I can do kind of the same thing here. Well ... I don't think you do that ..." (Figure 8)

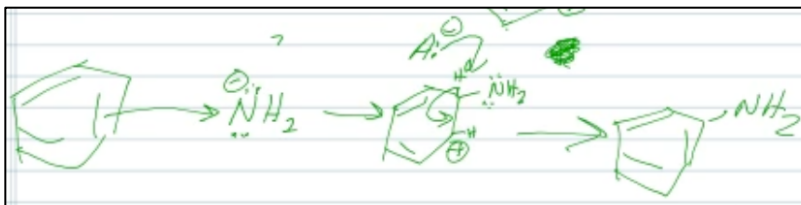


Figure 8. Work generated by Mason showing the synthesis of aniline from benzene.

Reduction of an aromatic nitro group is an anchoring concept in organic chemistry (Raker et al., 2013). However, only one participant was able to remember the reagents to correctly reduce nitrobenzene to aniline. As seen with Casey and Alex, several students focused on the topic of EAS and believed that in order to obtain aniline, you would need to create an electrophile. Emery and Mason focused on using a nucleophilic amide as a reagent to obtain aniline. Emery's synthesis, Figure 7, showed an "electrophilic hydrogen" forming a sigma bond to the benzene ring followed by a nucleophilic addition of amide to the benzonium intermediate. Mason's synthesis, Figure 8, showed an amide ion forming a sigma bond to the benzene ring with two electrons from the benzene forming the bond. Additionally, the second step shows a neutral amide substituent even with the additional electron from the new sigma bond.

Gaps in Understanding – Lewis Structures

One of the steps in answering synthesis problems was to show the generation of the electrophile in each case and to provide the mechanism in which the substituent bonds to the benzene. One participant, Kayden, correctly drew $\text{-SO}_3\text{H}$ as the sulfonic acid substituent, but was unable to show the mechanism for the sulfonation of benzene. Although, Kayden correctly identified the reagents sulfuric acid and sulfur trioxide that sulfonate benzene, he was unable to provide the mechanism. To support the possibility of drawing a mechanism, Kayden was asked to begin by drawing the Lewis structure of either sulfuric acid or sulfur trioxide. He began by trying to draw the Lewis structure of sulfur trioxide.

Kayden: "I know it has three oxygens, but I believe sulfur only has five valence electrons. And that makes it over the eight ..."

Interviewer: "So you could also start by trying to draw the Lewis structure of H_2SO_4 ."

Kayden: "Also don't really know how that one looks. I don't really know how the three oxygens ... the additional oxygens are connected to this. Yeah, I'm not entirely sure how this happens." (Figure 9)

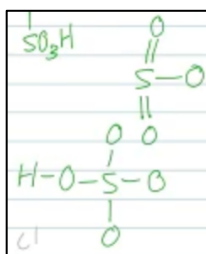


Figure 9. Kayden's skeletal structures when attempting to draw the Lewis structures of sulfur trioxide and sulfuric acid.

The ability to draw and use Lewis structures is identified in both the general and organic chemistry ACCM (Holme, Luxford, & Murphy, 2015; Raker et al., 2013). Even though Kayden

provided the correct reagents to synthesize benzenesulfonic acid, his inability to draw a reasonable Lewis structure of the molecules hindered him from providing a mechanism for the reaction.

Gaps in Understanding – Electron-Pushing Formalism

The ability to visualize molecules, show how they react, and use curved arrow notation to depict the movement of electrons are all identified in the organic chemistry ACCM (Raker et al., 2013). Cations and carbocations are formed when electrons are removed from an atom (Holme, Luxford, & Murphy, 2015). When asked to show why the OH substituent in phenol is an ortho and para director, Casey and Emery used the following language to describe the resonance structures of phenol:

Casey: *“When we do the resonance of this all we move [the carbocation] there. The carbocation would move to this place over here. Because of this, this electron can be donated here. Therefore the charge, sorry, the charge moves to the oxygen. Since oxygen is the more electronegative compound, or molecule, atom, it would be more stable that way. Because of that property, it would then do para. Same thing with ortho, if we had this example, Cl. The OH is here. The carbocation is directly there. It's the same thing as this. Therefore with the movement of the positive charge, sort of, the carbocation to the oxygen, that would be ... That would make the whole resonance structure more stable.”* (Figure 10)

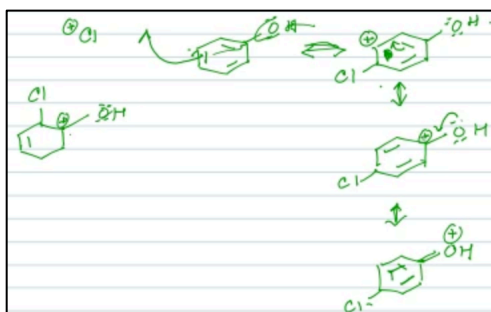


Figure 10. Casey's work showing his application of resonance structures to reason through why the hydroxy substituent in phenol is ortho and para directing.

Emery: *“So... Okay. I remember it something to do with the [oxygen] being able to take on the charge ... So I'm trying to remember exactly the details. So the positive charge can move along quite easily there. also the other option would be for to do something along these lines. You see how ... This one however I know it can't do that. Yeah I do have this right, right? Yeah. The reason being, when the charge moves around. Is this still ... Okay I get you. So say the charge moves like this, you'll have this, and a positive here. But then you move this to say the thing might me here, the positive's gonna on here, which means the [oxygen] can never take that positive charge. And so it has ...resonance effect. And of this one, again it'll work like [oxygen]. When you move it around it can be moved from here to here, and from here on to the [oxygen].”* (Figure 11)

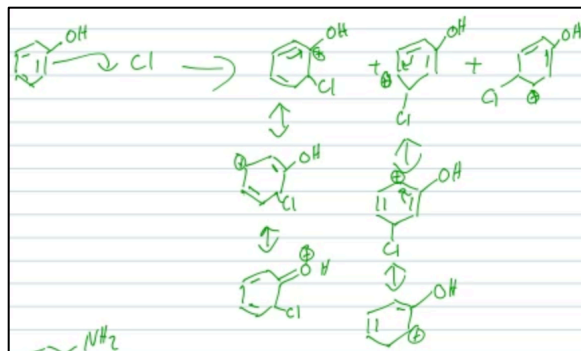


Figure 11. Emery's work showing his application of resonance structures to reason through why the hydroxy substituent in phenol is ortho and para directing.

When considering Friedel-Crafts alkylation versus Friedel-Crafts acylation, Peyton described the carbocation rearrangement as though it was the positive charge moving.

Peyton: "...because if I did a Friedel-Crafts alkylation, the positive charge could rearrange part, move somewhere else to a carbocation rearrangement."

Casey, Emery, and Peyton all described the reactions as the positive charge moving around, rather than the carbocation being formed from the absence of electrons. With the EPF convention, the movement of electrons is shown with the single- or double-headed arrows. Charges are created from the addition or absence of electrons, and EPF is not used to describe the movement of these charges.

Gaps in Understanding – Resonance

When solving the EAS synthesis problems, most participants (10 out of 11) would begin by drawing the target molecule before attempting a synthetic route. In the example below, Emery began his synthesis by drawing the target molecule of 4-chloro-2-nitroaniline, Figure 12. When he finished the synthesis, the double bonds had been drawn in a different location in the benzene ring.

Emery: "I drew this wrong. Okay. From that ... And so the final structure would be ... Should be that. Cl ... did I draw it right? No. Okay, and then when used in the Cl as an ortho, para. It'll form ... I'm also noticing how I'm doing this. I'm very sure the benzene ring, electron double-bonds can move around pretty freely, so I would assume I would have to use either some sort ... I'm not sure exactly how I would go about moving those, like purposely or anything." (Figure 12)

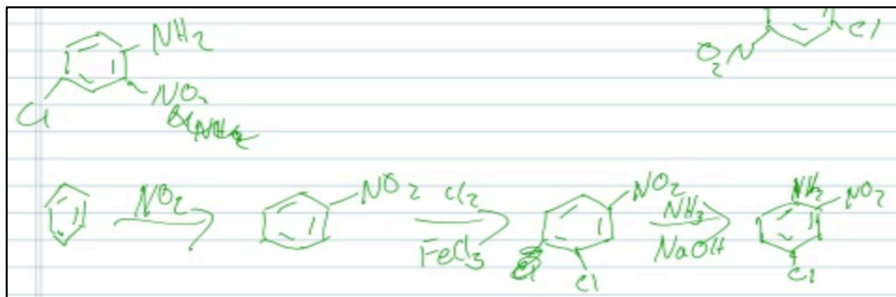


Figure 12. Emery's synthesis of 4-chloro-2-nitroaniline from benzene.

The concept of resonance and resonance structures are identified in both the general and organic chemistry ACCM (Holme, Luxford, & Murphy, 2015; Raker et al., 2013). Although Emery correctly stated that the double bonds in the benzene can “move around freely,” he ultimately believed his answer to be incorrect because on paper, the double bonds of his final product did not match the double bonds in the original depiction of the target molecule. However, the definition of resonance structures states that the only difference is “the absolute location of electrons” (pg. 3) (Raker et al., 2013).

Conclusions and Implications

The purpose of this study was to describe how organic chemistry students reason through EAS synthesis problems and to identify gaps in understanding that inhibit students from successfully solving these problems. Several conclusions regarding students’ approaches to solving EAS synthesis problems and gaps in understanding can be reached from the findings of this study.

One of the most important aspects of synthesizing molecules using EAS is understanding and applying the directing effects of different substituents. While most students were able to identify the directing effects of a substituent, they were unable to provide mechanistic reasoning for *why* a substituent had that effect. This shows that students are relying on memorizing the concepts associated in this topic without deeper understanding. Memorization without understanding in organic chemistry has been well documented. (Anderson & Bodner, 2008; Grove & Bretz, 2012, 2010; Pursell, 2009) It would be beneficial for instructors to include assessment questions in which students need to justify how a substituent activates or deactivates the benzene ring, or why a substituent has the directing effect(s) that it does.

Another important aspect of organic chemistry as a whole is being able to apply the numerous reactions taught in the course in synthesis problems. Students appeared to focus on the topic of the study, EAS, in which an electrophile is needed. Reactions that had been taught previously were forgotten, as seen in the creation of aniline with only one participant having the correct response. Additionally, the limitations of both Friedel-Crafts alkylation and Friedel-Crafts acylation were difficult for students to remember. Thus, it is important for instructors to consider the amount and types of reactions required to complete a synthesis question. It may be beneficial to remind students that EAS is just another set of reactions that they can use as tools for completing a synthesis, and that previous reactions can still be applicable.

Several gaps in understanding emerged in the data, including difficulties with concepts of Lewis structures and resonance – two topics taught in general chemistry. Students entering organic chemistry with an underdeveloped understanding of Lewis structures will have a difficult time drawing reagents needed in mechanisms. Emery was quick to conclude that their answer to the synthesis problem was incorrect when the double bonds didn’t match the ones drawn in the original structure. While the two structures are the same, Emery believed their answer was wrong. Instructors need to be aware that these underdeveloped understandings are still prevalent in students about to complete the course.

Limitations

This study describes the how eleven organic chemistry students reason through EAS reaction problems and the emergent concepts that inhibited students’ success at solving these types of problems. At the time of the interview these students were enrolled in a second-

semester organic chemistry for chemistry majors. The course was taught by the same instructor during both semesters. The findings would have been more generalizable by studying students in other organic chemistry courses taught by a sample of the instructors interviewed. The findings are also limited to the students enrolled in the course designed for chemistry majors. Multiple sources of data were used in this study; however, the data was collected in a limited time frame by one individual in the last month of the academic school years' of 2017 and 2018.

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