S_N2 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 docunent, and skip to any particular parts of the videos that cover 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

Problems begin on next page.

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_N2 reactions.

(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?

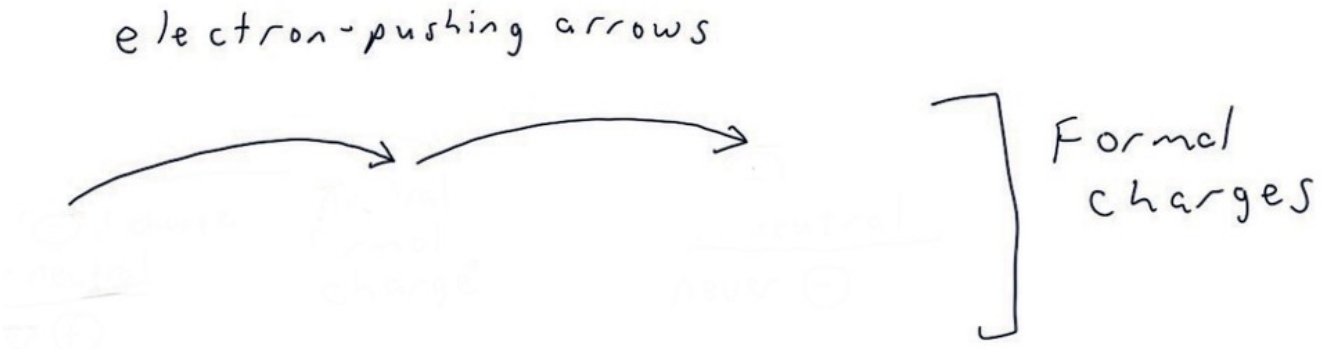
Does nature “like” or “dislike” charges?

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

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

Which atoms are most likely to participate in a reaction?

(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”.



(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?

(1d)

Identify the roles that these atoms are likely to play. Be specific about which atoms will play which roles.

$I^{\ominus}$, $Br^{\ominus}$, $^{\ominus}CN$, $CH_3CH_2O^{\ominus}$, $CH_3S^{\ominus}$

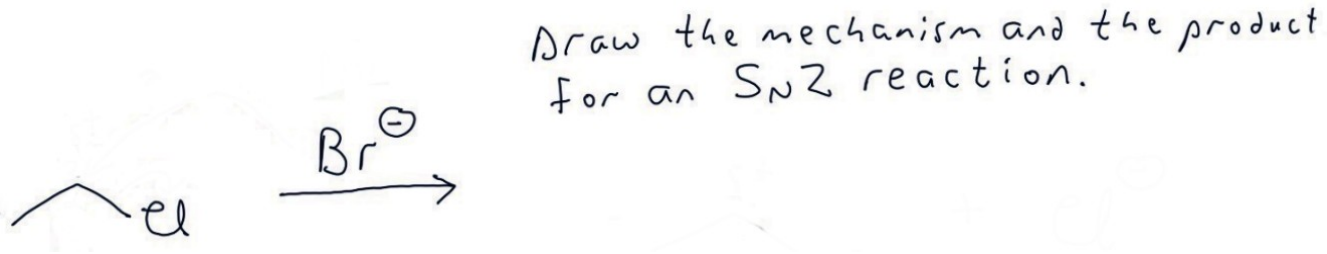
Also identify which carbons we will treat as the "α-carbons" in the above compounds.
What is the definition of "α-carbon" that is useful at this point in the course?

Video (2)

THE S_N2 MECHANISM

(2a)
How many steps are there in an S_N2 reaction?
What happens in those step(s)?

(2b)



(2c)
When you are drawing the products of a mechanism step, what is the most important part of the products to get right?

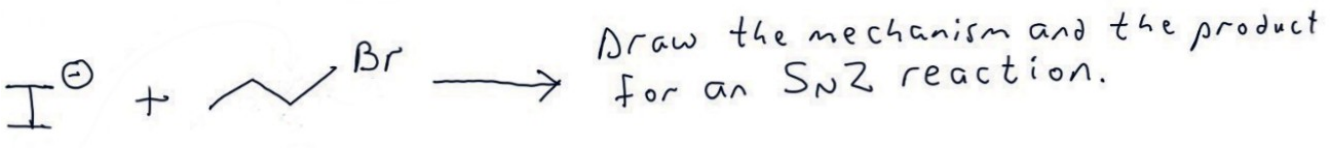
How many formal charges should you change for each mechanism step?

How do you know which formal charges to change for each mechanism step?

Checklist of things to do for each reaction

1. Number *all* the carbons in the starting materials. These numbers are for your personal reference, not for IUPAC naming, so it doesn't matter whether you number from right to left or from left to right.
2. Label which specific atoms will play which roles. Identify the "clues" that tell you which atoms will play which roles.
3. Draw electron-pushing arrows. Don't begin drawing the products until you have finished drawing the electron-pushing arrows.
4. Draw the products. Number *all* the carbons in the products. Make sure your numbers for the products are *consistent* with the numbers you used for the starting materials. The purpose of the numbers is to show you which carbons in the products are the same as which carbons in the starting materials.

(2d)



(2e)

In the name "S_N2" reaction:
what does the letter S stand for?
what does the letter N stand for?

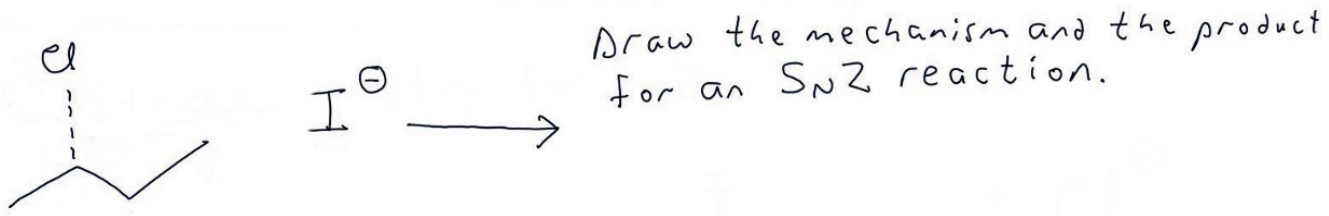
Does the number 2 in the term "S_N2" mean that there are two steps in an S_N2 reaction?

Review Quiz
Define the following terms: nucleophile, leaving group, electrophile

Video (3)

S_N2 STEREOCHEMISTRY

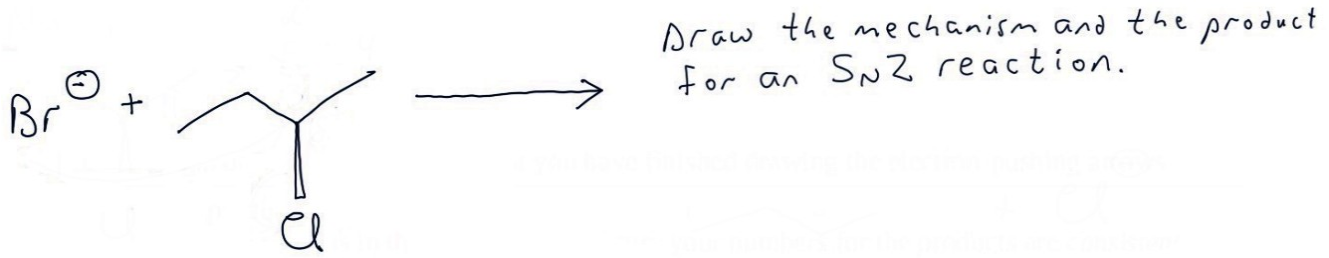
(3a)
When a nucleophile attacks an atom that is attached to a leaving group,
from what direction(s) does the nucleophile attack?



When an S_N2 reaction occurs at an α-carbon that is a stereocenter,
what will be the stereochemistry of the product(s)?

What is the definition of the term “stereocenter”?

(3b)



<u>Review Quiz</u>
How many steps are there in an S_N2 reaction?

What happens in that single step?

Video (4)

HOW TO USE IONIC BONDS TO DETECT FORMAL CHARGES

(4a)
Define: ionic bond
Define: covalent bond

How can you detect whether a bond in the starting materials is covalent or ionic?

Where do you find metals and nonmetals in the periodic table?

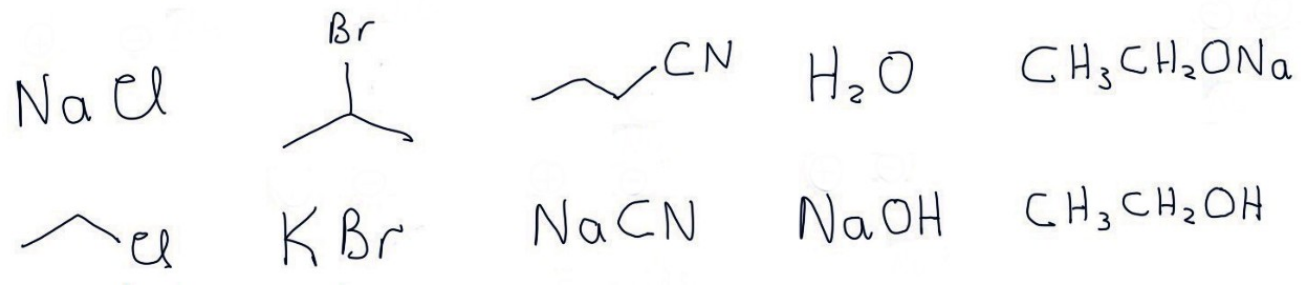
Which two metals commonly appear in the starting materials for S_N2 reactions?

Is hydrogen a metal or a nonmetal?
What do you need to know about the electronegativity of hydrogen?

How do you determine the formal charges for the starting materials for a reaction?

(4b)

Suppose each of the following is provided as the starting material for a reaction. Draw in any necessary formal charges.

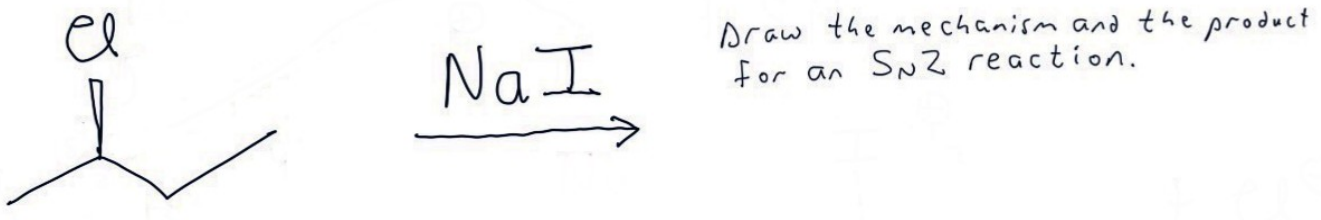


If a bond is represented by a solid line, or by a dashed line, or by a wedge, could the bond be covalent, ionic, or either?

What is the name of this compound: NaCN?

(4c)
What atoms in the starting materials are most likely to participate in the reaction?
What roles do metals with positive charges play in reactions?

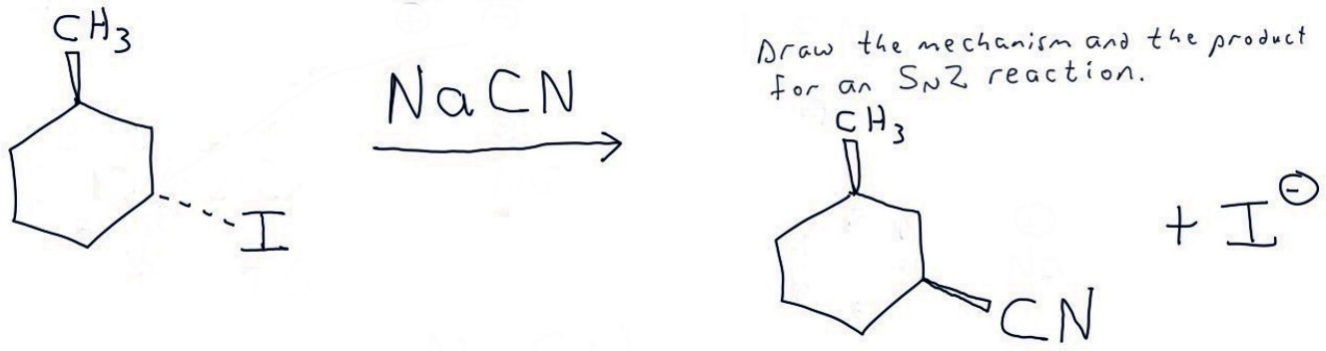
(4d)



Checklist of things to do for each reaction

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. Draw electron-pushing arrows. Don't begin drawing the products until you have finished drawing the electron-pushing arrows.
5. Draw the products. Number *all* the carbons in the products. Make sure your numbers for the products are *consistent* with the numbers you used for the starting materials.

(4e)



When do you break an ionic bond?

In general, which covalent bonds do you break?
In general, which covalent bonds do you not break?

Review Quiz

What is the most important tool for drawing the correct electron-pushing arrows?

What types of formal charges are likely to go at the beginning, middle, and end of a series of electron-pushing arrows?

Video (5)

HOW TO DETERMINE WHEN TO USE AN S_N2 MECHANISM

Problem (5a)

Define: primary carbon, secondary carbon, tertiary carbon, methyl carbon

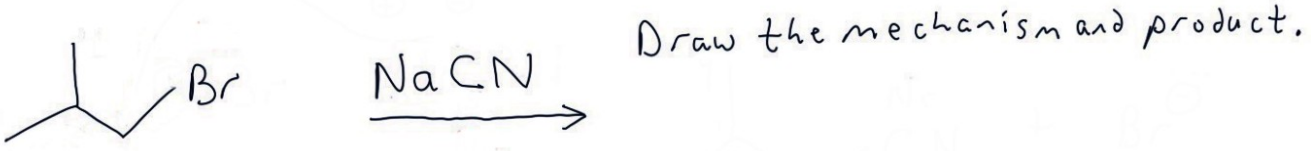
Label *all* of the carbons in each molecule as primary, secondary, tertiary, or methyl.
Label the α carbons. Are the α carbons primary, secondary, tertiary, or methyl?

Problem (5b)
How do you determine whether the mechanism for a reaction will be S_N2, S_N1, E2, or E1?

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

Problem (5c)

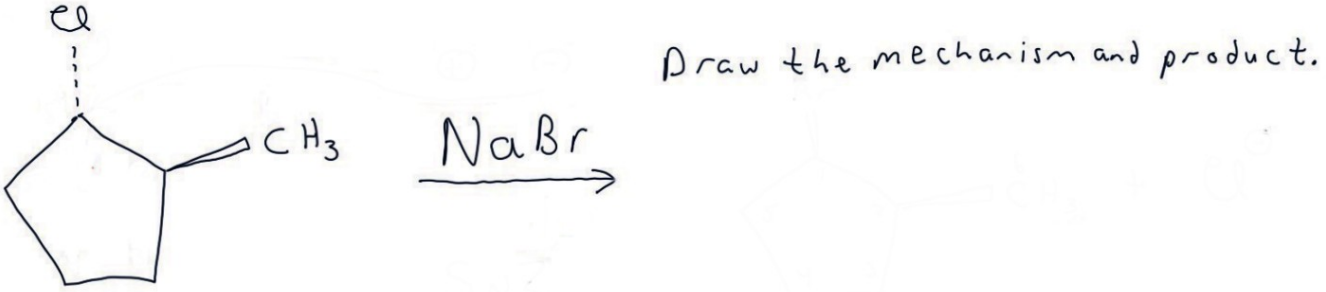


Do not *assume* that the mechanism is S_N2. **Use the table** to determine the correct mechanism.

Checklist of things to do for each reaction

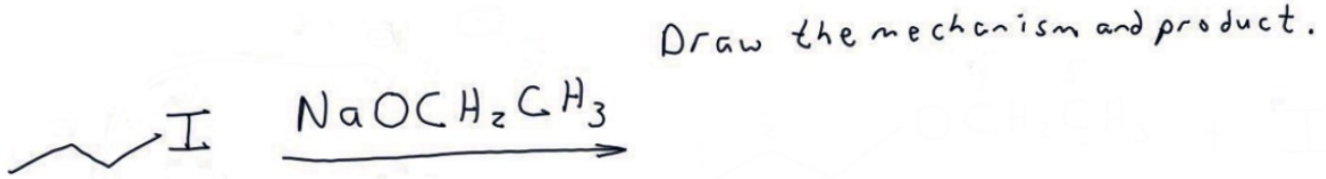
1. Number *all* the carbons in the starting materials.
2. Draw formal charges for any ionic bonds.
3. Label which specific atoms will play which roles. Identify the "clues" that tell you which atoms will play which roles.
4. **Label** the α-carbon. **Write down** whether the α-carbon is methyl, 1°, 2°, 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. Don't begin drawing the products until you have finished drawing the electron-pushing arrows.
7. Draw the products. Number *all* the carbons in the products. Make sure your numbers for the products are *consistent* with the numbers you used for the starting materials.

Problem (5d)



Do not *assume* that the mechanism is S_N2. **Use the table** to determine the correct mechanism.

Problem (5e)

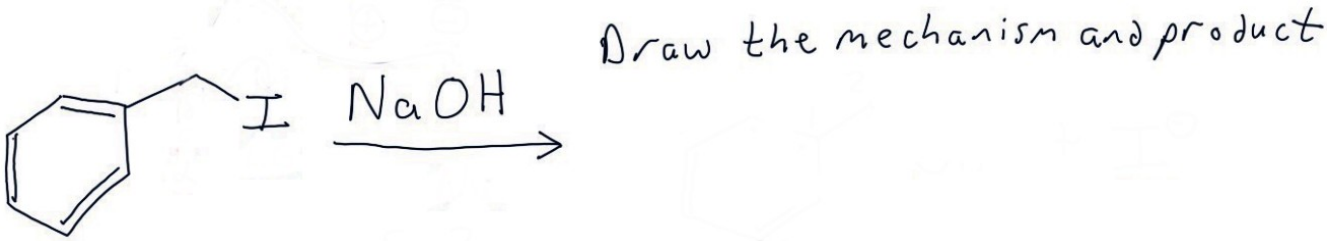


Do not *assume* that the mechanism is S_N2. **Use the table** to determine the correct mechanism.

Draw the structure of *tert*-butyl oxide.

Problem (5f)
Memorize the table for choosing between S_N2, S_N1, E2, and E1 reactions.
Then, write down the table **from memory**.

Problem (5g)



Do not *assume* that the mechanism is S_N2. **Use the table** to determine the correct mechanism.

<u>Review Quiz</u>
What clues have we learned so far for identifying when an atom will play the role of electrophile?
What clues have we learned so far for identifying when an atom will play the role of leaving group?
What clues have we learned so far for identifying when an atom will play the role of nucleophile?

Video (6)

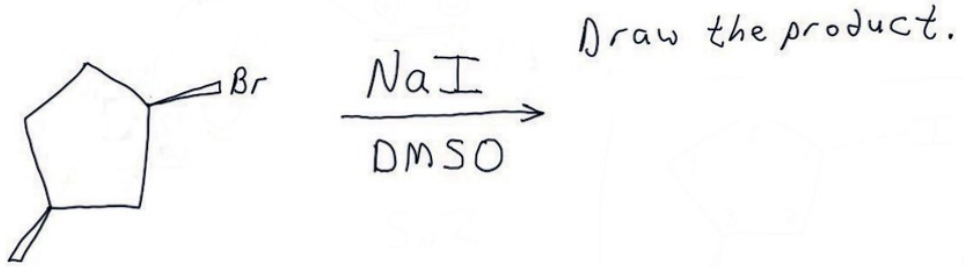
SOLVENTS

Problem (6a)
What is a “solvent”?
In general, when should you use a solvent as a participant in a reaction?

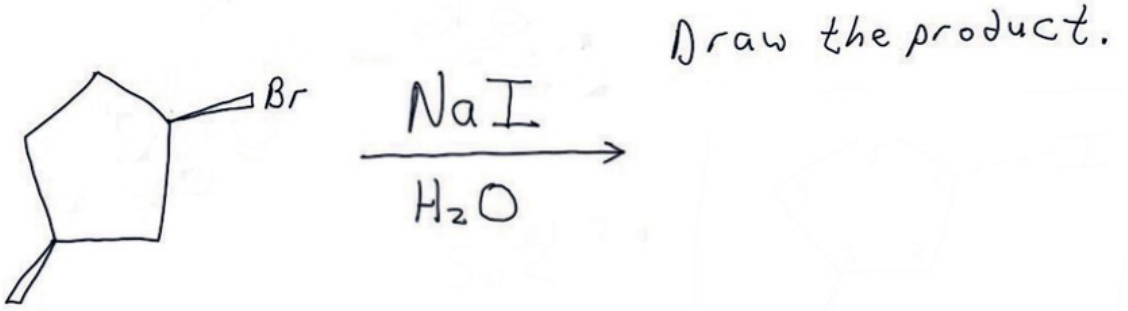
What are some common solvents used in S_N2, S_N1, E2, and E1 reactions?
What role do we expect these solvents to play in S_N2, S_N1, E2, and E1 reactions?

What is the definition of an “alcohol”?

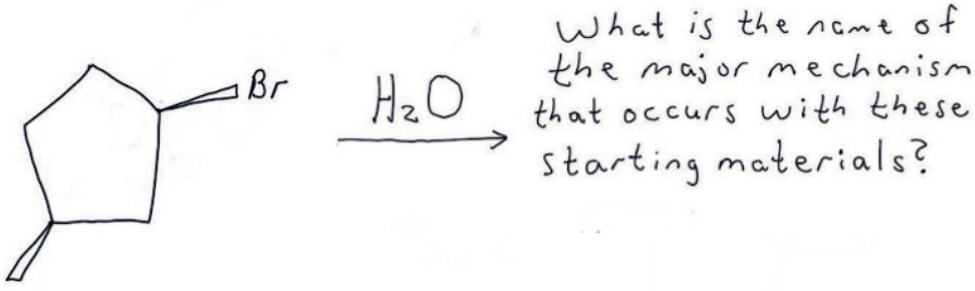
Problem (6b)



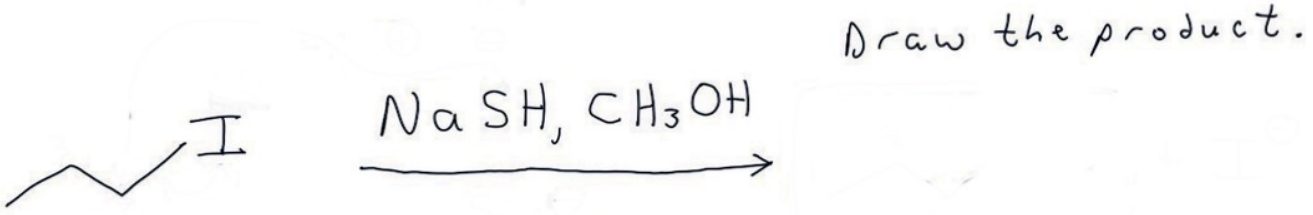
Problem (6c)



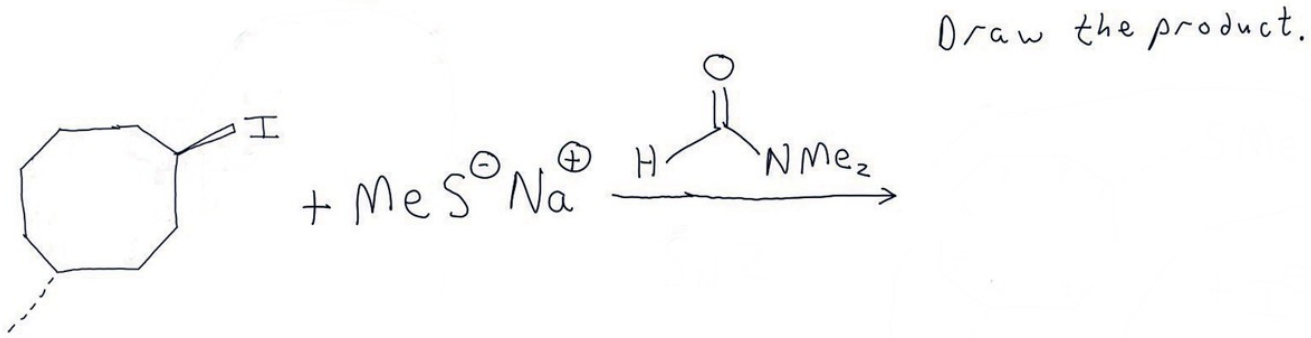
Problem (6d)



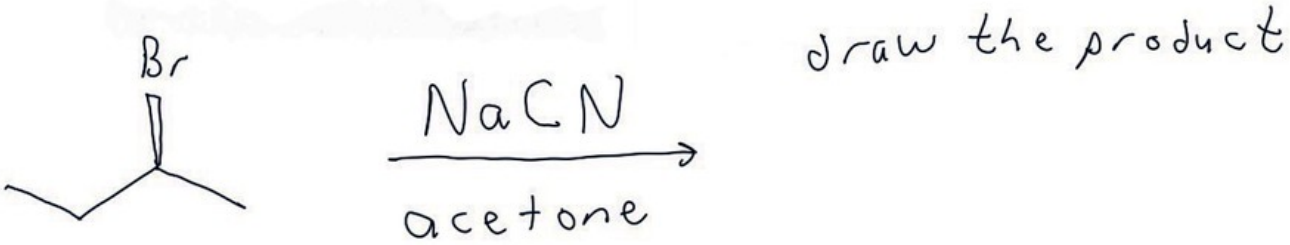
Problem (6e)



Problem (6f)



Problem (6g)



Review Quiz

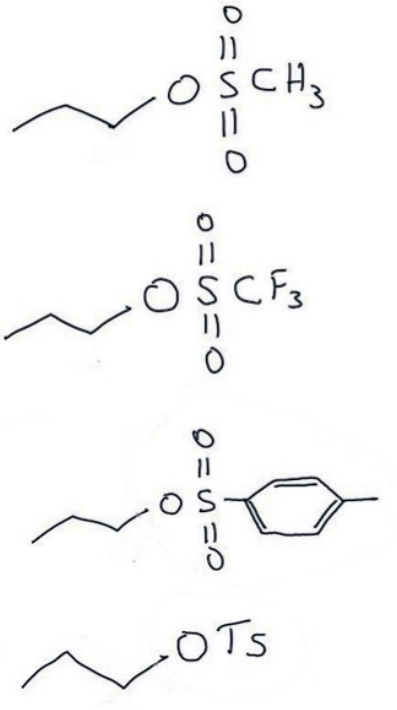
When a nucleophile attacks an atom that is attached to a leaving group, from what direction(s) does the nucleophile attack?

When an S_N2 reaction occurs at an α-carbon that is a stereocenter, what will be the stereochemistry of the product(s)?

Video (7)

ALKYL SULFONATES

The purpose of this video is to learn about a new type of leaving group: sulfonates
Here are some examples of molecules that contain sulfonate groups:

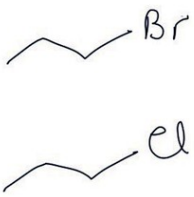


Problem (7a)

So far in this video series, what neutral atoms have we learned that can function as good leaving groups?

Define the term “alkyl”.

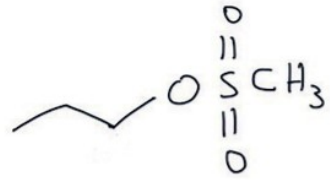
Give the general name for the functional group in each of the following molecules.

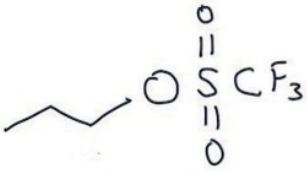


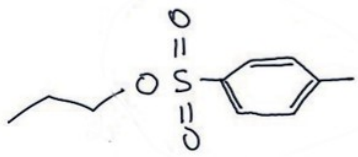
Problem (7a) continued

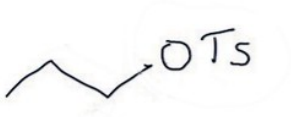
What is the general structure of an alkyl sulfonate?
Which part of the general structure is the "alkyl" group? Which part is the "sulfonate group"?
How do you identify the α carbon in an alkyl sulfonate?

Give the general name for the functional group in each of the following molecules.
Label the α carbon in each molecule.









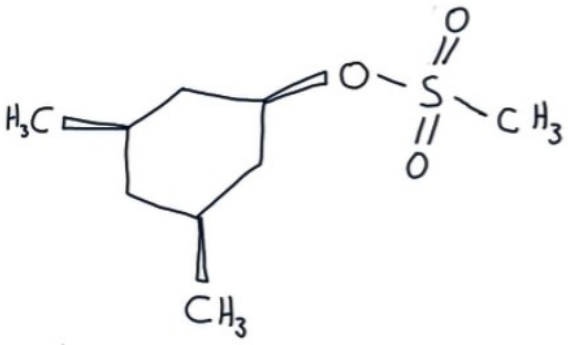
How many oxygens are there in a sulfonate group?

What neutral atoms have we now learned that are good leaving groups?

This table applies to what electrophiles?

	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^-
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

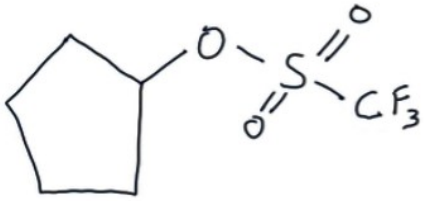
Problem (7b)



NaBr, CH_3OH →

Draw the product.

Problem (7c)



+ NaN_3 →

Draw the product.

So far in this video, we have learned that neutral sulfonate groups are good leaving groups, even though most other neutral atoms are not good leaving groups.
In the remainder of this video, we will learn *why* sulfonate groups are good leaving groups.

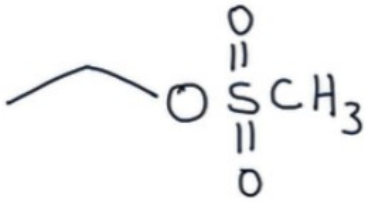
Problem (7d)
What is the most important factor in organic chemistry?

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

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

Does nature “prefer” charges to be concentrated or spread out?

Give the general names for the functional groups in each of the following molecules.
Does each of the following have an acceptable leaving group?



What is usually the best way to judge leaving group ability?

In the alcohol, the neutral alcohol group is not an acceptable leaving group.
In an alkyl sulfonate the neutral sulfonate group *is* an acceptable leaving group.
Explain why a neutral sulfonate is a good leaving group, while a neutral OH is not an acceptable leaving group.

Review Quiz

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

How many formal charges should you change for each mechanism step?

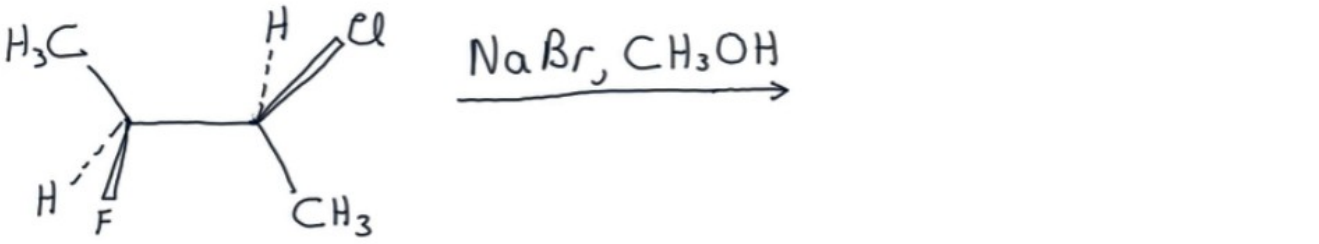
How do you know which formal charges to change for each mechanism step?

Video (8)

SUBSTRATES WITH MULTIPLE FUNCTIONAL GROUPS

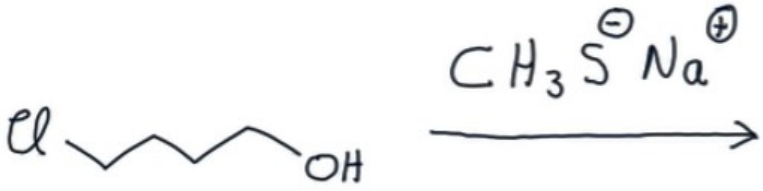
Problem (8a)

Draw the product.



Problem (8b)

Draw the product.



Review Quiz

Define the following terms: nucleophile, leaving group, electrophile

Explain the origin of the term “electrophile”.
Explain the origin of the term “nucleophile”.

Video (9)

S_N2 REACTIONS WITH NEUTRAL NUCLEOPHILES

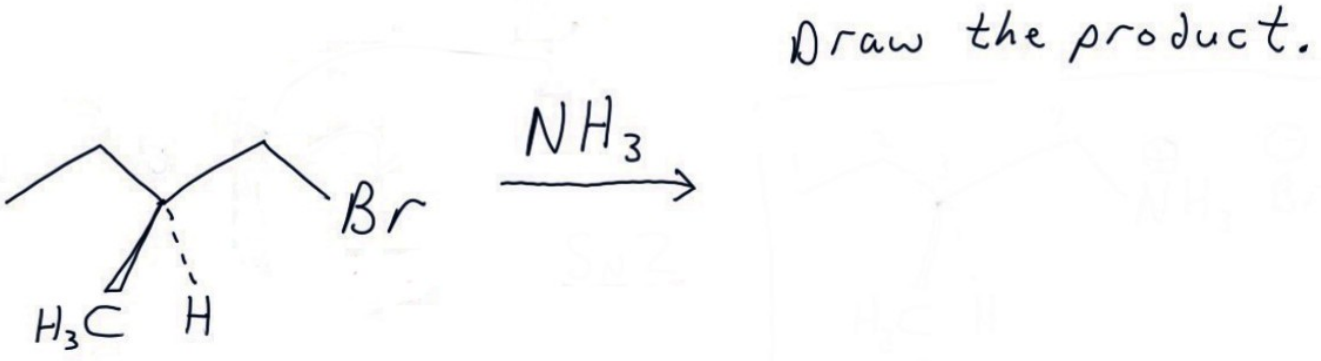
Problem (9a)
What is the definition of “nucleophile”?
Draw the electron-pushing arrow for a nucleophile.
What clue have we learned so far for identifying a nucleophile?

Problem (9b)
What types of neutral atoms can be used as nucleophiles?

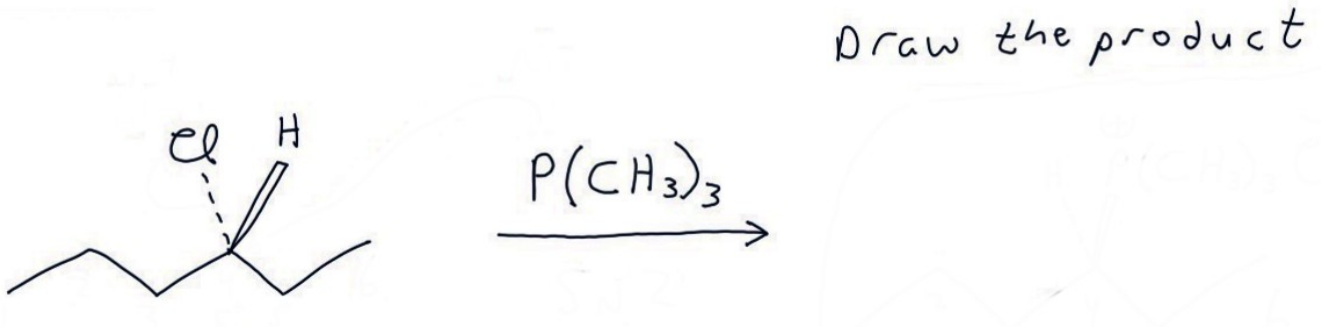
Problem (9c)
Which neutral atoms are considered “good” nucleophiles?
Which neutral atoms are considered “poor” nucleophiles?

Problem (9d)
Summarize the definitions for nucleophile, electrophile, and leaving group.
How do you draw the electron-pushing arrows for each of these roles?
What are the clues we have learned so far in this video series for identifying these roles?

Problem (9e)



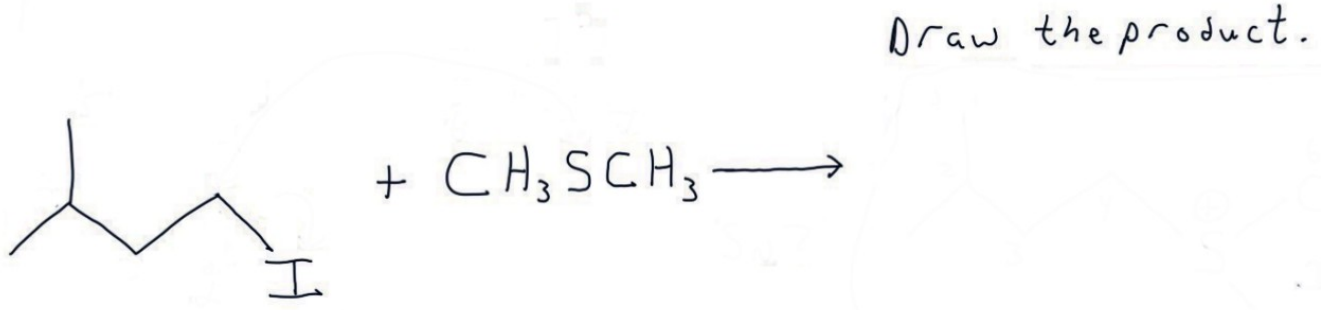
Problem (9f)



Problem (9g)

What is the rule for determining when a mechanism is finished?
What is an important exception to this rule?

Problem (9h)



Review Quiz

From memory: Draw the table for choosing between S_N2, S_N1, E2, and E1 reactions for alkyl halides and alkyl sulfonates.

Video (10)

FACTORS AFFECTING THE RATE OF 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_N2 mechanism.

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

Problem (10a)

Define: rate-determining step

How do we use the rate-determining step to determine what factors will affect the rate of a reaction?

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

Problem (10b)

Why does "S_N2 reaction" have the number "2" in its name? What does the "2" stand for?

What do the "S" and "N" stand for in the term "S_N2 reaction"?

Problem (10c)

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

Does an S_N2 reaction require a good leaving group? Why?

Can the following starting materials do an S_N2 reaction? Why?

Problem (10d)

Does the quality of the nucleophile affect the rate for an S_N2 reaction? Why?

Does an S_N2 reaction require a good nucleophile? Why?

How can you distinguish between "poor" nucleophiles and "good" nucleophiles?

Can the following starting materials do an S_N2 reaction?

Problem (10e)

What is the "big obstacle" to S_N2 reactions?

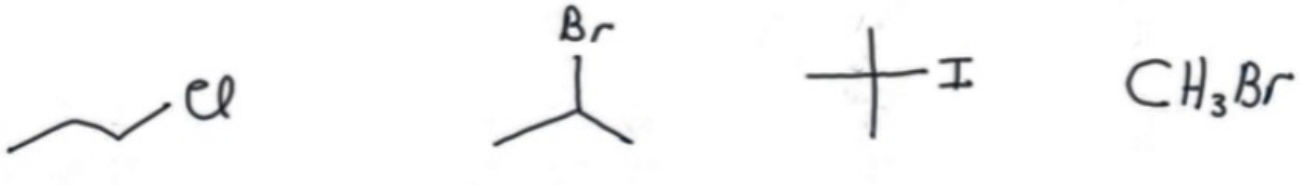
What does the term "steric hindrance" mean?

Why does steric hindrance that blocks the nucleophile affect the rate of an S_N2 reaction?

Problem (10f)

Define: Primary carbon, secondary carbon, tertiary carbon, methyl carbon

Determine whether the α carbons in each of the following are primary, secondary, tertiary, or methyl:



Problem (10g)

Rank the following, from slowest rate for S_N2, to fastest rate for S_N2:
Primary alpha carbon, secondary alpha carbon, tertiary alpha carbon, methyl alpha carbon

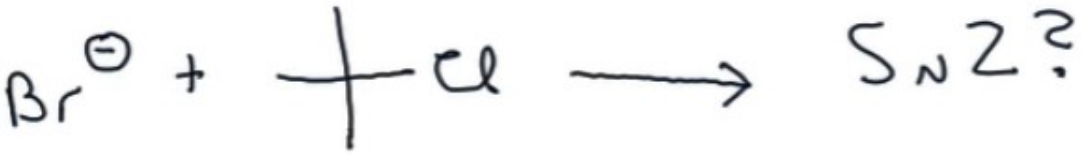
Explain your ranking.

Which types of alpha carbons cannot do S_N2 reactions? Why not?

Which types of α carbons *can* do S_N2 reactions?

Problem (10h)

Can the following starting materials carry out an S_N2 reaction? Explain.



Problem (10i)

Consider this table:

how to determine the mechanism for alkyl halide and alkyl sulfonate electrophiles

	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^-
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

In this table, the term "α-carbon" refers to the carbon attached to the leaving group.

Why are there no entries for "S_N2" reactions in the bottom row of the table?

Why are there no entries for "S_N2" reactions in the left column of the table?

Problem (10j)

Summarize the factors that do and do not affect S_N2 reactions that we have learned about in this video.

Explain why each factor does or does not affect S_N2.

Video (11)

FACTORS AFFECTING THE RATE OF AN S_N2 REACTION:
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.

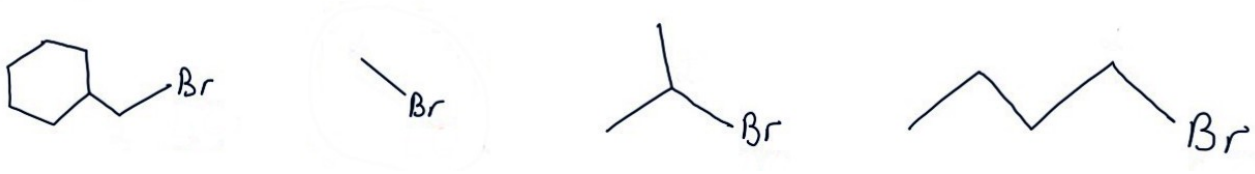
Problem (11a)

What does the term "substrate" mean when referring to an S_N2 reaction?

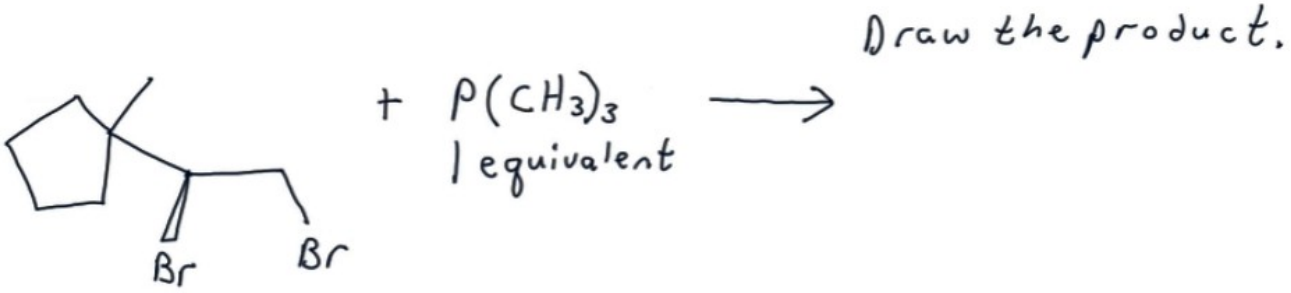
Problem (11b)

Choose the best substrate for an S_N2 reaction.

Explain your choice.



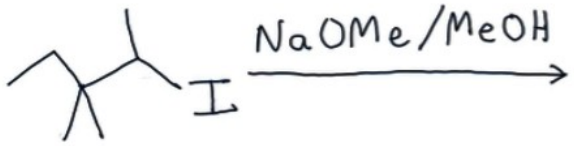
Problem (11c)



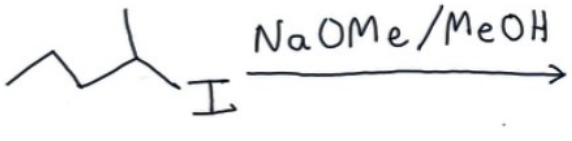
Problem (11d)

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.

Reaction A:



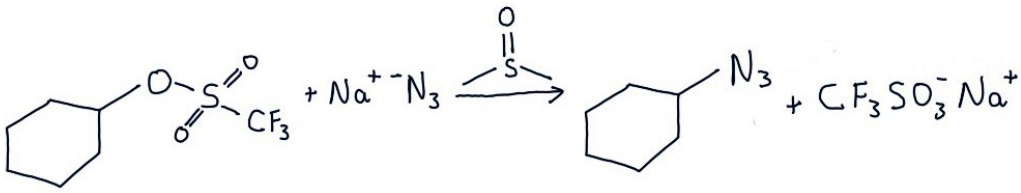
Reaction B:



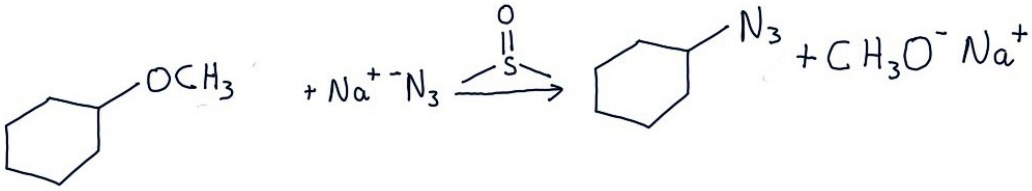
Problem (11e)

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.

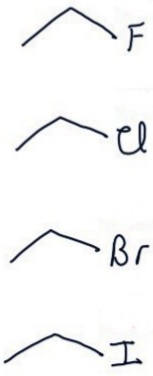
Reaction A:



Reaction B:



Problem (11f)



Rank the leaving groups in these compounds, from worst to best. Which are good leaving groups, and which are unacceptable leaving groups?

Problem (11g)

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 (11h)

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.

Reaction A:

Reaction B:

Problem (11i)

H_2O

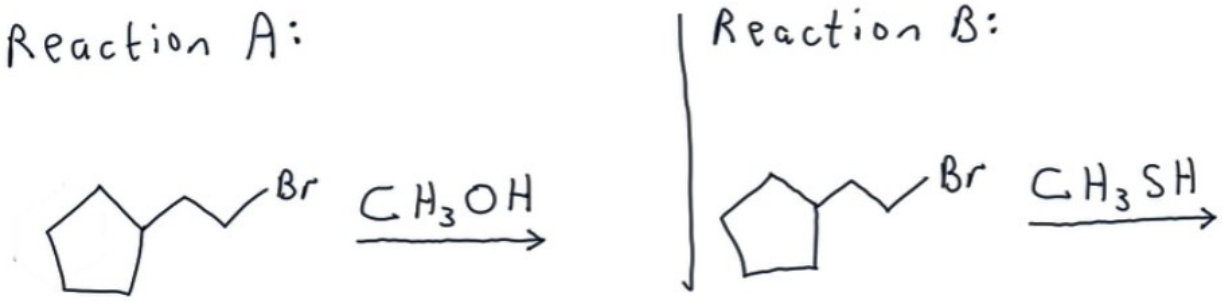
H_2S

(a) Which of these compounds is the better nucleophile? Justify your answer.

(b) Label each compound as a "poor nucleophile" or a "good nucleophile.

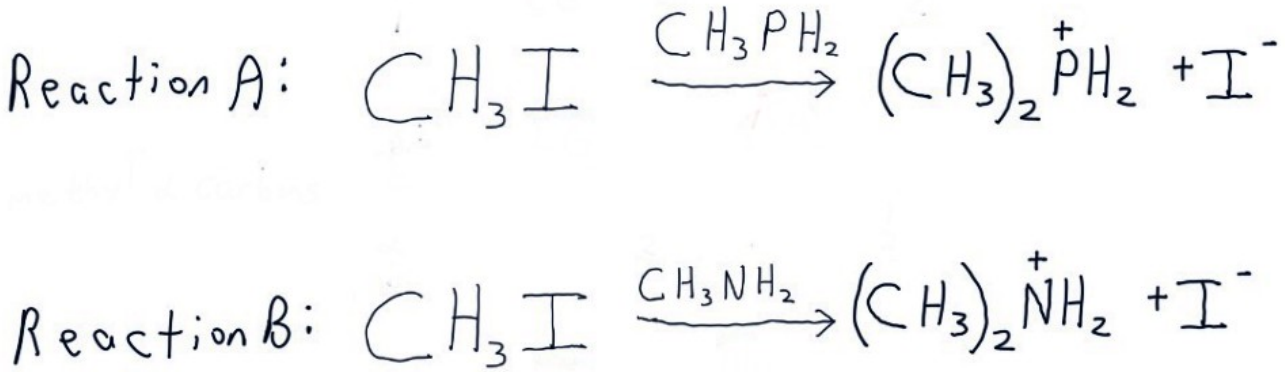
Problem (11j)

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 (11k)

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 (11l)

(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 (11) includes some additional comments on comparing leaving group ability and nucleophile ability. You can find a summary of these comments in the Answers document.

Review Quiz

Label the “head” and “tail” of an electron-pushing arrow.

An electron-pushing arrow shows the movement of _____.

The formal charge on an electron is:

Draw the electron-pushing arrow for a leaving group.

Draw the electron-pushing arrow for a nucleophile.

Draw the electron-pushing arrow for an electrophile.