Exam 3 Test Prep

Substitution and Elimination

Breaking down each reaction:

Sn2

E2

Sn1

E1

What is said to be the rate-determining step in an Sn1 or E1 reaction? (Circle the 2 answers)

A. Loss of a leaving group
B. Backside attack
C. Carbocation rearrangement
D. Formation of a carbocation
E. Mixing the solution of chemicals

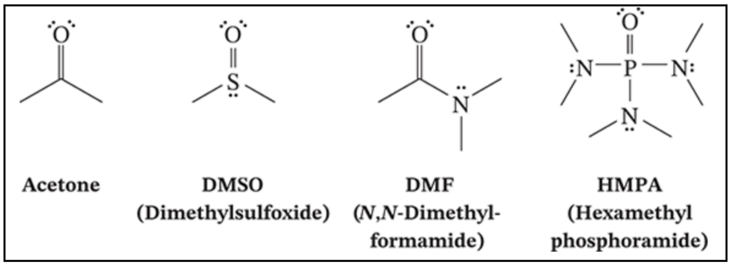
T/F: Rate-determining steps are typically very quick

Solvents

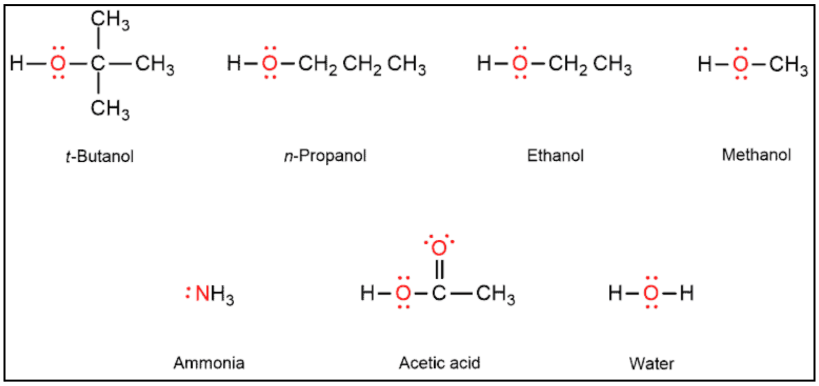
Generally, polar aprotic goes with ________________and polar protic goes with ______________

On of the major exceptions is ______________with ________________________

Polar Aprotic Solvents



Polar Protic Solvents



Determining Nucleophilicity

<u>Charge</u>: more _____________ charge, ________________ nucelophile

<u>Sterics</u>: smaller the nulceophile the ______________ it is

<u>Electronegativity</u>: In polar protic solvents, EN and nulceophilicity are ______________

<u>Polarizability:</u> The ability of a very large atom to __________________________, regardless of solvation

Is -SH or -OH a better nulceophile?

Determining Bascity

<u>Acid-base principle</u>: Look at the _________________________

Nulceophilicity parallels with basicity for compounds with the _________________________

$$RO^- > HO^- \gg RCO_2^- > ROH > H_2O$$

Nulceophilicity is not parallel to basicity for compounds with __________________________

$$HS^- > N\equiv C^- > I^- > HO^-$$

Identify the better nucleophile:

a. NaSH vs. H2S

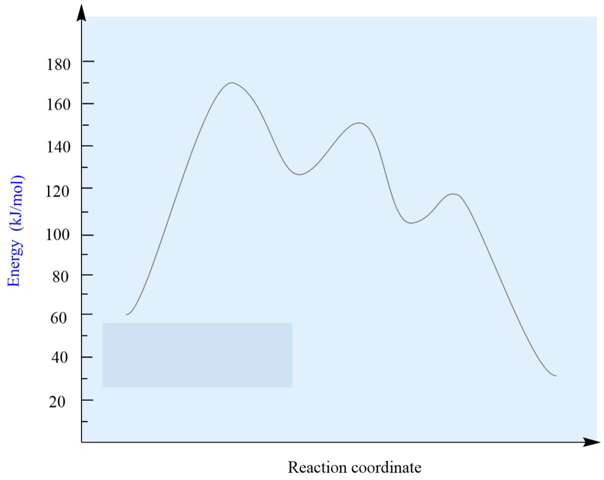
c. CH3O (In methanol) vs. CH3O (in DMSO)

d. Ethoxide CH3CH2O- vs. tert-butoxide (CH3)3O-

e. HO- vs. Cl-

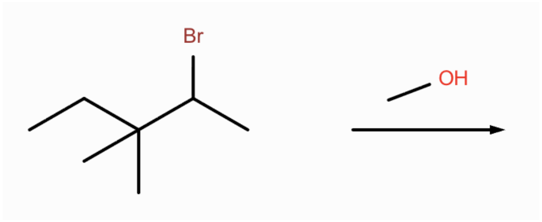
E & S Practice

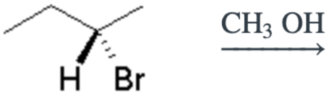
What is true about the free energy diagram below?



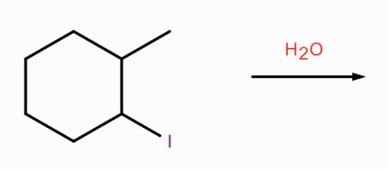
A. The reaction is an endergonic reaction, meaning Gibbs free energy is less than 0
B. The reaction is most likely an Sn2 reaction, which is unimolecular and exergonic
C. The reaction is a competing reaction between E2 and Sn2, both are endergonic, where Gibbs free energy is greater than 0
D. The reaction is most likely Sn1, which is exergonic, where Gibbs free energy is less than 0
E. The reaction is E1, an exergonic reaction, meaning Gibbs free energy is greater than 0

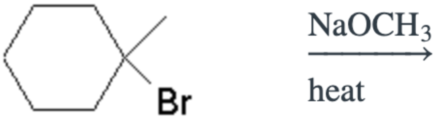
Give the major product and identify the reaction below:

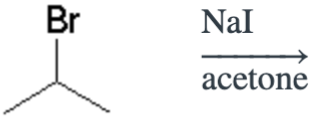





Br
(CH3)3 COK
heat


I
H2O


Br
NaOCH3
heat

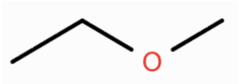

Br
NaI
acetone

Reaction Scenarios

1. Emily wants to make an ether compound using 1-bromo-1-methylcyclopentane. What kind of reagents would be good for this?

   From the previous problem above, Emily mixes the reagents and heats them up in an Erlenmeyer flask. When she is determining her final product, she notices she isn't getting the desired product. How can she change her reaction conditions to get the product she wants?

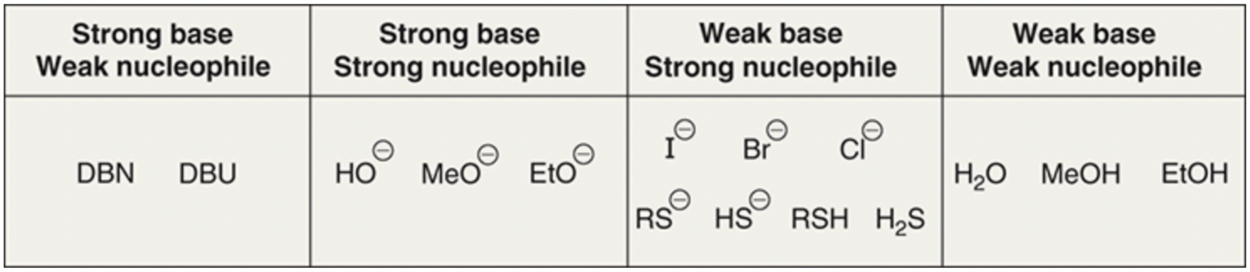
2. Harvey is working on synthesizing a new drug. One of his reactions is taking chloroethane, sodium methoxide, and turning it into the compound below

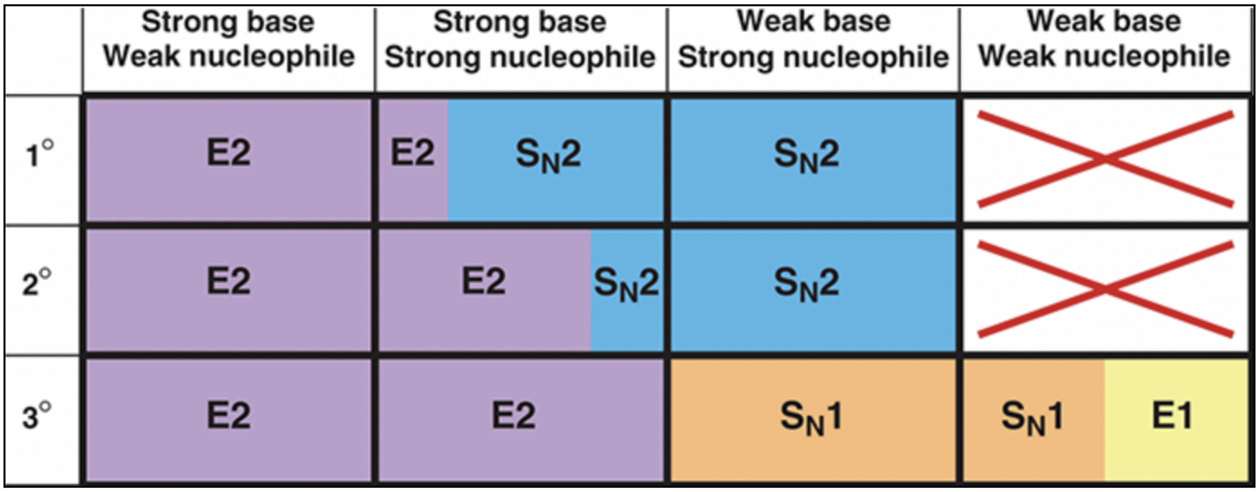
   Unfortunately, he is completely out of his stash of aprotic solvents. Can Harvey still complete his reaction? If so, how can he do it?

E&S Charts

	Regiochemistry	Stereochemistry
Sn2		
E2		
Sn1		
E1		



Strong base Weak nucleophile	Strong base Strong nucleophile	Weak base Strong nucleophile	Weak base Weak nucleophile
DBN DBU	$HO^{\ominus}$ $MeO^{\ominus}$ $EtO^{\ominus}$	$I^{\ominus}$ $Br^{\ominus}$ $Cl^{\ominus}$ $RS^{\ominus}$ $HS^{\ominus}$ RSH H_2S	H_2O MeOH EtOH



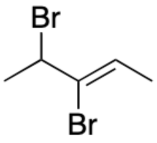
	Strong base Weak nucleophile	Strong base Strong nucleophile	Weak base Strong nucleophile	Weak base Weak nucleophile
1°	E2	E2 S_N2	S_N2	✗
2°	E2	E2 S_N2	S_N2	✗
3°	E2	E2	S_N1	S_N1 E1

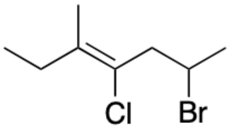
Alkenes

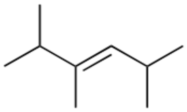
(E):

(Z):

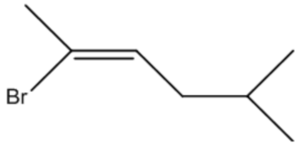
Designate E or Z for the compounds below:

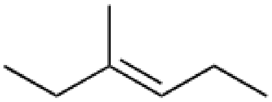




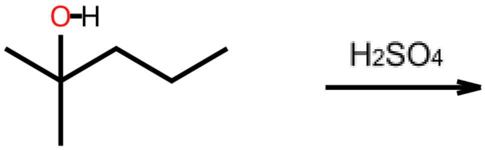


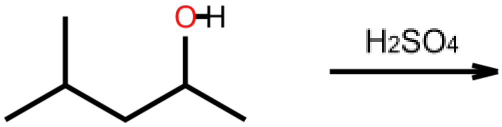
Name the compounds with E and Z configuration in mind:





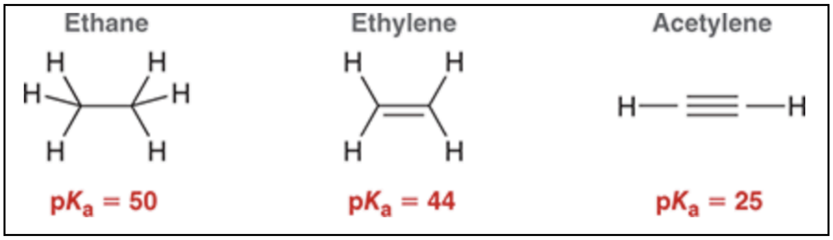
Predict the dehydration products below:



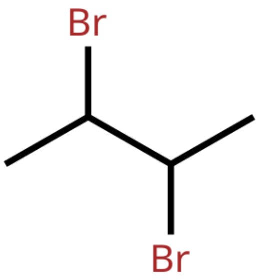
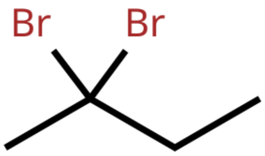


Alkynes

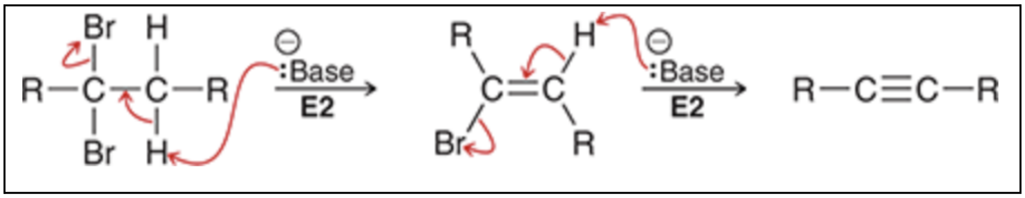
Acidity of alkynes



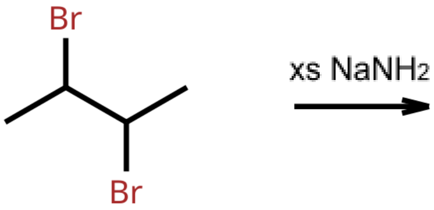
Synthesizing alkynes via dehydrohalogenation

Vicinal Dihalide	Geminal Dihalide
	

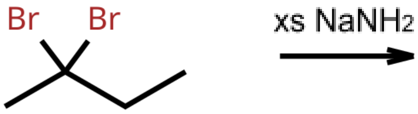
Mechanism:



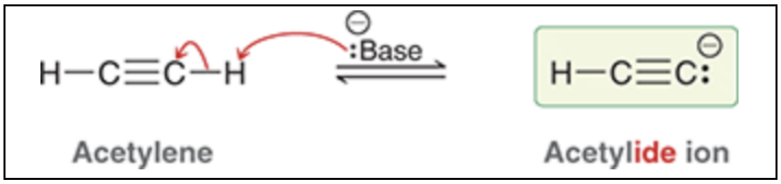
Vicinal Dihalide:



Geminal Dihalide:

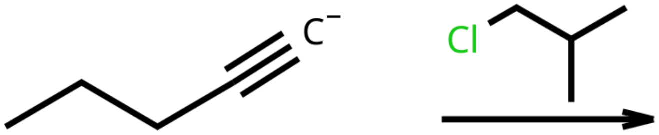


Acetylide Anion:

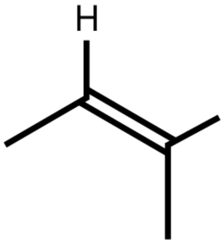
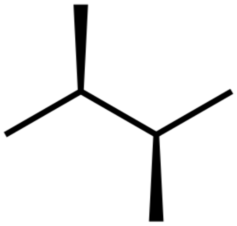
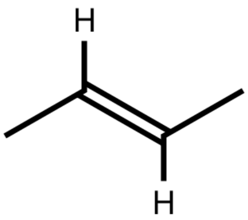
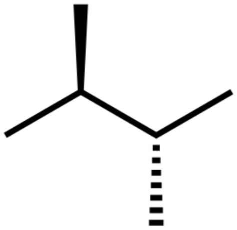


Synthesis:

Using acetylide ions in reactions



Syn and Anti-Addition

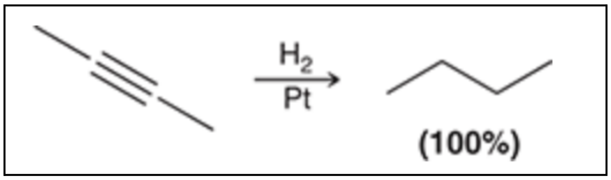
Syn-Addition	Anti-Addition
 OR 	 OR 

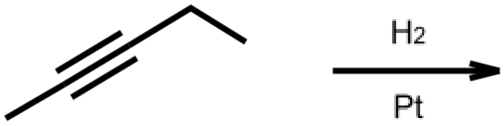
Reduction via catalytic hydrogenation

Similar to converting an alkene to an alkane, we can convert an alkyne to an alkane

Via________________________

Uses ________ addition

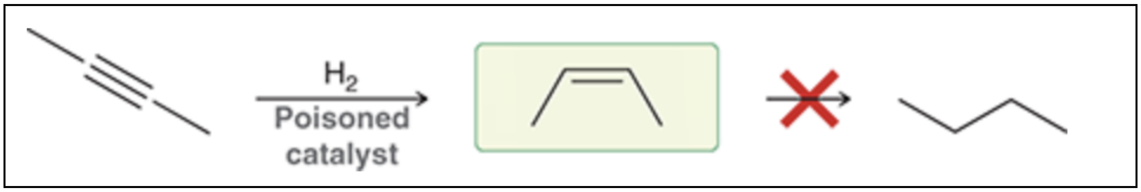




Using a poisoned catalyst

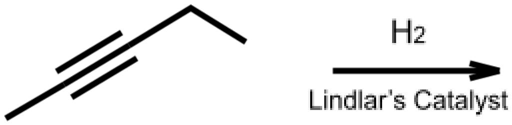
Under regular hydrogenation, it is difficult to isolate the cis-alkene intermediate. To stop the

reaction at a cis-alkene we use a ________________________________ (aka Lindlar's Catalyst or P-2)



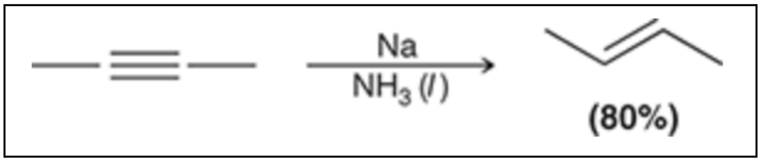
Lindlar's Catalyst:

P-2 Catalyst:

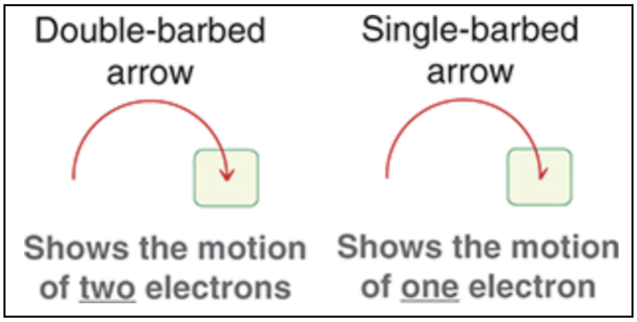


Dissolving Metal Reduction

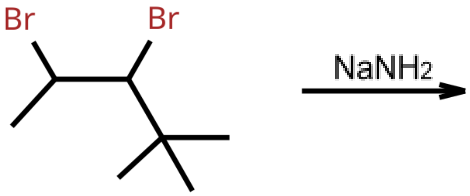
Alkyne to ____________ Alkene via an ______________ addition

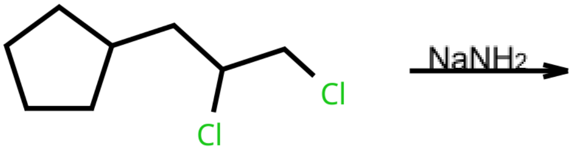


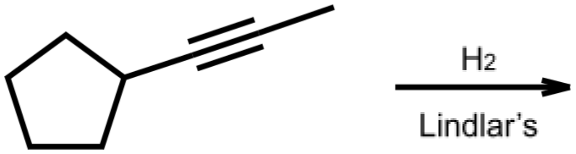
PSA: Pay attention to the arrows being used!

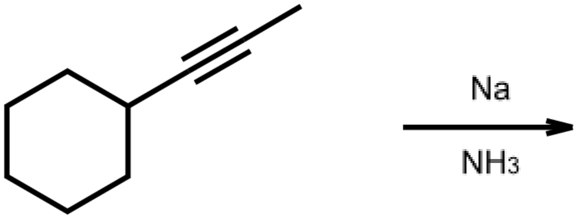


Practice






H2
Lindlar's


Na
NH3