

PRACTICE EXERCISE – ORGANIC CHEMISTRY I
Alkynes Synthesis and Reactions

FOR QUESTIONS 1-4, DRAW A LEWIS OR LINE-ANGLE FORMULA AND GIVE THE IUPAC NAME.

1) $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{CH}_3)\text{CCCH}(\text{CH}_3)_2$ 2) $\text{HCCCH}_2\text{CH}_2\text{CH}_3$ 3) $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCCCH}_3$ 4) $\text{BrCH}_2\text{CH}_2\text{CCCH}_2\text{CH}_3$

5) Draw acetylene

6) Draw (S)-5-phenyloct-2-yne

7) Draw hepta-3,6-dien-1-yne

8) The carbon-carbon triple bond of an alkyne is composed of

A) 3 σ bonds

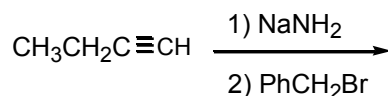
B) 3 π bonds

C) 2 π bonds and 1 σ bond

D) 1 π bond and 2 σ bonds

9) Why are terminal alkynes more acidic than other hydrocarbons?

10) Provide the structure of the major organic product(s) in the reaction below.



11) Which of the species below is **less basic** than acetylide?

A) CH_3Li

B) CH_3ONa

C) CH_3MgBr

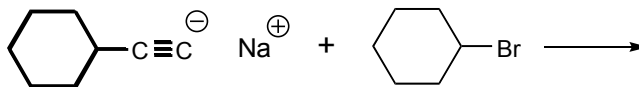
D) both A and C

E) all of the above

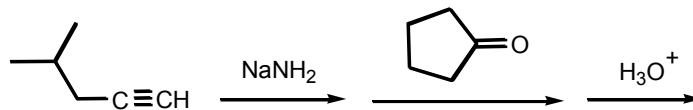
12) Describe a chemical test for distinguishing terminal alkynes from internal ones.

13) 2-Methylhex-3-yne can be prepared by the reaction of an alkynide with an alkyl halide. Does the better synthesis involve alkynide attack on bromoethane or on 2-bromopropane? Explain your reasoning.

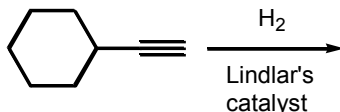
14) Provide the structure of the major organic product(s) in the reaction below.



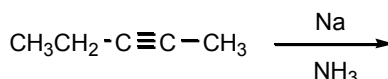
15) Provide the structure of the major organic product(s) in the reaction below.



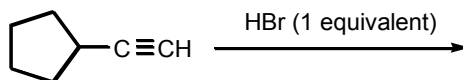
16) Provide the structure of the major organic product(s) in the reaction below.



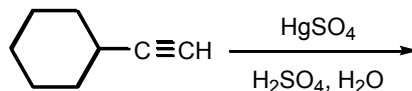
17) Provide the structure of the major organic product(s) in the reaction below.



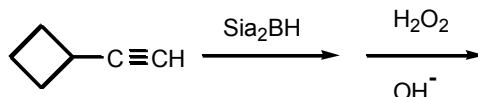
18) Provide the structure of the major organic product(s) in the reaction below.



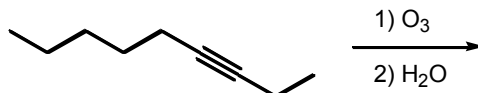
19) Provide the structure of the major organic product(s) in the reaction below.



20) Provide the structure of the major organic product(s) in the reaction sequence below.



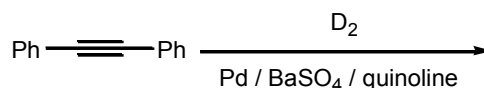
21) Provide the structure of the major organic product(s) in the reaction below.



22) To a solution of propyne in diethyl ether, one molar equivalent of CH_3Li was added and the resulting mixture was stirred for 0.5 hour. After this time, an excess of D_2O was added. Describe the major organic product(s) of this reaction.

- A) $\text{CH}_3\text{CCD} + \text{CH}_4$
- B) CH_3CCCH_3
- C) CD_3CCD_3
- D) CH_3CCCD_3
- E) $\text{CH}_3\text{CCD} + \text{CH}_3\text{D}$

23) Provide the structure of the major organic product(s) in the reaction below.



24) Which of the alkyne addition reactions below involve(s) an enol intermediate?

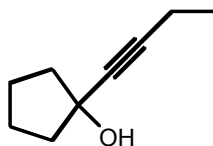
- A) hydroboration/oxidation
- B) treatment with HgSO_4 in dilute H_2SO_4
- C) hydrogenation
- D) both A and B
- E) none of the above

25) Draw the products which result when oct-3-yne is heated in basic potassium permanganate solution.

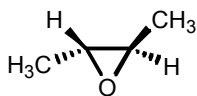
QUESTIONS 26-33 INVOLVE MULTISTEP SYNTHESSES. PROVIDE THE STEPS BY WHICH THE PRODUCT GIVEN CAN BE PREPARED FROM THE STARTING MATERIAL GIVEN.

- 26) Prepare racemic 2,3-dibromobutane from propyne
- 27) Prepare meso-2,3-dibromobutane from propyne
- 28) Prepare hept-1-yne from hept=1-ene.
- 29) Prepare butylbenzene from phenylacetylene
- 30) Prepare *trans*-pent-2-ene from propyne.

31) Prepare the compound shown below from acetylene.



32) Prepare the compound shown below from acetylene.



33) How many distinct alkynes exist with a molecular formula of C_4H_6 ?

- A) 0 B) 1 C) 2 D) 3 E) 4

34) Name the compound which results when pent-2-yne is subjected to catalytic hydrogenation using a platinum catalyst.

35) Which of the following reagents should be used to convert hex-3-yne to (*E*)-hex-3-ene?

- A) H_2 , Pt B) Na, NH_3 C) H_2 , Lindlar's catalyst D) H_2SO_4 , H_2O E) $HgSO_4$, H_2O

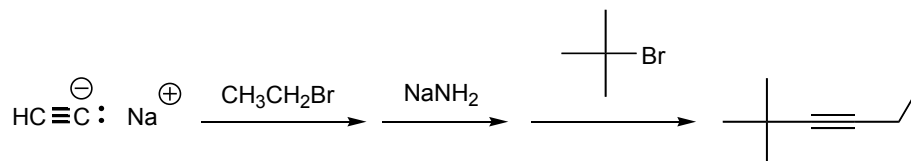
36) Which of the following reagents should be used to convert hex-3-yne to (*Z*)-hex-3-ene?

- A) H_2 , Pt B) Na, NH_3 C) H_2 , Lindlar's catalyst D) H_2SO_4 , H_2O E) $HgSO_4$, H_2O

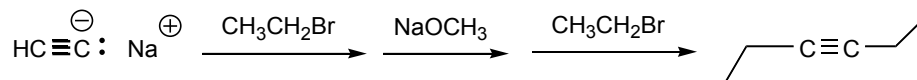
37) Draw the product that results when CH_3CCLi reacts with $CH_3CH_2COCH_2CH_3$ followed by addition of H_2O

38) Name the compound which results when pent-1-yne is treated with sodium in liquid ammonia.

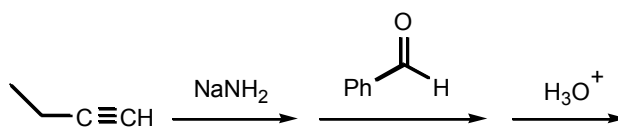
39) Explain why the synthetic route shown below would be unsuccessful.



40) Explain why the synthetic route shown below would be unsuccessful.

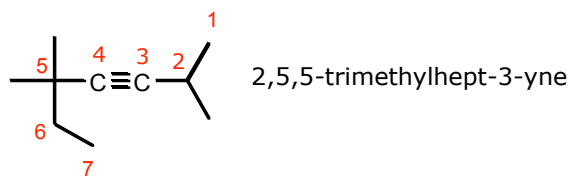


41) Provide the major organic product of the reaction shown below.



ANSWERS

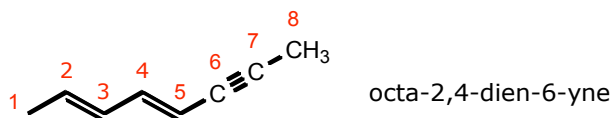
1)



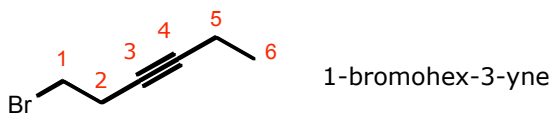
2)



3)



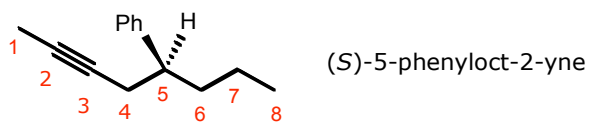
4)



5)



6)



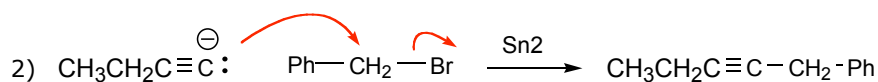
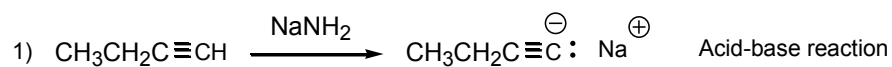
7)



8) D

9) The carbanion which results upon deprotonation of a terminal alkyne has the lone pair of electrons in an sp hybrid orbital. The greater % s character of this orbital gives this orbital a significantly lower energy.

10)

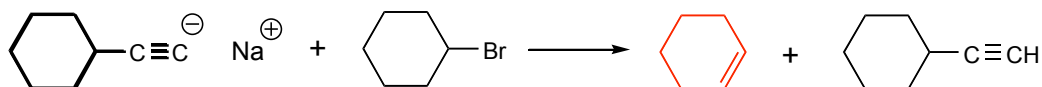


11) B

12) Add a solution of Cu^+ or Ag^+ . Terminal alkynes form insoluble metal acetylides and precipitate

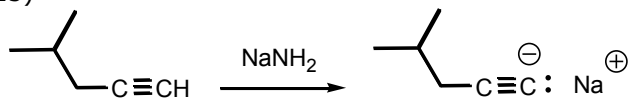
13) Attack on the less sterically hindered primary bromide (bromoethane) is more favorable. Reaction of an alkyne with the secondary (hindered) bromide would result mostly in elimination instead of substitution.

14)

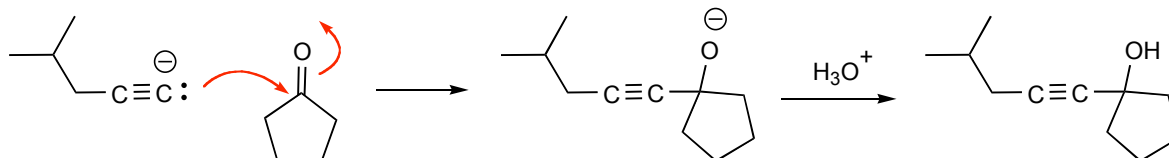


The attack of the strong base on a hindered bromide promotes elimination (E2) over substitution

15)



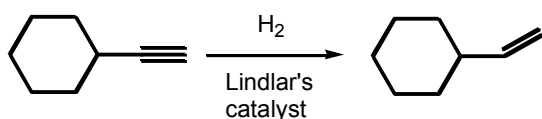
The first step is an acid-base reaction which produces the alkyne conjugate base, or alkynide ion (a nucleophile)



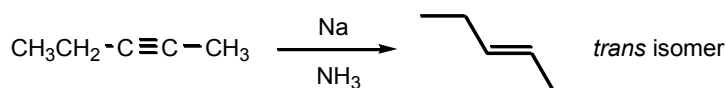
Nucleophilic attack on the ketone gives the alkoxide ion, which is the conjugate base of the 3° alcohol.

3° alcohols are produced from the reaction between carbon nucleophiles and ketones.

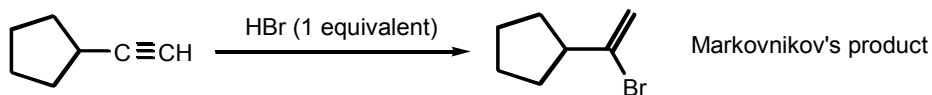
16)



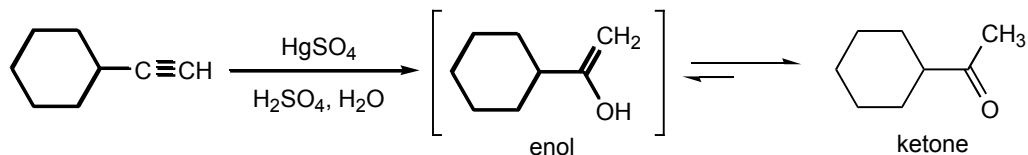
17)



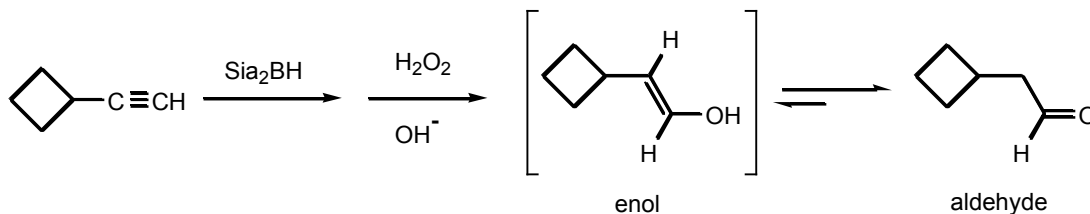
18)



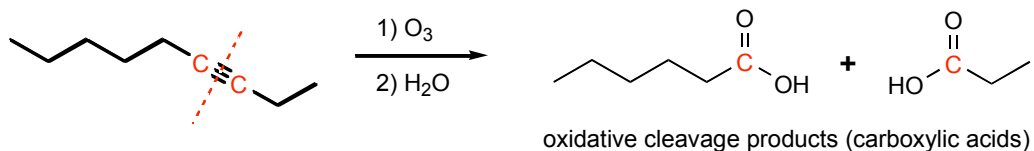
19) Markovnikov addition of water to the triple bond produces the enol, which then rearranges to the ketone.



20) Anti-Markovnikov addition of water to the triple bond produces the enol, which then rearranges to the aldehyde.

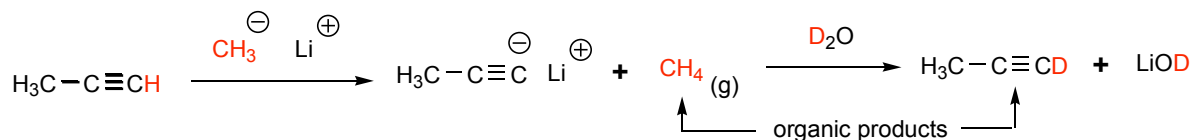


21)

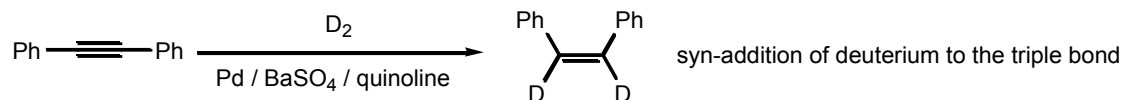


oxidative cleavage products (carboxylic acids)

22) This is simply a series of acid base reactions, as follows (the answer is **A**).



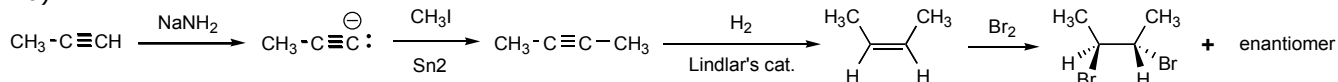
23)



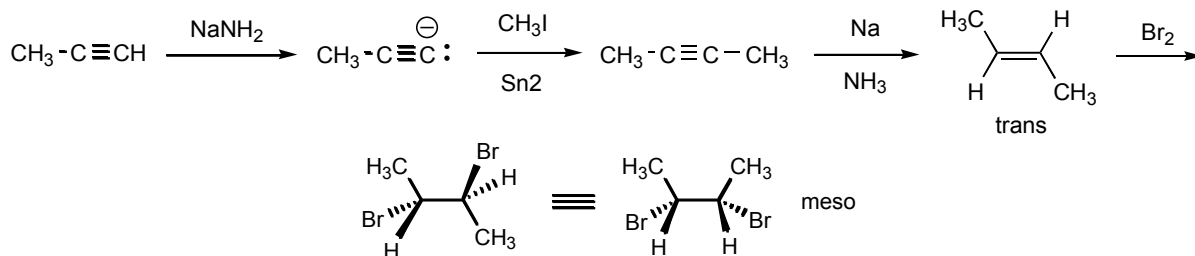
24) D

25) $\text{CH}_3\text{CH}_2\text{CO}_2^- \text{K}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2^- \text{K}^+$. These products are the conjugate bases of the carboxylic acids that would be produced if the pH was neutral or acidic. But because the KMnO_4 reaction involves basic medium (OH^-), the actual products are not the free carboxylic acids, but their conjugate bases.

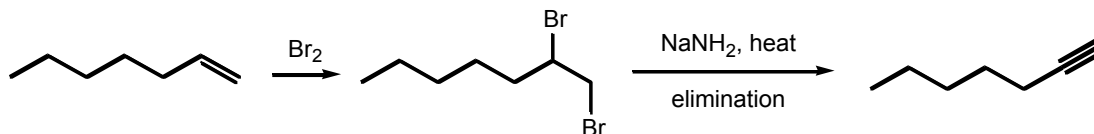
26)



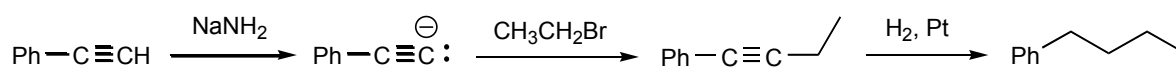
27)



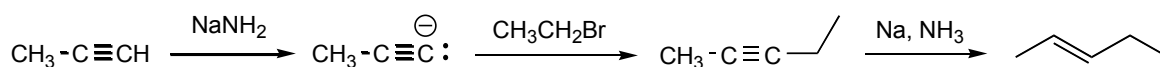
28)



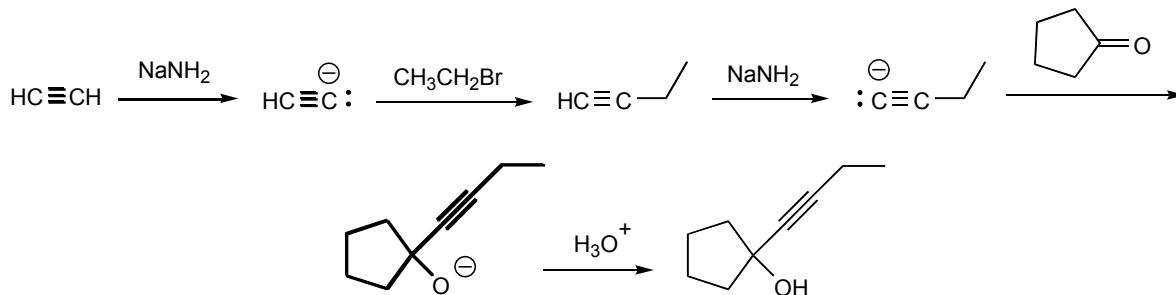
29)



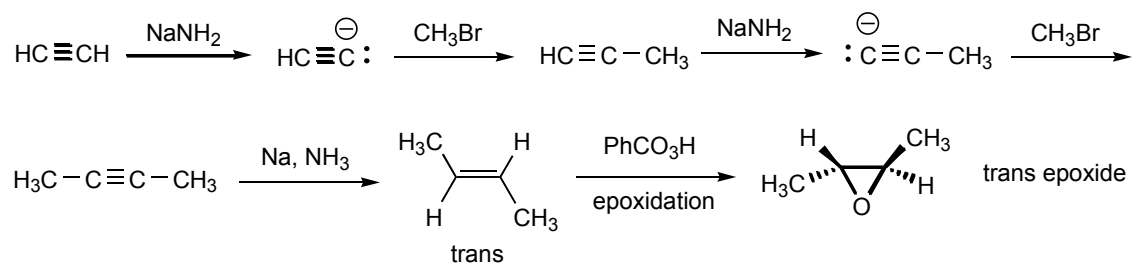
30)



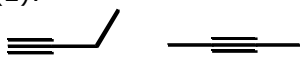
31)



32)

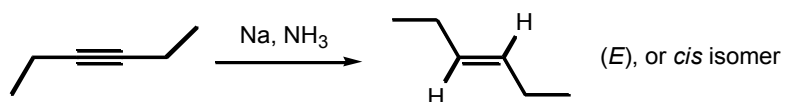


33) C (2):



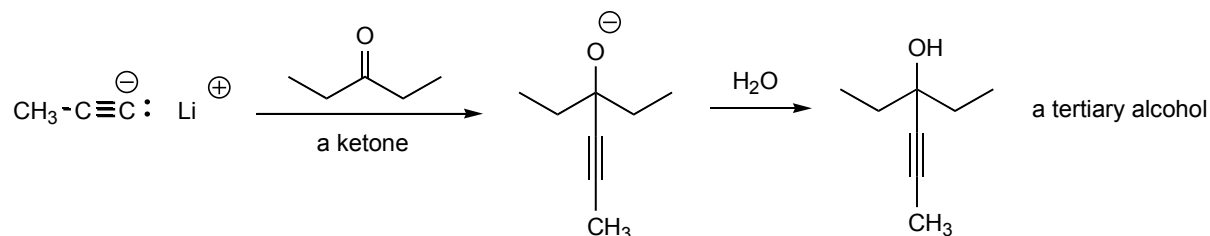
34) pentane

35) B



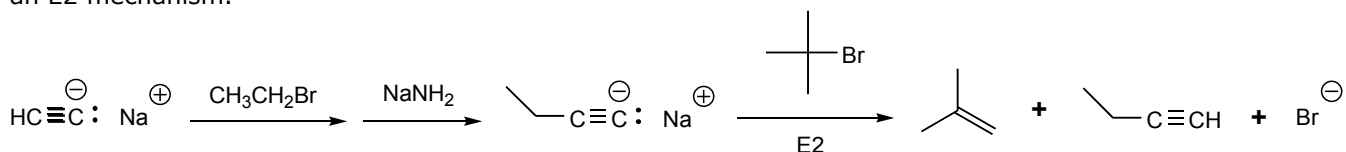
36) C

37)

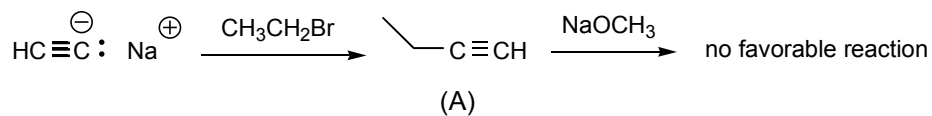


38) pent-1-ene

39) The *t*-butyl bromide would not undergo $\text{S}_{\text{N}}2$ when treated with the intermediate alkynide because the steric hindrance in the halide is too great. Instead, the alkynide would deprotonate the tertiary bromide via an $\text{E}2$ mechanism.



40) Sodium methoxide (NaOCH_3) is not a strong enough base to deprotonate the intermediate terminal alkyne (A):



41)

