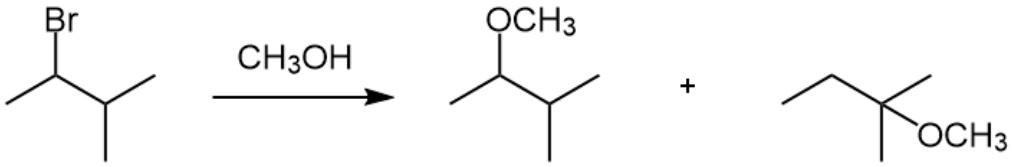
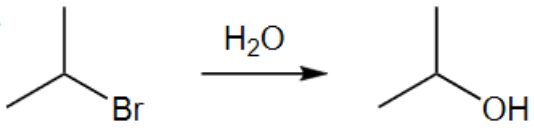
Provide a mechanism to account for both products formed.

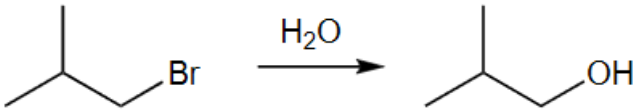


Which would be the faster reaction (A or B)? Explain. (Consider first: S_N2 or S_N1 mechanism?)

A



B



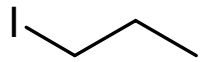
Summary of Substitution Reactions

Alkyl Group	S_N1	S_N2
3° (tertiary)	common	rare (N/R)
2° (secondary)	sometimes	sometimes
1° (primary)	rare (N/R)	common
CH_3 (methyl)	never (N/R)	common
allyl/benzyl	common	common (if not 3°)

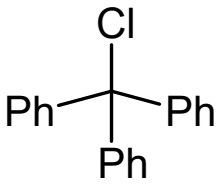
S_N2 vs. S_N1

S_N2 requires **strong Nu:** and **minimal steric hindrance**
S_N1 requires a **stable carbocation** and typically involves a **weak Nu:**

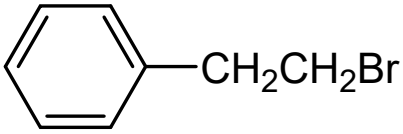
In the box provided, indicate the mechanism involved in each of the following reactions (S_N1 or S_N2). If no reaction is expected, write NR. Predict the major product(s) expected, and remember to indicate stereochemistry, when appropriate.

a) 

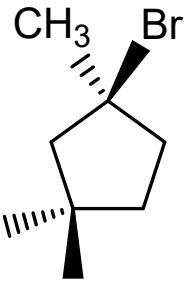
NaSH / acetone

b) 

CH_3CH_2OH

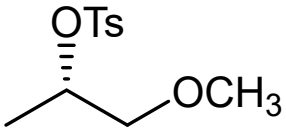
c) 

MeONa / MeOH

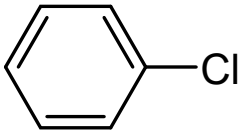
d) 

$CH_3-C(=O)-ONa$ / CH_3CO_2H

e) CH_3I
H_2O

f) 

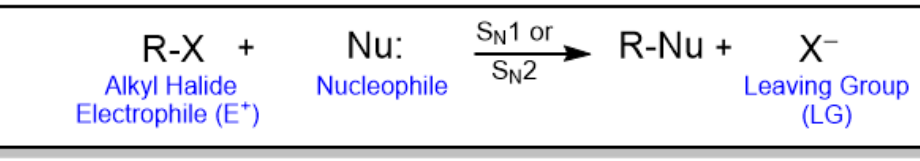
NH_3 (xs) / DMF

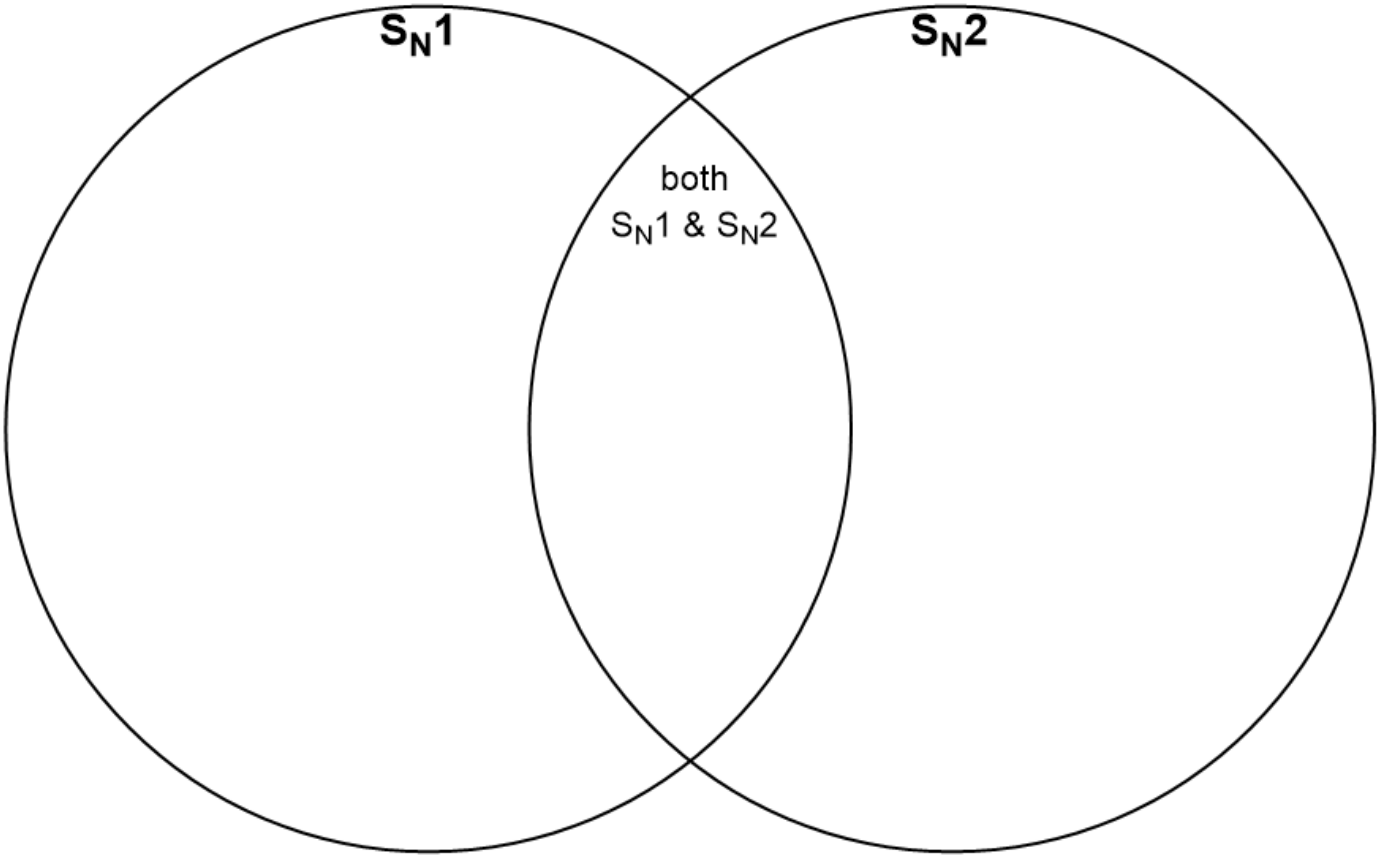
g) 

NaOH / H_2O

Comparison of S_N1 and S_N2 Mechanisms

Consider a substitution reaction:





Categorize each of the following items as being related to S_N1, S_N2, or both.

carbocation

bimolecular

good LG

MeOH Nu:

backside attack

a bond forms in rate-determining step

more than one transition state

3º RX

sterics

aprotic solvent

unimolecular

H_2O Nu:

solvolysis

MeI = fastest

no reaction on 1º RX

unhindered E^+

only one transition state

no reaction on vinyl RX

HO^- Nu:

Rate = *k*[RX]

weak Nu:

inversion of stereochemistry

NaOMe Nu:

protic solvent

2º RX

strong Nu:

Rate = *k*[RX][Nu:]

t-BuBr = fastest

no reaction on 3º RX

rearrangement

a bond breaks in rate-determining step

racemization

1º RX

Cal Poly Pomona, Dr. L. S. Starkey, Organic Chemistry I, CHM 3140

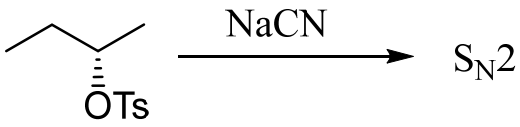
S_N2 and S_N1 Comparison Homework

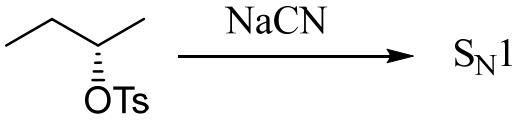
Name:_____ Section (day/time):_____

In the reaction of the tosylate shown and sodium cyanide, both S_N2 and S_N1 mechanisms are possible.

For each reaction: a) predict the major product(s) expected (stereochemistry?)
b) provide a complete mechanism (watch details: lone pairs, formal charges, arrows)
c) provide an E vs. POR diagram (**give structures for the transition states**)

Complete Lewis structure for NaCN	Complete Lewis structure for tosylate leaving group $^{\ominus}$OTs





BONUS Experimentally, how could you determine which mechanism has occurred? Explain.