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In the Classroom

# A Consistent System of Curved Electron Arrows

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*This system of electron arrows is superior because the rules can be more generally applied, the arrows reflect the nucleophilicity of electron pairs….*

Many students of organic chemistry find it difficult to properly use electron arrows. Traditional arrows do not end at one type of location. Whereas the vast majority end at an atom, an arrow that indicates formation of a π bond points to a bond instead. Rethinking electron arrows leads to the following four rules, which form a consistent system:

1. An electron arrow always begins at an electron pair, either bonding or nonbonding. One arrow begins at the nucleophilic electron pair, if any.
2. An electron pair always remains attached to an atom, normally indicated by its arrow.
3. An electron arrow always ends at an atom, not at a bond. One arrow ends at the electrophilic atom, if any.
4. In a series of arrows for one mechanistic step, a succeeding arrow begins by the atom where the preceding arrow ends.

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This system of electron arrows is superior because the rules can be more generally applied, the arrows reflect the nucleophilicity of electron pairs, the arrows carry more meaning, the arrows in a series flow more directly from one to the next, and the arrows clearly prescribe products.

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Why do our organic chemistry students have so much trouble drawing curved electron arrows to show the movement of electron pairs in reaction mechanisms? We professors tell our students that these arrows help us understand patterns of bond making and breaking. Yet, their many wrong arrangements of electron arrows suggest that students are not mastering this important lesson.

I believe the problem lies in the traditional use of electron arrows. In Figure 1 consider parts of eleven mechanisms, commonly found in organic chemistry textbooks [1–9].

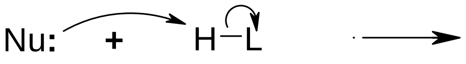
In the first column the mechanisms show the usual arrows, whereas the second column depicts my proposed arrows, to be discussed later. These 11 mechanisms contain 24 electron arrows. All 24 of the usual arrows begin at electron pairs, either bonding or nonbonding. Unfortunately they do not end at one type of location. Whereas 20 of the 24 arrows end at atoms, four arrows (marked with asterisks) in mechanisms 5–8 instead point to bonds.

Why do we tolerate this inconsistency? One rationalization states that each anomalous arrow shows the place where two atoms will share the electron pair in a π bond. By this rationalization the 12 electron arrows in Figure 1 that form σ bonds should also point between atoms, but instead they point to atoms. Such inconsistency frustrates the thoughtful student seeking to find rhyme or reason in electron arrows.

Any squeamishness about ending arrows at atoms can be dispelled on both pedagogic and theoretical grounds. It is pedagogically better to consistently end electron arrows at the same kind of molecular feature. Students can more dependably draw arrows if they always begin at electron pairs and always end at atoms. Furthermore, electron pairs are fundamentally nucleophilic (i.e., nucleus loving), not electrophilic. To emphasize this tendency it is better to show the electrons tending toward nuclei (i.e., atoms), not toward other electrons in bonds.

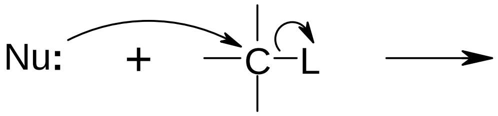
Usual arrows | Proposed arrows

### acid-base:



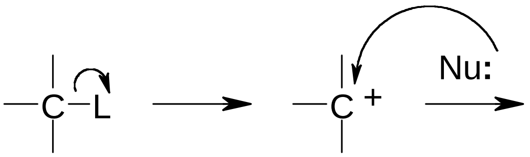
no change (1)

### $S_N2$:



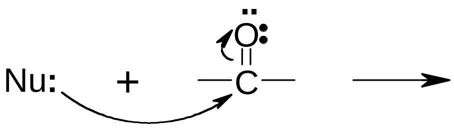
no change (2)

### $S_N1$:



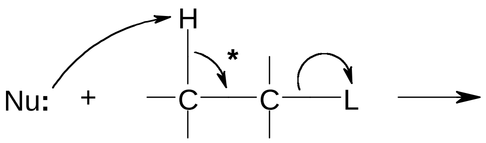
no change (3)

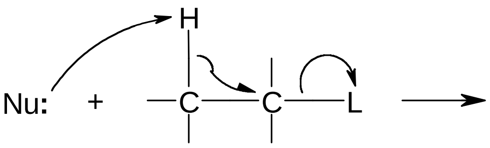
### carbonyl addition:



no change (4)

### E2:





(5)

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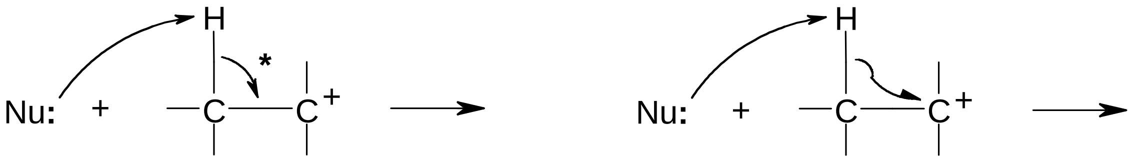
## E1, second step:



(6)

## acyl substitution, second step:

(7)

## Diels–Alder:

(8)

## alkene addition of acid, first step:

(9)

## carbocation rearrangement, hydride shift:

(10)

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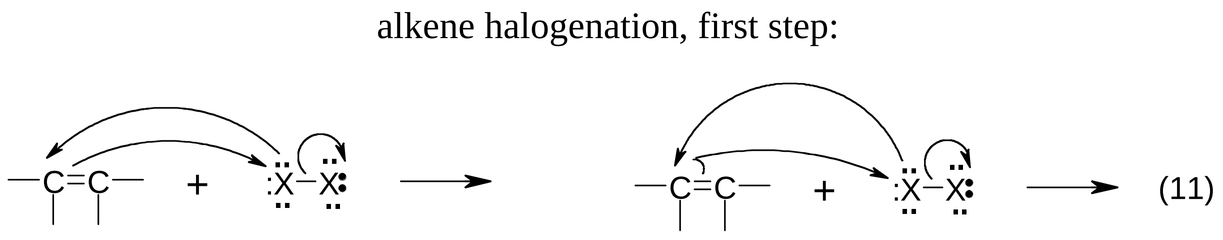

**FIGURE 1.** PARTS OF ELEVEN COMMON ORGANIC REACTION MECHANISMS.

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In addition, we should remember that the formation of a bond requires two atoms, not one. An electron arrow should clearly indicate the two atoms forming any bond.

Based on this rethinking of electron arrows, the following four rules form a consistent system:

1. An electron arrow always begins at an electron pair, either bonding or nonbonding. One arrow begins at the nucleophilic electron pair, if any.
2. An electron pair always remains attached to an atom, normally indicated by its arrow.
3. An electron arrow always ends at an atom, not at a bond. One arrow ends at the electrophilic atom, if any.
4. In a series of arrows for one mechanistic step, a succeeding arrow begins by the atom where the preceding arrow ends.

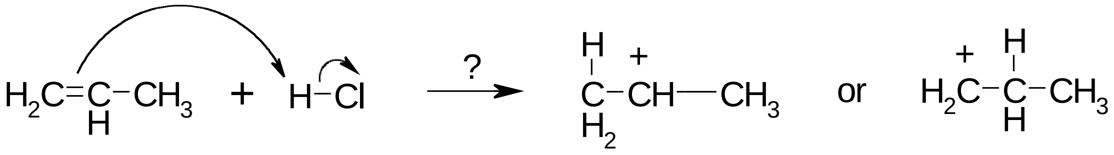
Although tradition accepts rule 1, it does not consistently observe rules 2–4. For example, consider the traditional arrows for the E2 mechanism, mechanism 5 in Figure 1:

The second arrow (marked with an asterisk) violates rule 3 by ending at a bond, not an atom. This arrow also violates rule 2 by not indicating that the carbon (not the hydrogen) remains with the bonding electron pair. Furthermore, by missing its target atom, the second arrow causes the third arrow to violate rule 4. My proposed arrangement, consistent with the systematic rules, uses a more curved second arrow.

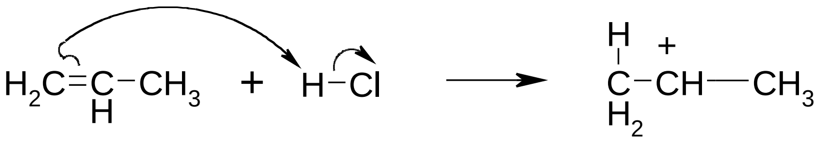
Likewise, in the second step of acyl substitution, mechanism 7 in Figure 1, one of the traditional arrows does not end at an atom.

Instead, both arrows should end at atoms.

The more curved arrow, consistent with rule 2, also helps visualize mechanisms where π bonds react as nucleophiles. For example, consider the traditional arrows for the addition of an acid to an alkene π bond.



The arrow beginning at the π bond does not show which of two carbons bonds to the acid's hydrogen. In contrast, a more meaningful, more curved arrow prescribes the carbocation to be expected.



A second justification for rule 2 lies in the mechanism of a hydride shift during a carbocation rearrangement, mechanism 10 of Figure 1. Without an extra curve in the arrow, the reaction might lead to either the rearranged carbocation or an alkene.

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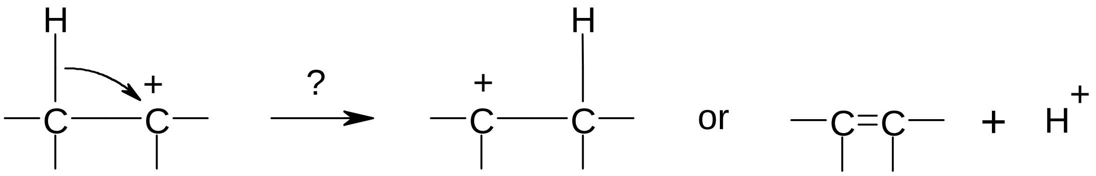
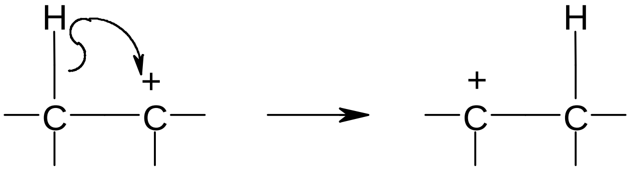


A more curved arrow, consistent with rule 2, prescribes the product without ambiguity.



This new system of electron arrows, therefore, is superior because the rules can be more generally applied, the arrows reflect the nucleophilicity of electron pairs (rules 1 and 3), the arrows carry more meaning (rules 1–3), the arrows in a series flow more directly from one to the next (rule 4), and the arrows clearly prescribe products (rule 2).

By using this system the last several years, my students now arrange electron arrows with more consistency and meaning, and write better mechanisms. Because the two systems of arrows are often not very different in practice and because of the inherent logic of the new system, students are not easily confused when seeing the traditional arrows. In fact, they enjoy “correcting” professors who display traditional arrows in later courses.

These rules apply to electron arrows that show electron pairs moving during reactions. They do not apply to “fishhook” arrows for unpaired electrons. They can be adapted, however, to generate resonance forms, as might be discussed in a later article.

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