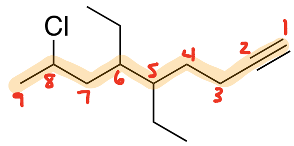
Answer Key

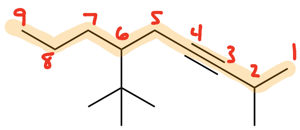
Chemistry 233
Chapter 9 Problem Set

Nomenclature

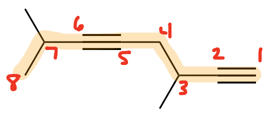
1) Provide the IUPAC name for each of the alkyne containing compounds below.



8-chloro-5,6-diethyl-1-nonyne
or
non-1-yne

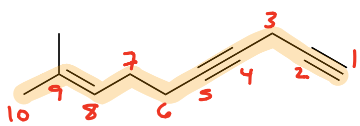


6-tert-butyl-2-methyl-3-nonyne
or
non-3-yne

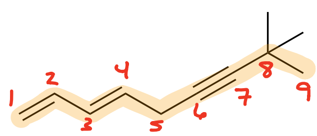


3,7-dimethyl-1,5-octadiyne
or
octa-1,5-diyne

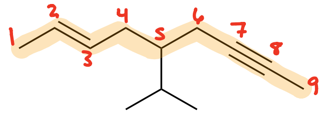
2) Provide the IUPAC name for each of the enyne compounds below.



9-methyl-8-decen-1,4-diyne
or
9-methyldec-8-en-1,4-diyne

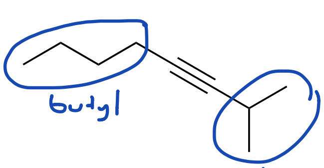


8,8-dimethyl-1,3-nonadien-6-yne
or
8,8-dimethylnona-1,3-dien-6-yne

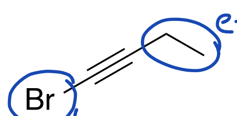


5-isopropyl-2-nonen-7-yne
or
5-isopropylnon-2-en-7-yne

3) Provide the common name for each compound below.

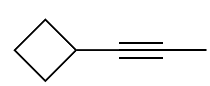


butyl
isopropyl
butylisopropylacetylene



ethyl
bromo
bromoethylacetylene

propyl
Propylacetylene

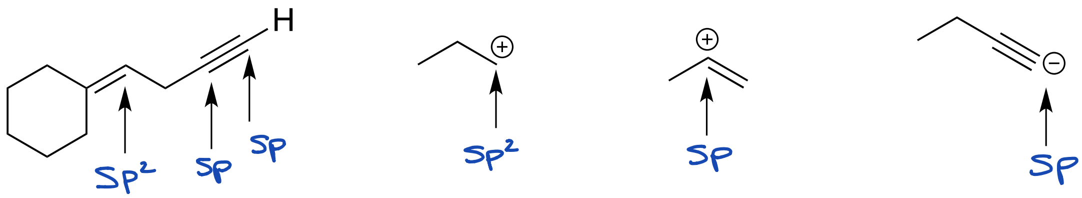


Cyclobutylmethyl acetylene

H−C≡C−H
acetylene

Structure and Properties of Alkynes

4) For each indicated carbon atom determine its hybridization.

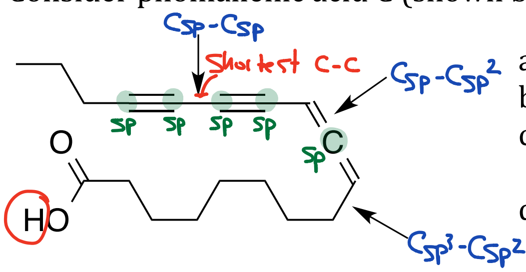


5) The smallest cycloalkyne that has been isolated and stored is cyclooctyne. Explain why alkynes do not exist in smaller rings.

Alkyne C's are sp hybridized and want a 180° bond angle

Constraining an alkyne in a ring results in substantial deviation from the 180° bond angle.
Rings with 8 or more C atoms are large enough to contain the alkyne without serious angle strain.

6) Consider phomallenic acid C (shown below), an inhibitor of bacterial fatty acid synthesis.



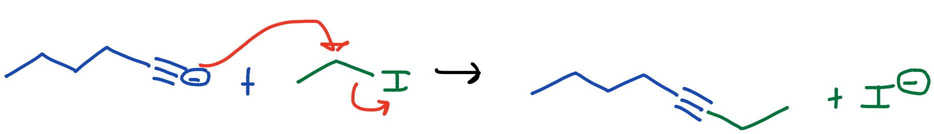
a. Circle the most acidic position.
b. What is the shortest C-C single bond?
c. How many sp hybridized atoms are present in the molecule? 5
d. For the bonds indicated with arrows, determine the orbitals that make up the bond.

7) Thinking back to our discussion of acid/base chemistry in Chapter 2, explain why sodium amide ($NaNH_2$) is a strong enough base to deprotonate a terminal alkyne. ⇒ yes, you should still know this.

Here, the acid is a stronger acid than the conjugate acid so the rxn lies to the right (side opposite the stronger acid)
We learned the exception that alkyne C-H is more acidic than amine N-H

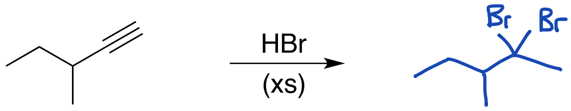
8) Draw the products from the acid base reaction shown below. Label the nucleophilic site in the product. Show curved arrows to demonstrate the flow of electrons.

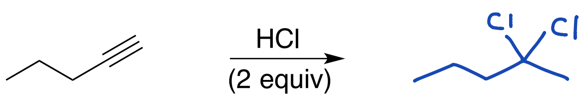
9) Show how the nucleophile generated above would react with iodoethane.

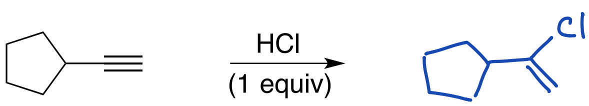


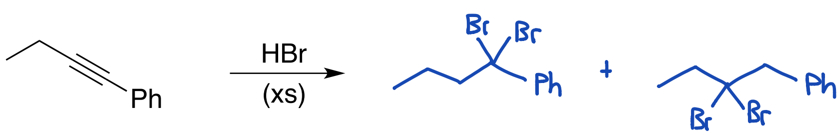
Reactions and Mechanisms

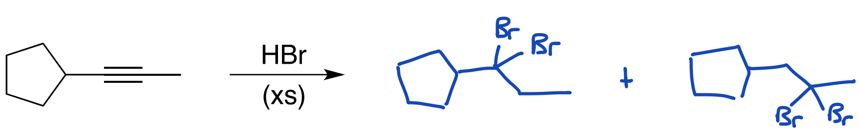
10)Predict the product(s) for each halogen addition below.

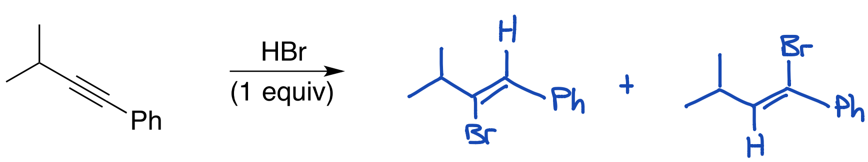




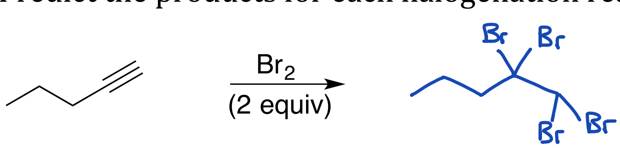


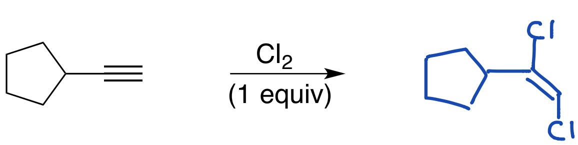


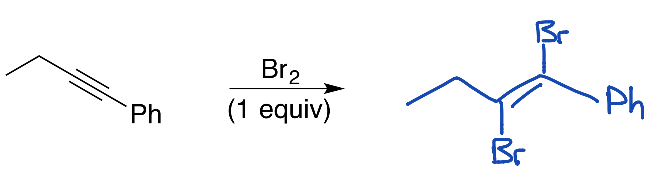


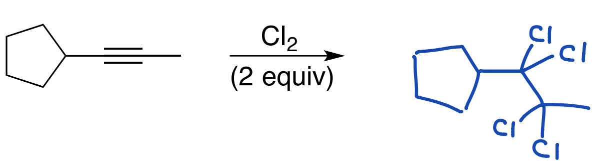


11)Predict the products for each halogenation reaction shown below.

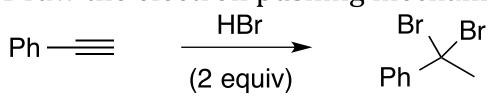






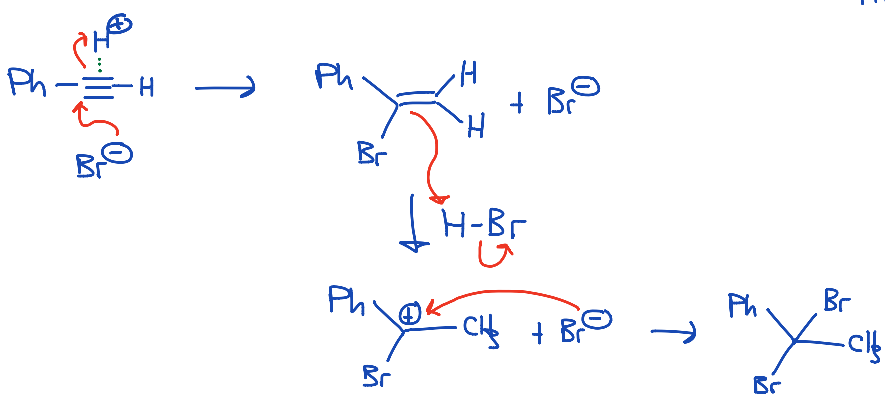


12) Draw the electron pushing mechanism for the reaction shown below.

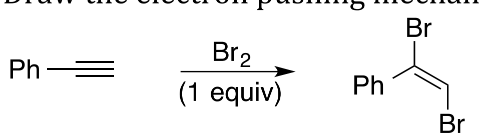


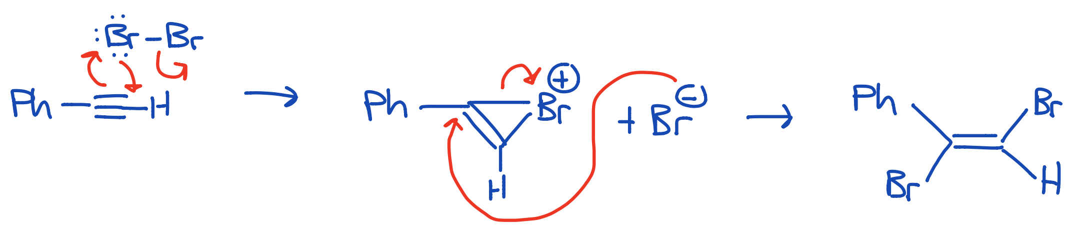
HBr provides a source of $Br^{\ominus}$

$HBr \rightleftharpoons H^+ + Br^-$

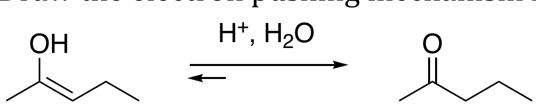


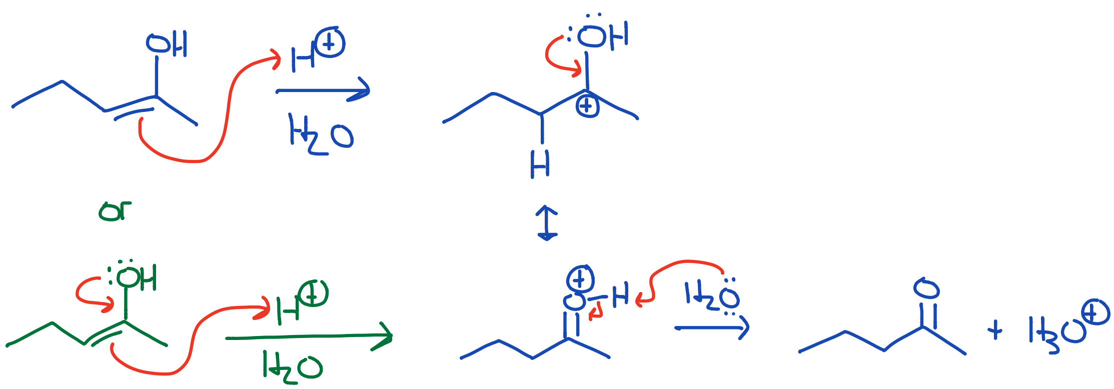
13) Draw the electron pushing mechanism for the reaction shown below.



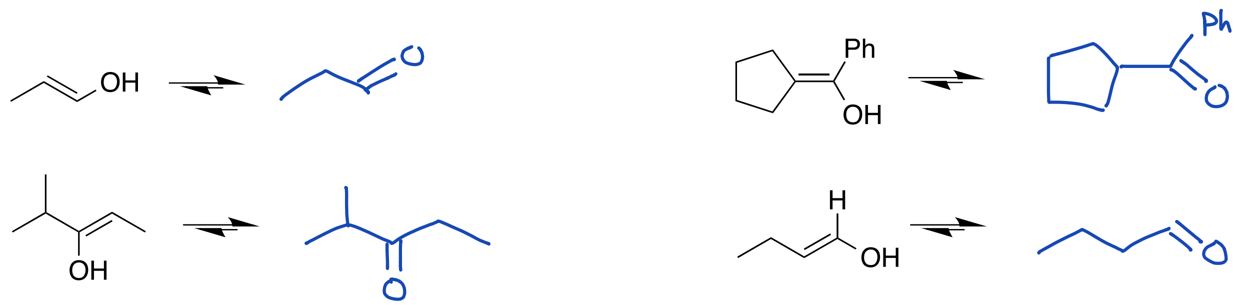


14) Draw the electron pushing mechanism for the acid catalyzed tautomerization of (*Z*)-2-penten-2-ol.

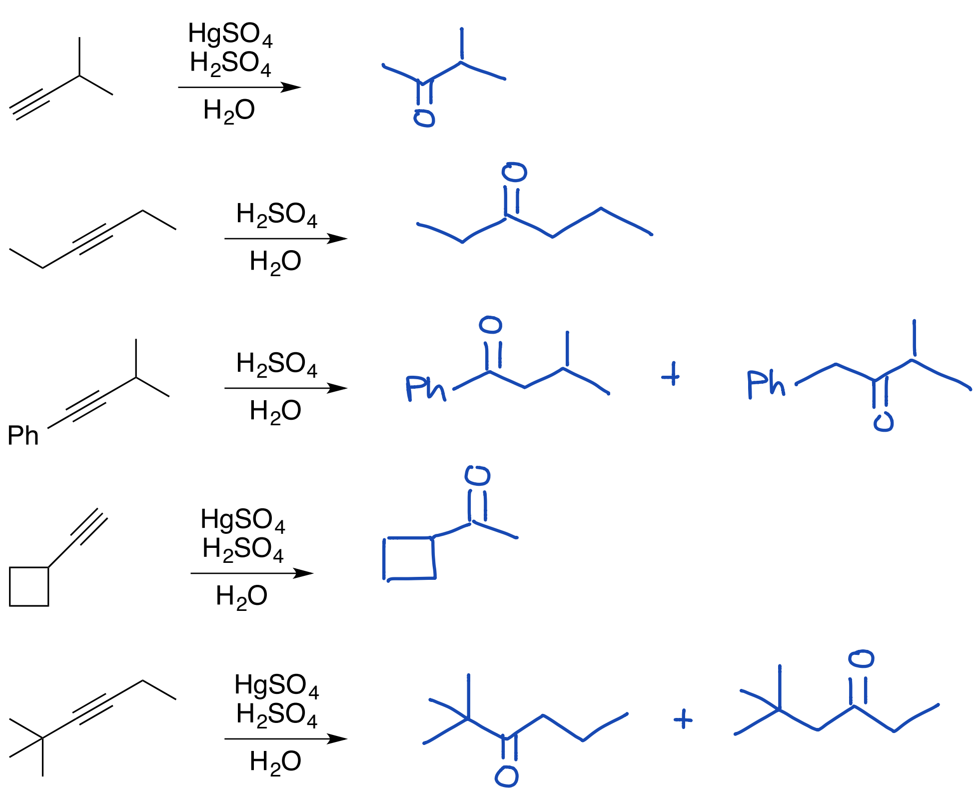




15)Draw the aldehyde/ketone form for the following enol tautomers

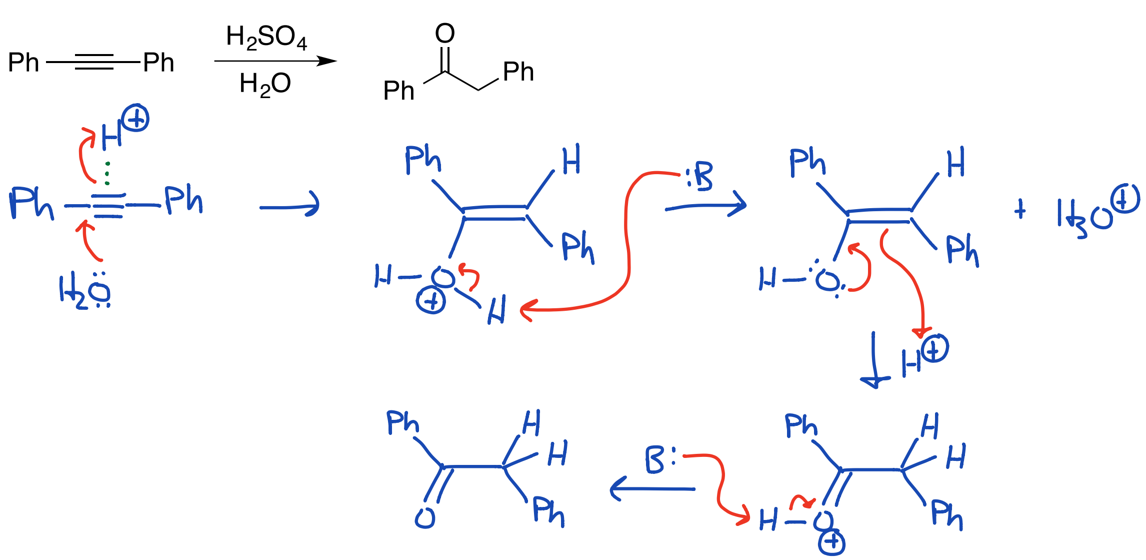


16)Predict the products for the acid and mercury(II) catalyzed hydration reactions shown below.

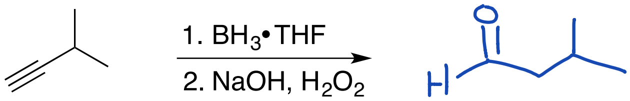


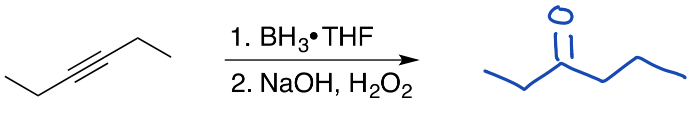
Although Hg^{2+} isn't necessary, it can be used to catalyze the hydration of internal alkynes.

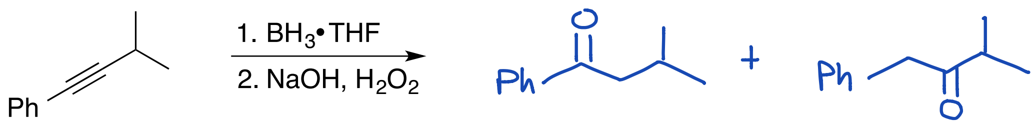
17)Draw the electron pushing mechanism for the acid catalyzed hydration reaction below.

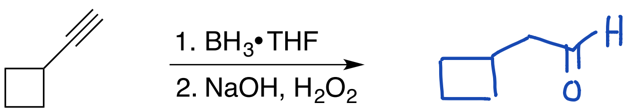


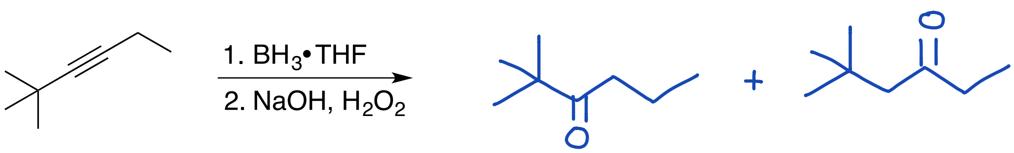
18) Predict the products for the hydroboration-oxidation reactions shown below.



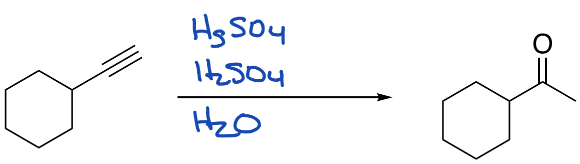


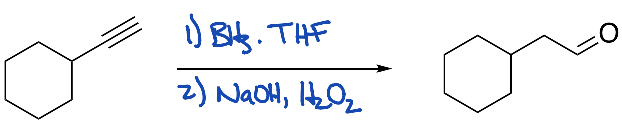


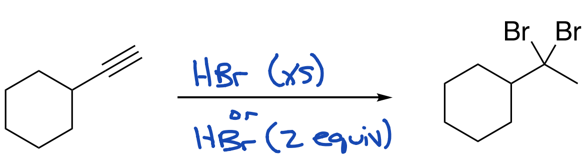


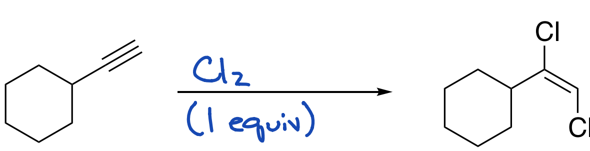


19) Determine the necessary reagents to carry out each of the interconversions shown below.

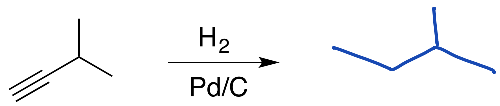


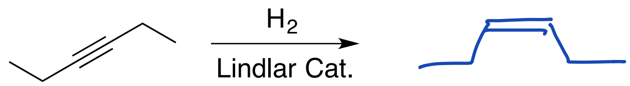


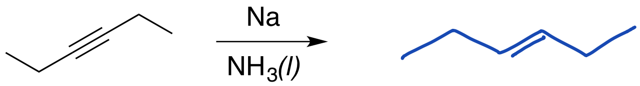


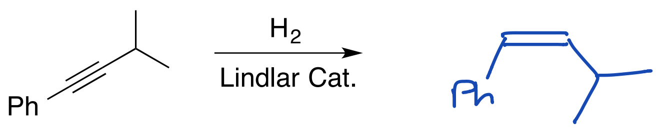


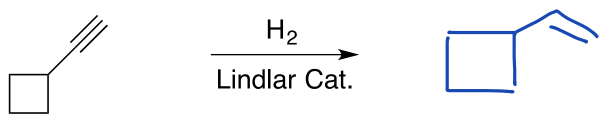
20)Predict the products for the alkyne reduction reactions shown below.

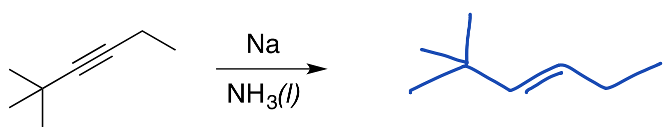




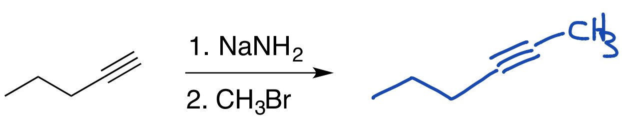


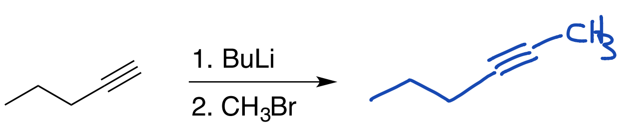


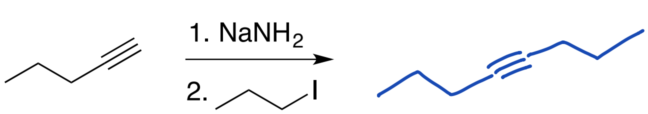


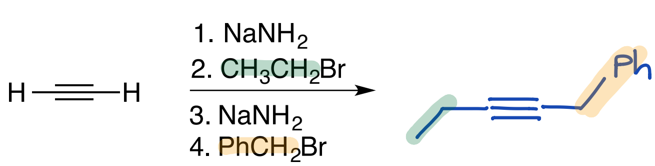


21)Predict the product for each alkylation reaction below.



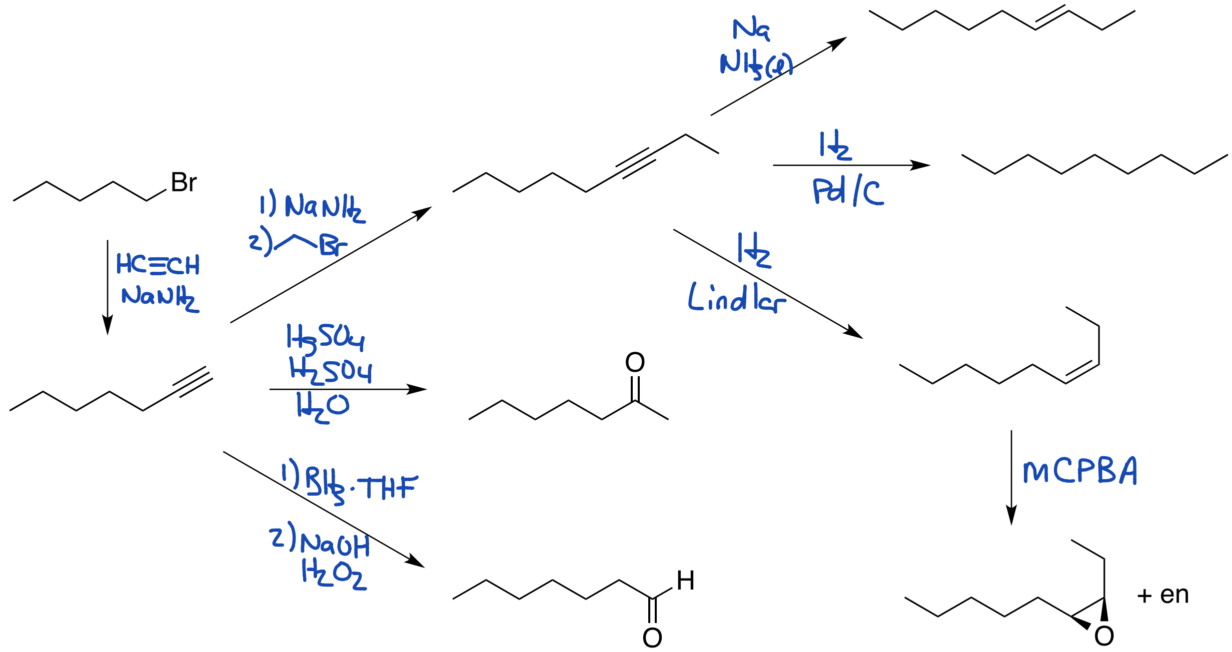




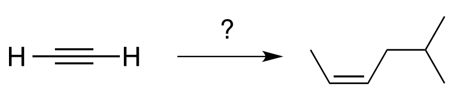


Synthesis

22)Provide the missing reagents in the synthetic sequence shown below.



23)Provide a reasonable synthesis for each of the following compounds using the provided starting material.



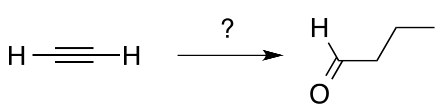
okay to switch order

1) $NaNH_2$
2) CH_3I

1) $NaNH_2$
2) I—(isobutyl)

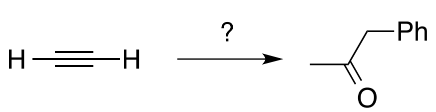
H_2
Lindlar

Cl + Br okay too



1) $NaNH_2$
2) (ethyl)Cl

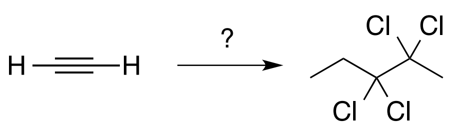
1) $BH_3 \cdot THF$
2) NaOH, H_2O_2



1) $NaNH_2$
2) $PhCH_2I$

$HgSO_4$
H_2SO_4
H_2O

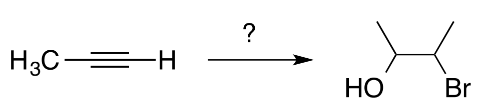
okay to swap steps



1) $NaNH_2$
2) CH_3I

1) $NaNH_2$
2) (ethyl)I

Cl_2
(xs)



1) $NaNH_2$
2) CH_3I

H_2
Lindlar or Na
$NH_3(l)$

Br_2
H_2O

Sterochem not given in prod so either reduction is fine.