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Article

## Precise-Source-Target Arrow (PSTA): A Modified Method for Drawing Curved Arrows in Organic Chemistry

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### Abstract

Curved arrows are indispensable explanatory tools routinely used by organic chemists to illustrate reaction mechanisms. However, for students, curved arrows are vague, useless, and difficult to understand owing to the ambiguity associated with their starting point or endpoint, leading to regioselectivity or formal charge uncertainty. The drawn curved arrows also affect students' understanding of the electron flow processes in chemical reactions, forcing them to resort to memorization and rote learning. Given the importance of this study, it aimed to develop a modified method for drawing arrows to clarify the ambiguity associated with curved arrows and enhance students' ability to understand and use them. This study also aimed to compare students' performance in predicting products of perplexing reaction patterns using traditional curved arrows and the new method to assess its efficiency. The newly developed method, *Precise-Source-Target Arrows*, (PSTA) was tested to locate the starting point (source) and endpoint (target) of drawn arrows and eliminate any regioselectivity or formal charge uncertainty. This study was conducted on 148 students enrolled in two organic chemistry courses at the Lebanese International University and used Edpuzzle videos to explain the new method and collect students' responses to the embedded questions. The study found out that the PSTA method enhanced students' performance in predicting products and assigning charges compared to the traditional method and effectively clarified the uncertainties associated with a wide variety of arrow pushing patterns. It also enhanced students' performance, their positive evaluation, high preference for using it as an alternative to the traditional method, and its applicability for a broad spectrum of mechanisms. The encouraging results of this preliminary study call for a more detailed study incorporating more reaction patterns, larger student samples, and an assessment of the short and long-term effects of using PSTA on student learning of reaction mechanisms.

### Keywords

Teaching; Organic Chemistry; Curved Arrows; Arrow Pushing; Mechanism

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Curved arrows are indispensable tools for practicing organic chemists (Bhattacharyya, 2014; Graulich, 2015; Levy, 2017; Vosburg, 2008), but most students consider them ambiguous, illogical, and a source of complexity (Bhattacharyya, 2014; Bhattacharyya & Bodner, 2005; Flynn & Featherstone, 2017; Gerlach et al., 2014; Schweiker et al., 2020; Webber & Flynn, 2018). Students' failure to develop a comprehensive understanding of arrows increased their reliance on memorizing mechanisms rather than understanding them, thus transforming organic chemistry into a challenging topic and an obstacle in the students' educational path, even those with highly distinguished academic performance (Anderson & Bodner, 2008; Ferguson & Bodner, 2008; Finkenstaedt-Quinn et al., 2020; Grove et al., 2008).

Curved arrows, first introduced by Kermack and Robinson (1922), are powerful pictographic tools routinely used by organic chemists to depict the flow of electrons in reaction mechanisms (Alvarez, 2012; Bhattacharyya, 2013, 2021; Loudon et al., 1995; Sykes, 1996). Mechanistic reasoning plays a vital role in developing a profound understanding of reaction outcomes, designing new reactions, and planning synthetic routes for target organic compounds (Bhattacharyya, 2013; Ferguson & Bodner, 2008; Flynn & Ogilvie, 2015; Graulich, 2015; Houchlei et al., 2021; Levy, 2017).

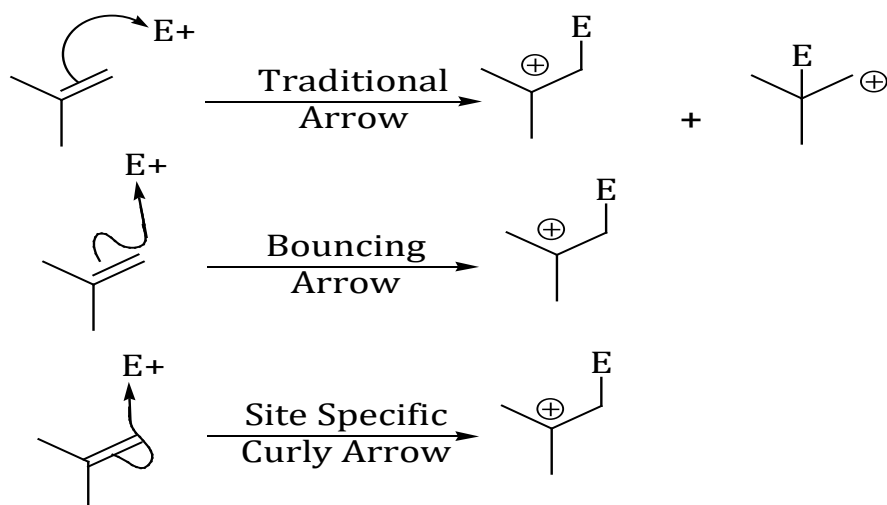
Students' incompetence to translate the information given by a drawn arrow to break bonds, form new ones, and redistribute charges usually prevents them from correctly using arrows to draw mechanisms and predict the products (Garcia-Martinez & Servano-Torregrose, 2015). This incomprehensive understanding of arrows is partially due to the vagueness associated with the starting point (source) of the arrow or its endpoint (target). Despite the importance of this topic and its impact on students' understanding of reaction mechanisms, only a few methods have been reported in the literature to solve this issue (Straumanis & Ruder, 2009b; Williams & Shaffer, 2017). The reported methods succeeded in clarifying some of the perplexing arrow-pushing patterns such as electrophilic addition reactions of alkenes, however, they have limitations and the development of simpler methods that can be applied to a broader spectrum of arrow-pushing patterns is necessary.

This study aimed to develop a modified method, *Precise-Source-Target Arrow (PSTA)*, for drawing curved arrows that precisely locates the source and target atoms of drawn arrows and eliminates any regioselectivity or charge uncertainties and assesses the efficiency of the new method and its impact on student learning in comparison with the traditional method. This research study was conducted at the Lebanese International University, a private university in Lebanon that has nine campuses and a big student population (> 35000). The study was conducted on students enrolled in two organic chemistry classes which are usually offered for students majoring in chemistry, biochemistry, and pharmacy.

## Literature Review

Despite being in use for almost a century, curved arrows are still attractive targets for researchers in the different fields of chemistry. Researchers in the chemical education field focused on the students' and educators' conceptual understanding of arrows, encountered challenges, and development of alternative approaches for teaching mechanisms and drawing arrows (Anderson & Bodner, 2008; Anzovino & Bretz, 2015; Bhattacharyya & Bodner, 2005; DeCocq & Bhattacharyya, 2019; Ferguson & Bodner, 2008; Flynn & Featherstone, 2017; Friesen, 2008; Galloway et al., 2017; Grove, Cooper, & Cox, 2012; Grove, Cooper, & Rush, 2012; Schweiker et al., 2020; Straumanis & Ruder, 2009a; Wilson & Varma-Nelson, 2018). Curved arrows have also been a subject of interest for some quantum computational studies that were used to propose plausible mechanisms for organic reactions (Schweiker et al., 2020), including organometallic ones (Sciortino et al., 2019). Recently, extended curved arrows were used to predict the structural effects on quantum interference in molecular junctions (O'Driscoll & Bryce, 2021).

Research studies and daily classroom experience revealed that curved arrows sometimes fail to fulfill their primary role in providing an informative image about the electron flow in reaction mechanisms (Schweiker et al., 2020), thus affecting the students' ability to understand and use arrows in predicting products. Two research groups tackled the regioselectivity perplexity in electrophilic addition reactions by changing the shape of the curved arrow. Straumanis and Ruder (2009b) proposed using a "bouncing curved arrow" that bounces back at the element that bonds to the target atom before completing its pathway. Williams and Shaffer (2017) suggested using a site-specific curly arrow, which acquired a trajectory that passed next to the element that bonds to the target site before completing its pathway (Figure 1).



**Figure 1:** Traditional, Bouncing & Site-Specific Curly Arrow

Although these two methods clarified the perplexity associated with the regioselectivity of electrophilic addition reactions by showing the atoms that form the new bond with the electrophile, however, there are some limitations. Using these methods in mechanisms involving multiple arrows or in situations where the target atom is improperly aligned reduces their usability since it adds complexity to the drawn mechanisms. The reported methods provided a qualitative study of students' and instructors' opinions toward the new methods through a short survey but lacked a detailed quantitative analysis of the efficiency of these two new methods on different arrow-pushing patterns in comparison with the traditional method and their impact on student learning.

## Methodology

### Research Design

The implemented strategy for developing the new method and assessing its efficiency was based on: identifying the most common sources of confusion in arrow pushing patterns in undergraduate organic chemistry courses; modifying traditional curved arrows to clarify the perplexing patterns; and comparing the students' performance in predicting products of perplexing arrow pushing patterns using the traditional and the PSTA methods.

### Identification of “Confusion Sources”

By carefully reviewing the most common arrow pushing patterns in undergraduate organic chemistry courses and using our experience (> 10 years) in teaching organic chemistry, we identified the most common “confusion sources” that prevent students from understanding traditional curved arrows and reaction mechanisms. Traditional curved arrows can be drawn starting from lone pairs, *sigma*, or *pi*-bonds as their electron sources and can end at bonds or atoms as their targets. For students, most of the arrow pushing patterns that start from lone pairs are clear (Figure 2, patterns 1 and 2). Students' confusion starts with pattern 3 which shows a change in the target of the arrowhead from atoms (patterns 1 and 2) to bonds (pattern 3), although the end result was forming a new bond between the source atom (X) and the target atoms (Y) or (Z) in all of them.

Arrows starting from the middle of bonds are usually more perplexing than those starting from lone pairs. Such arrows usually lead to regioselectivity or charge uncertainties in the products since they do not clearly show the source element that loses the electron and the element that bonds to the target atom, especially if the reagents are placed inappropriately, or the curvature of the arrow does not clearly show the direction of electrons flow (Anzovino & Bretz, 2015). In some patterns, such as the electrophilic addition reaction (pattern 4), an arrow starting from the middle of a *pi*-bond can have two possible source atoms and gives two possible products (pattern 4). In others, such as the three-membered ring cyclization reaction (pattern 5) and allylic resonance (pattern 6), although the arrow is starting from the same bond, there is only one possible product, and the nature of the formed product depends on the endpoint of the arrow.

Similarly, arrow pushing patterns that start from *sigma*-bonds can also lead to different products depending on the endpoint of the arrow, such as the rearrangement pattern (pattern 7) and fragmentation pattern (pattern 8). Such differences in interpreting arrows with similar starting points and the differences between the endpoints of different arrow patterns are usually the main reasons that prevent students from understanding arrows, thus resorting them to memorizing patterns rather than understanding them.

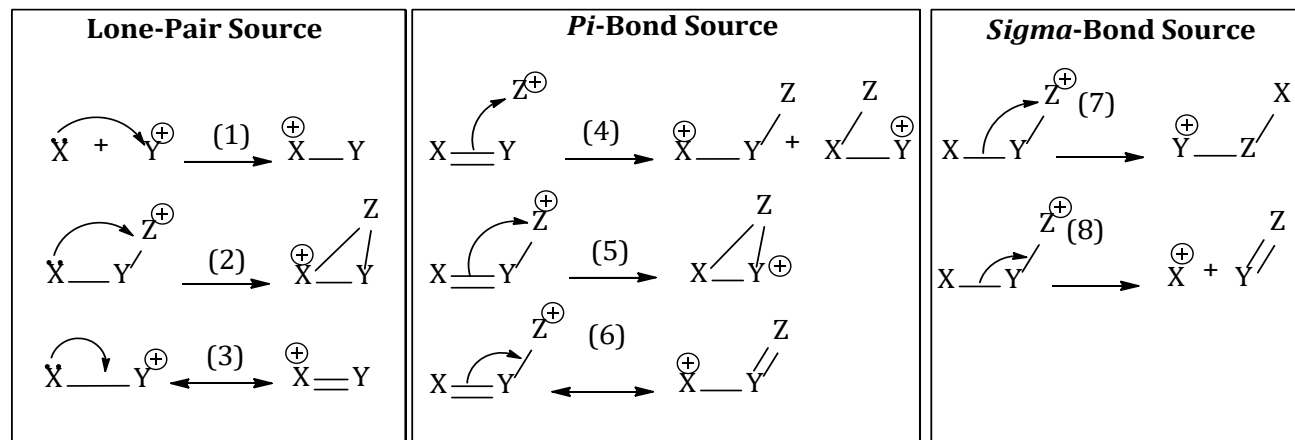


Figure 2. Confusion sources in common arrow pushing patterns.

Based on the above analysis, we modified the traditional arrows by precisely locating their starting point (source) and endpoint (target) to eliminate any regioselectivity or formal charge uncertainty and we named them “Precise Source-Target Arrow” (PSTA) to distinguish them from traditional ones.

### Precise-Source-Target Arrow (PSTA)

The “Precise Source-Target Arrow” (PSTA) method precisely locates the source and target atoms in any electron pushing process. Unlike other methods that rely on modifying the shape of the curved arrow (Figure 1), the PSTA method modifies either the starting point, endpoint, or both of a curved arrow without changing its traditional shape. Arrows drawn according to the PSTA method, neither begin from nor end at bond centers; they always start at bond sides and end at target atoms. According to the PSTA method, the arrow’s tail starts precisely from the bond side near the atom that loses the electron (*tail atom*), the head ends at the atom that gains the electron (*target atom*), and the new bond always forms between the *bonding atom*, which is adjacent to the tail atom, and the target atom (Figure 3).

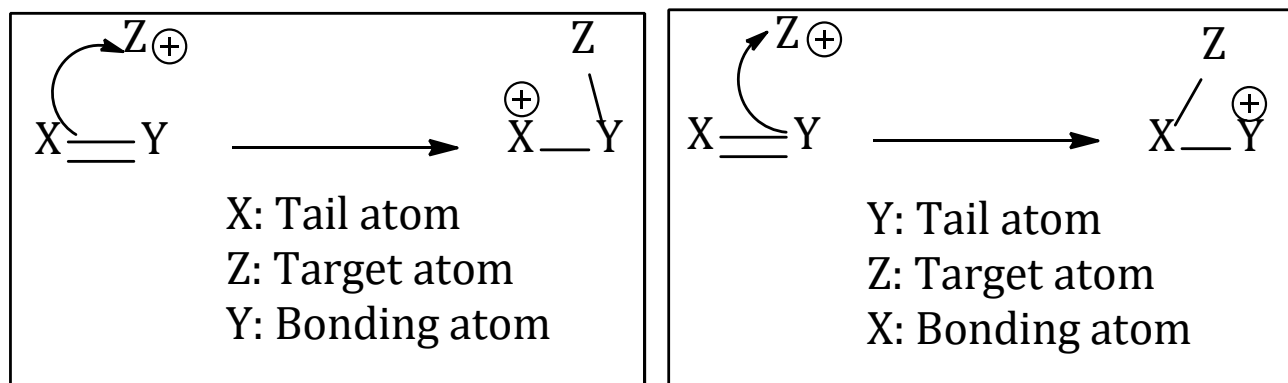


Figure 3. Precise Source-Target Arrow (PSTA)

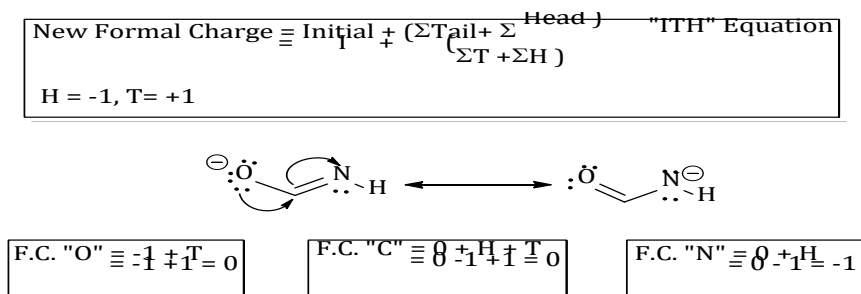
The physical significance of the PSTA method and traditional curved arrows is debatable (O’Driscoll & Bryce, 2021). We choose the starting point of the arrow (tail) to be at the bond side, not in the middle, and the endpoint (head) to be always at the target atom rather than at atoms and bonds as in the traditional method because

such an arrow clearly shows the atom that loses the electron (tail atom) and the atom that gains the electron (target atom), thus reducing students' confusion when placing charges. In addition to facilitating charge assignments, the PSTA method clarifies the perplexing regioselectivity by precisely locating the bonding atom that forms the new bond with the target atom. Table 1 summarizes the main types of modifications needed to convert traditional arrows into PSTA ones.

**Table 1.** Conversion of traditional arrows into PSTA

Traditional	Modification Site	PSTA
	Head	
	Tail	
	Head-Tail	

The PSTA method also fruited a student-friendly equation, the "Initial-Tail-Head" (ITH) equation, to track the formal charge changes during arrow pushing. According to the PSTA method, an arrow leaves a "+1" charge at the tail atom that loses the electron and affords a "-1" charge at the target atom that gains the electron. The ITH equation calculates the formal charge change based on the number of heads (H; H=-1) and tails (T; T=+1) at any element (Figure 3). The formal charges at the different elements involved in the resonance arrow pushing pattern in Figure 4 were calculated using the ITH equation. Initially, oxygen was negatively charged; the tail at oxygen indicates that it lost one electron, and its formal charge became zero. The formal charge of the central carbon does not change because the head and tail effects cancel each other. The formal charge of nitrogen changes from zero to (-1) because it gained one electron (head).



**Figure 4.** "Initial-Tail-Head" (ITH) Equation

### Research Sampling

To assess the efficiency of the PSTA method in clarifying the perplexing arrow pushing patterns and enhancing the students' performance in predicting products of selected patterns, a comparative study between the traditional and PSTA methods was conducted on a group of 200 students enrolled in two organic chemistry courses (organic I & II) at the Lebanese International University. Students enrolled in the organic chemistry I course had little experience with arrows since this study was conducted at the beginning of the fall semester and they were mainly familiar with resonance and acid-base reactions arrow patterns. On the other hand, students enrolled in the organic chemistry II course had more experience with arrows and were familiar with substitution, elimination, and addition reactions arrow patterns.

## Research Instruments and Procedure

The comparative study was done via Edpuzzle, a self-paced video learning platform with multiple useful features for online learning such as embedding questions, preventing video-skipping mode, and monitoring students' progress (Pulukuri & Abrams, 2020). Students were asked to watch a recorded video lecture about the traditional and PSTA methods and answer the embedded questions that popped up after finishing each section based on their understanding.

In the recorded video, initially, both methods were introduced briefly and the main differences between them were highlighted. In section one, the arrow pushing patterns that start from lone pairs were introduced, and then students were asked to answer question one. In section two, the arrow pushing patterns that start from *pi*-bonds were introduced briefly based on the traditional and PSTA methods respectively, and after explaining each method, students were asked to answer a set of three consecutive questions. In section three, students were asked to answer a set of questions related to arrow pushing patterns that start from *sigma*-bonds. The first two questions were related to the traditional method and the second two were related to the PSTA method. Finally, students were asked to choose their preferred method based on their performance in the previous questions and their understanding of both methods.

## Assessment Questions

The study questions were selected based on our preliminary analysis of the most common perplexing arrow pushing patterns, "confusion sources." In all questions (except question 2), the general symbols "X, Y, Z" were used to represent atoms instead of real atomic symbols to check the students' ability to understand the drawn arrows and translate them into products regardless of any prior knowledge about reactions or arrow pushing patterns. The choices in all questions were selected based on the frequently encountered mistakes related to charge location or misunderstanding of an arrow pattern with a similar one. Since the same group of students were evaluating both methods and answering similar questions, the order of questions that have similar answers such as the rearrangement and fragmentation patterns were reversed for traditional and PSTA methods to avoid any effect on the students' performance.

## Data Analysis

Data were statistically analyzed using Excel, categorical data were presented using counts and percentages. A Chi-Square test was carried out as a suitable comparison of categorical variables. A *p*-value of less than 0.05 was considered statistically significant.

## Results

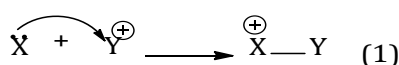
Students' participation in this project was voluntary, and out of the 200 students, 148 students completed the video and answered all the questions. Initially, the students' results were divided into two groups based on their class (organic I or II), later on, the results were combined since we did not find a significant difference between both data sets and this is probably due to our use of the general symbols "X, Y & Z" which forced students to mainly depend on their understanding of the material explained in the video and not their prior knowledge about arrows.

In question one, students were asked to compare patterns 1 to 3 and choose their preferred method for drawing pattern 3 (Figure 5). The traditional and PSTA methods share patterns 1 and 2, wherein both the arrow starts from the lone pair and ends at the target atom. The two methods differ in patterns 3 and 3a, which depict the formation of a *pi*-bond between two adjacent elements. In pattern 3, the arrowhead is directed toward the bond, and in 3a, it is pointed toward the target atom itself. The PSTA method for drawing such arrows (3a) was significantly preferred by 68 % of the students compared to 32 % that preferred the traditional one (3) (*p* < 0.00). During a class discussion conducted at the end of this study, students indicated that pattern 3a was preferable since it is more consistent with the first two patterns where the arrow always ends at the target atom when forming a new bond.

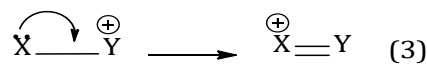


## Question 1

## Traditional &amp; PSTA



## Traditional



## PSTA

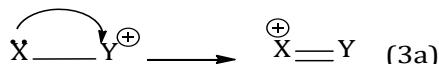
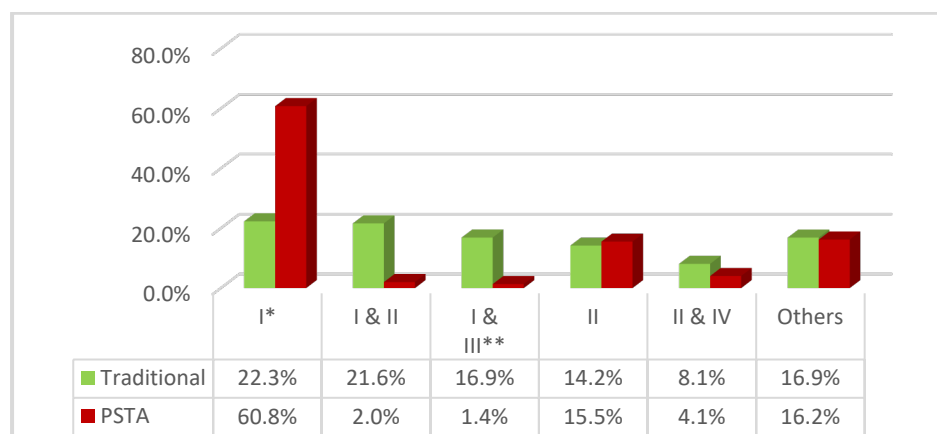
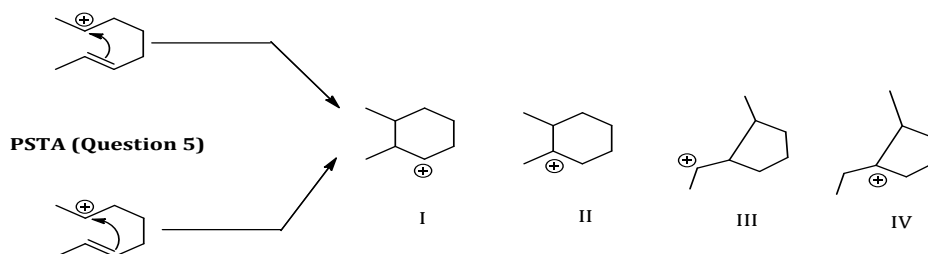


Figure 5. Lone pair sources

In section two of the video, arrows that start from  $\pi$ -bonds were introduced briefly according to the traditional method, and students were asked to answer questions 2 to 4, then the PSTA method was introduced for similar arrow patterns and students were asked to answer questions 5 to 7. In questions 2 and 5 (Figure 6), students were asked to predict the intermediates of an intramolecular electrophilic addition cyclization reaction using the traditional and PSTA methods, respectively. The results in Figure 6 show that 60.8 % of the students predicted the correct answer (I) for question 5 using the PSTA method compared to only 16.9 % that chose the correct answer (I & III) for question 2 using the traditional method. The p-value ( $p < 0.00$ ) was calculated based on the students' choice of the correct answer and indicated a significant difference between the two methods.

## Traditional (Question 2)

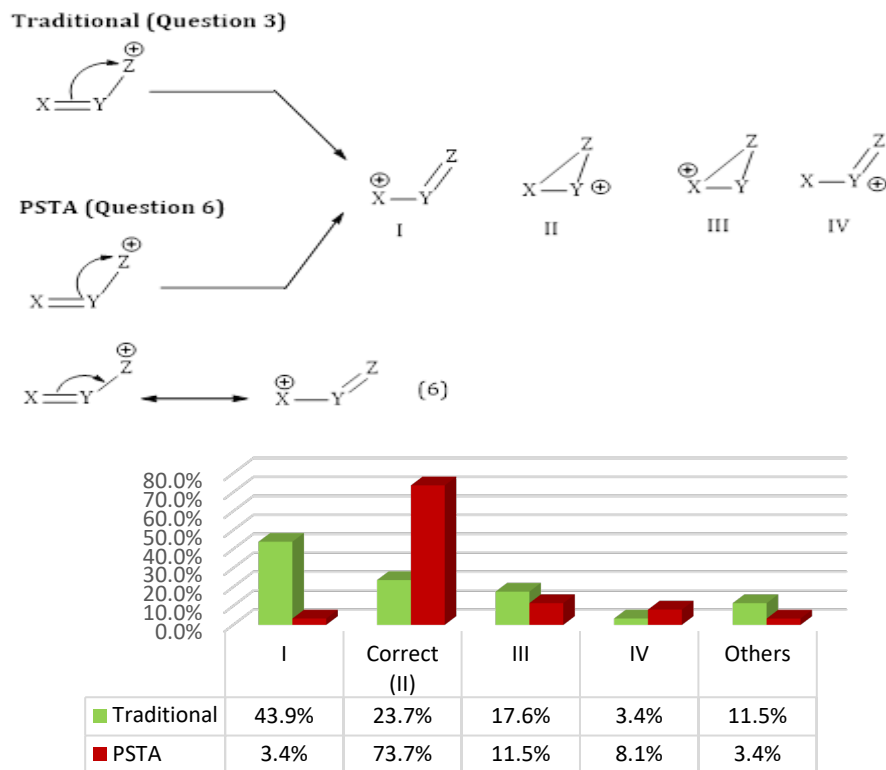


\*\* Correct answer for question 2

\* Correct answer for question 5

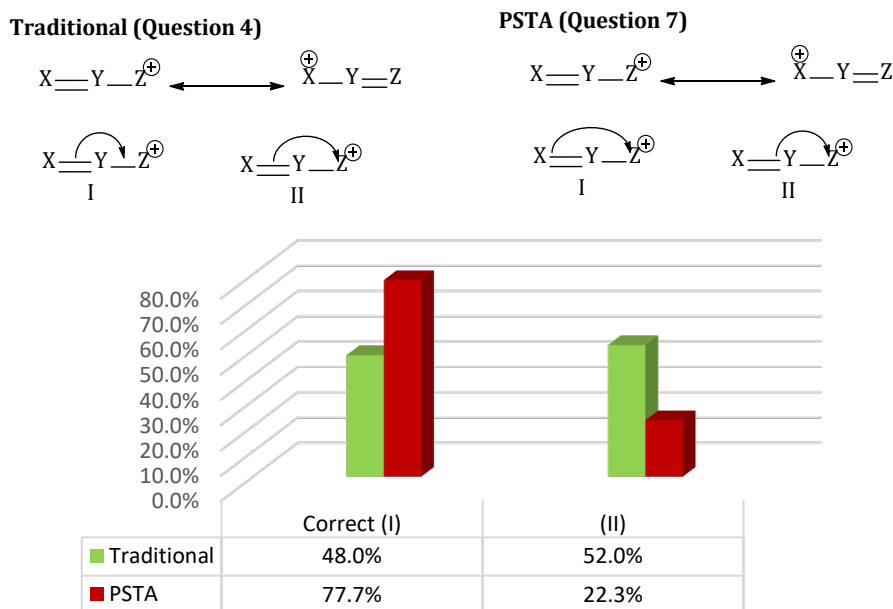
Figure 6. Intramolecular electrophilic addition reaction

In questions 3 and 6 (Figure 7), students were asked to predict the product of the three-membered ring cyclization reaction, which is often confused with the allylic cation resonance pattern (equation 6) that differs only in the endpoint of the arrow, that is directed toward the Y-Z bond. Using the traditional method, 43.9 % of the students chose the incorrect resonance product (I) and only 23.7 % predicted the correct cyclization product (II). However, using the PSTA method, 73.7 % of the students significantly predicted the correct cyclization product (II) and only 3.4% selected the incorrect product (I) ( $p < 0.00$ ).



**Figure 7.** Cyclization vs Resonance

The students' ability to select the right arrows based on the given products was tackled in questions 4 and 7 (Figure 8). In these questions, students were asked to select the correct arrow for the allylic cation resonance pattern using the traditional (question 4) and PSTA (question 7) methods. Using the traditional method, only 48 % of the students chose the correct arrow (I), whereas using the PSTA method 77.7 % selected the correct arrow (I) ( $p < 0.00$ ). The results of questions 3 and 4 clearly show that students often face difficulties distinguishing between very close arrow pushing patterns using the traditional method whereas, using the PSTA method (questions 6 and 7), students had more success in predicting the products and choosing the correct arrows.



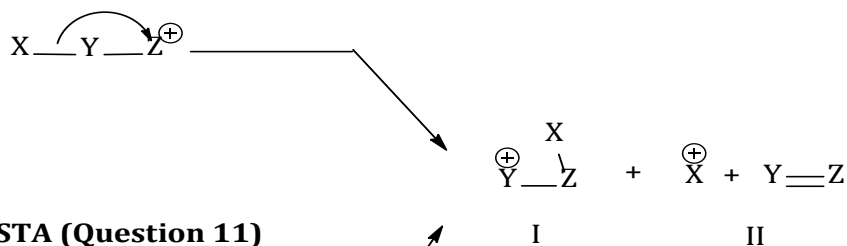
**Figure 8.** Resonance arrows



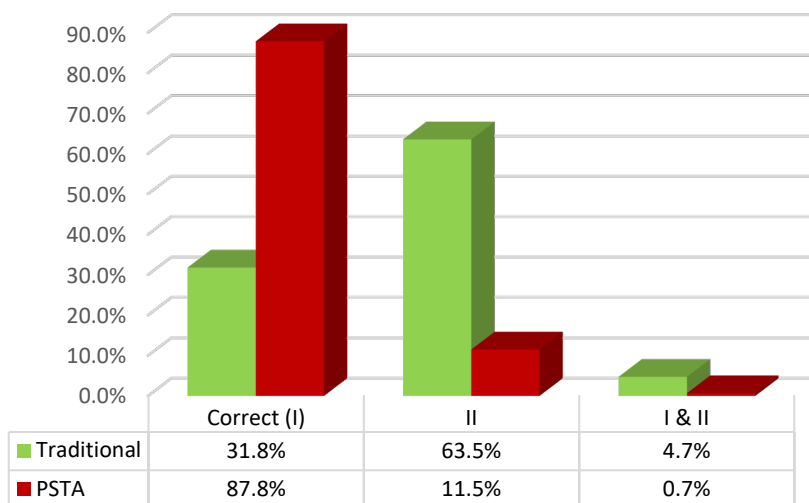
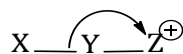
In section three of the video, arrow-pushing patterns that start from *sigma*-bonds were addressed in questions 8 to 11. Rearrangement and fragmentation arrow pushing patterns are often confusing for students using the traditional method since they only differ in the endpoint of the arrow, which is directed toward the target atom in rearrangements (Figure 9, question 8) and toward the bond in fragmentation (Figure 10, question 9). To compare the students' performance using both methods and evaluate the efficiency of the PSTA method in minimizing such confusions, students were asked to predict the products for the arrow pushing patterns in questions 8 to 11 (Figure 9 and Figure 10).

The order of similar questions was reversed in this section to avoid any effect on students' performance and to ensure that students were choosing products based on their understanding of the drawn arrows. In questions 8 and 11, students were asked to predict the product of the rearrangement pattern. Only 31.8 % of the students were able to correctly choose the rearrangement product (I) using the traditional method compared to 87.8 % using the PSTA method (Figure 9). This significant difference ( $p=0.00$ ) in the students' ability to choose the correct products using the two methods indicated an enhancement in the students' ability to predict products using the PSTA method.

### Traditional (Question 8)



### PSTA (Question 11)



**Figure 9.** Rearrangement

For the fragmentation pattern (Figure 10), 81.8 % of students selected the correct fragmentation product (II) using the PSTA method versus 74.3 % using the traditional one. The difference in this case was not significant ( $p = 0.21$ ), but the results of questions 8 and 9 confirm our primary analysis which indicated that students were not able to distinguish between the rearrangement pattern (question 8) and the fragmentation pattern (question 9) using the traditional method although they were consecutively asked and selected the same fragmentation product (II) in both questions (63.5 % in 8 and 74.3 % in 9). On the other hand, using the PSTA method students successfully differentiated between both patterns and selected the correct products with high percentages.



The PSTA method and the ITH equation enabled students to precisely identify the bonding atom and predict the correct ring size based on the drawn arrows (Figure 6). Using the PSTA method, students easily distinguished between the allylic resonance and three-membered cyclization patterns. Similarly, PSTA enabled students to successfully differentiate between rearrangement and fragmentation patterns whereas using the traditional method students failed to do so (Figures 9 and 10). By precisely locating the bonding atom, target atom, and the adjacent atom, the PSTA method proved to be more student-friendly, easier to apply, and enabled students to predict the products based on their understanding of the drawn arrows and not memorization, even for unfamiliar arrow pushing patterns.

The results of this study confirm the results of previous studies that illustrated the perplexity associated with traditional curved arrows and provided a quantitative analysis to support these findings (Anderson & Bodner, 2008). These results also provided a preliminary data confirming that students' learning and satisfaction was enhanced using a modified version of curved arrows which is consistent with the findings of similar studies done before (Straumanis & Ruder, 2009a).

The PSTA method can be used in classroom in parallel with the traditional method which remains the primary method for drawing curved arrows in reaction mechanisms. Similar practices have been used in well-known textbooks to clearly show the flow of electrons in perplexing patterns (Clayden et al., 2001). An example of the parallel use of both methods in the classroom is illustrated in Figure 11. In equations 9a and 9b, the PSTA method is used to explain the formation of both products in the electrophilic addition reaction of alkenes to hydrogen bromide. In 9a and 9b, the PSTA method clearly shows the source atom that lost the electron (disubstituted & mono-substituted carbons respectively), the trajectory of the moving electron as it moves toward the target atom "H", which uses this electron to make the new bond.

Another example of using PSTA in the classroom to explain charge changes in rearrangements is illustrated in Figure 11. Using the PSTA method, the drawn arrow clearly shows the transfer of an electron from the tertiary carbon toward the target atom (secondary carbocation) that makes the new bond with the migrating hydride (equation 10a) and clarifies any confusion that might arise. Using the PSTA method enabled students to visualize the electron flow processes depicted by the drawn arrows in a better way and correctly predict the charges and products.

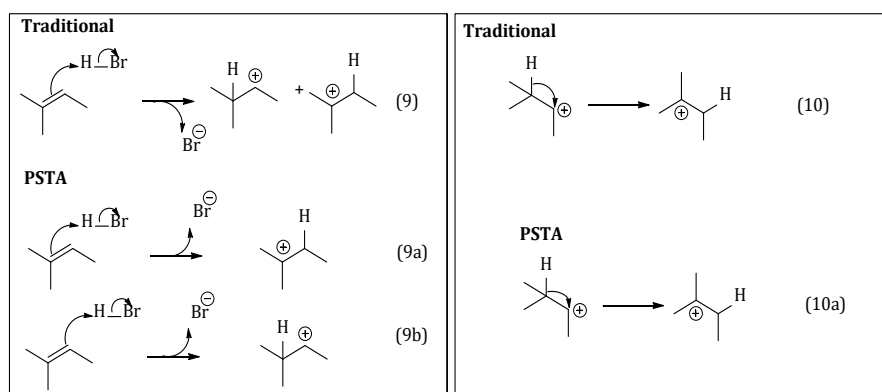


Figure 11. Clarifying traditional arrows using PSTA in classroom

## Conclusion

This paper presented a modified method (PSTA) that simplified the depiction and use of arrows by specifying precisely their sources and targets, thus demystifying any regioselectivity and charge uncertainties. Using the PSTA method and the "ITH" equation, students successfully translated mechanistic steps into products and differentiated between similar arrow pushing patterns. The students' improved performance, positive evaluation, and high preference for the PSTA method over the traditional one make it a student-friendly, successful, and easy-to-use tool and a forward step in restoring the role of curved arrows as successful explanatory tools. The applicability of the PSTA method for a broad spectrum of mechanisms makes it good support to the traditional method and an effective tool in the organic chemists' toolbox.

Using PSTA in classrooms has limitations since the traditional method of drawing arrows remains the primary tool of drawing mechanisms in our classrooms and in textbooks, and students are urged to learn and use the traditional method to pursue their studies and take standardized exams. The PSTA method can be still used in parallel as a supporting explanatory tool to clarify the ambiguous points. Although this method provided positive results regarding students' ability to predict products of reactions, however more detailed studies using larger samples, students from different educational backgrounds and different question styles are needed to provide solid evidence of its usability and efficiency. The positive preliminary results of this study can also provide the basis for more research studies that focus on the long-term effects of using PSTA on students' conceptual understanding of organic reactions and mechanisms. Further investigations of the students' ability to draw reasonable reaction mechanisms using PSTA if they were given the products can be also one of the future research plans.

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