S_N1 REACTIONS
Problems document

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This video series is intended for students who find this material to be difficult, so in the videos I proceed slowly and repeat myself a lot. If you find the videos to move too slowly, you can simply try the problems in this Problems document, check your answers against the Answers document, and skip to the video explanations for any problems that you find confusing.

There is a table of contents for each individual video in the progress bar at the bottom of the video. You can use this table of contents to find particular problems you want to review.

TABLE OF CONTENTS FOR THE VIDEO SERIES

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Video (1)

OCHEM FUNDAMENTALS

This first video in the series covers fundamental concepts and techniques for understanding ochem reactions in general.

Then, beginning with the second video in the series, we will show how to use these fundamental concepts and techniques to understand specific S_N1 reactions.

The material in this video is partly a review of material we covered in the series on S_N2 reactions, but this video also contains new material not covered in the S_N2 series.

Problem (1a)
What is the most important factor in organic chemistry?

What is the most important tool for predicting what will happen in a reaction?

When you draw the products of a mechanism step, what is the most important part of the products to get right?

Does nature “like” or “dislike” formal charges?

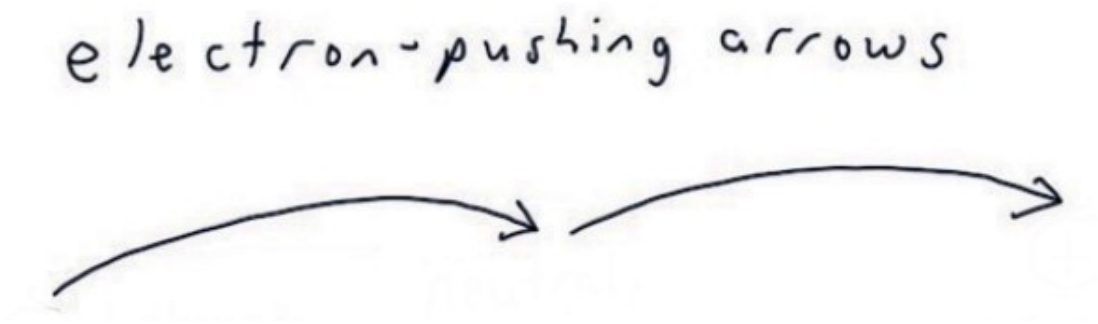
Does nature “prefer” atoms to be charged or neutral?

Does nature “prefer” formal charges to be big or small?

Which atoms are most likely to participate in a reaction?

Problem (1b)

Show the formal charges that we place at the beginning, middle, and end of a series of electron-pushing arrows.
The choices are “positive”, “negative”, and “neutral”.



For a mechanism step that consists of a single electron-pushing arrow,
show the formal charges that we place at the beginning and end of the electron-pushing arrow.

Problem (1c)
Define each of the following roles: nucleophile, electrophile, leaving group
How do you draw the electron-pushing arrows for each of these roles?
What are some clues that we can use to identify which atoms will play each of these roles?

Problem (1d)
What types of *neutral* atoms can be used as nucleophiles?

Problem (1e)
What are the clues for an electrophile?

What role does a metal with a positive formal charge play?

Video (2)

Problem (2a)

How many steps are there in an S_N2 reaction?

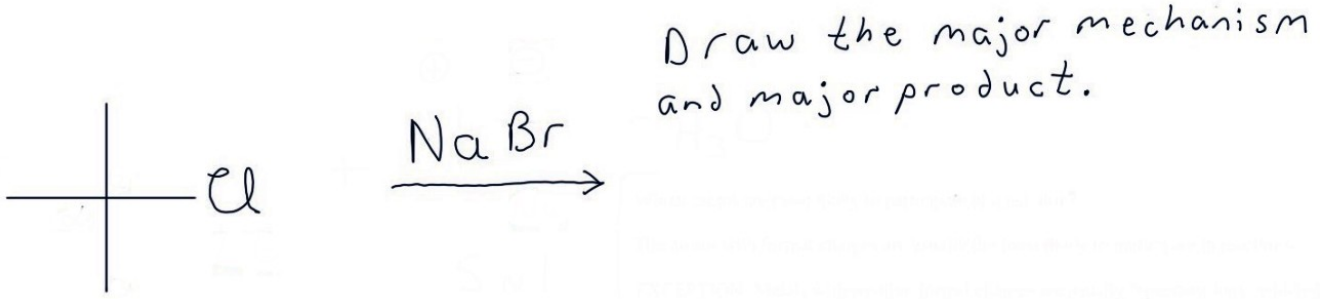
What happens during that one step?

Define “α carbon”.

How many steps are there in an S_N1 reaction?

What happens during those two steps?

Problem (2b)



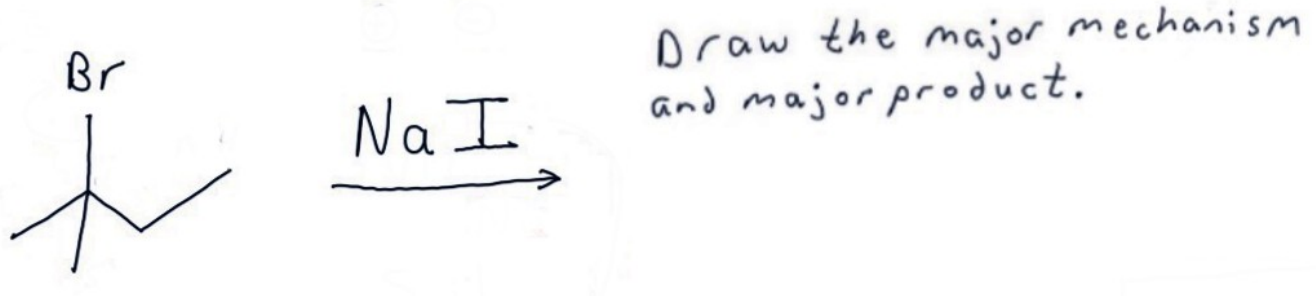
Checklist of things to do for the *first* step in a mechanism

1. Number *all* the carbons in the starting materials.
2. Draw formal charges for any ionic bonds.
3. Label which specific atoms will play which roles. Identify the "clues" that tell you which atoms will play which roles.
4. Label the α-carbon. Write down whether the α-carbon is methyl, 1°, 2°, or 3°.
5. Use the table to determine whether the reaction is S_N2, S_N1, E2, or E1. Write down the name of the mechanism.
6. Draw electron-pushing arrows for a mechanism step. Don't begin drawing the products for a mechanism step until you have finished drawing the electron-pushing arrows for that step
7. Draw the products of the mechanism step Number *all* the carbons in the products. Make sure your numbers for the products of a step are *consistent* with the numbers you used for the starting materials of the step.
8. Ask whether you have finished the mechanism, or require another mechanism 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_N2 reaction can have a formal charge.

Checklist of things to do for each step in a mechanism *after* the first step

1. Label which specific atoms will play which roles. Identify the "clues" that tell you which atoms will play which roles.
2. Draw electron-pushing arrows for the mechanism step. Don't begin drawing the products for a mechanism step until you have finished drawing the electron-pushing arrows for that step
3. Draw the products of the mechanism step Number *all* the carbons in the products. Make sure your numbers for the products of a step are *consistent* with the numbers you used for the starting materials of the step.
4. Ask whether you have finished the mechanism, or require another mechanism 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_N2 reaction can have a formal charge.

Problem (2c)



Problem (2d)
In the term "S_N1," what does the "S" stand for?

In the term "S_N1," what does the "N" stand for?

Problem (2e) (Review problem)

How many steps are there in an S_N1 reaction?

What happens during those two steps?

Video (3)

ACID-BASE STEPS

Most S_N1 mechanisms include an *acid-base step*.
In this video, we will learn how to draw the general mechanism for an acid base step.
Then, in the next video, we will learn how to draw an S_N1 mechanism that includes an acid-base step.

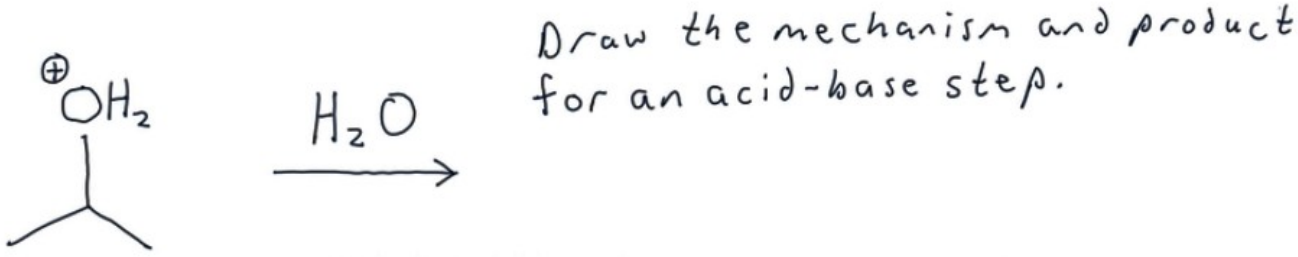
Problem (3a)
Define these roles: base, acid

Problem (3b)
Draw the electron-pushing arrow for a base.
Draw the electron-pushing arrow for an acid.

Problem (3c)
How is a base similar to a nucleophile?
How is a base different from a nucleophile?
Verbally describe how to draw the *first* arrow for an acid-base step.

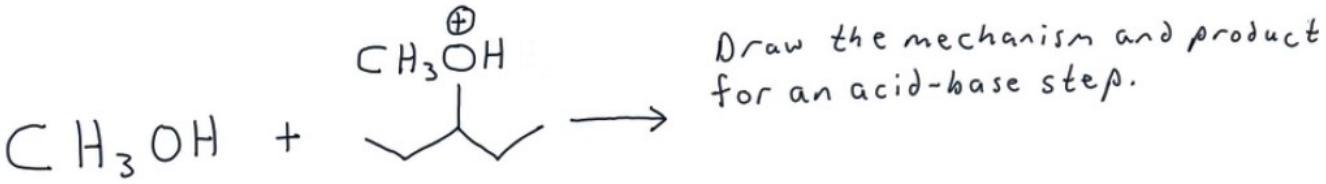
Problem (3d)
What are the clues that indicate an atom can be a base?
What are the clues that indicate an atom can be an acid?

Problem (3e)



When drawing the products of a mechanism step, what is the most important aspect of the products to draw correctly?
How many formal charges do you change for every mechanism step?
How do you know which formal charges to change for each mechanism step?

Problem (3f)



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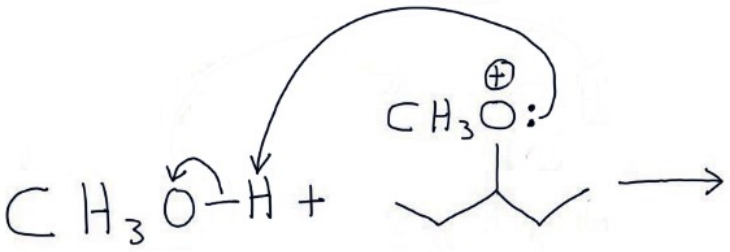
Problem (3g)

Are these reasonable or unreasonable electron-pushing arrows? Explain.



Problem (3h)
What is the difference between a strong base and a weak base?
What is the difference between a strong acid and a weak acid?

Are water and alcohols strong or weak bases?

Is an atom with a positive formal charge a strong or weak acid?

Who is more reactive, strong or weak acid?
Who is more reactive, strong or weak base?

Determine whether an acid-base step can occur for each set of starting materials below

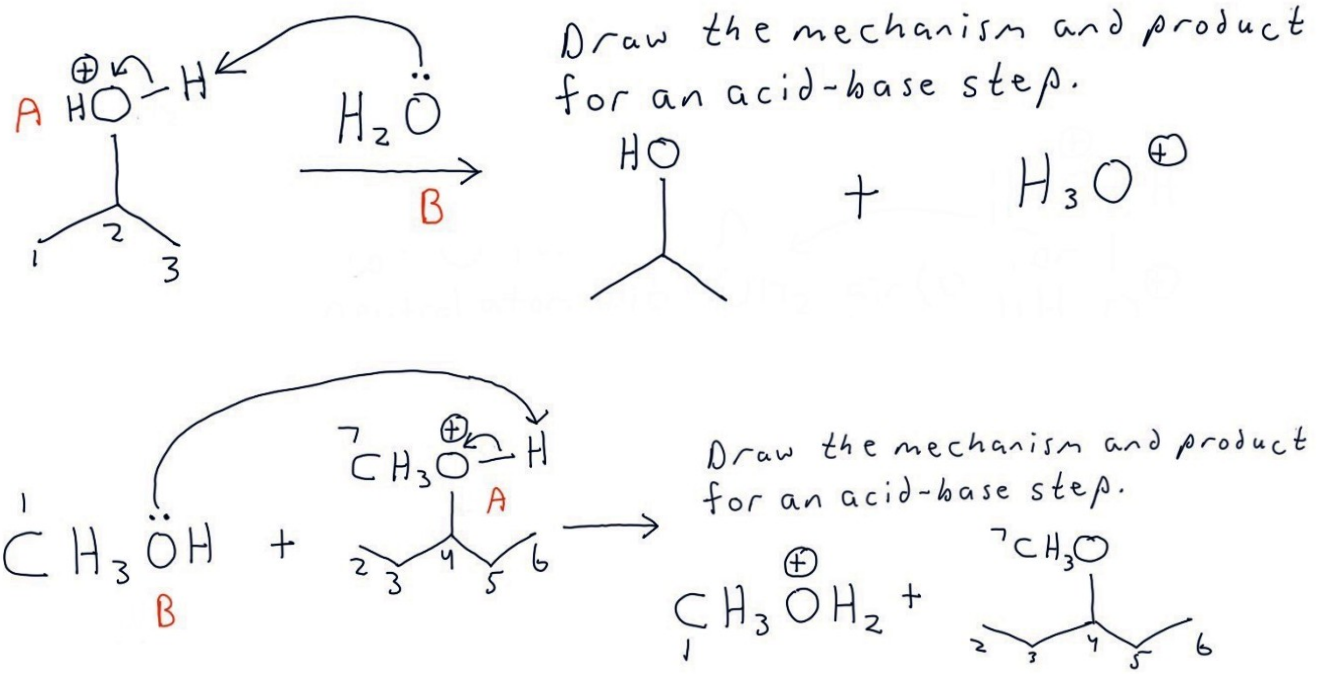
Can an acid-base step occur?

strong acid + strong base ⟶
strong acid + weak base ⟶
weak acid + strong base ⟶
weak acid + weak base ⟶

Problem (3i)

For each of the reactions that we saw earlier in the video, identify whether each acid or base is strong or weak. The reactions and our previous answers are shown below.

Confirm that an acid-base step can occur for each of the reactions we saw earlier in this video.



Problem (3j)

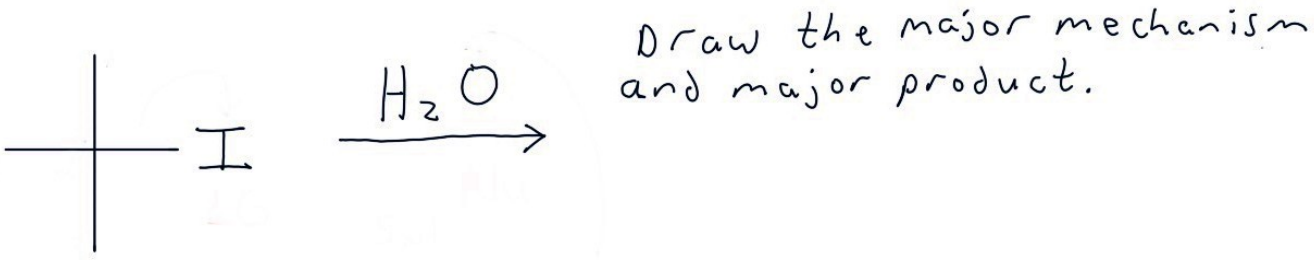
Are Cl^-, Br^-, and I^- strong or weak bases?

Are neutral Cl, Br, and I basic?

Video (4)

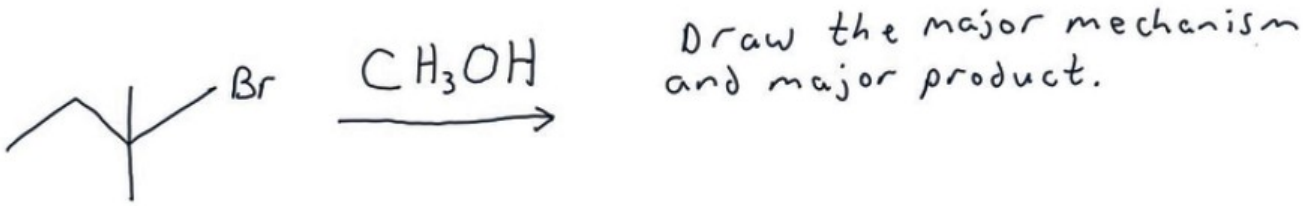
S_N1 REACTIONS INVOLVING AN ACID-BASE STEP

Problem (4a)



How can you tell when a mechanism is finished?

Problem (4b)



Problem (4c)
How many steps are there in an S_N1 reaction?
What happens during those steps?

Video (5)

S_N1 STEREOCHEMISTRY

Problem (5a)
What is the basic fact about S_N2 stereochemistry?
What is the justification for this fact?

What is the definition of the term “carbocation”?

Define these terms: cation, anion
How can you remember these definitions?

Does an S_N1 reaction have a carbocation intermediate?
Does an S_N2 reaction have a carbocation intermediate?

Problem (5b)
When does a carbon have tetrahedral geometry?
When does a carbon have trigonal planar geometry?

What is the geometry of a carbocation?

Most atoms that participate in ochem reactions have complete octets. What is the most important example in organic chemistry of an atom with an incomplete octet?

Problem (5c)

Draw the correct geometry for all the atoms attached to carbon 2.

Draw the correct geometry for all the atoms attached to carbon 5.

What is the correct way to draw the geometry for a tetrahedral atom?
What is the correct way to draw the geometry for a trigonal planar atom?

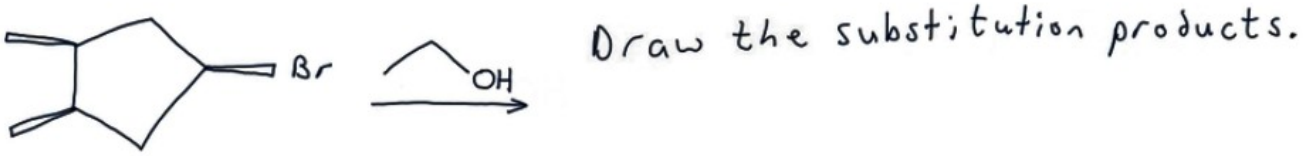
Problem (5d)
When a nucleophile attacks an atom with trigonal planar geometry, from what direction does the nucleophile attack?

Problem (5e)

Draw the major products.

Problem (5f)
What is the key fact about S_N1 stereochemistry? What is the justification for this fact?
What is the key fact about S_N2 stereochemistry? What is the justification for this fact?

Problem (5g)

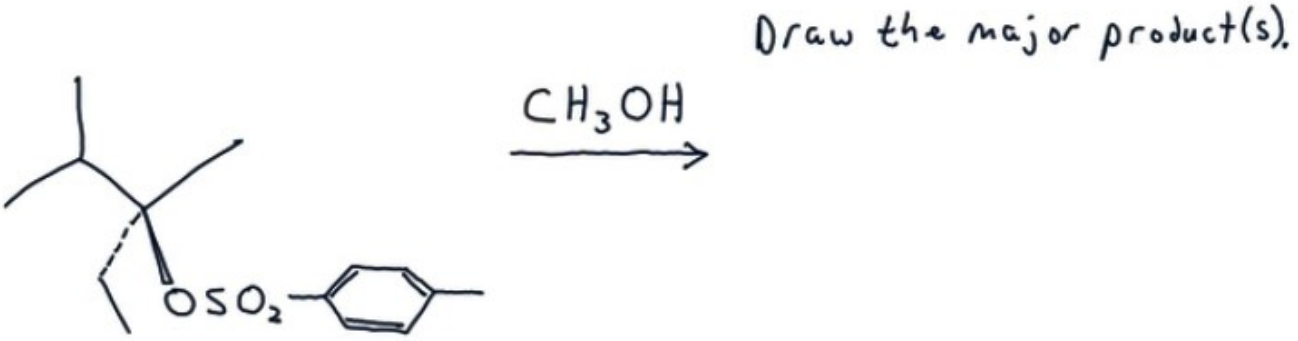


problems for Video (5) continue on next page

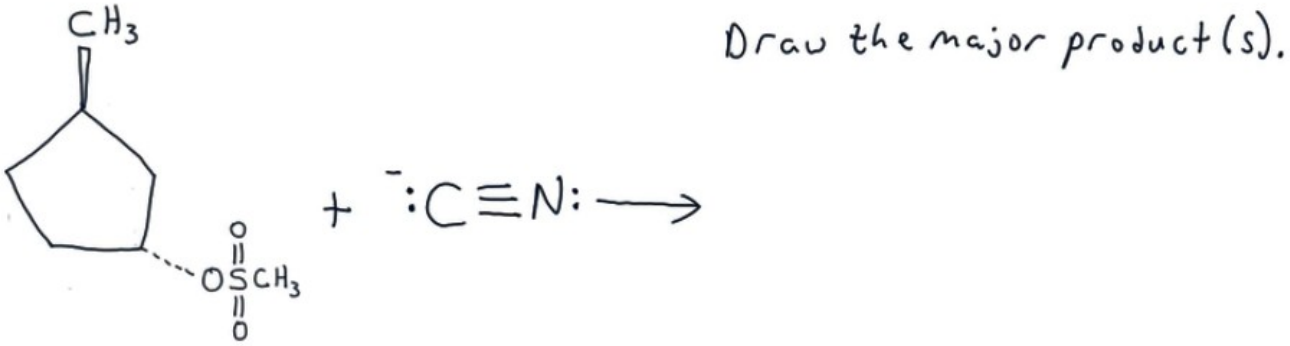
Problem (5h)

Now, in the mechanism you drew for Problem (5g), draw in the hidden hydrogen on the α carbon on the starting material, intermediates, and final products. Be careful to draw the correct geometry for these hydrogens.

Problem (5i)

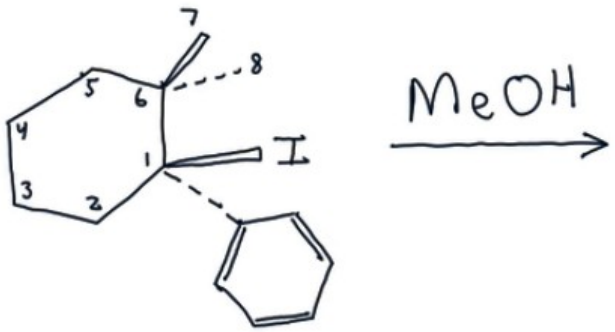


Problem (5j)



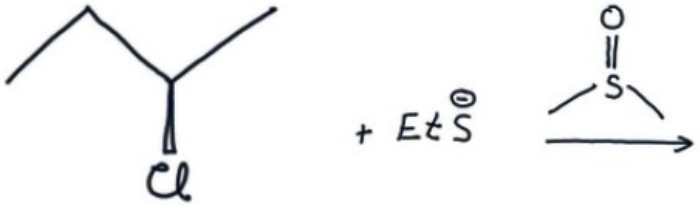
Problem (5k)

Draw the major product(s).



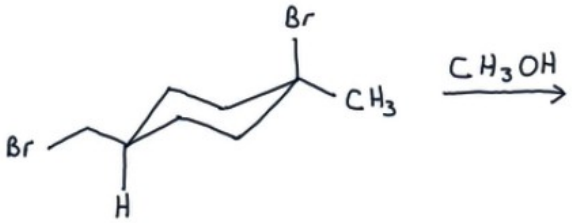
Problem (5l)

Draw the major product(s).



Problem (5m)

Draw the major product.
If more than one stereoisomer of the major product is produced, include all the stereoisomers.



Problem (5n)

What is the key fact about S_N1 stereochemistry? What is the justification for this fact?
What is the key fact about S_N2 stereochemistry? What is the justification for this fact?

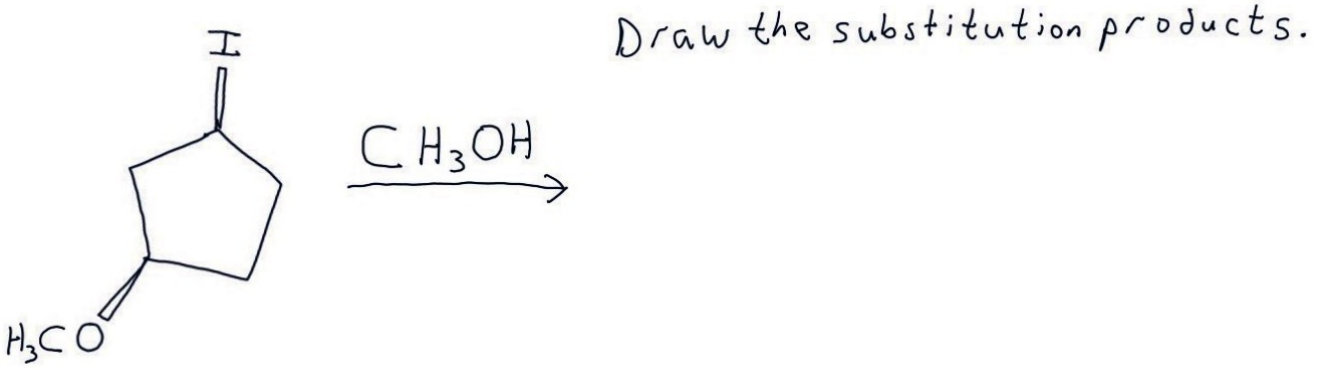
Review Quiz

What are the names of the five main roles in organic chemistry?
How is a base similar to a nucleophile?
How is a base different from a nucleophile?
Draw the electron-pushing arrows for an acid-base step.

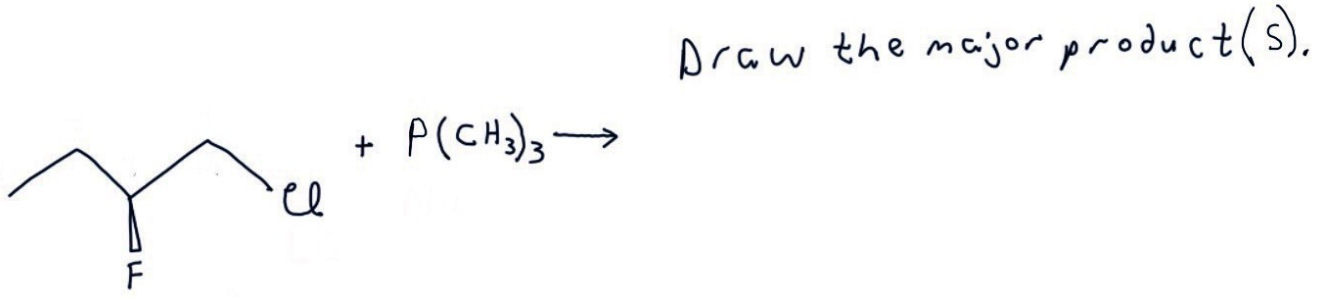
Video (6)

SUBSTRATES WITH MULTIPLE FUNCTIONAL GRUOPS

Problem (6a)



Problem (6b)



Review Quiz

Which roles in organic chemistry involve donating electrons?

Which roles in organic chemistry involve receiving electrons?

Video (7)

FACTORS THAT AFFECT THE RATE OF S_N1 AND S_N2 REACTIONS:
THE RATE-DETERMINING STEP

In this video we will use the concept of the "rate-determining step" to determine what factors can affect the rate of an S_N1 or S_N2 mechanism.

Then, in the next video, we will see how to apply this material to typical problems.

Problem (7a)

Define: rate-determining step

How can we use the rate-determining step to determine which factors affect the rate of a reaction and which factors do not affect the rate of a reaction?

What is the rate-determining step for an S_N1 reaction?

What is the rate-determining step for an S_N2 reaction?

Problem (7b)

In the terms "S_N1" and "S_N2", what does the letter *S* stand for?

What does the letter *N* stand for?

What do the numbers *1* and *2* stand for?

Problem (7c)

Does leaving group quality matter for the rate of an S_N1 reaction?

Does an S_N1 reaction require a good leaving group?

Does leaving group quality matter for the rate of an S_N2 reaction?

Does an S_N2 reaction require a good leaving group?

How can you tell whether an atom is a good leaving group?

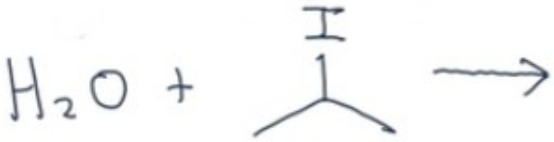
Can the following starting materials carry out an S_N1 reaction?

Can they carry out an S_N2 reaction?

Problem (7d)
Does nucleophile quality matter for the rate of an S_N1 reaction?
Does an S_N1 reaction require a good nucleophile?

Does nucleophile quality matter for the rate of an S_N2 reaction?
Does an S_N2 reaction require a good nucleophile?

Can the following starting materials carry out an S_N2 reaction?
Can they carry out an S_N1 reaction?



Which atoms are poor nucleophiles?
Which atoms are good nucleophiles?

Problem (7e)
What is the "big obstacle" to an S_N2 reaction?

Rank the types of α carbons (1°, 2°, 3°, and methyl) in terms of the rate of an S_N2 reaction, from slowest to fastest. Explain your ranking.

For which types of α carbons does S_N2 occur quickly enough to be a practical reaction? For which types of α carbons does S_N2 occur too slowly to be practical?

Problem (7f)
Is steric hindrance that blocks the nucleophile from joining the α-carbon a big obstacle for an S_N1 reaction? Why or why not?

Problem (7g)
Define: carbocation

Does an S_N1 reaction have a carbocation intermediate?
Does an S_N2 reaction have a carbocation intermediate?

Are carbocations “happy” or “unhappy”?
Do carbocations have too few electrons, or too many?

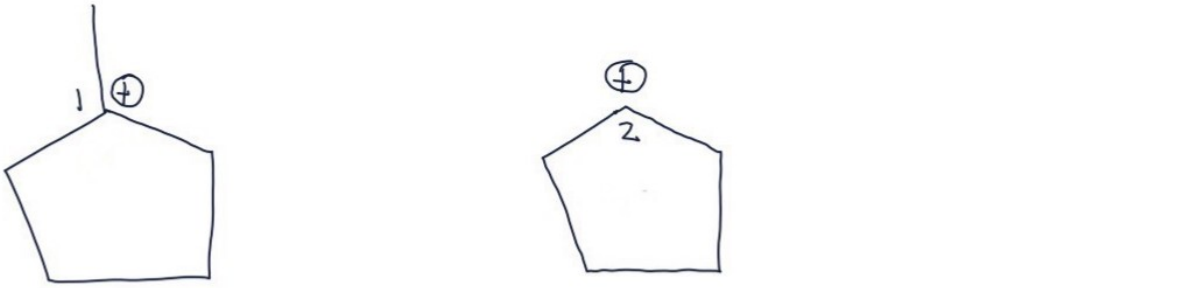
Problem (7h)
Are carbon chains (“alkyl groups”) electron-donating or electron-withdrawing?
Do carbon chains help to stabilize or destabilize a carbocation? Why?

Problem (7i)
Rank the types of carbocations (primary, secondary, tertiary, or methyl) from least stable to most stable. Justify your ranking.

What types of carbocations are stable enough to be formed during typical reaction mechanisms? What types of carbocations are usually too unstable to form?

Problem (7j)

(a)



Which is more stable, carbon 1 or carbon 2?

(b)

Which is more stable, carbon 3 or carbon 4?

(This is a trick question!)

Problem (7k)

Rank the different types of α carbons (primary, secondary, tertiary, or methyl) from slowest S_N1 rate to fastest S_N1 rate. Justify your ranking.

For which types of α carbons does S_N1 occur quickly enough to be a practical reaction? For which types of α carbons does S_N1 occur too slowly to be practical?

Problem (7l)

What is the "big obstacle" to an S_N1 mechanism?

Why does the stability of the carbocation intermediate matter for an S_N1 reaction?

Why doesn't "the stability of the carbocation intermediate" matter for an S_N2 reaction?

Problem (7m)
Can these starting materials carry out an S_N1 mechanism? Why or why not?
Can they carry out an S_N2 mechanism? Why or why not?

Problem (7n)

how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	**good Nu / weak base** Cl^-, Br^-, I^-, ^-CN, S^-, N_3^- or N, P, or S with no formal charge	**good Nu / strong base** O^-, N^-
methyl α-carbon **1° α-carbon**	no reaction	S_N2	S_N2 Exception: E2 with *t*-butyloxide and 1° α-carbon
2° α-carbon	S_N1 major, E1 minor	S_N2	E2
3° α-carbon	S_N1 major, E1 minor	S_N1 major, E1 minor	E2

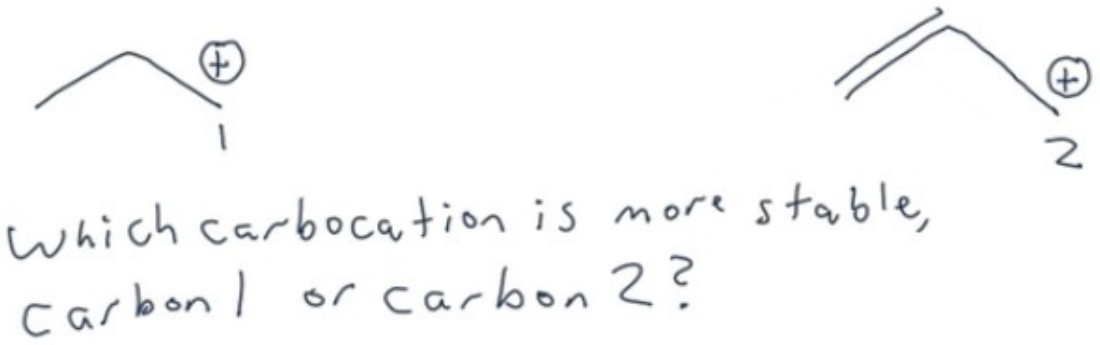
Why does the top left cell of the table predict "no reaction"?

Why are there no S_N1 reactions predicted in the top row of the table?
Why are there no S_N2 reactions predicted in the bottom row of the table?
Why are there no S_N2 reactions predicted in the left column of the table?

Problem (7o)

FROM MEMORY: Write out the complete table for determining the mechanism for alkyl halides and alkyl sulfonates.

Problem (7p)



Justify your answer.

Problem (7q)

Rank the following types of carbocations from least stable to most stable:
primary, secondary, tertiary, methyl, and primary with resonance stabilization

What types of carbocations from the list above are stable enough to be formed during typical reaction mechanisms? What types of carbocations are usually too unstable to form?

Problem (7r)

Rank the following types of α carbons from slowest S_N1 rate to fastest S_N1 rate:
primary, secondary, tertiary, methyl, and primary with resonance stabilization

Problem (7s)

Summarize all the factors that affect the rate S_N1 reactions and S_N2 reactions that we have discussed in this video.

Video (8)

FACTORS THAT AFFECT THE RATES OF S_N1 AND S_N2 REACTIONS:
PROBLEMS

In the previous video we used the concept of the "rate-determining step" to determine what factors can affect the rate of an S_N1 or S_N2 mechanism.

Now, in this video, we will see how to apply this material to typical problems.

Problem (8a)

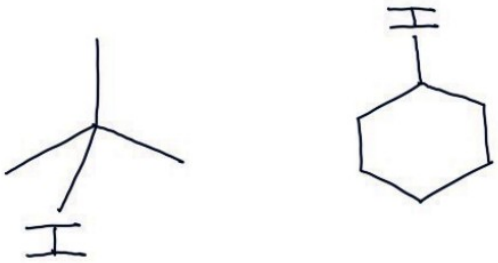
Rank the following carbocations in order of increasing stability.
(1 = least stable, 4 = most stable).

Problem (8b)

What is an example of a "solvolysis" reaction?

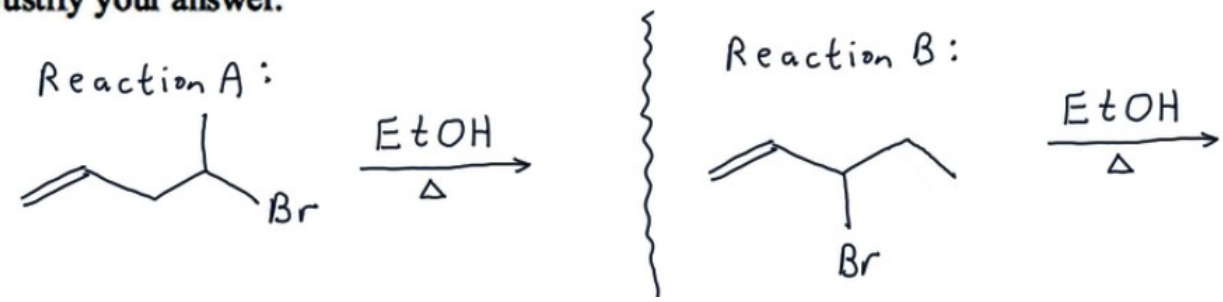
Problem (8c)

Which substrate undergoes the faster solvolysis reaction in H_2O? Why?



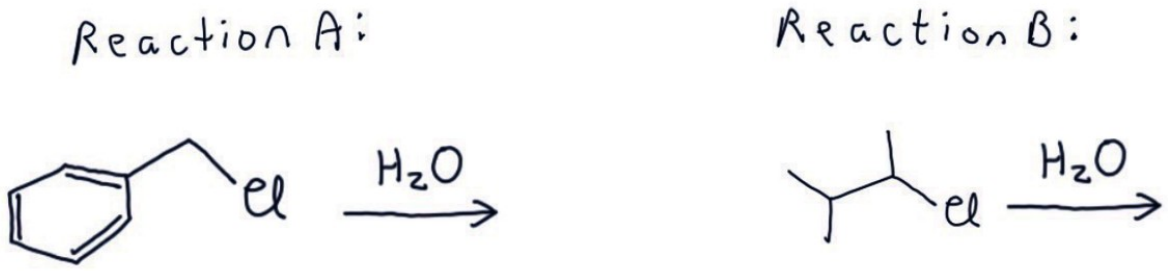
Problem (8d)

For the reactions below, which reaction will have the faster rate for an S_N1 mechanism? Or will the two reactions both occur at the same rate for S_N1? Justify your answer.



Problem (8e)

For the reactions below, which reaction will have the faster rate for an S_N1 mechanism? Or will the two reactions both occur at the same rate for S_N1? Justify your answer.

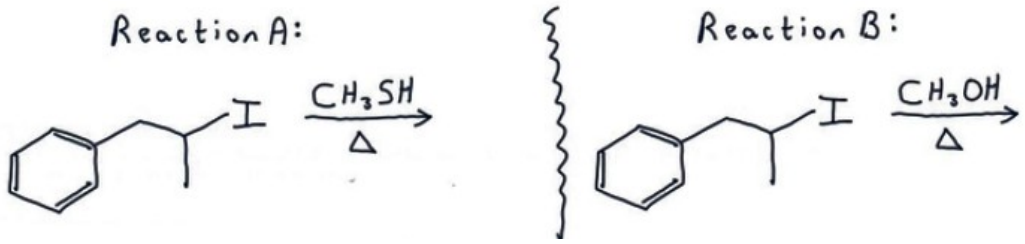


Problem (8f)

For the reactions below, which reaction will have the faster rate for an S_N2 mechanism? Or will the two reactions both occur at the same rate for S_N2? Justify your answer.

Problem (8g)

For the reactions below, which reaction will have the faster rate for an S_N1 mechanism? Or will the two reactions both occur at the same rate for S_N1? Justify your answer.

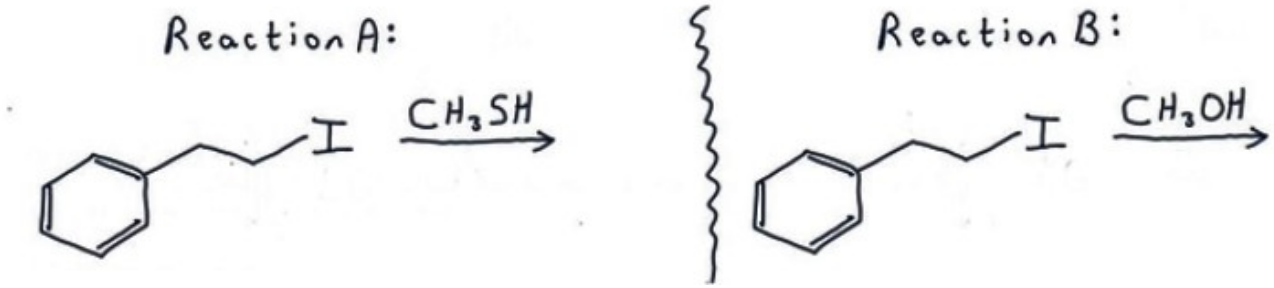


Problem (8h)

Which is the better nucleophile, CH_3OH or CH_3SH?
Justify your answer.

Problem (8i)

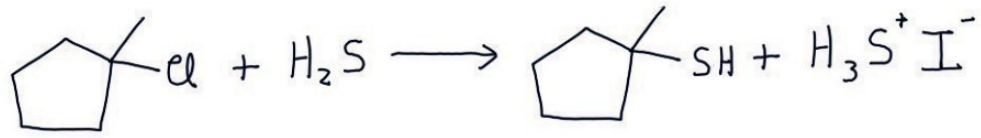
For the reactions below, which reaction will have the faster rate for an S_N2 mechanism? Or will the two reactions both occur at the same rate for S_N2? Justify your answer.



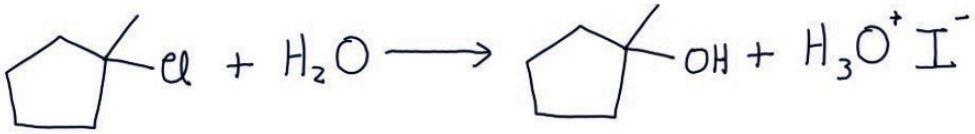
Problem (8j)

For the reactions below, which reaction will have the faster rate?
Or will the two reactions both occur at the same rate?
Justify your answer.

Reaction A:



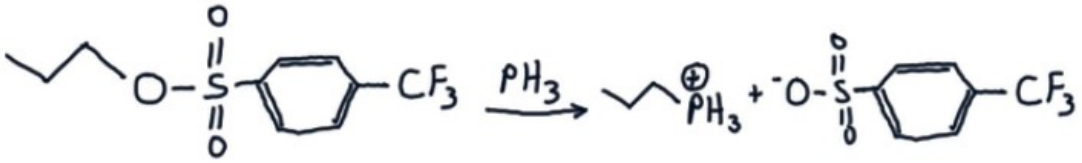
Reaction B:



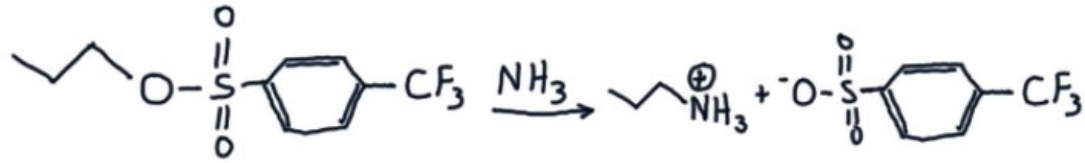
Problem (8k)

For the reactions below, which reaction will have the faster rate?
Or will the two reactions both occur at the same rate?
Justify your answer.

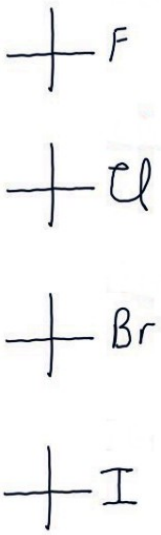
Reaction A:



Reaction B:



Problem (8l)



(a) Rank the leaving groups in these compounds, from worst to best.

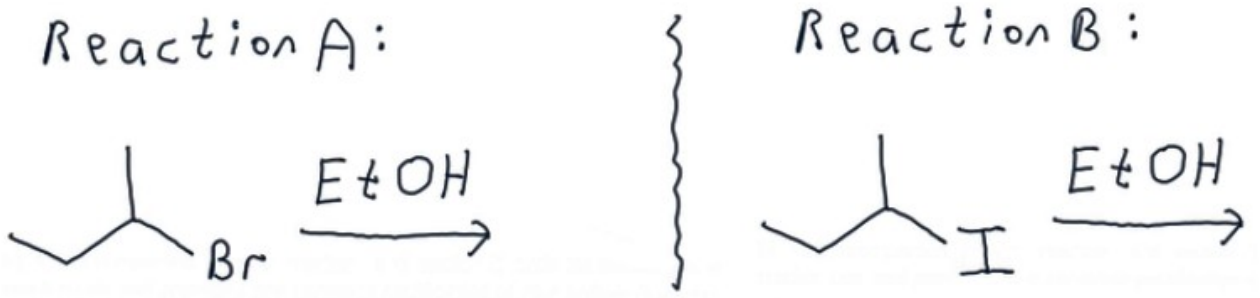
(b) Which are good leaving groups, and which are unacceptable leaving groups?

Problem (8m)

When comparing elements from the same column of the periodic table, leaving group ability increases as you move down a column. Give an *explanation* for this pattern.

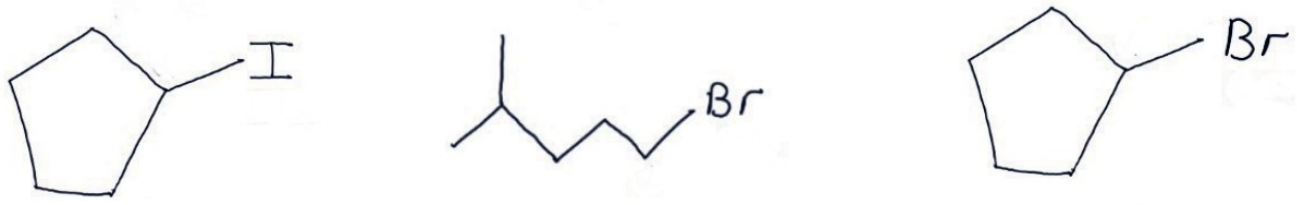
Problem (8n)

For the reactions below, which reaction will have the faster rate for an S_N1 mechanism? Or will the two reactions both occur at the same rate for S_N1? Justify your answer.



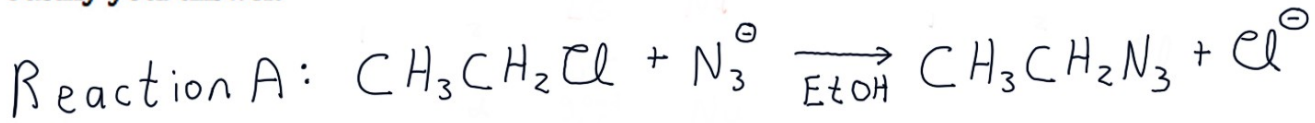
Problem (8o)

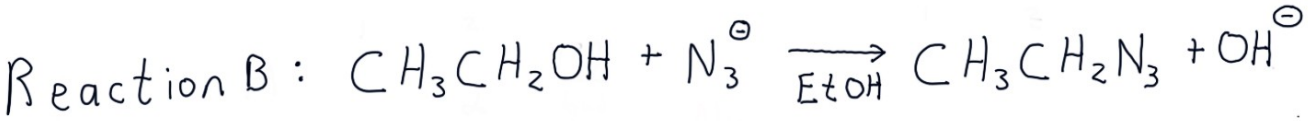
Rank the following alkyl halides in order of decreasing S_N1 reactivity. (1 is fastest, 3 is slowest.)



Problem (8p)

For the reactions below, which reaction will have the faster rate?
Or will the two reactions both occur at the same rate?
Justify your answer.





Problem (8q)

(a) As you move down a column in the periodic table, does leaving group ability increase or decrease?

(b) When comparing neutral nucleophiles, as you move down a column in the periodic table, does nucleophilicity increase or decrease?

The end of video (8) includes some additional comments about comparing electronegativity, and a “warning” about using atomic size to compare leaving group ability and nucleophile ability. You can find a summary of these comments in the Answers document.

Review Quiz

What are the names of the five main roles in organic chemistry?
What are the definitions for each of these roles?