E1 REACTIONS Solutions document

Step-by-step discussions for each of these solutions are available in the "E1 reactions" videos. There is also a "Brief Answers" document containing brief answers to each problem. You can find links to these resources at my website: <u>www.freelance-teacher.com</u>

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Solutions begin on next page.

Video (1)



Use the table to determine the mechanism.

	\checkmark how to determine the mechanism for alkyl halides and alkyl sulfonates						
		poor Nu / weak base)	good Nu / weak base	good Nu / strong base			
		O with no formal charge	Cl [•] , Br [•] , I [•] , CN, S [•] , N ₃ [•]	0', N			
		(water or alcohol)	or N, P, or S with no formal charge				
	methyl a-carbon	no reaction	S _N 2	S _N 2			
	1° a-carbon			Exception: E2 with t-butyloxide and 1° α-carbon			
$ \rightarrow $	2° α-carbon	S _N 1 major,	S _N 2	E2			
/		(El minor)					
	3° α-carbon	S _N 1 major,	S _N 1 major,	E2			
		E1 minor	E1 minor				
	Y						

We draw the minor E1 mechanism, rather than the major $S_N 1$ mechanism, because the problem specifies an "elimination reaction". (E1 and E2 are "elimination" reactions; $S_N 2$ and $S_N 1$ are "substitution" reactions.)

The reaction involves "heat". Heat is often used in $S_N 1$ or E1 mechanisms on a 2° α carbon. But, for this problem, the presence of heat plays no significant role in our solution to the problem.

Solution continues on next page

solution for Video (1), continued



Carbocation intermediate

E1 is a two-step mechanism: First step: Leaving group leaves α carbon Second step: Base takes β hydrogen, π bond forms between α and β carbons

 α carbon: the carbon attached to the leaving group, or the carbon with a positive formal charge β carbon: A carbon attached to the α carbon

We have labeled the "roles" played by atoms in the mechanism. In Step One, the neutral Br is the leaving group (LG). In Step Two, the water is the weak base (WB) and the β carbon is the strong acid (SA). Remember that a base is defined as something that "donates electrons to take a H⁺ from an acid". You can see that the oxygen in the water does play the role of a base. It donates electrons (since it is at the tail of the electron-pushing arrow) to take a proton from the β carbon.

Notice that we use H₂O as the weak base for Step Two, rather than Br⁻.

Cl⁻, Br⁻, and I⁻ are *very* weak bases, so, when water or alcohol solvent (ROH) is present, it is generally preferable to use the water or alcohol as the base, rather than the Cl⁻, Br⁻, or I⁻.

(HCl, HBr, and HI are very strong acids. Cl⁻, Br⁻, and I⁻ are the conjugates of HCl, HBr, and HI. The conjugate of a very strong acid is a very weak base.)

alkyl halide: a carbon chain ("alkyl" group) attached to a halogen (usually Cl, Br, or I). carbocation: A carbon ("carbo") with a positive formal charge ("cation"). alkene: A carbon-carbon double bond

Notice that the E1 mechanism shown above uses an alkyl halide as a starting material. The product is an alkene. The E1 mechanism has a carbocation intermediate. (An "intermediate" is a molecule that is the product of one step, and the starting material for the next step.) Solution continues on next page.

solution for Video (1), continued



Carbocation intermediate

For each mechanism step:

First, draw the electron-pushing arrows for that step.

Then, use the electron pushing arrows to draw the products of that mechanism step.

For each electron-pushing arrow: Erase a bond, or draw a new bond, or both.

Break a bond when the tail of the electron-pushing arrow is on a bond.

<u>Form a σ bond</u> when the arrow head is pointing to an atom which was not already sharing the electrons at the tail of the arrow. [This rule is discussed in more detail in Video (2).]

Form a π bond when the arrow head is pointing to a bond.

Examine each electron-pushing arrow in the mechanism above and determine whether it tells us you to erase a bond, draw a bond, or both!

It is crucial to get all the formal charges correct! For each mechanism step:

Make the atom that loses electrons at the *start* of the chain of arrows one step less negative i.e., one step more positive.

And make the atom that gains electrons at the *end* of the chain of arrows one step more negative —i.e., one step less positive.

THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

So be especially careful to check that:

In the product of Step One, carbon 2 should be positive.

And in the product of Step Two, the oxygen should be positive.

Solution continues on next page

solution for Video (1), continued



Carbocation intermediate

Carbon 1 and carbon 3 both have the same "connectivity", so you get the same product if you use either carbon 1 or carbon 3 as the β carbon. (You will usually lose credit if you include a "redundant" product in your answer.)

To describe the "connectivity" of a particular atom in a molecule, describe the *complete series* of all the atoms that the atom is connected to, and all the atoms that those atoms are connected to, etc., for the entire length of the molecule.

The connectivity of carbon 1 is: "Carbon 1 is attached to three hydrogens and a C⁺; the C⁺ is attached to one hydrogen and a methyl."

The connectivity of carbon 3 is: "Carbon 3 is attached to three hydrogens and a C⁺; the C⁺ is attached to one hydrogen and a methyl."

You can see that Carbon 1 and Carbon 3 have the same connectivity, so using either Carbon 1 or Carbon 3 as the β carbon results in the same E1 product.

To confirm this further, here are the two products you get from using either Carbon 1 or Carbon 3 as the β carbon. It should be apparent that these are two different pictures of the *same* molecule, just rotated differently.



guidelines for drawing an E1 mechanism

Label the α carbon and the β carbon(s) you will use in the mechanism.

Only a β carbon attached to one or more hydrogens can be used for E1.

If two β carbons have different "connectivity", they result in different E1 products.

If two β carbons have the same "connectivity", they result in the same E1 product.

Exception: If the E1 product has one or more stereocenters, then two β carbons with the same connectivity *may* result in different E1 products.

Video (2)



Use the table to determine the mechanism.

how to determine the mechanism for alkyl halides and alkyl sulfonates							
		poor Nu / weak base	good Nu / weak base	good Nu / strong base			
		Owith no formal charge	Cl., Br., I., CN, S., N ₃	0', N'			
		(water of alcohol)	or N, P, or S with no formal charge	STC22 5 141			
	methyl a-carbon	no reaction	S _N 2	S _N 2			
\rightarrow	1° α-carbon			Exception: E2 with t-butyloxide and 1° a-carbon			
	2° α-carbon	S _N 1 major,	S _N 2	E2			
		El minor					
	3° α-carbon	S _N 1 major,	S _N 1 major,	E2			
		E1 minor	E1 minor				

We draw the minor E1 mechanism, rather than the major S_N1 mechanism, because the problem specifies an "elimination reaction". (E1 and E2 are "elimination" reactions; S_N2 and S_N1 are "substitution" reactions.)

solution for Video (2) continued



E1 is a two-step mechanism: First step: Leaving group leaves α carbon Second step: Base takes β hydrogen, π bond forms between α and β carbons

We label the "roles" played by atoms in the mechanism: LG (leaving group), WB (weak base), and SA (strong acid).

Remember that a base is defined as something that "donates electrons to take a proton from an acid". You can see that the oxygen in the alcohol does play the role of a base. It donates electrons (since it is at the tail of the electron-pushing arrow) to take a proton from the β carbon.

In the carbocation intermediate, carbon 1 and carbon 3 obviously have different "connectivity". (For example, carbon 1 is directly connected to three hydrogens, while carbon 3 is directly connected to only one hydrogen.) So you get a different product if you use carbon 1 rather than carbon 3 as the β carbon. Since the problem asks for the "product(s)", for full credit we must draw mechanisms and products resulting from using both carbon 1 and carbon 3 as the β carbons, as shown above.

Solution for Video (2), continued



We have labeled the functional groups in the starting materials (alkyl halide, alcohol), intermediate (carbocation intermediate), and products (alkenes) above.

Alcohol: An OH group attached to one or more carbon chains.

Notice that we use CH_3OH alcohol as the weak base for Step Two, rather than Br^- .

Cl⁻, Br⁻, and I⁻ are *very* weak bases, so, when water or alcohol solvent (ROH) is present, it is generally preferable to use the water or alcohol as the base, rather than the Cl⁻, Br⁻, or I⁻.

Elimination mechanism: A mechanism in which one or more groups is eliminated from a molecule, and no groups are added.

E1 is an elimination mechanism. (The "E" in "E1" stands for "elimination.") For example, in the E1 mechanism above, we eliminated two groups from the alkyl halide: the leaving group, and the β hydrogen. No groups were added to the alkyl halide.

Solution for Video (2), continued



For each mechanism step: First, draw the electron-pushing arrows for that step. Then, *use* the electron pushing arrows to draw the products of that mechanism step.

For each electron-pushing arrow: Erase a bond, or draw a new bond, or both.

Break a bond when the tail of the electron-pushing arrow is on a bond.

<u>Form a σ bond</u> when the arrow head is pointing to an atom which was not already sharing the electrons at the tail of the arrow. (This rule is discussed in more detail in the video explanation.)

Form a π bond when the arrow head is pointing to a bond.

Examine each electron-pushing arrow in the mechanism above and determine whether it tells you to erase a bond, draw a bond, or both!

It is crucial to get all the formal charges correct! For each mechanism step:

Make the atom that loses electrons at the *start* of the chain of arrows one step less negative i.e., one step more positive. And make the atom that gains electrons at the *end* of the chain of arrows one step more negative—i.e., one step less positive.

THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows. So be especially careful to check that:

In the product of Step One, carbon 2 should be positive.

And in the product of Step Two, the oxygen should be positive.

Rules for using electron-pushing arrows to draw the products of a mechanism step

Number all the carbons in the starting materials, and in the products you draw.

Number the products *consistently* with how you numbered the starting materials.

For each electron-pushing arrow: Erase a bond, or draw a new bond, or both.

Break a bond when the tail of the electron-pushing arrow is on a bond.

Form a σ bond when the arrow head is pointing to an atom which was not already sharing the electrons at the tail of the arrow.

Form a π bond when the arrow head is pointing to a bond.

Change two formal charges.

Make the atom that loses electrons at the *start* of the chain of arrows one step less negative i.e., one step more positive.

Make the atom that gains electrons at the *end* of the chain of arrows one step more negative i.e., one step less positive.

Do not change the formal charge for any atom in the *middle* of the series of arrows.

THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

guidelines for drawing an E1 mechanism

Label the α carbon and the β carbon(s) you will use in the mechanism.

Only a β carbon attached to one or more hydrogens can be used for E1.

If two β carbons have different "connectivity", they result in different E1 products.

If two β carbons have the same "connectivity", they result in the same E1 product.

Exception: If the E1 product has one or more stereocenters, then two β carbons with the same connectivity *may* result in different E1 products.

Checklist of things to do for each reaction

Number *all* the carbons in the starting materials, intermediates, and products. Make sure your numbers for the intermediates and products are *consistent* with the numbers you used for the starting materials.

Label which specific atoms will play which roles.

Identify the "clues" that tell you which atoms will play which roles.

Label the α -carbon. *Write down* whether the α -carbon is methyl, 1°, 2°, or 3°.

Use the table to determine whether the reaction is $S_N 2$, $S_N 1$, E2, or E1. *Write down* the name of the mechanism.

Don't begin drawing the products for a mechanism step until you have *finished* drawing the electronpushing arrows for that step

The reaction is usually finished when the "main product" of a mechanism step has no formal charge. When the "main product" of a step has a formal charge, you usually need to continue the mechanism. Exception: the "main product" of an S_N 2 reaction can have a formal charge.

Video (3)



The instructions are to "Draw the product(s)", which implies we should draw both the S_N1 and E1 products for this reaction. Since the instructions for this problem don't mention the mechanism, on an exam you wouldn't need to write out the mechanism for this problem to get full credit. But it's still good practice to write out the full mechanism when you are practicing.



Be aware that "Me" stands for "Methyl", so "MeOH" is methanol (methyl alcohol).

What happens in an $S_N 1$ mechanism: First main step: Leaving group leaves α carbon Second main step: Nucleophile joins α carbon There may also be an acid/base step.

We have labeled the roles played by participating atoms: LG (leaving group), Nu (nucleophile), and E (electrophile), SA (strong acid), WB (weak base).

Notice that Step Two of the S_N1 mechanism uses a nucleophile, not a base. Compare that with E1. Step Two of an E1 mechanism uses a base, not a nucleophile.

In Step Two, the nucleophile is attacking a trigonal planar carbocation. Therefore, the nucleophile can attack from either in front of the page or from behind the page. Therefore, in the Step Two product, the oxygen can end up either on a wedge (retention of original starting material's configuration) or on a dash (inversion of the original starting materials configuration). For full credit, we must include both S_N1 products in our answer.

When a nucleophile attacks an atom with trigonal planar geometry, the nucleophile can attack from *either* of the two directions that are perpendicular to the flat plane.

1 stereochemistry

If the α -carbon in the product is a stereocenter, (or if the α carbon's stereochemistry matters because of cis/trans relationships around a ring) an S_N1 reaction will produce some products with *inversion* of configuration at the α -carbon, and

some products with retention of configuration at the α -carbon.

SNZ stereochemistry

When a nucleophile attacks an atom that is attached to a leaving group, the nucleophile will attack from the side *opposite* to the leaving group.

If the α -carbon in the product is a stereocenter (or if the α carbon's stereochemistry matters because of cis/trans relationships around a ring), the product of an S_N2 reaction will have *inversion* of configuration at the α -carbon.

Make sure you know the difference between S_N1 stereochemistry and S_N2 stereochemistry.



THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

The most common mistake on this mechanism is forgetting that, in the product of Step Two, the oxygen should be positive.

The "main" product of Step Two still has a formal charge (the positive formal charge on the oxygen). This is a clue that the mechanism needs one more step: an Acid-Base Cleanup step, to "clean up" the formal charge on the main product. (Notice that, if you forget to change the oxygen's charge to positive in the Step Two product, you won't realize that you need this Acid-Base Cleanup step!)

We use the MeOH as the weak base for this clean up step. Remember that Br⁻ is a very weak base, so it is preferable to use MeOH as our base, rather than Br⁻.

The MeOH alcohol is the solvent for the reaction. Since solvent is always present in large excess, we don't have to worry about running out of solvent molecules. So, even though we already used MeOH as the nucleophile in Step Two, there is plenty of MeOH left to act as a weak base in Step Three.

In general, a reaction is usually finished when the "main product" of a mechanism step has no formal charge. When the "main product" of a step has a formal charge, you usually need to continue the mechanism. (Exception: the "main product" of an $S_N 2$ reaction can have a formal charge.)

What happens in an $S_N 1$ mechanism: First main step: Leaving group leaves α carbon Second main step: Nucleophile joins α carbon There may also be an acid/base step.

Notice that, while an $S_N 1$ mechanism has two "main" steps, there may also be an acid/base step. In fact, *most* $S_N 1$ mechanisms that you see on exams will include an acid/base step, such as acid/base clean up step we used in Step Three of the mechanism above.



For each mechanism step:

First, draw the electron-pushing arrows for that step.

Then, use the electron pushing arrows to draw the products of that mechanism step.

For each electron-pushing arrow: Erase a bond, or draw a new bond, or both.

Break a bond when the tail of the electron-pushing arrow is on a bond.

Form a σ bond when the arrow head is pointing to an atom which was not already sharing the electrons at the tail of the arrow.

Form a π bond when the arrow head is pointing to a bond.

Examine each electron-pushing arrow in the mechanism above and determine whether it tells you to erase a bond, draw a bond, or both!

It is crucial to get all the formal charges correct! For each mechanism step:

Make the atom that loses electrons at the *start* of the chain of arrows one step less negative i.e., one step more positive.

And make the atom that gains electrons at the *end* of the chain of arrows one step more negative —i.e., one step less positive.

THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

The most common mistake on this mechanism is forgetting that, in the product of Step **Two, the oxygen should be positive.** This positive oxygen is the clue that tells us that we need Step Three, Acid-Base Cleanup.

Also check that, in the product of Step One, carbon 4 should be positive. And in the product of Step Three, the oxygen in MeO^+H_2 should be positive.

I discuss $S_N 1$ reactions in much more detail in the " $S_N 1$ reactions" video series.



Be aware that "Me" stands for "Methyl", so "MeOH" is methanol (methyl alcohol).

What happens in an E1 mechanism: First step: Leaving group leaves α carbon Second step: Base takes β hydrogen, π bond forms between α and β carbons

In the carbocation intermediate, carbon 3 and carbon 5 obviously have different "connectivity". (For example, carbon 5 is directly connected to three hydrogens, while carbon 3 is directly connected to only one hydrogen.) So you get a different product if you use carbon 3 rather than carbon 5 as the β carbon. Since the problem asks for the "product(s)", for full credit we must draw products resulting from using both carbon 3 and carbon 5 as the β carbons, as shown above.

Be sure that you got all the formal charges correct.

THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

So a common mistake for this problem would be to forget to the change the oxygen's charge to positive in the product of Step Two.



What happens in an E1 mechanism	What happens in an $S_N 1$ mechanism
Step One: Leaving group leaves α carbon	Step One: Leaving group leaves α carbon
Step Two: Base takes β hydrogen, and	Step Two: Nucleophile joins α carbon
π bond forms between α and β carbons	
	There may also be an acid-base step.

How is E1 similar to $S_N 1$? How is E1 different from $S_N 1$?

E1 is similar to S_N1 in that they have the same first step: Leaving group leaves the α carbon, forming the carbocation intermediate. Notice that the carbocation intermediate formed for S_N1 is identical to the carbocation intermediate formed for E1. The difference between E1 and S_N1 is that Step Two of S_N1 uses a nucleophile, while Step Two of E1 uses a base.

How is a base similar to a nucleophile? How is a base different from a nucleophile?

A base is similar to a nucleophile because both a base and a nucleophile are electron donors. The difference between a base and a nucleophile is that a nucleophile donates electrons *to join another molecule*, while a base donates electrons *to take a proton from another molecule*.



What is a substitution mechanism?

A substitution mechanism is a mechanism in which one or more groups is eliminated from a molecule, and no groups are added.

The "S" in S_N1 and S_N2 stands for "substitution". Notice, that, in the S_N1 mechanism above, the MeOH substitutes for the Br. (The "N" in S_N1 and S_N2 stands for "nucleophilic". The MeOH is a nucleophile, so S_N1 is a "nucleophilic" substitution.)

What is an elimination mechanism?

An elimination mechanism is a mechanism in which one or more groups is eliminated from a molecule, and no groups are added.

The "E" in E1 and E2 stands for "elimination". Notice that, in the E1 mechanism above, two groups are eliminated from the molecule (the Br leaving group, and the β hydrogen), while no groups are added.

This problem asks only for the "product(s)", not for the mechanism, so for this problem you can get full credit, even if you don't draw the mechanism. And if you saw this problem on an exam, it would likely be too time consuming to write out the *full* mechanism as we did above. Nevertheless, as a beginning ochem student, I recommend that you *should* draw the full mechanisms hen practicing, in order to get practice with the mechanism and gain insight into the reactions. And, on an exam, you could still find it helpful to draw an "abbreviated" version of the mechanism.

Video (4)



how to determine the mechanism for alkyl halides and alkyl sulfonates

		poor Nu / weak base	good Nu / weak base	good Nu / strong base
		Owith no formal charge	Cl', Br', I', 'CN, S', N ₃ '	0', N'
		(water or alcohol)	or N, P, or S with no formal charge	
	methyl a-carbon	no reaction	S _N 2	S _N 2
	1° a-carbon			Exception: E2 with <i>t</i> -butyloxide and $1^{\circ} \alpha$ -carbon
->	2° a-carbon	(S _N 1 major,	S _N 2	E2
		E1 minor		
1	3° a-carbon	S _N 1 major,	S _N 1 major,	E2
		E1 minor	E1 minor	

The instructions say to draw "all possible organic products", which indicates that we should draw both the $S_N 1$ and the E1 products. You can see from the title of the table above that it applies, not only to alkyl halides, but also to alkyl sulfonates. The starting material for this problem is an alkyl sulfonate.



The starting material is an alkyl sulfonate. The sulfonate group is a good leaving group.

The α carbon in a sulfonate is the carbon attached to the oxygen, not the carbon attached to the sulfur. Therefore, the α carbon for this starting material is carbon 1, not the carbon attached to the sulfur.

What happens in an $S_N 1$ mechanism: First main step: Leaving group leaves α carbon Second main step: Nucleophile joins α carbon There may also be an acid/base step.

In Step Two, the nucleophile is attacking a trigonal planar carbocation. Therefore, the nucleophile can attack from either in front of the page or from behind the page. Therefore, in the Step Two product, the oxygen can end up either on a wedge (retention of original starting material's configuration) or on a dash (inversion of the original starting material's configuration). For full credit, we must include both S_N1 products in our answer.

The stereochemistry at carbon 1 matters because carbon 1 is a stereocenter, attached to four different groups. Notice that, if we travel counterclockwise from carbon 1, it takes two "steps" to reach the methyl group (on carbon 5), whereas if we travel clockwise around the ring, it take four "steps" to reach the methyl group. Therefore, for purposes of checking for a stereocenter, the counterclockwise and clockwise paths do count as two different "groups" attached to carbon 1.

We do not change the stereochemistry at carbon 5, because carbon 5 is not participating in the reaction. An S_N1 reaction produces some products with inversion of configuration *at the* α *carbon*, and some products with retention of configuration *at the* α *carbon*. An S_N1 reaction makes no changes to the stereochemistry at any carbons *other* than the α carbon. In this problem, the α carbon 1, not carbon 5. So this S_N1 mechanism affects the stereochemistry at carbon 1, not at carbon 5.



alkyl sulfonate



THE MOST COMMON MISTAKE is forgetting to change the formal charge on the atom that loses electrons at the *start* of the chain of arrows.

The most common mistake on this mechanism is forgetting that, in the product of Step Two, the oxygen should be positive.

The most important factor in organic chemistry is the formal charges, because the formal charges are our main tool for determining what will happen in each step.

Therefore, when drawing the products of a mechanism step, the most important part to get right is the formal charges.

We need a third, Acid-Base Cleanup step to clean up the positive charge on the oxygen. If you forget to change the oxygen's charge to positive in the Step Two product, you won't realize that you need Step Three.

This problem does not require you to write out the mechanism to get full credit. But remember that, while you might not have time to write the full mechanism for this problem during an exam, it is still good practice to write the full mechanisms for the problems you solve during your initial practice. And you may find it helpful to write an "abbreviated" mechanism for this problem if you see it on an exam.

The electron-pushing arrow mechanisms are your *tools* for getting the right products!

When drawing a mechanism step, *first* draw all the electron-pushing arrows for the step. *Then* draw the products of that step. Don't begin drawing the products for a mechanism step until you have *finished* drawing the electron-pushing arrows for that step. The electron-pushing arrow mechanisms are your *tools* for getting the right products. In order to use that tool, you must draw the electron-pushing arrows for a mechanism step *before* you begin the drawing the products of that step.

This process is illustrated in the videos.

Solution continues on next page



What happens in an E1 mechanism: First step: Leaving group leaves α carbon Second step: Base takes β hydrogen, π bond forms between α and β carbons

In the carbocation intermediate, carbon 2 and carbon 6 have different "connectivity". You can see this because carbon 6 is one "step" away from the methyl group (on carbon 5), while carbon 2 is three "steps" away from the methyl group. Therefore, we must draw the products resulting from using both carbon 6 and carbon 2 as the E1 β carbons.

Notice that the "connectivity" of a particular atom in a molecule is based on the *complete series* of all the atoms that the atom is connected to, and all the atoms that those atoms are connected to, etc., for the entire length of the molecule. Carbon 6 is *directly* attached to the same four types of atoms as carbon 2 (two hydrogens and two carbons); but the "connectivity" of carbon 6 is still different than the connectivity of carbon 2 when we take into account the *complete series* of all the atoms that they are connected to through the entire length of the molecule.

You should be able to confirm that the two alkene products we get from using carbon 6 or carbon 2 as the β carbon are different from each other. In the first alkene product shown above, the double bond is one step away from the methyl group (on carbon 5), whereas in the second alkene product shown above, the double bond is two steps away from the methyl group. This confirms that the two alkenes are different molecules, which confirms that we need to include both alkenes among the products in our answer to the problem.

Solution to bonus question on next page

Bonus question

Here are alternative arrows that some students might have tried drawing for Step Three of the $S_N 1$ mechanism. Are these reasonable or unreasonable electron-pushing arrows? *Why*?



The electron-pushing arrows above are *unreasonable*, because the series of arrows begins on a positive formal charge.

A positive formal charge makes an atom want to receive electrons. But the atom at the beginning of the series of arrows is an atom that the arrows predict will donate electrons. The atom at the end of the series of arrows is the atom that the arrows predict will receive electrons. Therefore, an atom with a positive formal charge should be placed at the end of a series of arrows, to indicate that that atom wants to receive electrons. An atom with a positive formal charge should never be placed at the beginning of a series of arrows, since that is the position for an atom that wants to donate electrons.

You might find it tempting to put the positive oxygen at the beginning of the series of arrows because of its lone pair. You might argue that the lone pair makes positive oxygen want to donate electrons. This logic is false, however, because the importance of the positive formal charge "overrides" the importance of the lone pair.

An atom with a negative formal charge and a lone pair wants to donate electrons, and can be placed at the beginning of a series of arrows.

An atom with a neutral formal charge and a lone pair may also want to donate electrons, and may also be placed at the beginning of a series of arrows.

But an atom with a positive formal charge and a lone pair wants to receive electrons, and should be placed at the end of the series of the arrows, not at the beginning.

solution to Bonus question continues on next page

Solution to Bonus problem, continued Here are the correct arrows for Step Three of the S_N1 mechanism: $A \cap O = A$ $A \cap O = A$ A

Notice that these arrows put the positive oxygen at the end of the series of arrows, showing that the positive formal charge makes the oxygen want to receive electrons.

At the beginning of the series of arrows we put the neutral oxygen, showing that the lone pair makes the neutral oxygen want to donate electrons.

In a neutral oxygen, the lone pair makes the oxygen want to donate electrons.

But in a positive oxygen, the positive formal charge makes the oxygen want to receive electrons, despite the fact that the positive oxygen also has a lone pair.

The most important factor in organic chemistry is the formal charges. This is because the formal charges are our most important tool for drawing reasonable electron-pushing arrows.

Here are the rules for using formal charges to draw reasonable electron-pushing arrows.



At the beginning of the series of arrows, put a negative or neutral atom, never a positive atom. At the end of the series of arrows, put a positive or neutral atom, never a negative atom. In the middle of the series of arrows, put neutral atoms, not positive or negative atoms.¹

continued on next page

¹ There are some exceptions to this rule in introductory ochem.



Notice how our electron-pushing arrows in the correct mechanism below obey the rules we have discussed. At the end of each series of arrows is an atom with a positive formal charge. (Or, for Step One, a neutral atom.)

For this mechanism, we put a neutral atom at the beginning of each series of arrows; but we know that on other mechanisms we will often put negative atoms at the beginning of the series of arrows. We will never put a positive atom at the beginning of a series of arrows.



The most important factor in organic chemistry is the formal charges!

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