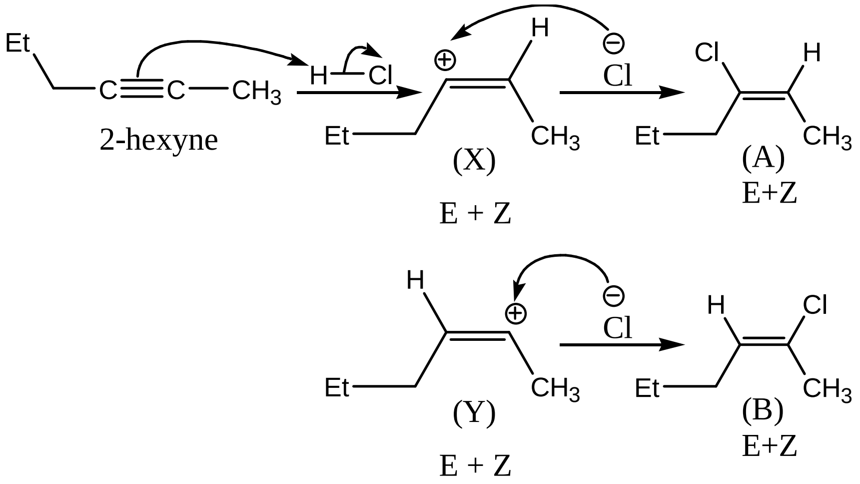
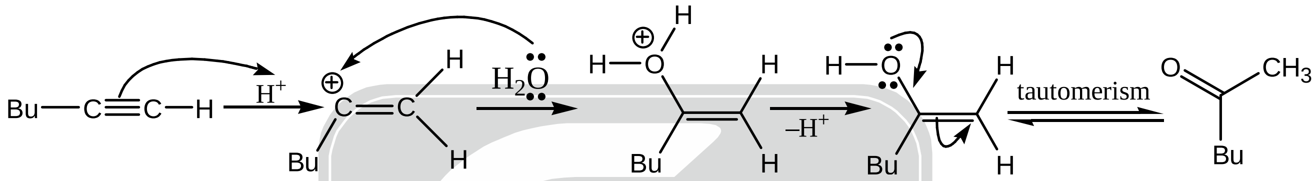
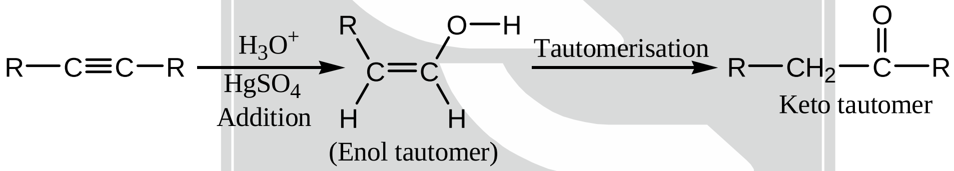


1-Hexyne reacts with a catalytic amount of sulfuric acid is an aqueous solvent to give vinylic carbocation, followed by reaction with water on tautomerism generate ketones.

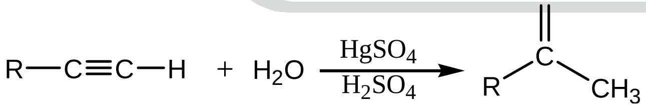


Hydration of alkynes and Tautomerism:

Addition of water to alkynes requires a strong acid. The initial product from the addition of water to an alkyne is an enol and this immediately rearranges to more stable keto tautomer.



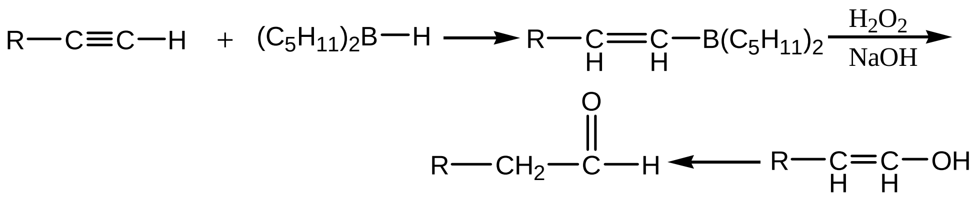
$$H—C\equiv C—H \;+\; H_2O \xrightarrow[H_2SO_4]{HgSO_4} H_3C—CHO$$



Hydroboration Reaction:

Diborane react readily with alkynes.

Addition of disiamylborane to alkyne, as with alkenes, the B–H reagent group adds in an apparently anti-Markovnikov manner, due to the fact that the boron is the electrophilic not the hydrogen.



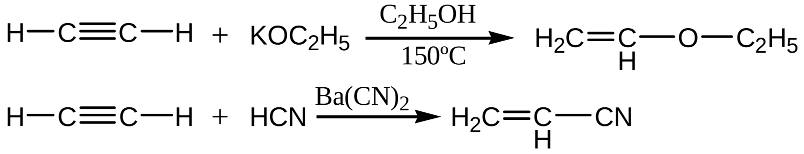
Oxidation: Reaction of alkynes with oxidising agents such as potassium permaganate and ozone usually result in cleavage of triple bond to give carboxylic acid products.

$$R—C\equiv C—R' \;+\; [O] \longrightarrow RCO_2H \;+\; R'COOH$$

Nucleophilic addition reactions:

The sp-hybrid carbon atoms of the triple-bond rendr alkynes more electrophilic than similarly substituted alkenes.

As a result, alkynes sometimes undergo addition reaction iniaited by bonding to nucleophile.



$$H-C\equiv C-H + KOC_2H_5 \xrightarrow[150^\circ C]{C_2H_5OH} H_2C=\underset{H}{C}-O-C_2H_5$$

$$H-C\equiv C-H + HCN \xrightarrow{Ba(CN)_2} H_2C=\underset{H}{C}-CN$$

Acidity of terminal alkyne:

pK_a value of ethene is estimated at 44, and pK_a of ethyne (acetylene) is found to be 25. This increase in acidity permits the isolation of insoluble silver and copper salts of such compounds.

$$R-C\equiv C-H + Ag(NH_3)_2 \xrightarrow{NH_4OH} R-C\equiv C-Ag + NH_3 + \overset{\oplus}{NH_4}$$

$$R-C\equiv C-H + NaNH_2 \xrightarrow{ether} R-C\equiv C-Na + NH_3$$

$$R-C\equiv C-H + H_3C-I \longrightarrow R-C\equiv C-CH_3 + NaI$$

$$H_3C-C\equiv C-H + NaNH_2 \xrightarrow{ether} H_3C-C\equiv C-Na + NH_3$$

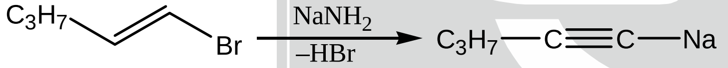
$$H_3C-C\equiv C-Na + C_2H_5-Br \longrightarrow H_3C-C\equiv C-C_2H_5 + NaBr$$

The enhanced acidity of terminal alkynes relative to alkanes also leads to metal exchange reaction when there compounds are treated with organolithium or Grignard reagents.

$$R-C\equiv C-H + C_2H_5MgBr \xrightarrow{ether} R-C\equiv C-MgBr + C_2H_6$$

$$H-C\equiv C-CH_2-CH_2-Br + Mg \xrightarrow{ether} H-C\equiv C-CH_2-CH_2-MgBr$$

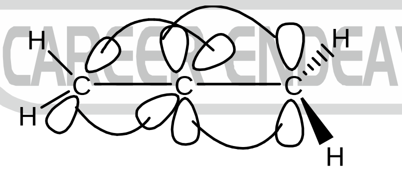
$$BrMg-C\equiv C-CH_2-CH_2-MgBr \xleftarrow{C_2H_5MgBr}$$



$$C_3H_7-CH=CH-Br \xrightarrow[-HBr]{NaNH_2} C_3H_7-C\equiv C-Na$$

5.1. (I) Addition to Allene

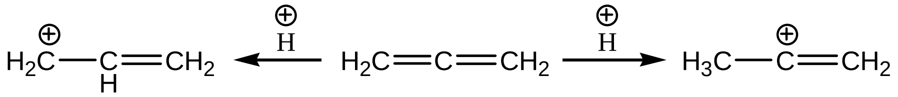
$$H_2C=C=CH_2$$



Orbital description

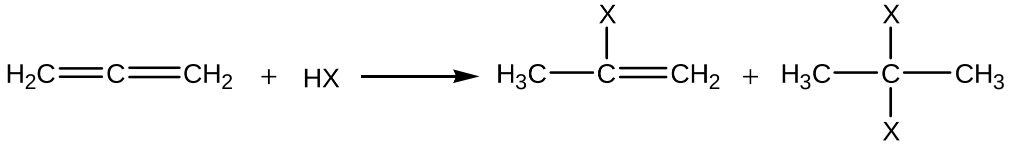
(Terminal atoms are perpendicular to each other)

The attack by a proton on allene might conceivably lead to the allyl cation or the 2-propyl cation.



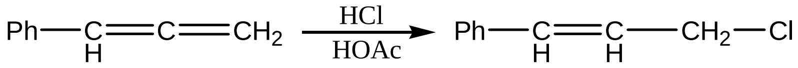
$$H_2\overset{\oplus}{C}-\underset{H}{C}=CH_2 \xleftarrow{\overset{\oplus}{H}} H_2C=C=CH_2 \xrightarrow{\overset{\oplus}{H}} H_3C-\overset{\oplus}{C}=CH_2$$

Protonation at the centre carbon without rotation of one of the terminal methylene group leads to a primary carbocation that is not stabilised by resonance, because the adjacent π-bond is orthogonal to empty p-orbital. As a result, protonation both in solution and gas phase occurs at a terminal carbon to give the 2-propenyl cation, not the allylic cation. The addition of HCl, HBr, HI to allene has been studied in some detail. In each case a 2-halopropene is formed, corresponding to a protonation at terminal carbon.



$$H_2C=C=CH_2 + HX \longrightarrow H_3C-\overset{X}{C}=CH_2 + H_3C-\underset{X}{\overset{X}{C}}-CH_3$$

The presence of phenyl group results in the formation of products from protonation at the centre carbon.

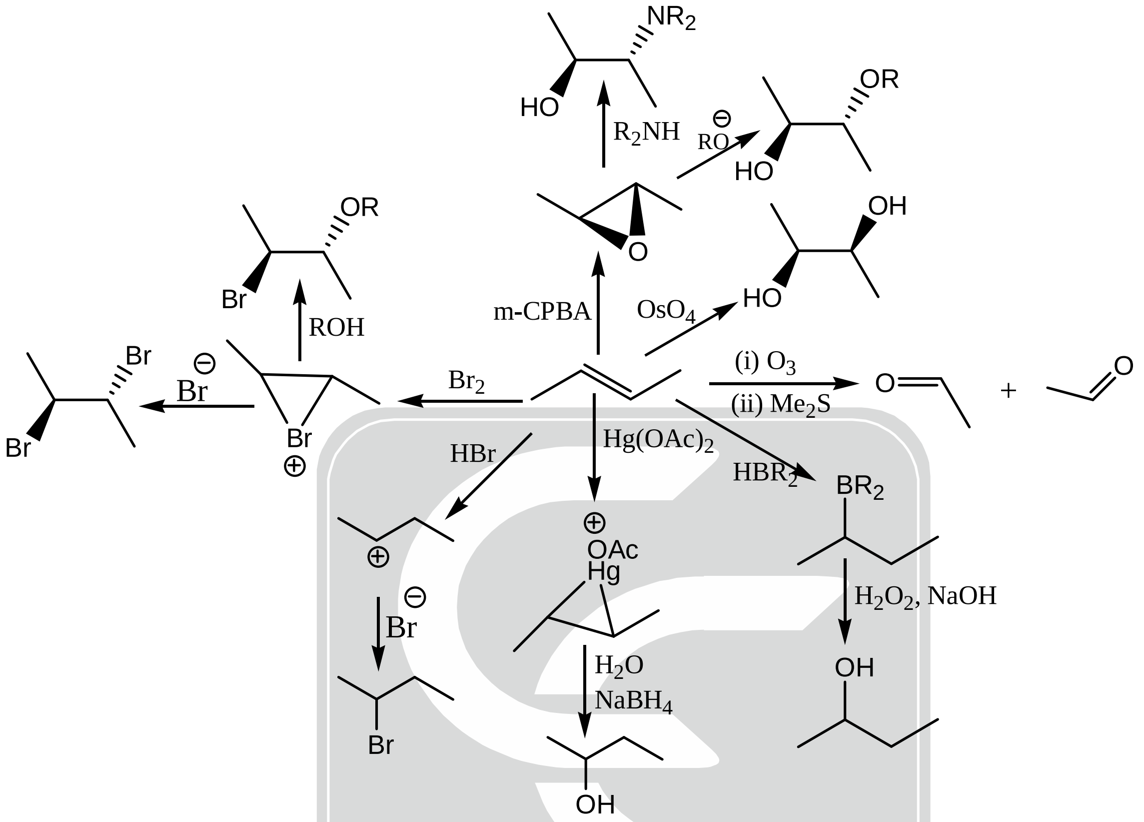


$$Ph-\underset{H}{C}=C=CH_2 \xrightarrow[HOAc]{HCl} Ph-\underset{H}{C}=\underset{H}{C}-CH_2-Cl$$

Two alkyl substituents, as in 1, 1-dimethlyallene, also lead to protonation at the centre carbon.

$$(H_3C)_2C=C=CH_2 \xrightarrow{HCl} (H_3C)_2C=CHCH_2Cl$$

5.1. (J) SUMMARY



5.1. (K) PRACTICE SET

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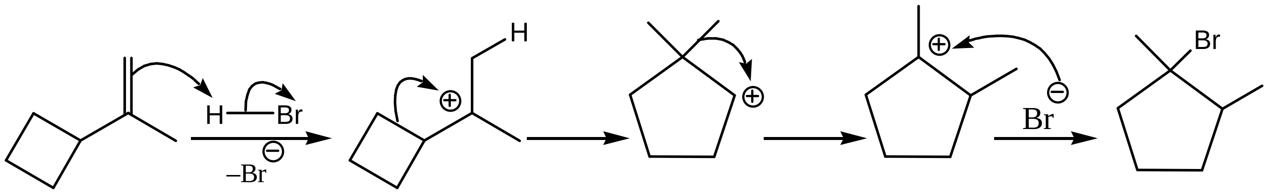

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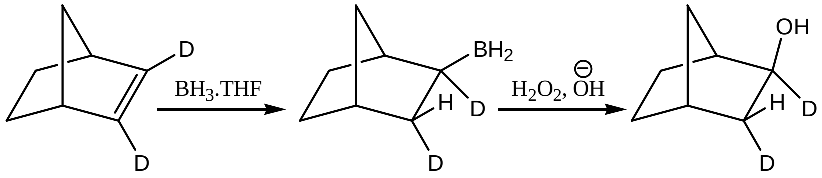

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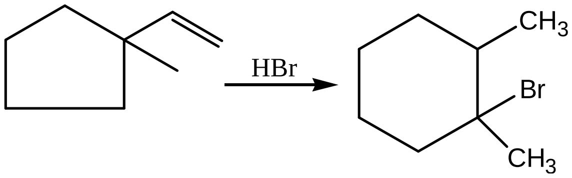

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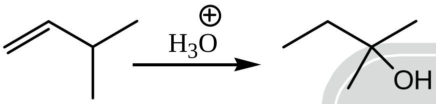

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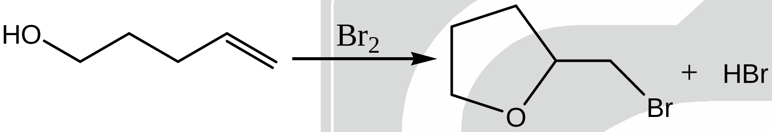

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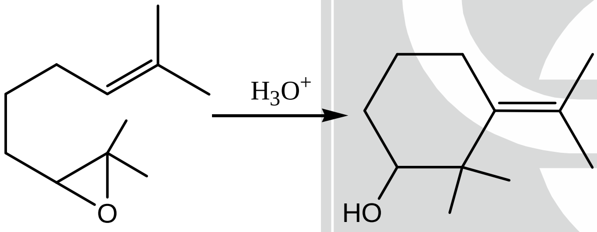

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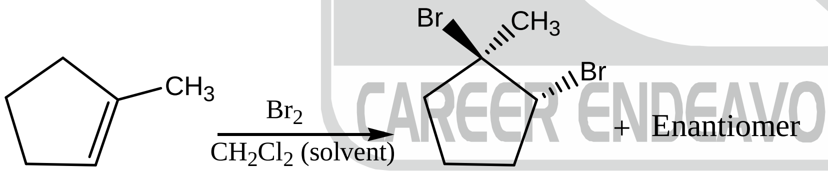

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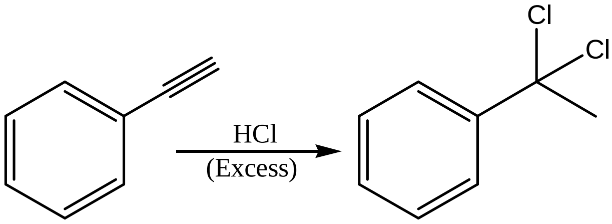

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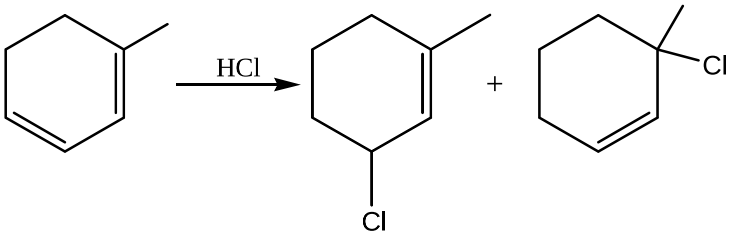

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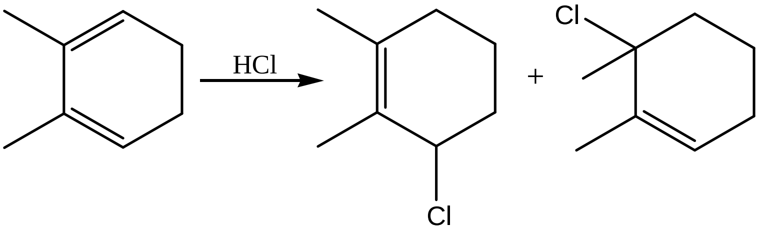

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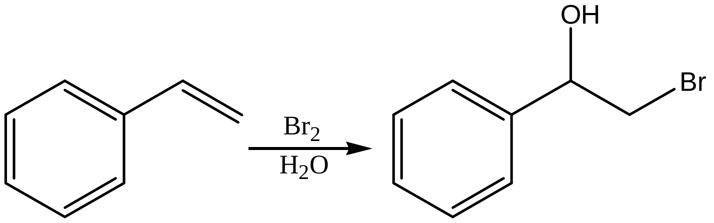

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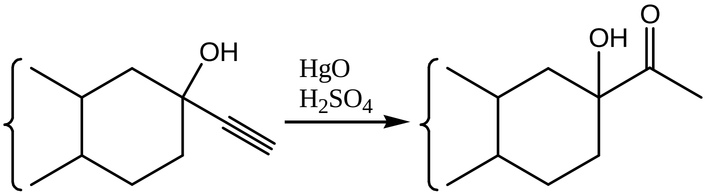

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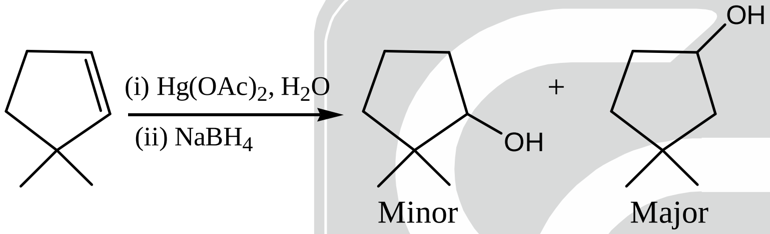

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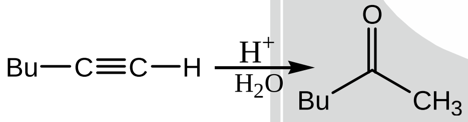

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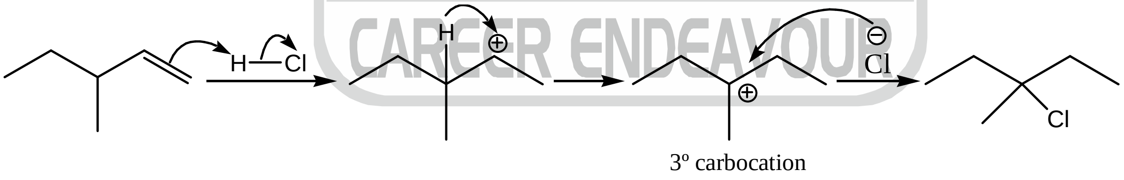

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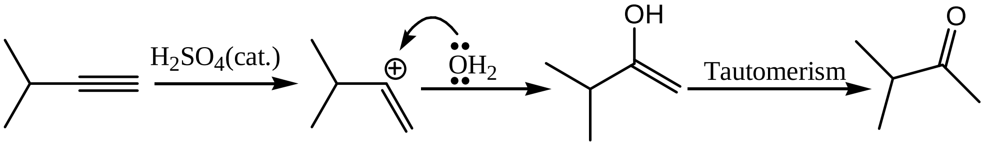

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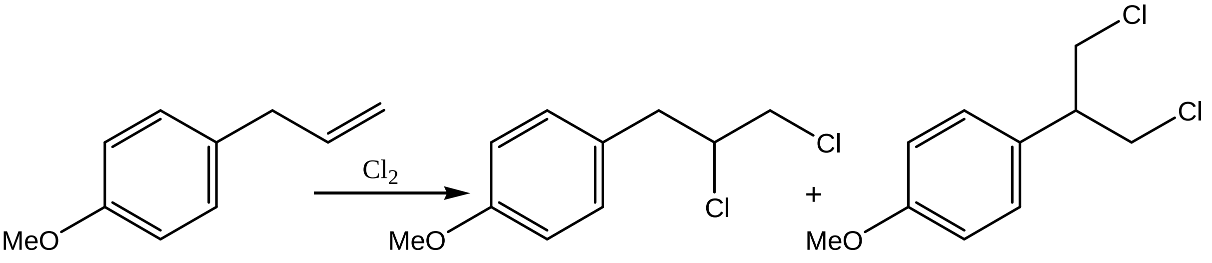

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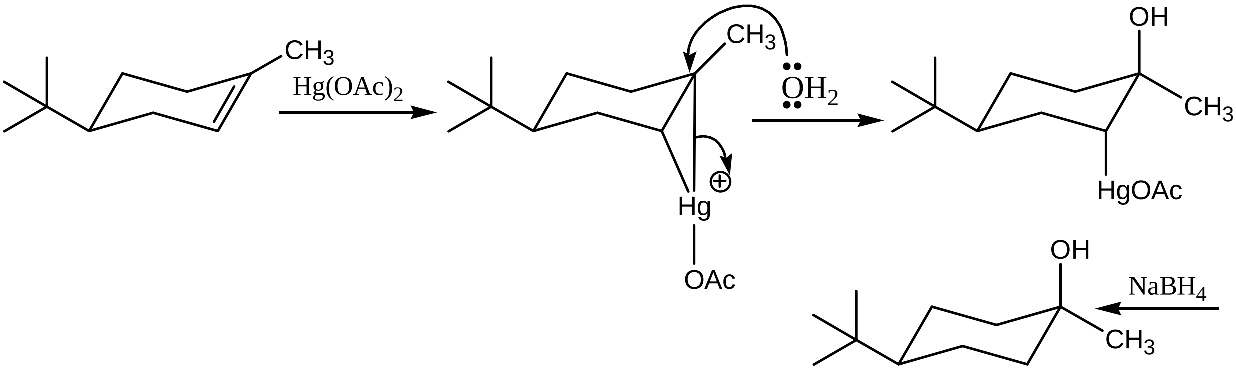
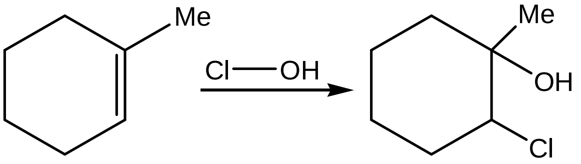
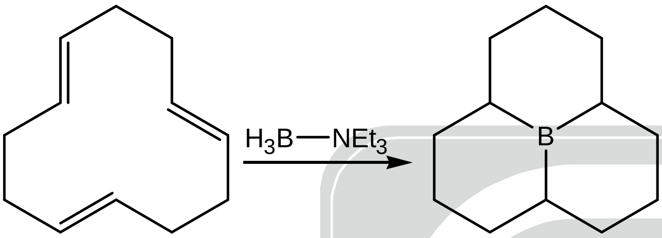

CH3
Hg(OAc)2
CH3
Hg
OAc
OH2
OH
CH3
HgOAc
OH
CH3
NaBH4

19.


Me
Cl—OH
Me
OH
Cl

20.


H3B—NEt3
B