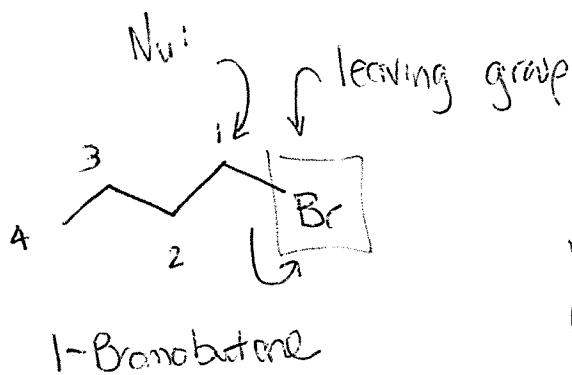
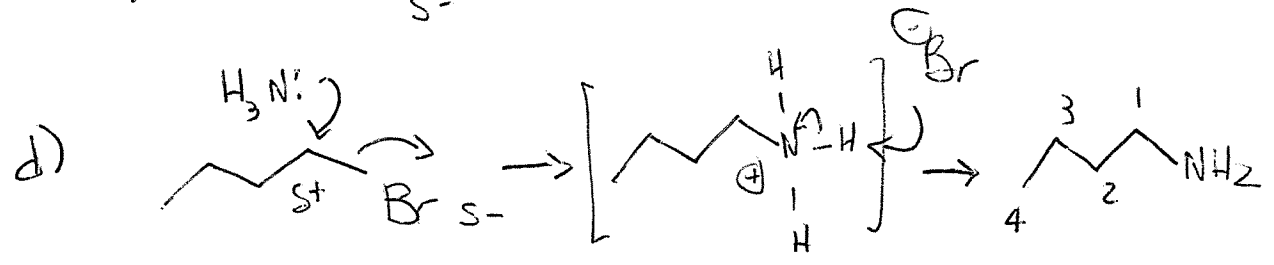
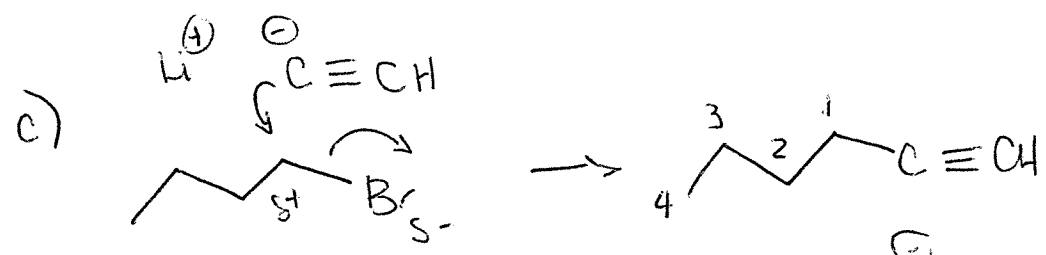
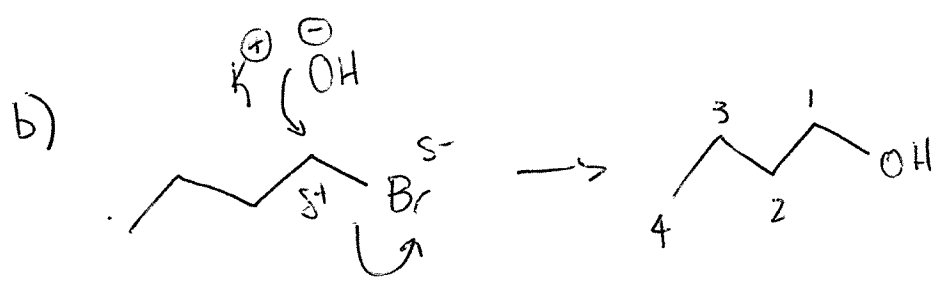
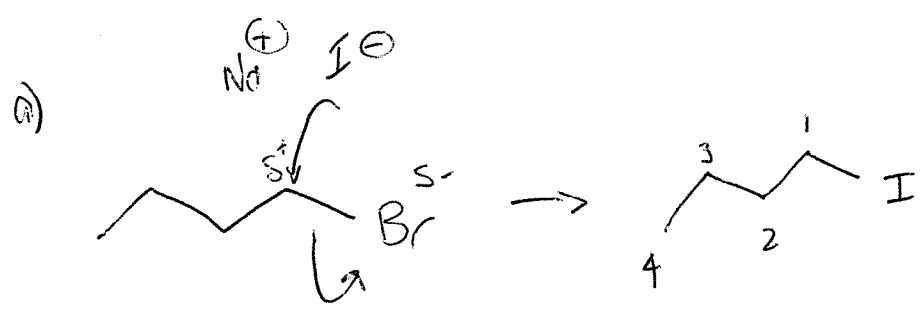
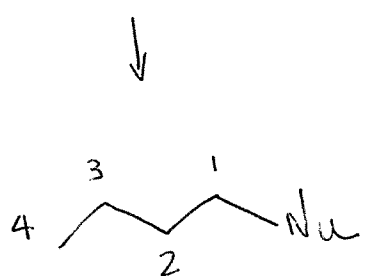


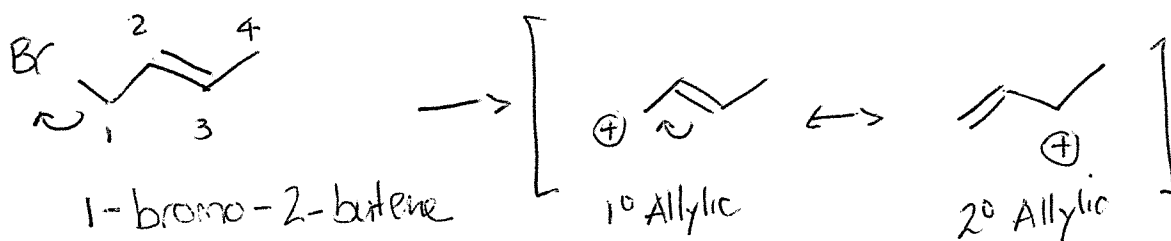
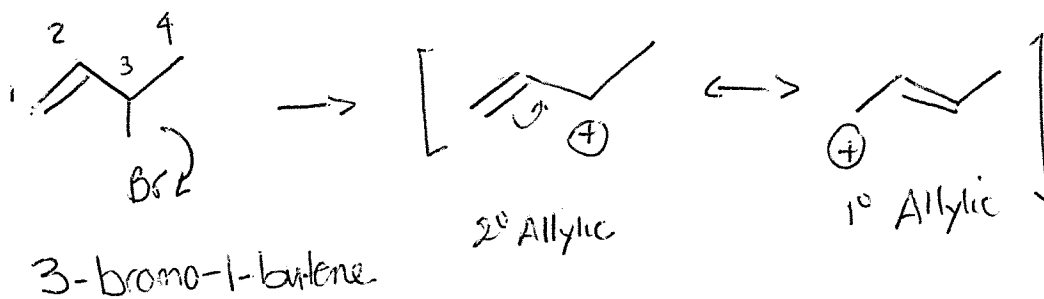
11.4



In an S_N2 reaction, the nucleophile reacts at the carbon atom bonded to the LG.

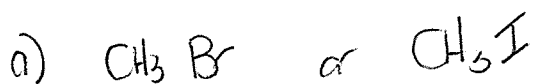


11.12



In the S_N1 mechanism, the rate determining step involves breaking the carbon-leaving group bond to generate a carbocation. In both of the above cases, allylic carbocations are generated and each of these have two resonance forms, a 1° allylic and a 2° allylic. Therefore, the stability of the carbocations (together) are equally stable, regardless of the starting material from which they are generated. Since the carbocations are equally stable, both of these reactions occur at the same rate.

11. 27



Among the halogens, the least electronegative are the best leaving groups

Weak bases are the best LG

Weak bases are best able to "hold" and keep their electrons.

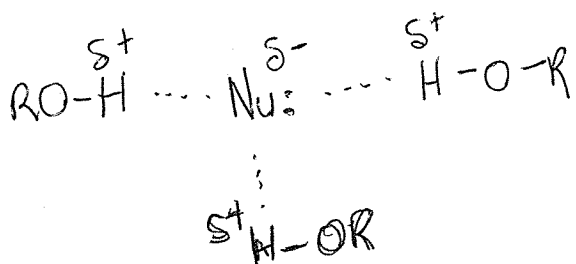
For halogens.....



↑
best
LG

↑
worst
LG

b) $\text{S}_\text{N}2$ reactions are most favored in POLAR, APROTIC solvents. The solvent affects the "strength" (or \ominus character) of the Nu^- . In protic solvents, the Nu^- tends to associate its \ominus character with the solvent via H-bonding, thus weakening its negative character and nucleophile strength.



(PROTIC SOLVENT)

- weakens Nu^- so $\text{S}_\text{N}2$ rxn is slower (less reactive)

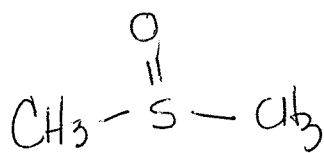
ETHANOL IS A PROTIC SOLVENT

11.27 (cont'd)

Aprotic solvents do not H-bond with the Nu:
 So the Nu⁻ retains its \ominus character. S_N2 reactions
 occur faster with APROTIC solvents.

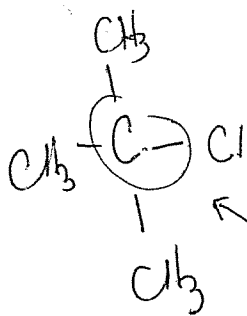
Dimethyl sulfoxide is an APROTIC solvent

S_N2 rxn occurs
 faster in DMSO

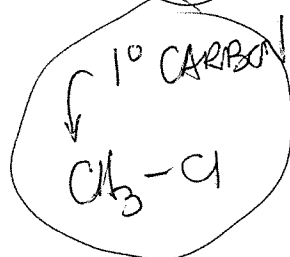


DIMETHYL SULFOXIDE
 (DMSO)

c)



vs.

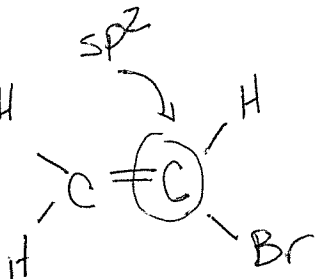


3° Carbon

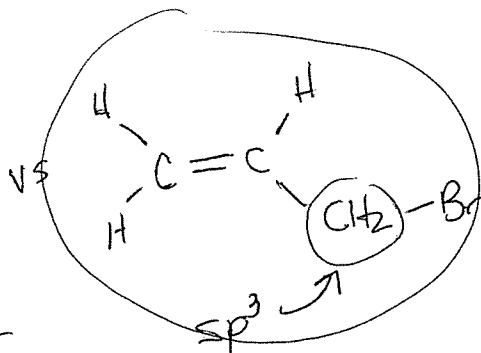
1° > 2° > 3°
 FASTEST
 S_N2
 SLOWEST
 S_N2

Least substituted carbons
 bonded to LG react fastest.

d)



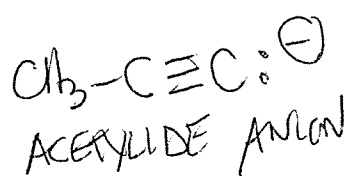
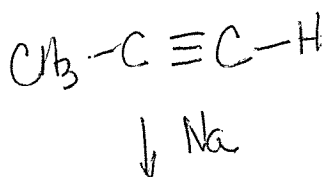
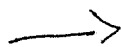
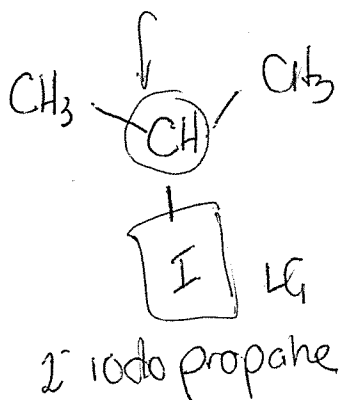
sp² C bonded to
 LG DO NOT REACT
 IN S_N2



11.31

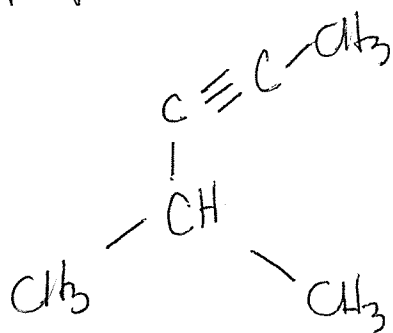
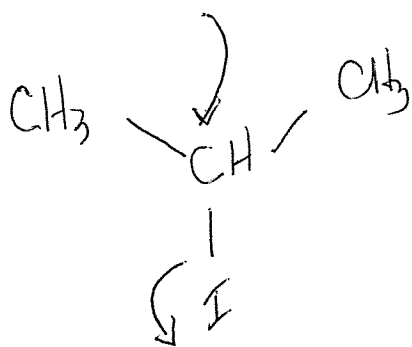
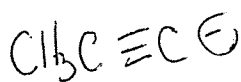
2° sp³ C

a)

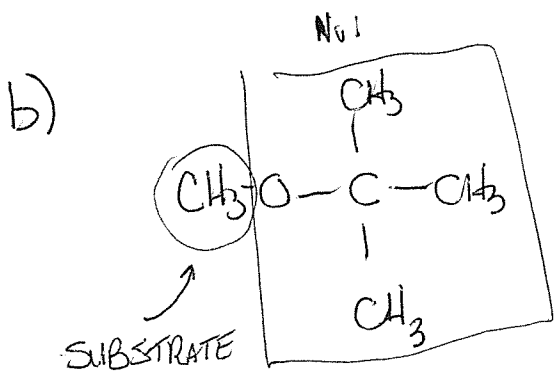


Treatment of a terminal alkyne with sodium metal (Na) forms an acetylide anion.

The acetylide anion behaves as a Nu⁻ in an S_N2 with 2-iodopropane



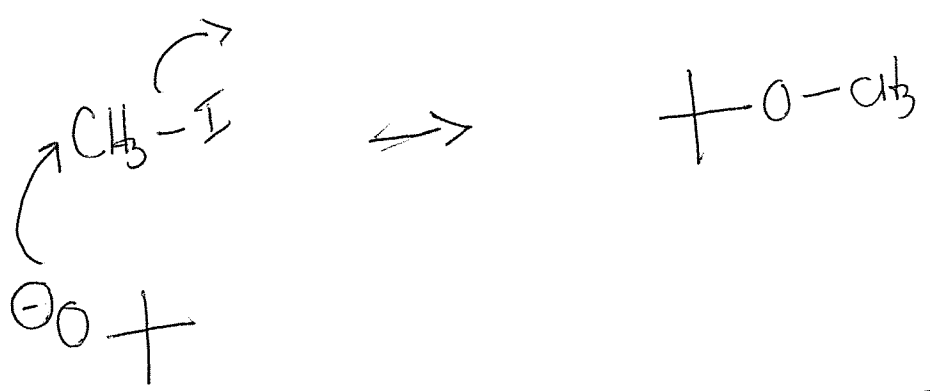
11.31 (cont'd)



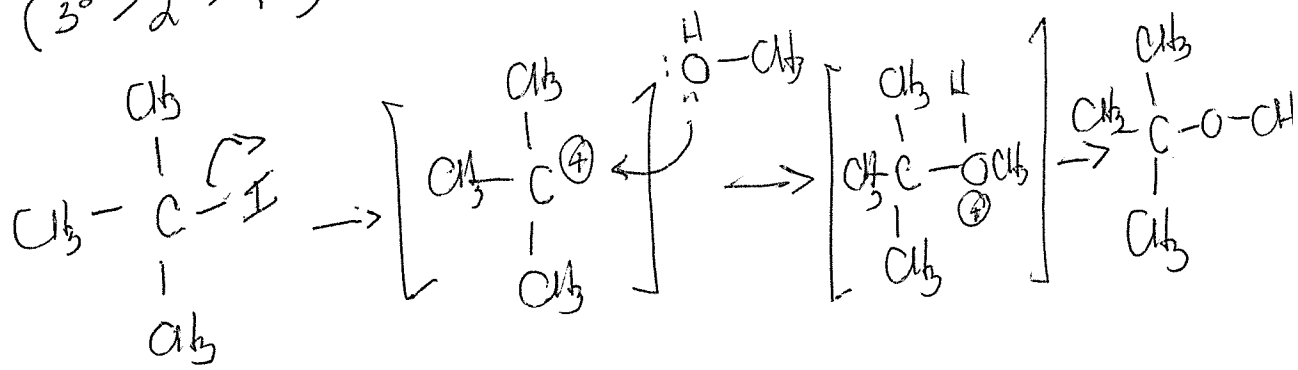
Can make this compound by either $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$

For $\text{S}_{\text{N}}2$, substrate C (i.e. sp^3 carbon bonded to the LG) should be LEAST substituted (i.e. Methyl $> 1^\circ > 2^\circ > 3^\circ$)

Nu1 is *t*-butoxide, derived from *t*-butyl alcohol

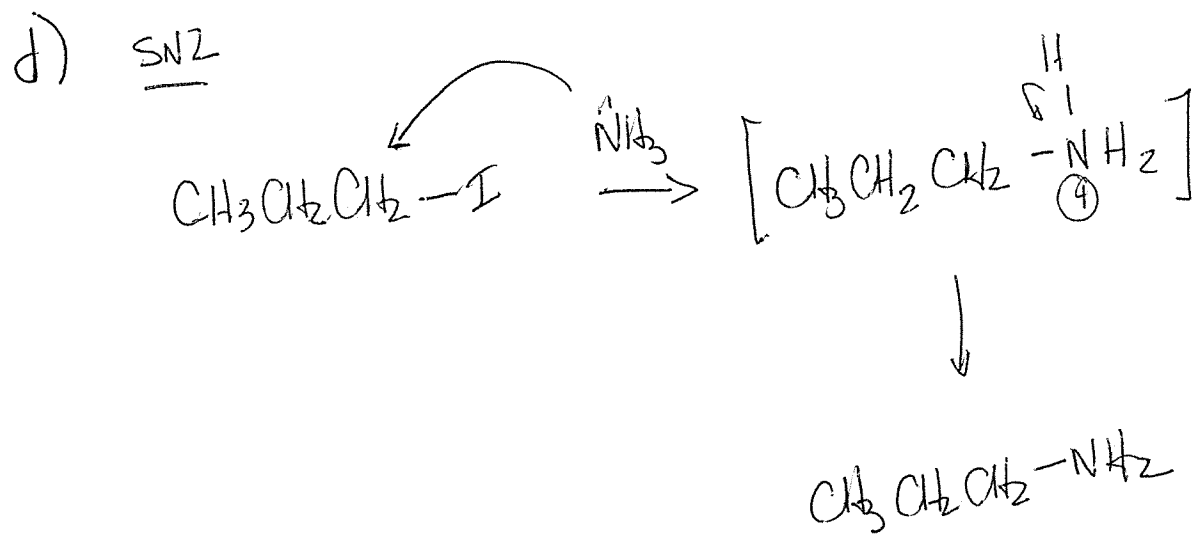
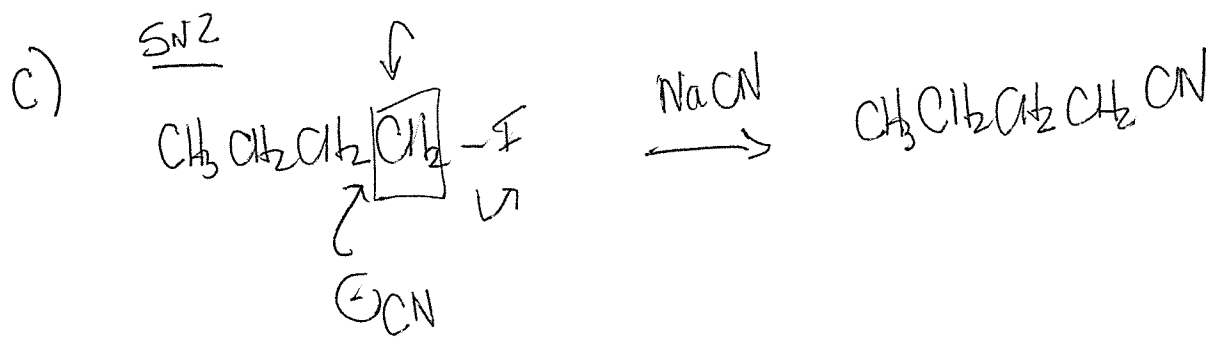


For $\text{S}_{\text{N}}1$, substrate carbon should be MOST substituted ($3^\circ > 2^\circ > 1^\circ$) Nu1 is methanol

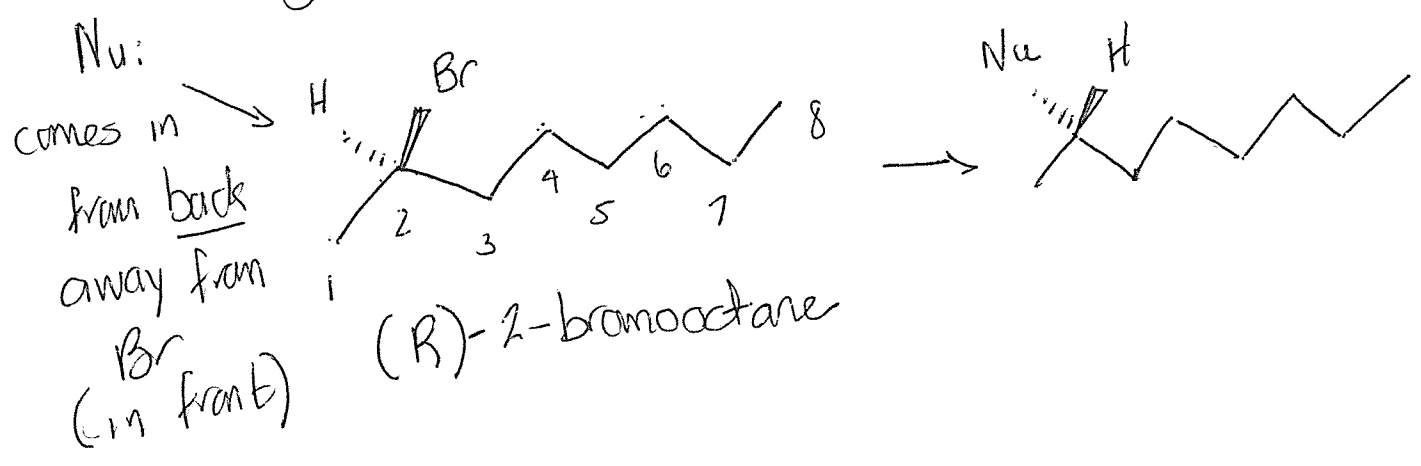


11.31 (cont'd)

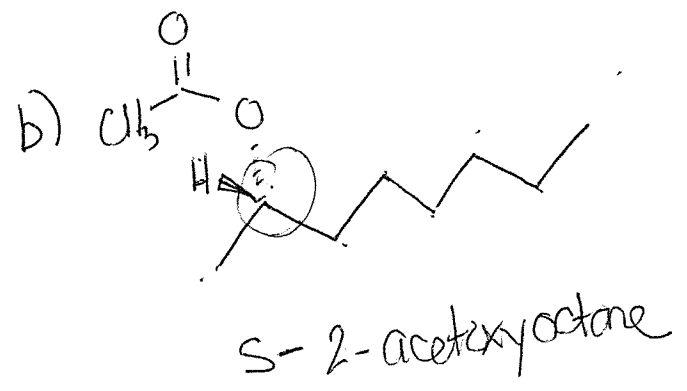
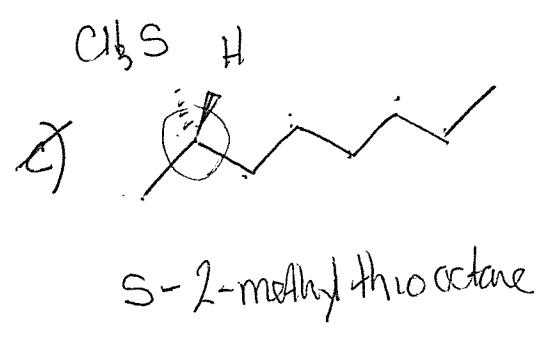
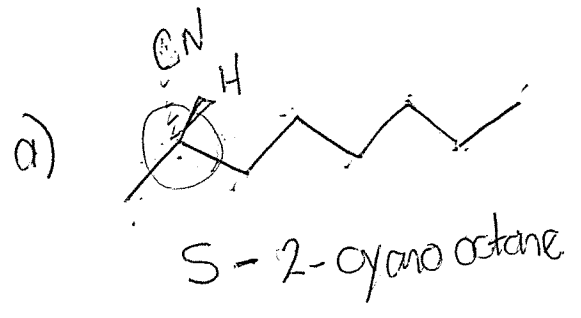
10 carbon (S_N2 better approach)



11.33 The S_N2 reaction occurs where the nucleophile attacks the carbon bonded to the leaving group 180° away from the LG (backside attack)



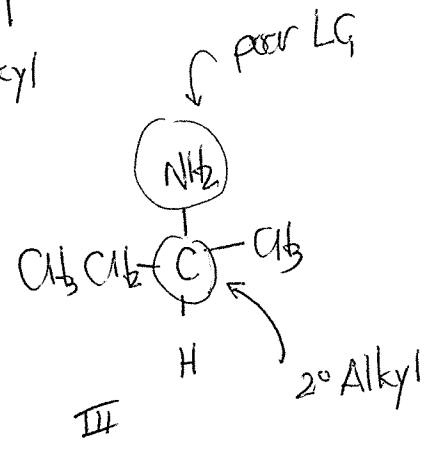
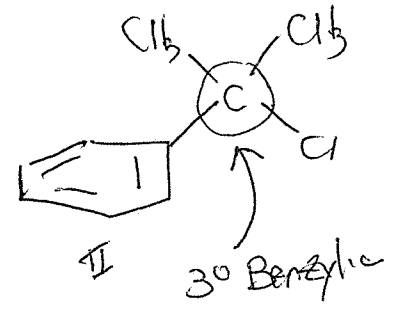
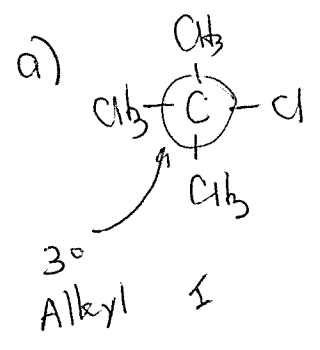
11.33 (cont'd)



11.41 SN₁ reactivity

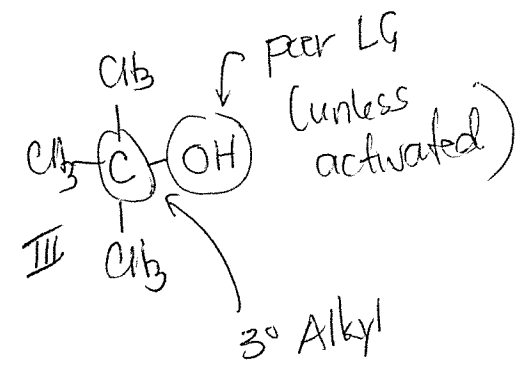
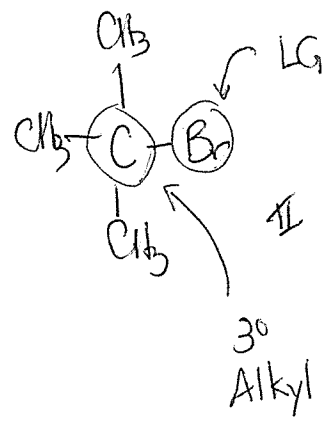
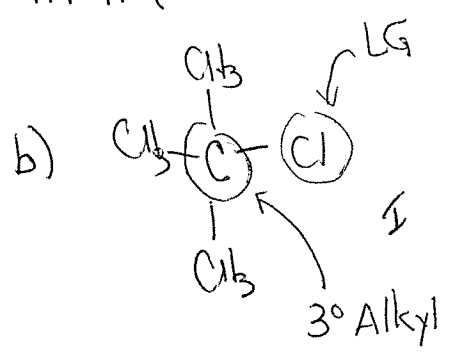
3° > 2° > 1°

Benzylic > Allylic > Alkyl



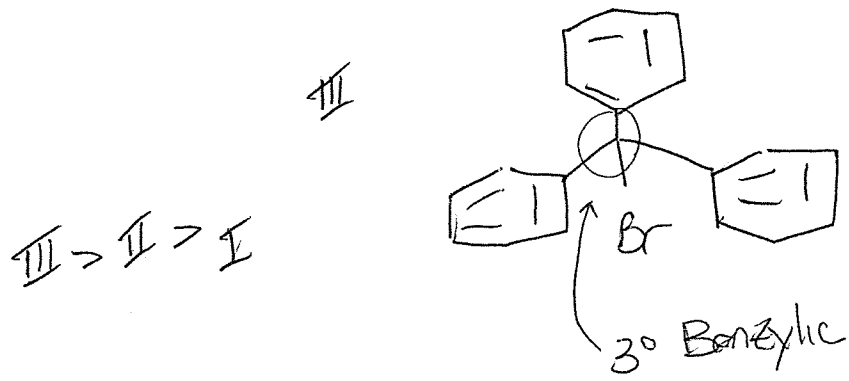
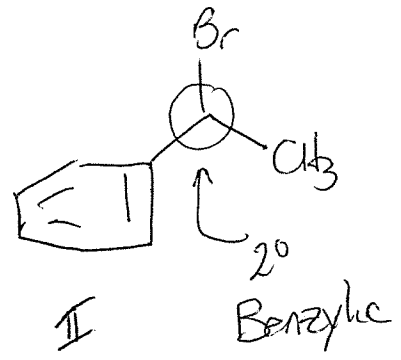
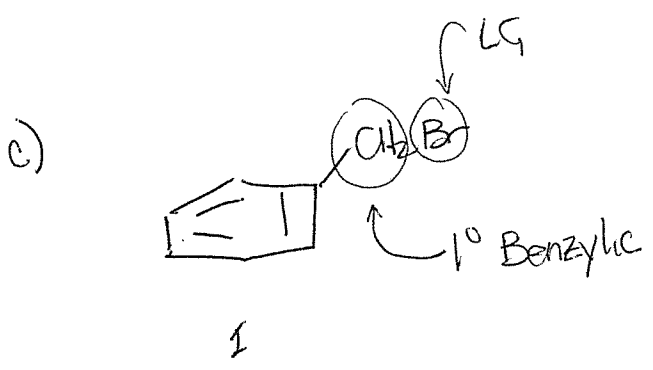
II > I > III

11.41 (cont'd)



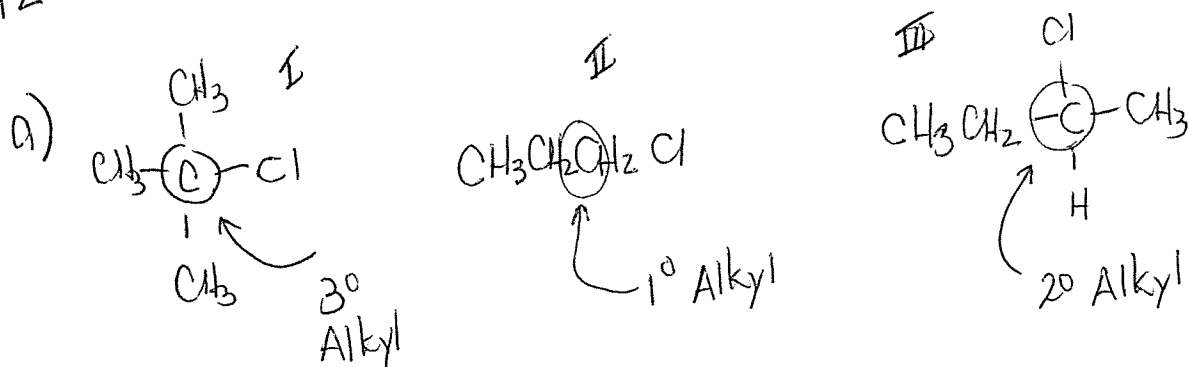
Br better leaving group than Cl

II > I > III

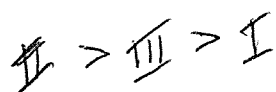
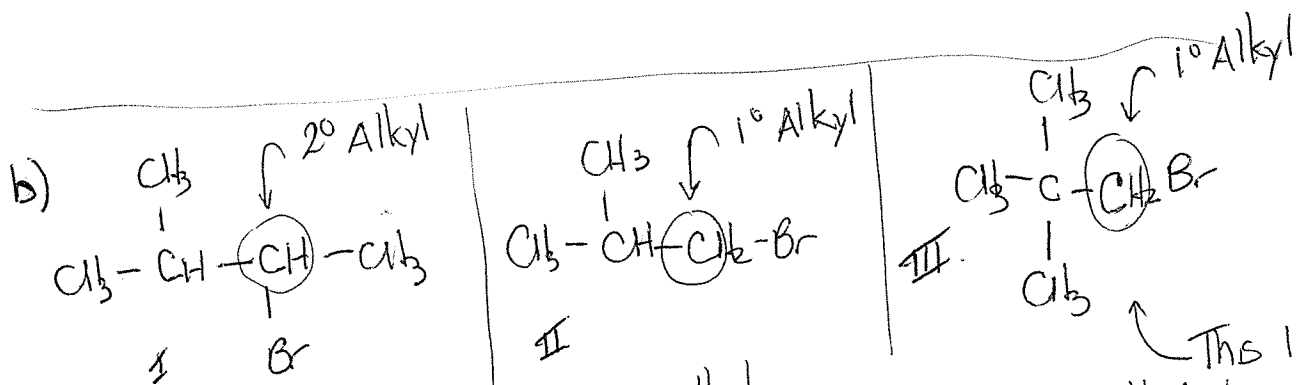
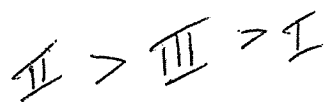


III > II > I

11.42



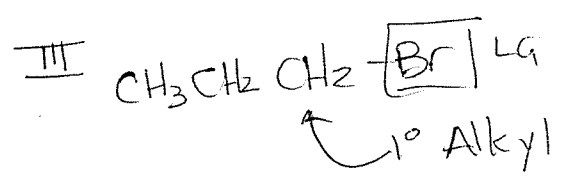
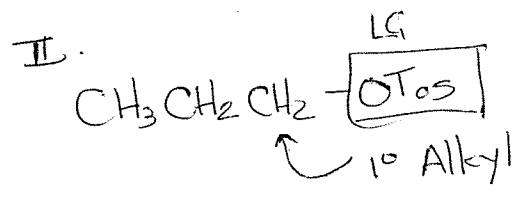
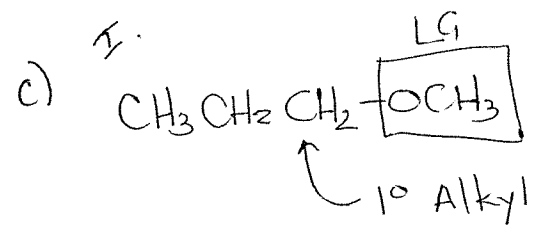
For S_N2 reactivity, $1^\circ > 2^\circ > 3^\circ$
No difference between benzylic/allylic and alkyl since NO carbocation involved in rds.



This 1° alkyl bromide is next to a 2° carbon. This has an impact b/c it contributes to sterics around the reacting carbon.

This 1° alkyl bromide is next to a 3° carbon. More steric crowding than II.

11.42 (cont'd)



II > III > I

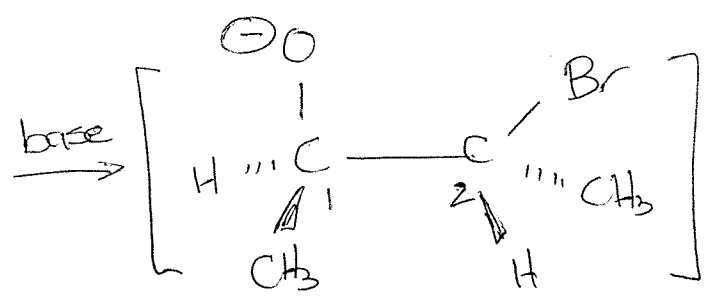
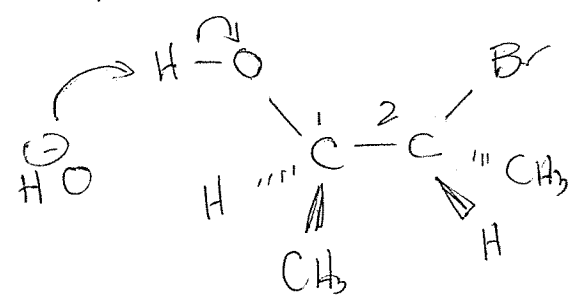
Best LG reacts
fastest. Tosylate (Tos)

$\left(\text{O}=\text{S}(=\text{O})\text{-C}_6\text{H}_4\text{-CH}_3 \right)^{\ominus}$ best LG

b/c it stabilizes \ominus
charge via resonance.

Br better able to
"handle" lone pair
than OCH_3

11.45

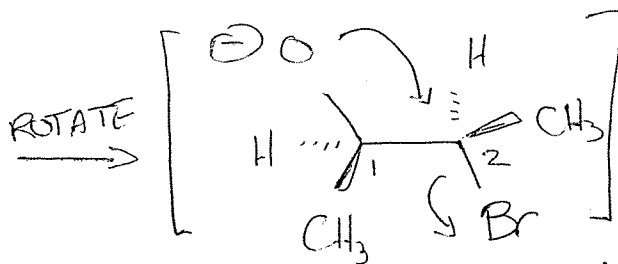
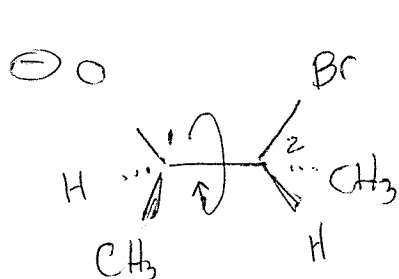


Alkoxide / Alkyl bromide

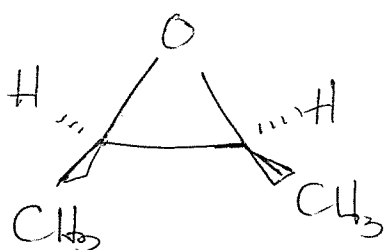
Treatment of the alcohol with strong base
gives rise to an alkoxide. The alkoxide
may serve as a nucleophile in an $\text{S}_{\text{N}}2$

11.45 (cont'd)

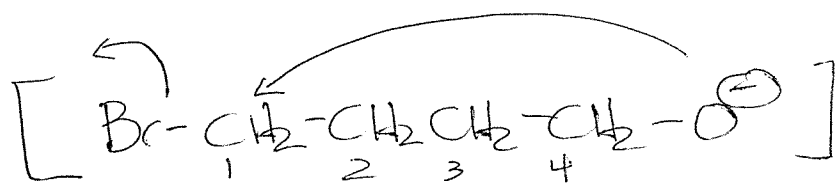
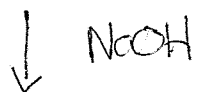
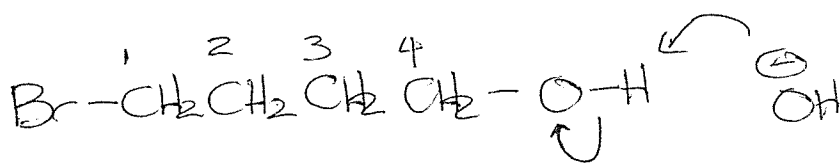
The S_N2 reaction may occur INTRAMOLECULARLY with the alkyl bromide however, the Br must be 180° away from the alkoxide Nu $^-$, so must rotate around the C_1-C_2 bond to achieve this required orientation.



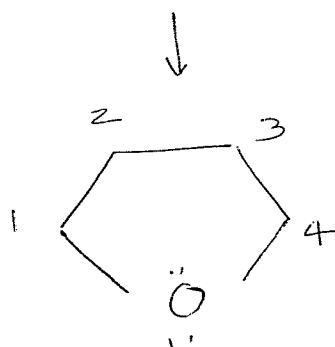
Once this orientation is achieved, the O $^-$ attacks C $_2$ and displaces the Br LG



11.47

Generate
alkoxide

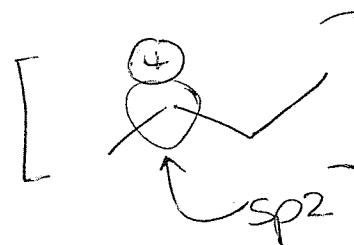
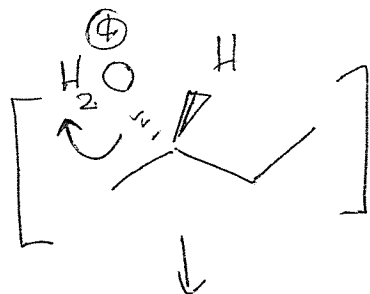
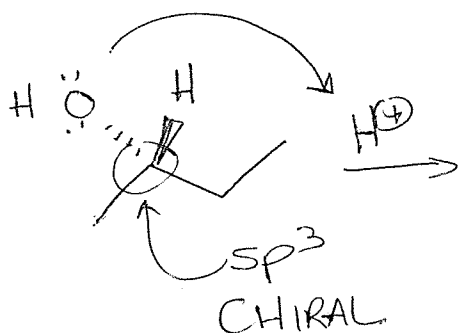
O^- reacts with
 C_1 to form a
ring and
displace Br^-



PRODUCT

11.57

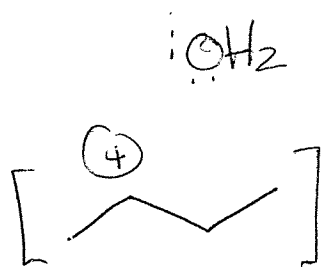
S-2-butanol



In the
presence of
acid, the
alcohol reacts
to form
a carbocation.

NOT CHIRAL

11.57



This carbocation then may react with H_2O from the top side or bottom side to give both the R- and S- 2-butanol

