Teaching Devices to Make Learning Undergraduate Organic Chemistry Easier

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Testing of a teaching device, the Nucleophile/Electrophile (Nu/E) Guide which enables students to visualize reaction mechanisms is described. The device consists of two sheets of card stock, one sheet showing nucleophiles and one showing electrophiles, and allows students to align the selected nucleophile with the selected electrophile. Results of tests, carried out in the Chemistry Department of the University of Oklahoma, show a 20% higher test score in the group using the device outside class than in the group not using the device at all. Because of the success of this device, a similar device for electrophilic aromatic substitution (EAS) was developed and is described herein. Each device includes a large amount of information, with similar data grouped, and the groups are juxtaposed in order to facilitate pattern recognition and differentiation. This in turn facilitates visualization, retention, understanding, and use of the information presented. ©2000 Oklahoma Academy of Science

INTRODUCTION

The periodic table still provides guidance to modern research (1-7) 130 years after its original development. It is of lasting and continuing value because it can include large amounts of information about each of the elements, with similar elements grouped, and the groups are juxtaposed in order to facilitate pattern recognition and differentiation. This in turn facilitates visualization, retention, understanding, and use of the data presented. One very important function of the periodic table in research has been as a data organizer and systematizer. It is not merely a teaching device (such as flash cards), a data holder (such as a lookup table), or a calculation aid (such as a slide rule), although the periodic table certainly can function in each of these roles. It is well-known that Mendeleev used his periodic table to predict the existence of undiscovered elements. In doing so, he charted known information in a highly systematic way, which provided a map leading to exploration of new territory.

Although the events have become legendary, application of this technique to other areas of chemistry is not one routinely reported. However, it should be of great utility in dealing with projects having a broad range. These projects could be sets with many members, such as investigations encompassing many different elements, reactions, mechanisms, etc.

Organic chemistry is often described as a difficult discipline because there is such a large amount of data to be learned. Particular attention is paid to learning mechanisms of the reactions, which often involve nucleophiles and electrophiles. In order to facilitate pattern recognition and retention of nucleophiles, electrophiles, and the mechanisms describing their reactions, we developed a Nucleophile/Electrophile (Nu/E) Reaction Guide (8-12) containing a page of nucleophiles and a page of electrophiles, grouped according to similarities. The two pages can be juxtaposed in order to visualize the mechanisms of reactions of nucleophiles and electrophiles common to organic chemistry and to facilitate remembering and differentiating (a) the electrophiles and nucleophiles, (b) the active site(s) in each, and (c) the arrow(s) designating the flow of electrons in the reaction of the two. An additional result of aligning nucleophiles and electrophiles in order to visualize reactions, was identification of potential reactions not covered in the classroom. Thus, just as in the original development of the periodic table, with the "holes" predicting undiscovered elements, users of this guide quickly identified potential reactions that had not been revealed to them. Thus, the enterprise led to a discovery that the organization and systematization techniques applied to previous territories can also be applied more universally, to aspects of organic chemistry.

However, reactions of electrophilic aromatic substitution (EAS) are somewhat more complicated. In order to make the data manageable, most treatments apply some organization, such as categorizing the reactions with respect to the patterns exhibited in the mechanisms, and by the effects of the substituents in the aromatic compounds on the reaction rate and regiochemistry. However, usually a separate reaction which provides the active reagent must also be considered, as well as the active site(s) in the reactant, the active site(s) in the reagent, and stabilizing charge delocalization caused by induction, conjugation, or both, in the intermediate. The multitude of variables in these reactions made it impossible to include EAS reactions as an entry in the Nu/E Reaction Guide. Therefore, it was necessary to develop a separate but similar organizational device for EAS.

This manuscript presents an evaluation of one hand-held device, the Nu/E Reaction Guide for facilitating students' understanding of reaction mechanisms in organic chemistry. (9,10) Future similar investigations are planned for the EAS Tool.

I. MEASURING EFFECT OF THE Nu/E REACTION GUIDE

A. Method

The participants were enrolled in a firstsemester organic chemistry course for science and engineering majors at a comprehensive public university. The sample consisted of 126 students; 63 were assigned to a control group, 17 were assigned to out-ofclass device group, 25 were assigned to in-

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class device group, and 21 were assigned to use the device both in class and out of class (Table 1). Assignments were random, and the course met for a total of 150 min/wk for the 15-wk semester. There were four different groups organized according to device use. Group YY saw demonstrations of how to use the device in class, mimicked the use of the device in class, and then used it unsupervised outside class. Each student in an in-class device group (Group YN) saw the demonstration, mimicked the demonstration with a device, continued to use the device in class, but did not use the device outside class. Each student in the out-of-class device group (Group NY) saw demonstrations of how to use the device in class and then used the device unsupervised outside class. The students in the control group (Group NN) did not use the guide at all. Thus, the uses of the device by Group YY would be a combination of those of the in class group (Group YN) and of the out of class group (Group NY) described above.

The experimental design is a posttestonly control group design for both content knowledge and problem solving. The questions used in the posttest are given in Table 2. A Control Unit Achievement Test (CUAT) (13) showed that the groups were approximately equivalent in their chemical knowledge before the treatment. There were no other variables in the groups, such as different TA's. Periodic checks were made to insure no use of the device by the Group NN students through sharing with students from other groups.

B. Results and Discussion

The results from the Nu/E Reaction Guide study are shown in Table 1, and the test questions are in Table 2. The questions were designed to determine student knowledge of various aspects of nucleophiles, electrophiles, and reactions and/or mechanisms involving nucleophiles and electrophiles. The percent correct response for each test question for each of the sample groups, Group YY, YN, NY, and NN (columns 1-3 and 5), as well as for a weighted average of all groups using the device in any manner (column 4), is shown (Table 1).

	Use of Nucleophile / Electrophile Reaction Guide				
	in and out of class (YY)	in class only (YN)	out of class only (NY)	any use (wt. ave.) (YY, YN, NY)	none (control) (NN)
Count	21	25	17	63	63
GPA	3.23	3.38	3.38		3.25
CUAT score	66.1	69.8	62.8	66.4	66.8
control score - group score	0.7	-3.0	4.0	0.4	0.0
% correct Q1 Q2 Q3 Q4 Q5	66.7 85.7 57.1 52.4 90.5	76.0 84.0 80.0 52.0 76.0	70.6 82.4 82.4 52.9 76.5	71.4 84.1 73.0 52.4 81.0	66.7 80.9 68.3 42.9 61.9
Ave Q1-Q5	70.5	73.6	73.0	72.4	64.1
average Q1-Q5 w/CUAT correctior	71.2 า	70.6	77.0	72.8	64.1

TABLE 1. Data for use of the Nu/E Reaction Guide based on student responses.

The CUAT scores for the groups, the last row of entries in Table 1, indicate that there was no difference between the three treatment groups and the control group: YY, 66.1%; YN, 69.2%; NY, 62.8%; NN, 66.8%. The weighted average for all groups using the device is 66.4%, almost identical to that of the control group.

The average of the five questions for each group is given in Table 1 (Ave Q1-Q5). The results are as follows: Group YY, 70.5%; Group YN, 73.6%, Group NY, 73.0%, Group NN, 64.1%. All three of the groups which used the Nu/E Guide (Groups YY, YN, and NY) performed significantly better than those of the control group (Group NN), and the weighted average of all groups using the device is 72.4%. Curiously, of the three groups using the device, the group which used the device both in and out of class scored marginally lower than the other two. The control group had the lowest average score on every test question except one (Q3), and in that one it had the next to the lowest score. Comments of some students using the Nu/E Guide in List 1 indicate that the students valued the device.

If the average results (Ave Q1-Q5) are normalized by using factors obtained from the CUAT scores (control score - group score), the corrected averages (corrected average Q1-Q5) become Group YY, 71.2%; Group YN, 71.2%; Group NY, 77.0%; Group NN, 64.1%. This analysis of the results shows that Group NY shows the most improvement from use of the Nu/E Guide. The reason for this may be that the student using the guide only out of class, puts more thought into determining how to use the guide, and did not merely follow the demonstration. Therefore, these students learned more from the independent effort invested.

II. ELECTROPHILIC AROMATIC SUB-STITUTION (EAS) TOOL

A prototype for such a device was created and used in the classroom and described at a national ACS meeting. (10) It was compared (11, 12) to a slide rule, because it consists of two surfaces which slide against each other with arrows to align in order to

TABLE 2. Test questions used for study of effect of the Reaction Guide upon learning.

- 1. Which is true of an electrophile?
 - A. It has room in an orbital to accept a pair of electrons.
 - B. It is pointed to by the head of an arrow in a reaction mechanism.
 - C.) Both of the above.
 - D. Neither of the above.
- 2. Match the components of the reaction below to their descriptions.



3. Which of the following electrophiles reacts fastest with I⁻ in an SN2 reaction?



4. Of those listed, the strongest nucleophile is:

А. Н ₂ О В. ОН ⁻ (С.) NH ₂ - D	D.	D. F
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5. In which of the following are both the reaction and the reaction mechanism drawn correctly?



pair reactants. The device is similar to a slide rule, but different as it also contains a great deal of organized and systematized information. As a result of the comparison, (11, 12)we received inquiries about the device from universities, from business, but mostly from industry. Because of the apparent interest in the device, we present a description of it and of the application of the organization and systematization techniques to EAS.

The device consists of two sheets of card stock, presenting EAS data in an organized fashion to facilitate pattern recognition and retention. One sheet can be placed over the other in order to visualize the mechanism between the substituted aromatic compound selected and the chosen reagent. On separate pages, it gives two aspects of EAS and then demonstrates interactively how these aspects inter-relate. The two aspects are: (a) the substitution itself, including the identity of the electrophile, the reagent(s) needed to generate it, and the substituent in the product and (b) the electronic effects of the groups in the aromatic compounds on the intermediate(s) and the structure of the product.

Sheet A (Figure 1) presents a discussion of and a table of representative electrophiles, the reagents needed to generate them, and the general class of product obtained from the reaction of each electrophile with an aromatic compound. In the first column, the electrophile (E or E+) undergoing attack by the π -electrons of the aromatic compound is listed. Each electrophile in the "E or E+" column has a head half of an arrow leading from the side of the page and pointing to an atom which is the reactive site in the electrophile, usually the atom bearing the highest amount of positive charge. This atom is the one to which the aromatic ring will become attached. In the second column are the reagents which generate the electrophiles in the first column. The third column lists the final product obtained by treating the aromatic compound with the reagent(s) in the second column. On the obverse of Sheet A are an introduction and additional discussion, including definitions of the aromatic ring positions relative to the group in the reactant, and an explanation of the four different types of electronic effects caused by substituents in the aromatic reactants. These four different categories of electronic effects are (a) ERG (π -system) = Electron Releasing Group via the π -system, (b) ERG (σ -system) = Electron Releasing Group via the σ -system, (c) ECG = Electron Conjugating Group, and (d) EWG = Electron Withdrawing Group.

Sheet B bears a table consisting of columns of information concerning EAS in general. Information is categorized with respect to the type of electronic effects caused by the substituents in the aromatic reactant; the members and characteristics of each category are placed next to each other to facilitate pattern recognition and thereby retention of the data presented. The first column contains a series of mono-substituted aromatic compounds as reactants categorized according to the type of electronic effects (defined at the bottom of the table) caused by the substituent present. Examples of substituents causing each type of electronic effect and a general description of its characteristics are below each substituted aromatic compound. The arrow leading from the reactant molecule to E+ represents the electrophilic attack of the π electrons upon the general electrophile (the rate-determining step of the reaction). The second column has the most stable resonance structure(s) of the most-favored intermediate(s) of the reaction, with arrows depicting electron withdrawal or donation justifying why that intermediate is disfavored. Since the position of the C-E bond has been established by this point, each intermediate leads logically to the major product(s), which are given in the third column. The fourth column shows the disfavored intermediate, with arrows depicting electron withdrawal or donation and justifying why that intermediate is disfavored.

In order to consider the reaction of a specific electrophile with a type of aromatic reactant under the effects of its substituent(s), it is necessary to juxtapose Sheet A and Sheet B. Bringing together the two reactants enables one to visualize the mechanism of the rate-determining step of a specific reaction while considering and tracking all of the variables involved. Attack at each specific



Figure 1. Reduction of a portion of Sheet A of the device placed over two-thirds of Sheet B in order to visualize the mechanism of the rate-determining step of the chlorination of phenol. The arrow halves are juxtaposed in order to show the flow of electrons; the arrow so created in this example has been made bold.

E or E+ is shown in the far left column of Sheet A, with arrows leading to each from the edge of the card. Attack by the aromatic compound upon a general electrophile E+ is shown in the left one-third of Sheet B, with arrows leading from the aromatic compound to E+. Therefore, in order to visualize the rate-determining step of a specific reaction, place Sheet A over the right two-thirds of Sheet B and align the head of the appropriate arrow on Sheet A with the base of the appropriate arrow on Sheet B. The steps involved in this process are (a) select the aromatic structure bearing the desired group type, (b) locate the corresponding base half of the arrow desired, (c) select the desired reagent(s) to be used or the electrophile provided, (d) determine the corresponding head half of the arrow desired, and (e) visualize the mechanism leading to the correct intermediate(s) by placing Sheet A over the right two-thirds of Sheet B and aligning the selected head half-arrow with the selected base half- arrow.

Two examples demonstrating the use of the EAS organization device to visualize the

mechanistic attack of the aromatic compound upon the electrophile (E or E+), leading to the intermediate and product with the proper regiochemistry are given on the reverse of Sheet B in the device. They are (a) Friedel-Crafts acylation of a halobenzene and (b) chlorination of phenol. The latter example is reproduced in Figure 1.

CONCLUSION

The effect upon learning brought about by using a teaching device has been measured. This device, the Nu/E Guide, consists of two sheets of card stock, one with nucleophiles, and one with electrophiles. The student can visualize a reaction mechanism by juxtaposing the two sheets in order to line up the selected nucleophile and the selected electrophile. Analysis of the results of the study shows that students using the device outside of class scored higher on pertinent exam questions (77%) than students not using the device (64%). The reason for this may be that students using the guide only out of class, put more thought into determining how to use the guide, and did not merely follow the demonstration. Therefore, these students learned more from the independent effort invested.

The success of the Nu/E Guide prompted development of a similar device dealing with electrophilic aromatic substitution (EAS), called the EAS Tool. To use this new device, one sheet is placed over the other in order to visualize the mechanism between the substituted aromatic compound selected and the chosen reagent. Testing of the EAS Tool is in progress.

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List 1. Comments of organic chemistry students using the Nucleophile/Electrophile Reaction Guide.

"I think the Nucleophile/Electrophile Reaction Guide is very beneficial in getting an overall view of the course's reactions. It provides us with an easy method to figure out the reactions in the course."

"One of my big problems was visualization of reactions. The Nucleophile/Electrophile Reaction Guide helped me to see where reactive sites were on the different functional groups."

"The Nucleophile/Electrophile Reaction Guide has helped immensely with my ability to learn and understand organic reactions. Although it does not give the detailed mechanisms, the table is a great tool to learn the fundamental reactions of Organic Chemistry. The ability to visualize which nucleophiles will react with the electrophiles has helped me build a foundation for my study of organic chemistry."

"The Nucleophile/Electrophile Reaction Guide helped me see how all of the reactions were interrelated and how there was a pattern between the reactions."

"I like the fact that the guide provides a condensed reference to facilitate learning the reactions. The sheets condense multiple chapters of information, and thus make it easier to find a specific reaction."

"The Nucleophile/Electrophile Reaction Guide was very helpful in the respect of time saving capabilities. For instance, all electrophile/nucleophile reactions which can occur are readily available for examination on two sheets of paper. One doesn't have to locate all reactions throughout the text for this valuable information."

"The Nucleophile/Electrophile Reaction Guide allows students to see the various reaction pathways that are possible."

"Organic chemistry has so much memorization. This Guide has provided a system to weeks of class material."

"The use of the Nucleophile/Electrophile Reaction Guide has made recognition of such reactions quicker and simpler to understand."

"The Nucleophile/Electrophile Reaction Guide has saved a great deal of time in studying these types of reactions."

"Nucleophile/Electrophile Reaction Guide is a most valuable tool for chemistry students. It has been of great benefit to me, and I'm sure it will be of great benefit to future students."

"The methods of study needed for Organic Chemistry are often as difficult as the subject itself. To quote a recent marketing campaign, often "the system is the solution." Much of chemistry study is often finding patterns or systems for understanding. The Nucleophile/Electrophile Reaction Guide provides a system in a format that easily, as well as expeditiously, provides one with a system for effective learning."

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