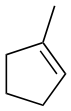
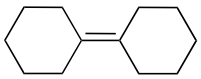
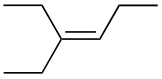
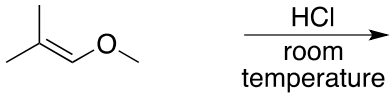
Question 1 – Draw the predominant intermediate carbocation that is formed when each of the following compounds is treated with HBr:

a)  b)  c)  d) 

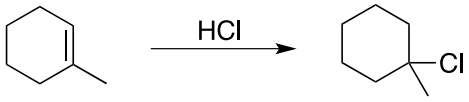
Question 2 – When 1-methoxy-2-methylpropene is treated with HCl, the major product is 1-chloro-1-methoxy-2-methylpropane, which is the product of *anti*-markovnikov addition. Although this reaction proceeds via an ionic mechanism (through a carbocation formation), the Cl is ultimately positioned at the less substituted carbon. Draw a mechanism that is consistent with this outcome, and then explain why the less substituted carbocation intermediate is more stable in this case.

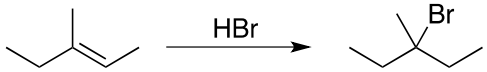


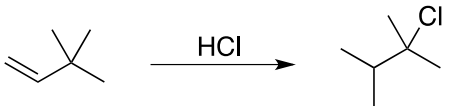
1-methoxy-2-methylpropene

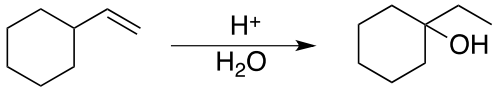
1-chloro-1-methoxy-2-methylpropane
(Major, *anti*-markovnikov addition product)

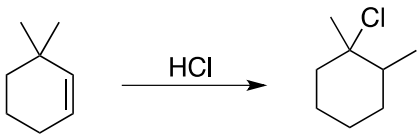
Question 3 – Using curved-arrows, draw the mechanism for each of the following transformations:

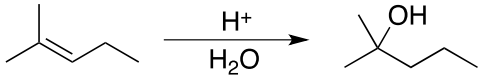
1) 

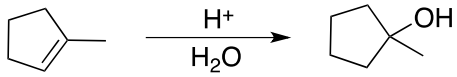
2) 

3) 

4) 

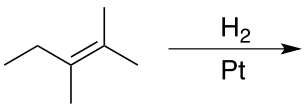
5) 

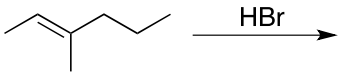
6) 

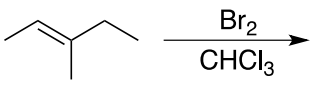
7) 

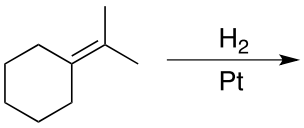
Question 4 – For each of the following examples, with the guidelines below in mind, draw the expected major product(s).

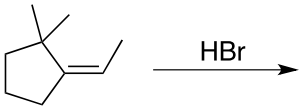
1. *What are the identities (which two groups) of the groups being added across the double bond?*
2. *What is the expected regioselectivity (Markovnikov or anti-markovnikov addition)?*
3. *What is the expected stereospecificity (syn or anti addition)?*

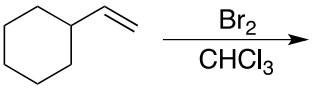
1) 

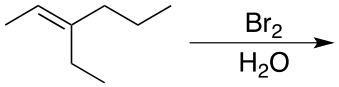
2) 

3) 

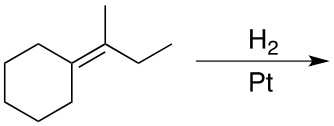
4) 

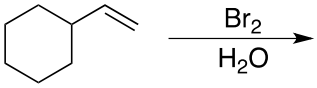
5) 

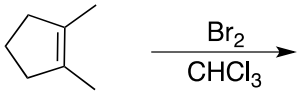
6) 

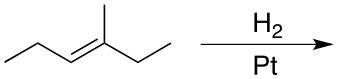
7) 

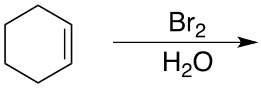
8) 

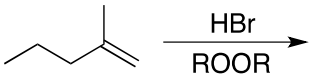
9) 

10) 

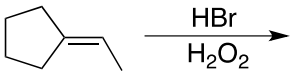
11) 

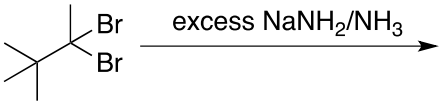
12) 

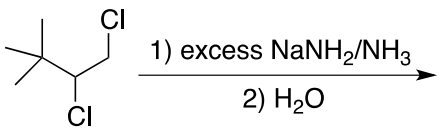
15) 

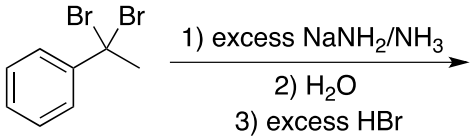
16) 

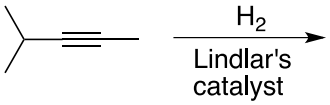
17) 

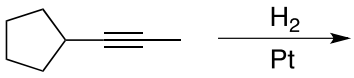
18) 

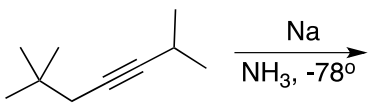
21) 

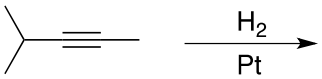
22) 

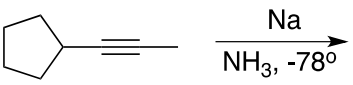
23) 

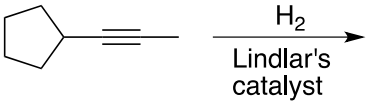
28) 

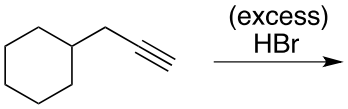
29) 

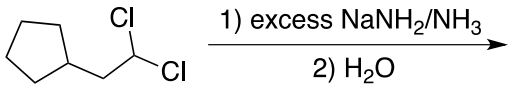
30) 

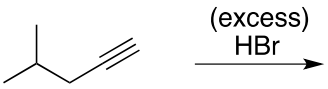
31) 

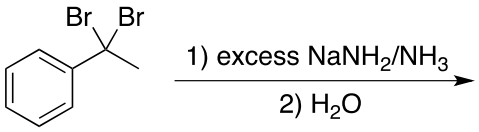
32) 

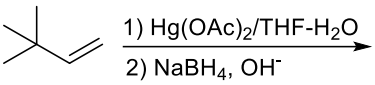
33) 

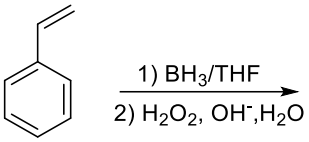
34) 

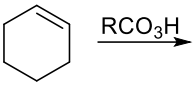
35) 

36) 

37) 

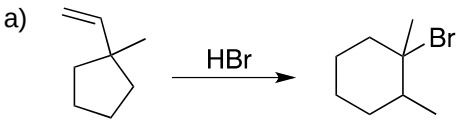
38) 

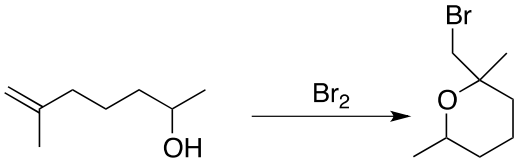
39) 

40) 

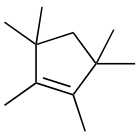
Question 5 - Using curved-arrows, draw the mechanism for reaction 6, 10, 16 and 36 from Question 4.

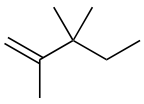
Question 6 – Draw the mechanisms for each of the following transformation:

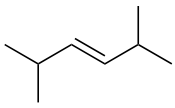
a) 

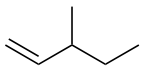
b) 

Question 7 – Predict the product(s) when each of the following compounds is treated with NBS and irradiated with UV light.

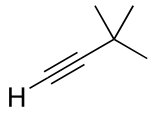
a) 

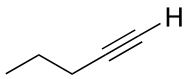
b) 

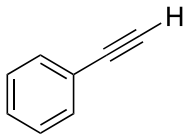
c) 

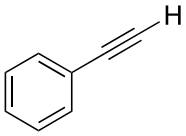
d) 

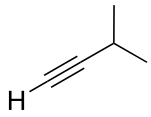
Question 8 – In each of the following cases, determine if the base is sufficiently strong to deprotonate the terminal alkyne. That is, determine whether the equilibrium favours formation of the alkynide ion (i.e. conjugate base of alkyne).

a)  + $NaNH_2$

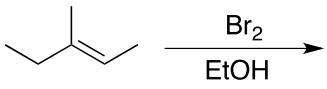
b)  + NaOEt

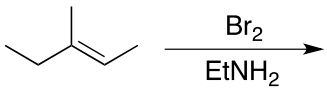
c)  + NaOH

d)  + BuLi

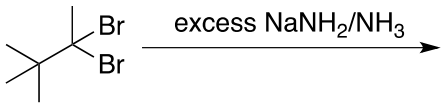
e)  + t-BuOK

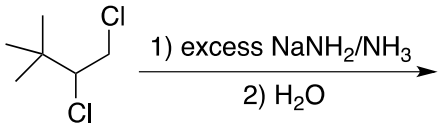
Question 9 – Halonium ions can be captured by nucleophiles other than water. Predict the products of each of the following reactions:

a) 

b) 

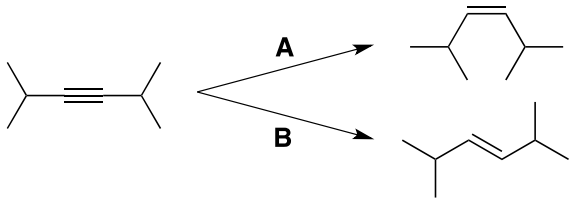
Question 10 – For each of the following transformations, predict the major product, and draw a mechanism for its formation:

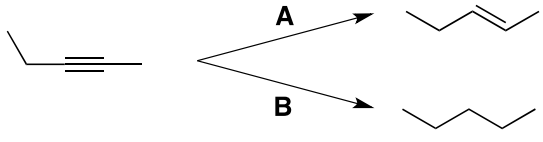
a) 

b) 

Question 11 – When 2-methyl-2-butene is treated with NBS and irradiated with UV light, five different monobromination products are obtained, one of which is a racemic mixture of enantiomers. Draw all five bromination products and identify the product that is obtained as a racemic mixture.

Question 12 – Identify the reagents you would use to achieve each of the following transformations:

a) 

b) 

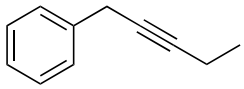
Question 13 – An alkyne with molecular formula C_5H_8 was treated with sodium in liquid ammonia to give a disubstituted alkene with molecular formula C_5H_{10}. Draw the structure of the alkene.

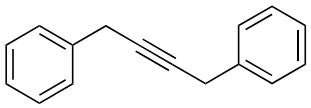
Question 14 – An alkyne with molecular formula C_5H_8 is treated with excess HBr, and two different products are obtained, each of which has molecular formula $C_5H_{10}Br_2$. Draw the structure of the starting alkyne and the two products.

Question 15 – Suggest reagents that would achieve the following transformation. Note that the transformation may involve more than one step.

Question 16 – Starting with acetylene (C_2H_2), show the reagents you would use to prepare the following compounds. Note that some preparations may involve more than one step.

a) 1-butyne b) 2-butyne c) 3-hexyne d) 2-hexyne
e) 1-hexyne f) 2-heptyne g) 3-heptyne h) 2-octyne
i) 2-pentyne j) k)

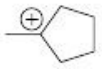
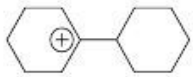
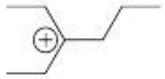




Question 17 – Preparation of 2,2-dimethyl-3-octyne cannot be achieved via alkylation of acetylene. Explain.

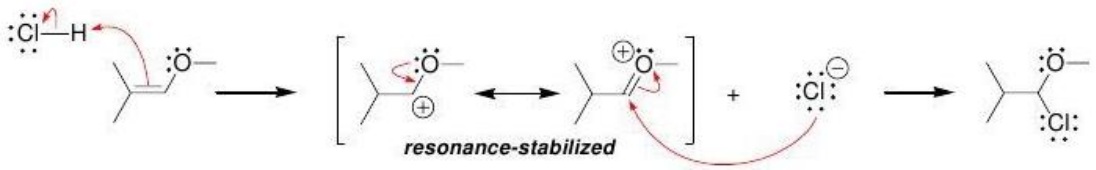
Solutions

Question 1 – Draw the predominant intermediate carbocation that is formed when each of the following compounds is treated with HBr:

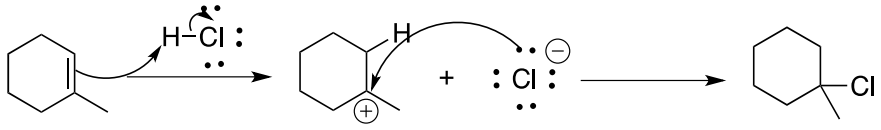
a)  b)  c)  d) 

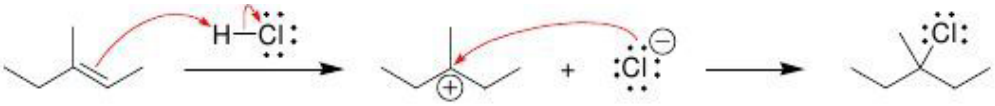
Question 2 – When 1-methoxy-2-methylpropene is treated with HCl, the major product is 1-chloro-1-methoxy-2-methylpropane, which is the product of *anti*-markovnikov addition. Although this reaction proceeds via an ionic mechanism (through a carbocation formation), the Cl is ultimately positioned at the less substituted carbon. Draw a mechanism that is consistent with this outcome, and then explain why the less substituted carbocation intermediate is more stable in this case.

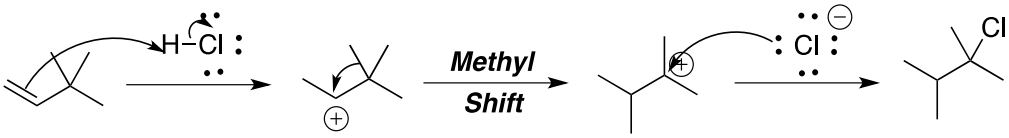
In this case, the less-substituted carbocation is more stable because it is resonance-stabilized.

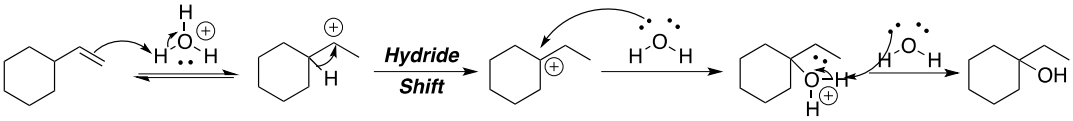


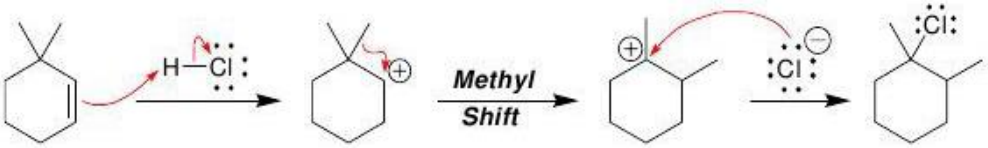
Question 3 – Using curved-arrows, draw the mechanism for each of the following transformations:

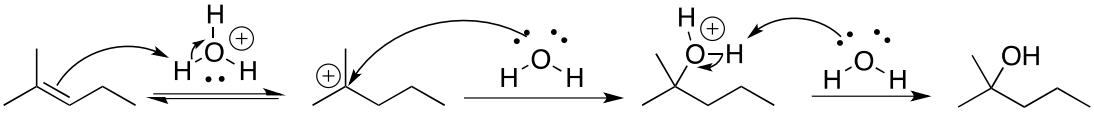
1) 

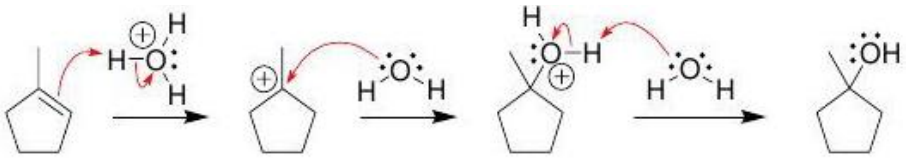
2) 

3) 

4) 

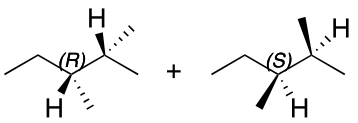
5) 

6) 

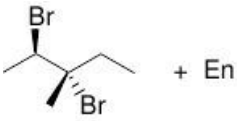
7) 

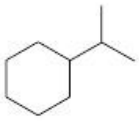
Question 4 – For each of the following examples, with the guidelines below in mind, draw the expected major product(s).

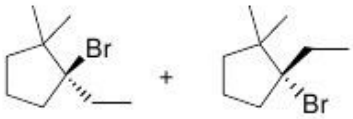
*En = Enantiomer

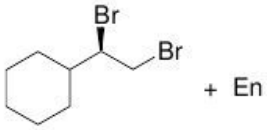
1) 

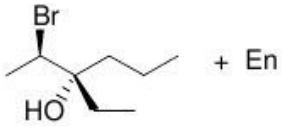
2) 

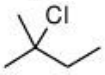
3) 

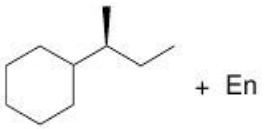
4) 

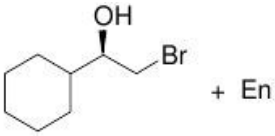
5) 

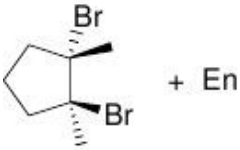
6) 

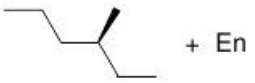
7) 

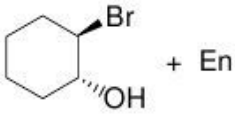
8) 

9) 

10) 

11) 

12) 

15) 

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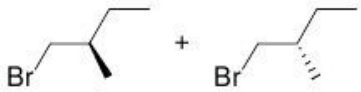
17) 

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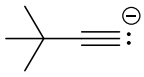
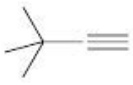
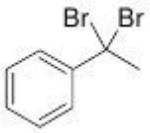
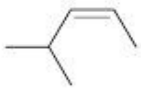
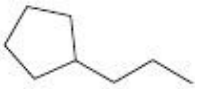
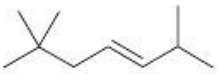
21) 

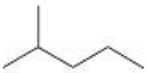
22) 

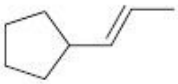
23) 

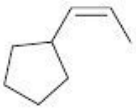
28) 

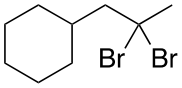
29) 

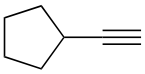
30) 

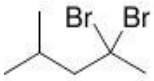
31) 

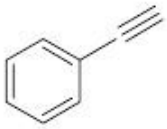
32) 

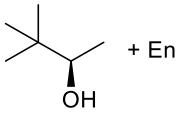
33) 

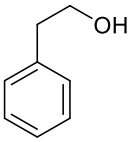
34) 

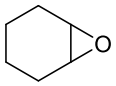
35) 

36) 

37) 

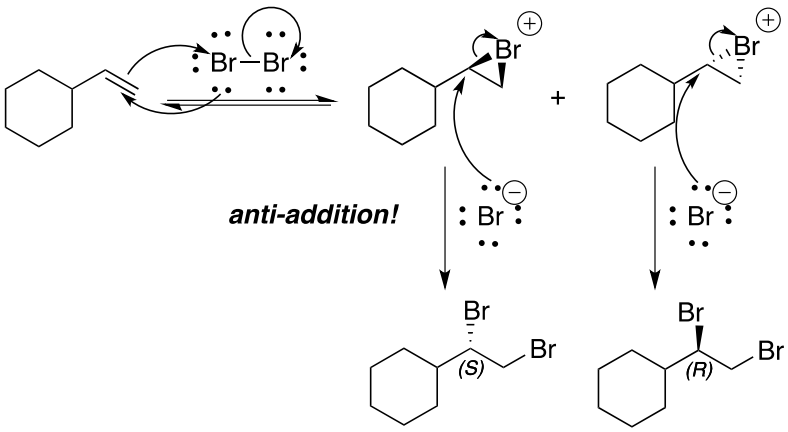
38) 

39) 

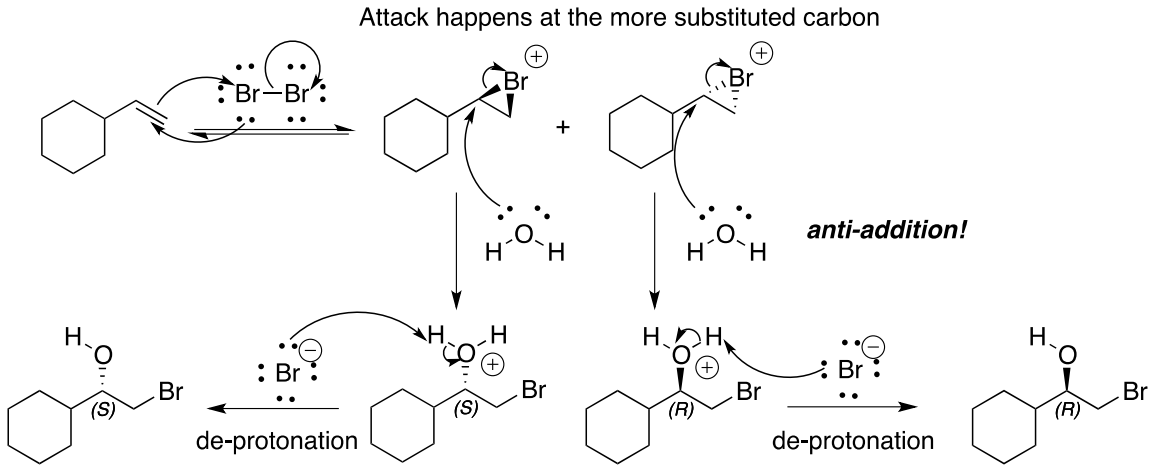
40) 

Question 5 - Using curved-arrows, draw the mechanism for reaction 6, 10, 16 and 36 from Question 4.

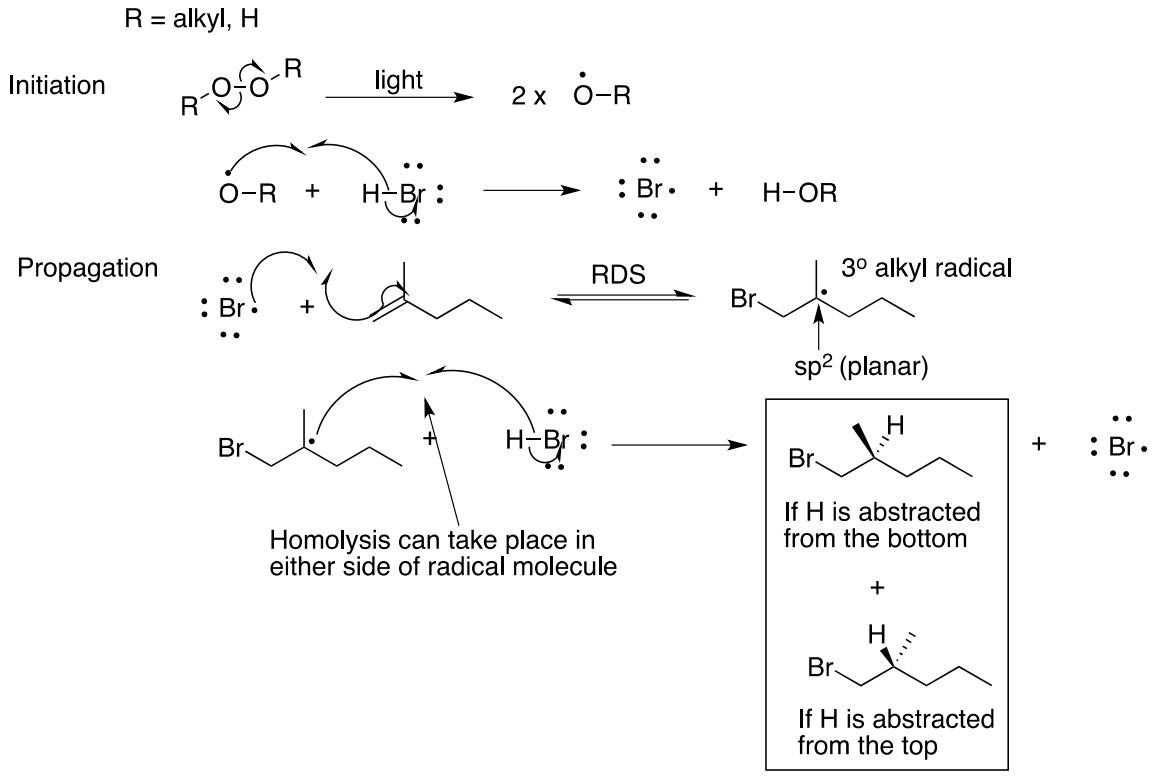
<u>Reaction 6 – Addition of Bromine</u>



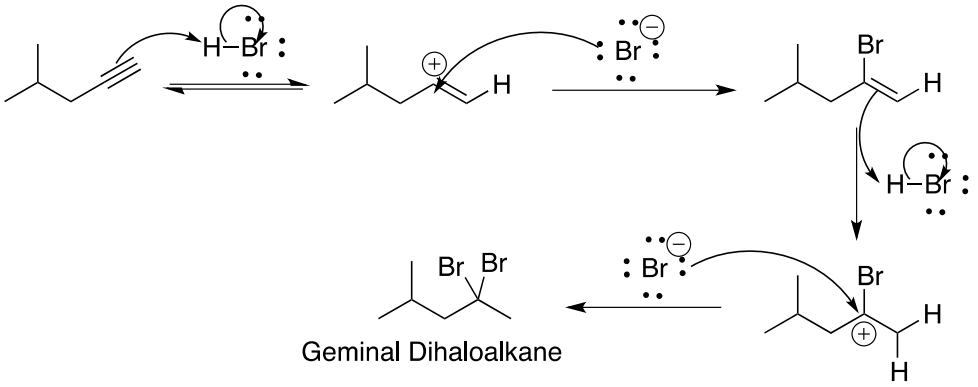
Reaction 10 – Halohydrin formation



Reaction 16 – Radical Addition of HBr (*anti*-Markovnikov addition)

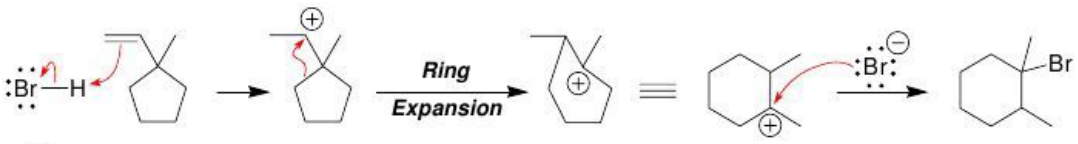


Reaction 36 – (Double) Addition of Hydrogen bromide

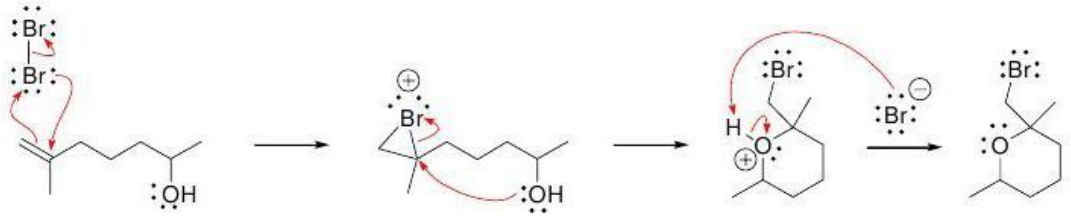


Question 6 – Draw the mechanisms for each of the following transformation:

a)

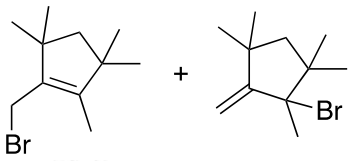


b)



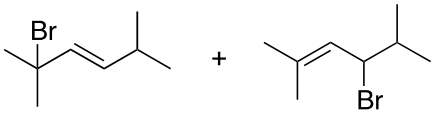
Question 7 – Predict the product(s) when each of the following compounds is treated with NBS and irradiated with UV light.

a)



b)

c)

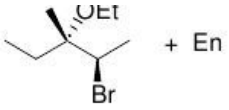


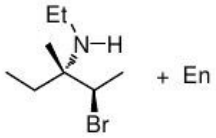
d)

Question 8 – In each of the following cases, determine if the base is sufficiently strong to deprotonate the terminal alkyne. That is, determine whether the equilibrium favours formation of the alkynide ion (i.e. conjugate base of alkyne).

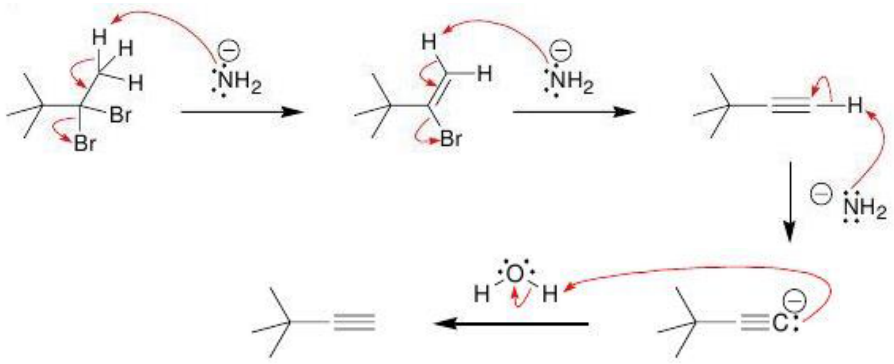
a) Equilibrium favours the products (Forward)
b) Equilibrium favours the Reactants (Reverse)
c) Equilibrium favours the Reactants (Reverse)
d) Equilibrium favours the products (Forward)
e) Equilibrium favours the Reactants (Reverse)

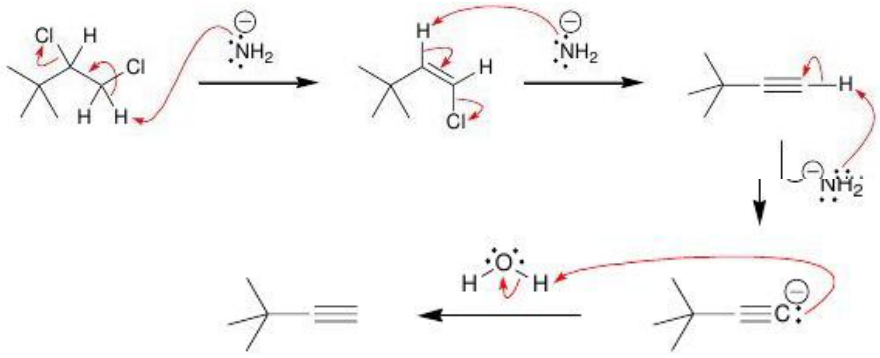
Question 9 – Halonium ions can be captured by nucleophiles other than water. Predict the products of each of the following reactions:

a) 

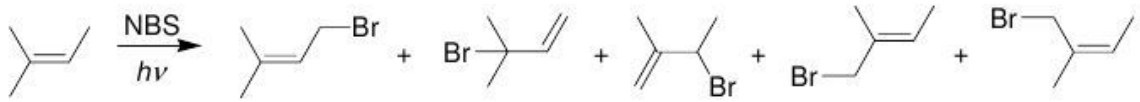
b) 

Question 10 – For each of the following transformations, predict the major product, and draw a mechanism for its formation:

a) 

b) 

Question 11 – When 2-methyl-2-butene is treated with NBS and irradiated with UV light, five different monobromination products are obtained, one of which is a racemic mixture of enantiomers. Draw all five bromination products and identify the product that is obtained as a racemic mixture.



(racemic mixture)

Question 12 – Identify the reagents you would use to achieve each of the following transformations:

a) **A** – H_2 + Lindlar's Catalyst; **B** – Na, NH_3(l)

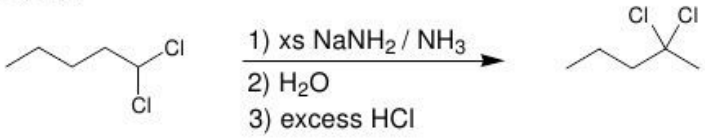
b) **A** - Na, NH_3(l); **B** – H_2 + Pt

Question 13 – An alkyne with molecular formula C_5H_8 was treated with sodium in liquid ammonia to give a disubstituted alkene with molecular formula C_5H_{10}. Draw the structure of the alkene.

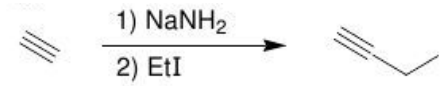
Question 14 – An alkyne with molecular formula C_5H_8 is treated with excess HBr, and two different products are obtained, each of which has molecular formula $C_5H_{10}Br_2$. Draw the structure of the starting alkyne and the two products.

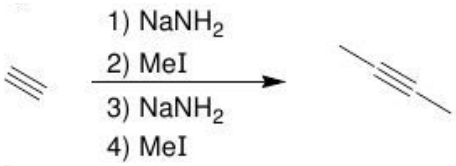
If two products are obtained, then the alkyne must be internal and unsymmetrical.

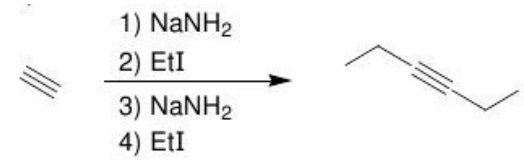
Question 15 – Suggest reagents that would achieve the following transformation. Note that the transformation may involve more than one step.

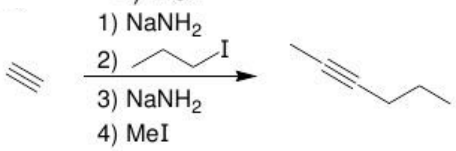


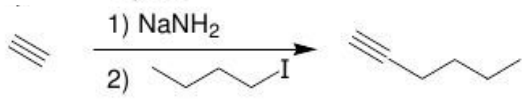
Question 16 – Starting with acetylene (C_2H_2), show the reagents you would use to prepare the following compounds. Note that some preparations may involve more than one step.

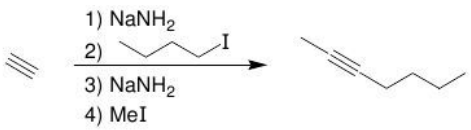
a) 

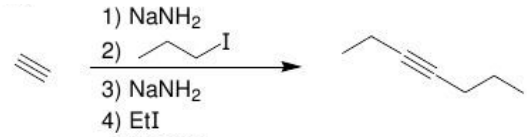
b) 

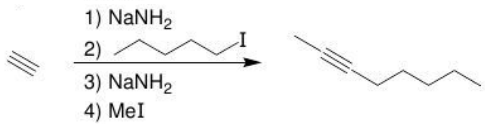
c) 

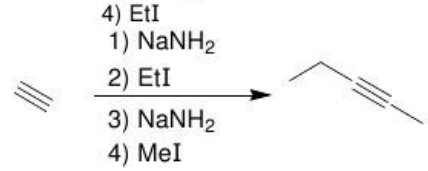
d) 

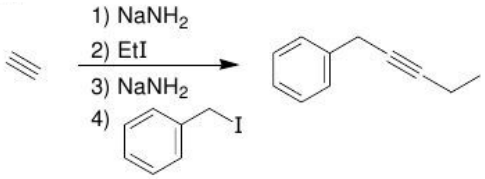
e) 

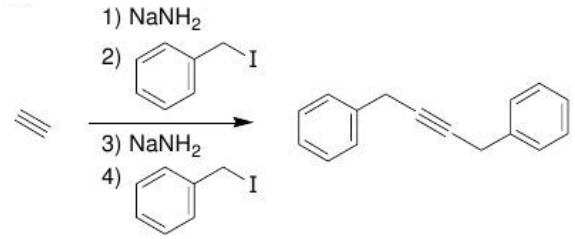
f) 

g) 

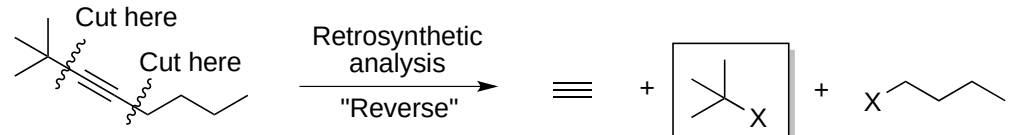
h) 

i) 

j) 

k) 

Question 17 – Preparation of 2,2-dimethyl-3-octyne cannot be achieved via alkylation of acetylene. Explain.



2,2-dimethyloct-3-yne

Problem!

(alkyl halide used in alkylation must be primary!)

*With a bulky alkylhalide, E2 is favoured. In order for alkylation chemistry to be successful, SN2 must be applied.