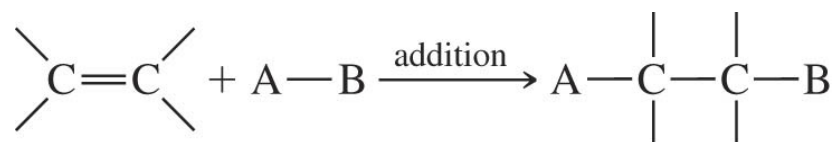
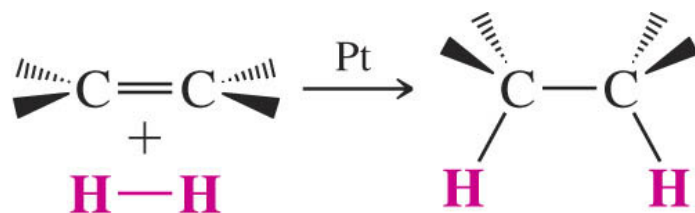


第8章 烯烴的加成反應

1) 烯烴的加成反應概述

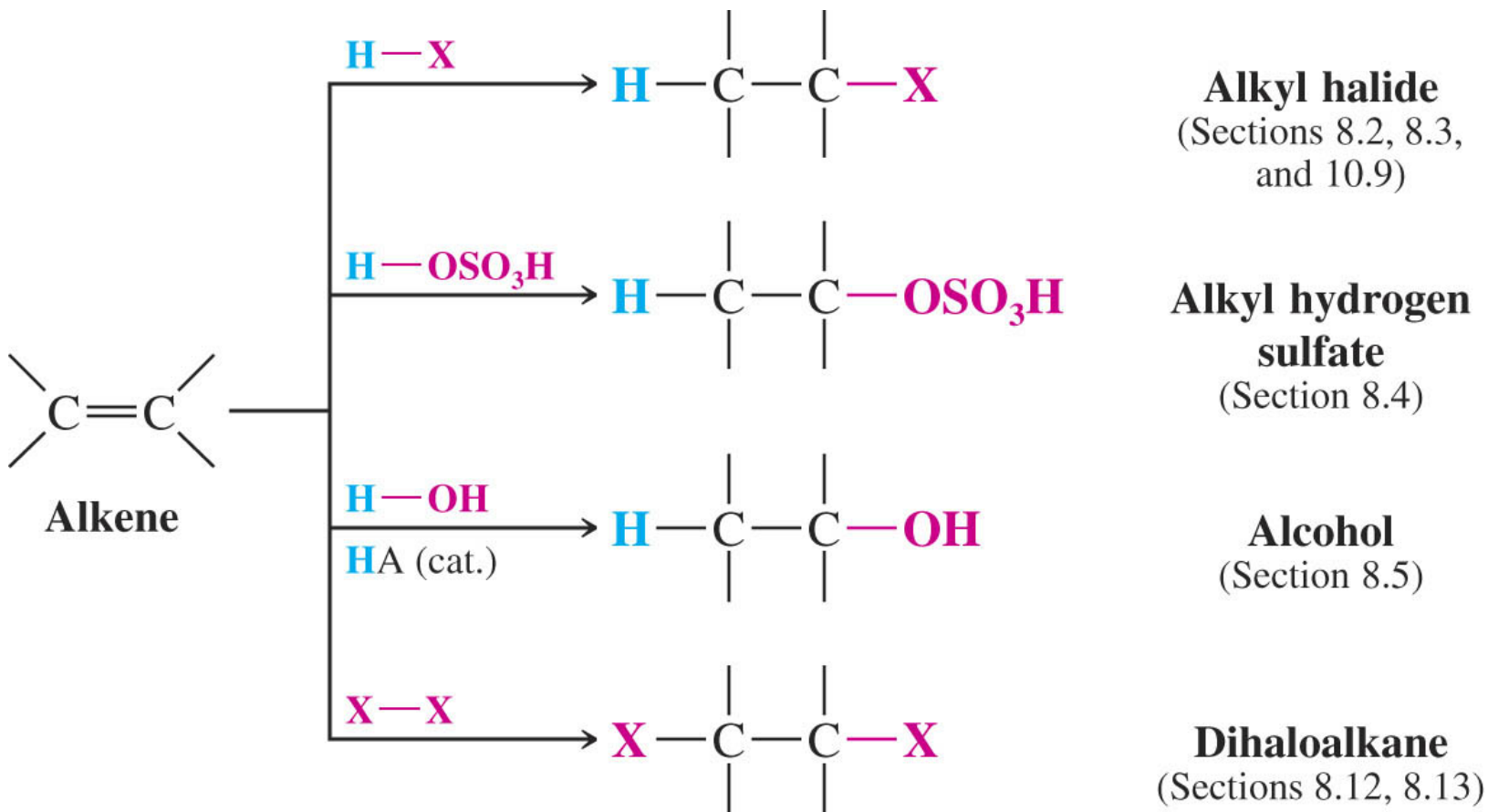


第一類：非離子型加成反應：氫化反應



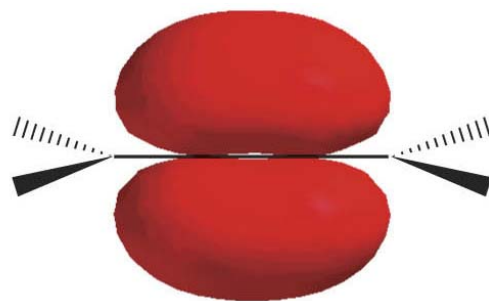
Catalytic hydrogenation is a syn addition.

第二類：離子型加成反應：與親電試劑(electrophiles)的加成反應：

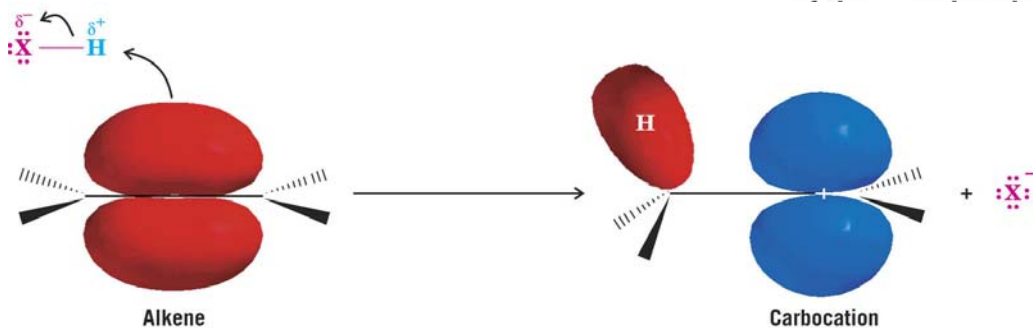


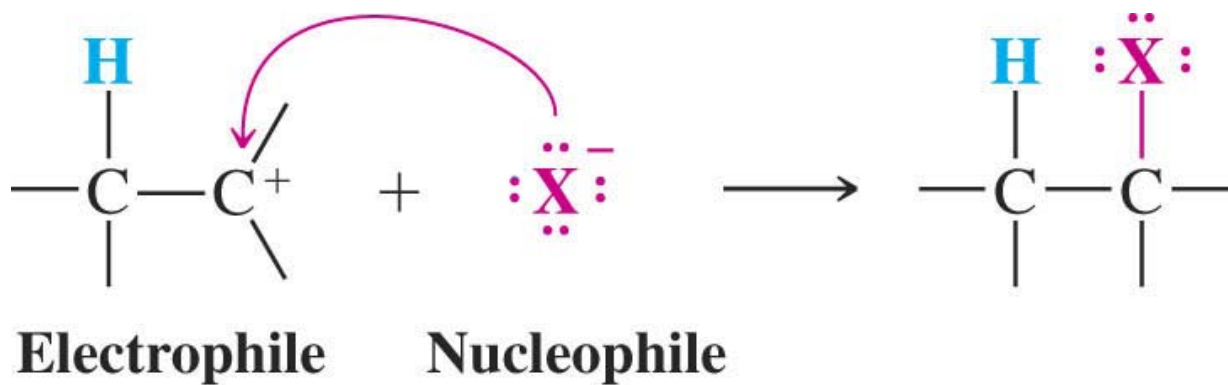
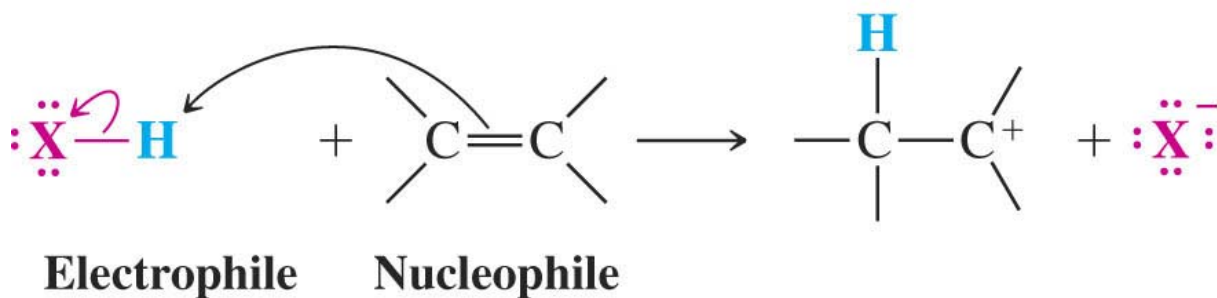
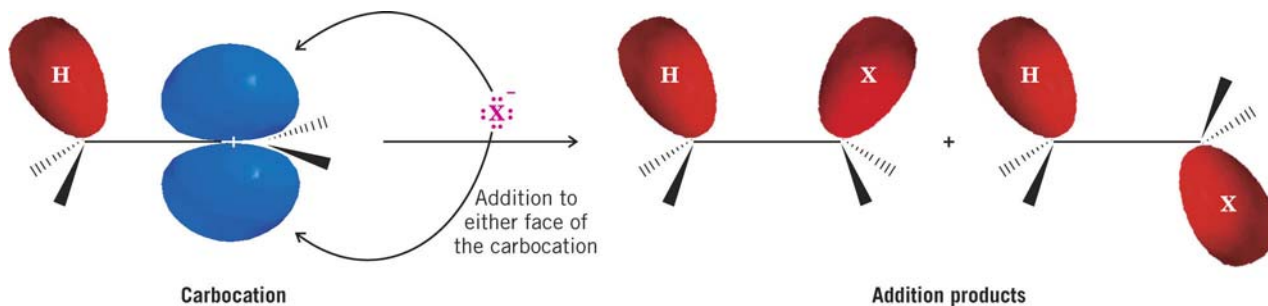
在加成反應過程中，需斷裂一個 π 鍵和 δ 鍵，並形成兩個新的 δ 鍵，反應通常為放熱(exothermic).

烯烴由於鬆散的p電子的存在，故可以作為親核試劑，而受到親電試劑(electrophiles)的進攻。



The electron pair of the π bond is distributed throughout both lobes of orbital.



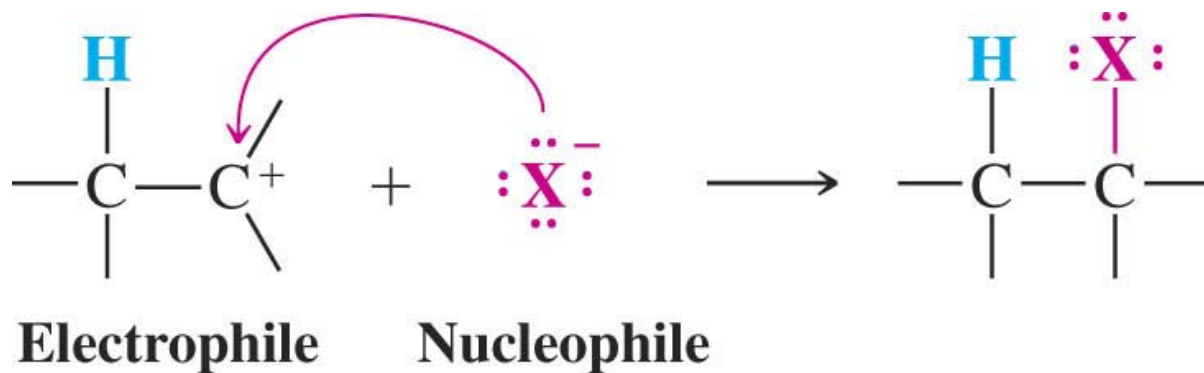
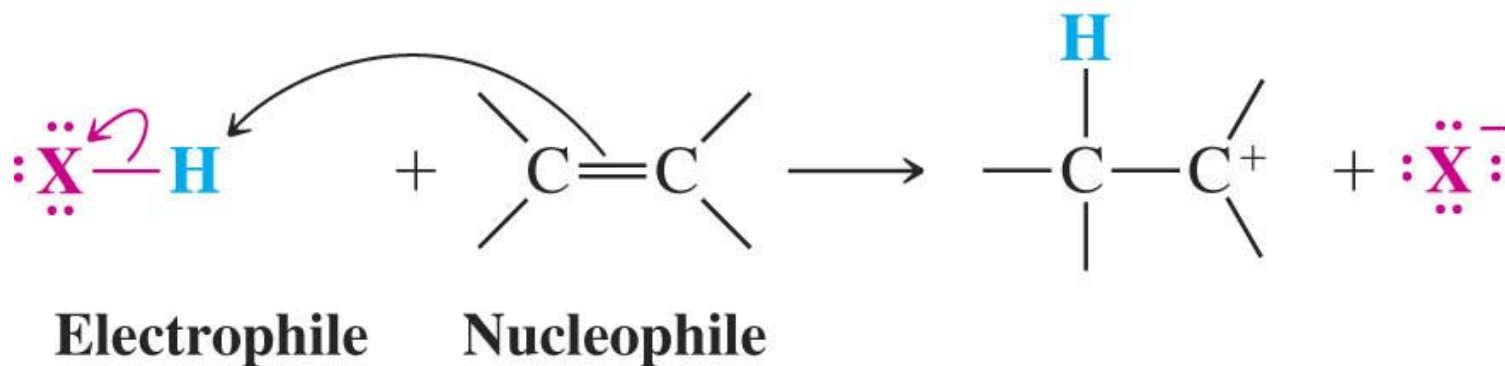
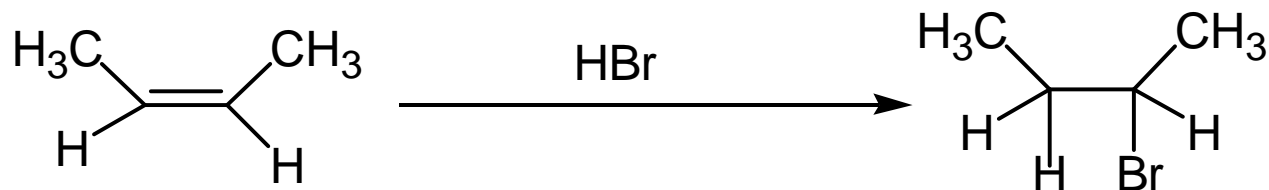


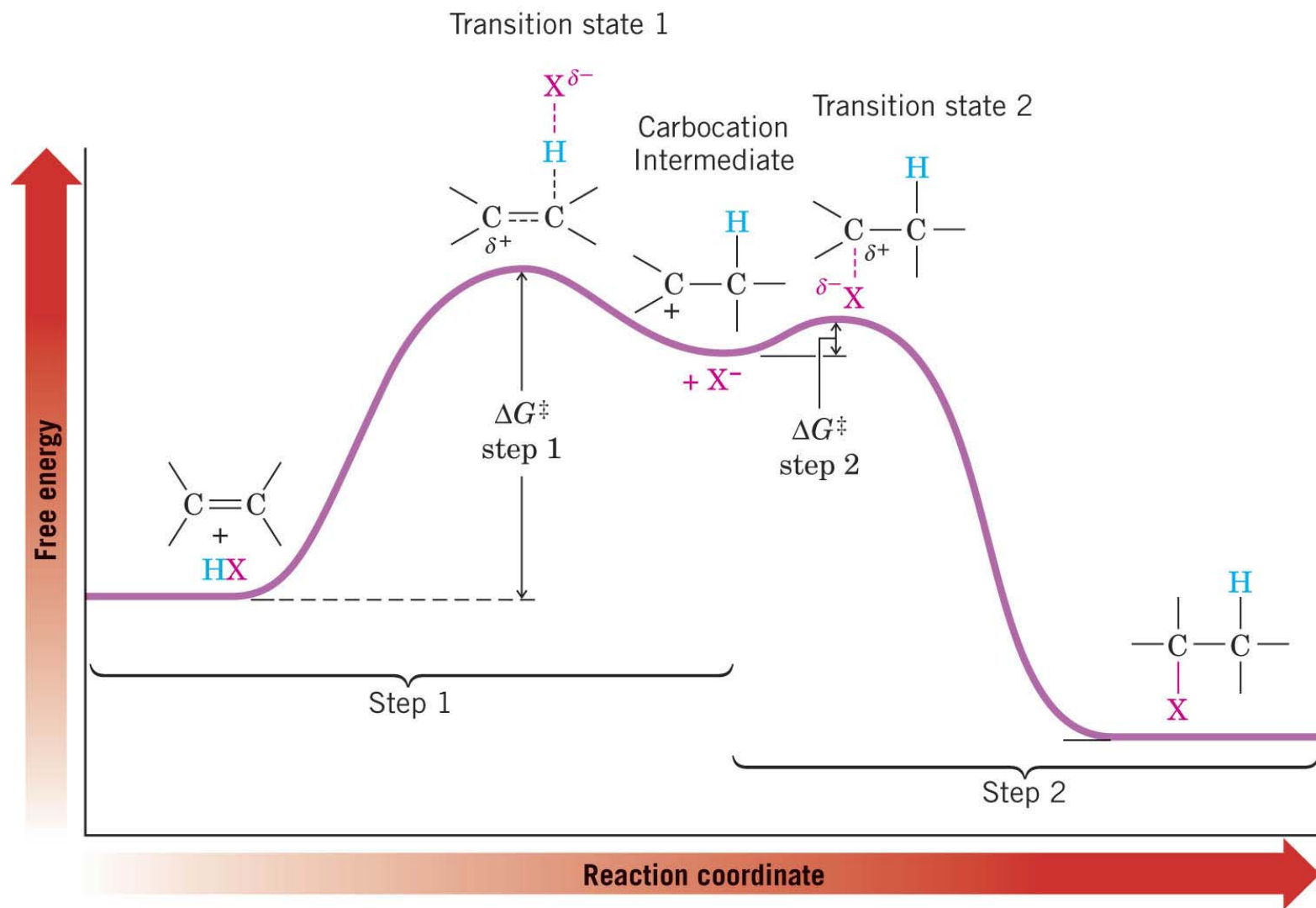
想想看，在上述過程當中，哪一個試劑是Lewis acid, 哪一個試劑是Lewis base?

2) 與鹵化氫的加成反應(Addition of hydrogen halides)

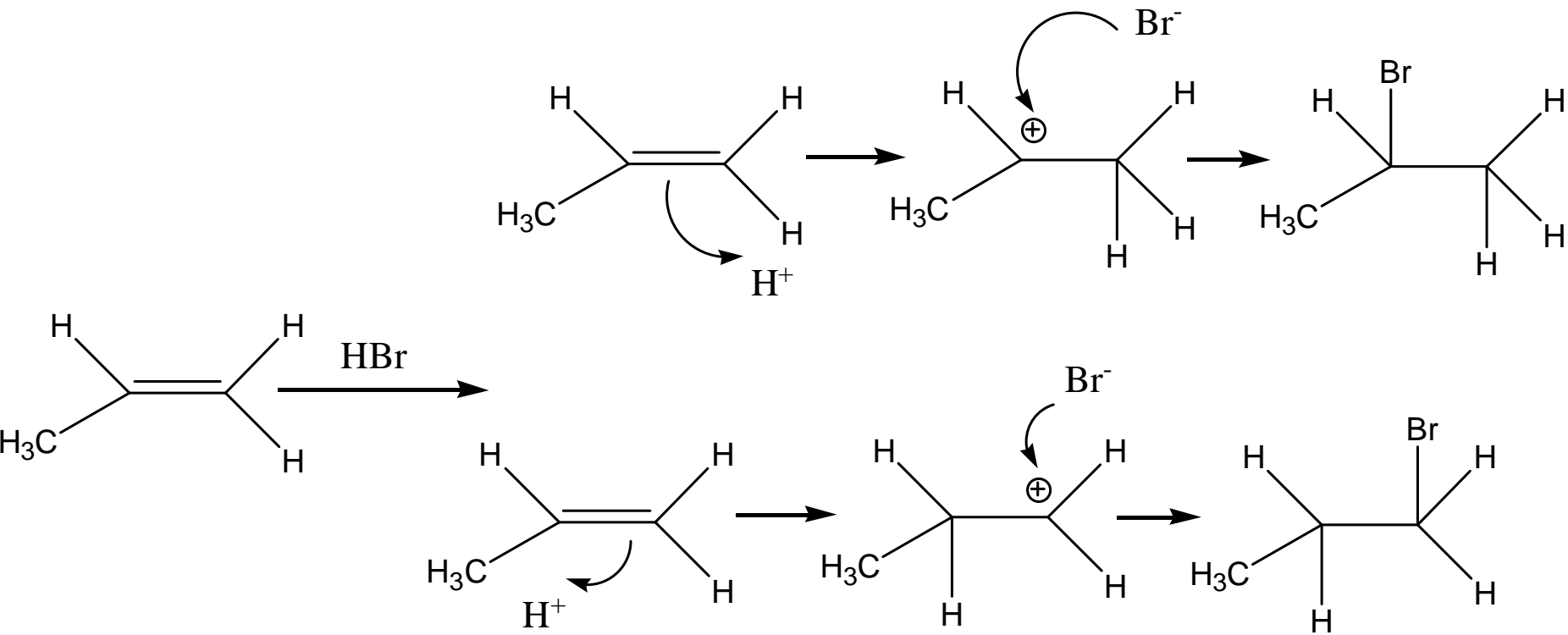
a) 反應活性： $\text{HI} > \underline{\text{HBr}} > \text{HCl} > \text{HF}$

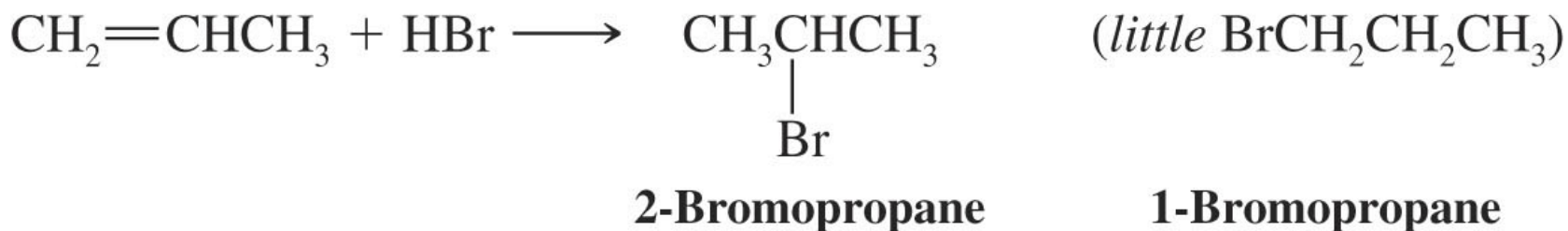
b) 反應的機制：



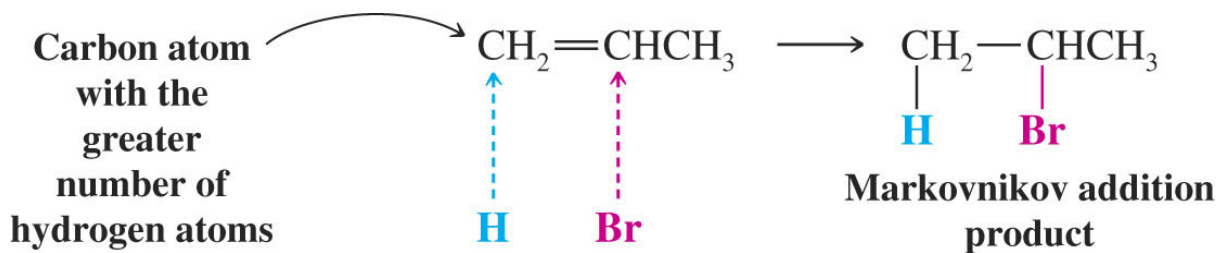


c) 反應的選擇性(regioselectivity)：Markovnikov規則



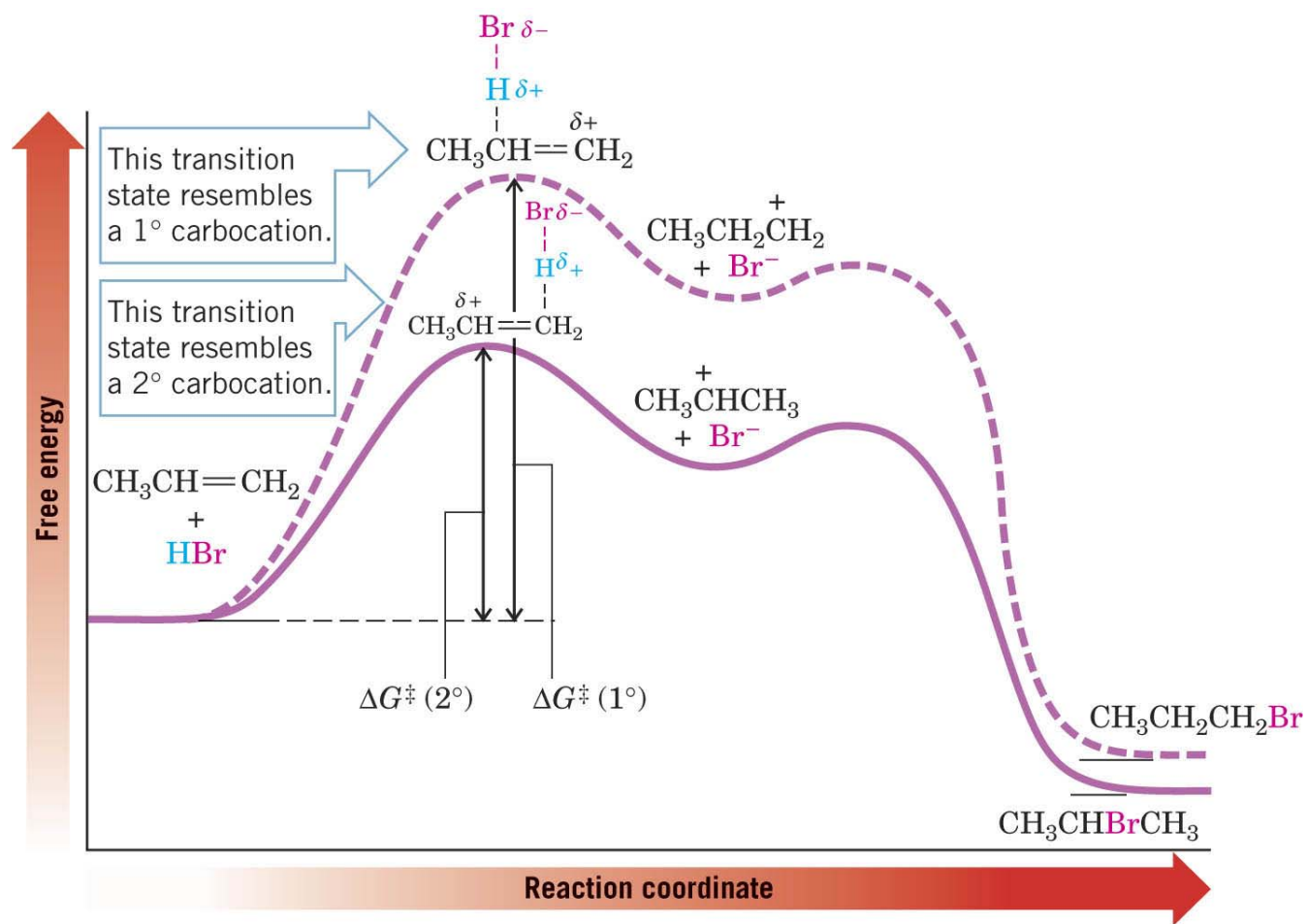


Markovnikov' rule: 在HX與部分不對稱烯烴的反應中;H+總是加在含氫原子較多的碳原子上。

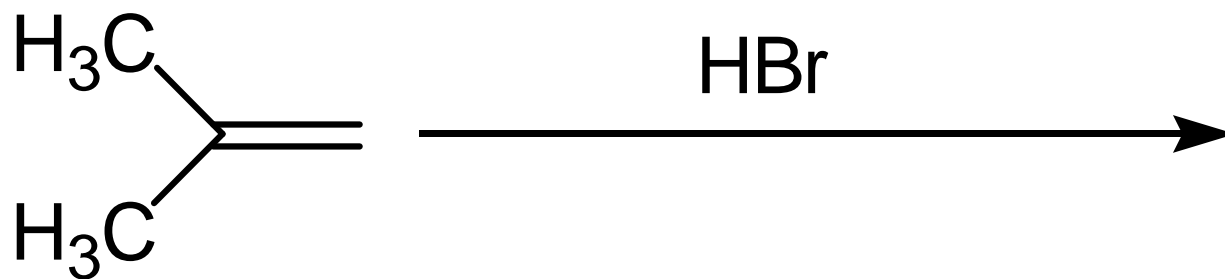


Markovnikov' rule的理論解釋:正碳離子越穩定,它所形成的速度就越快,所對應產物的形成就越多。

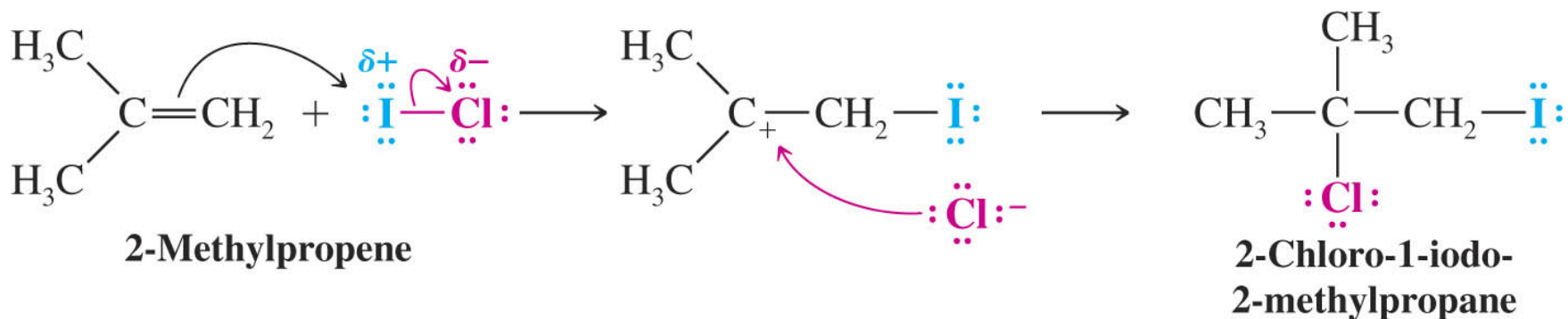
Rate-determining step



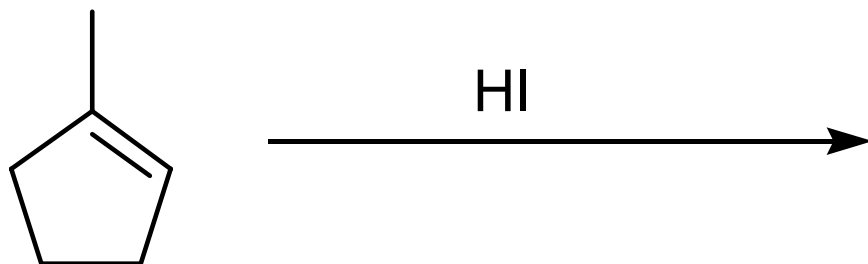
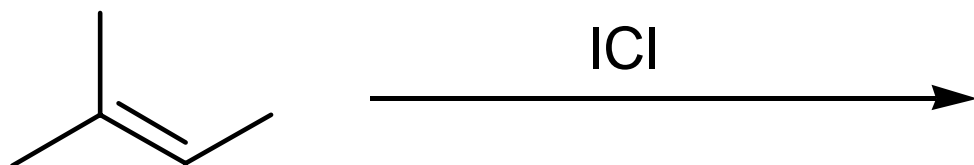
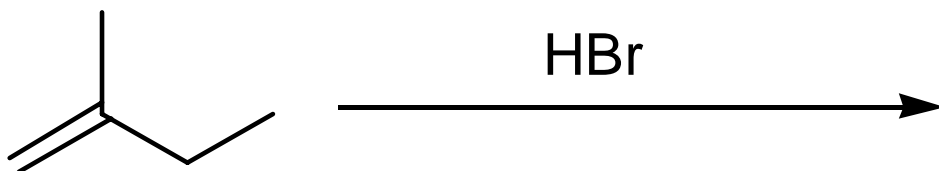
給出反應之major product:



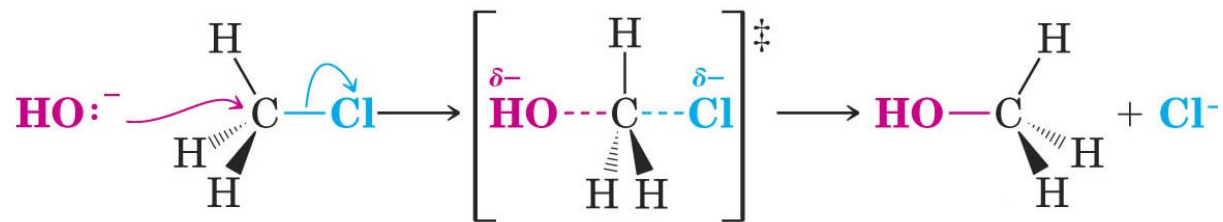
d) Markovnikov' rule的現代理論:在部分離子型不對稱烯烴的加成反應中;形成穩定的正碳離子的反應方向佔優勢。



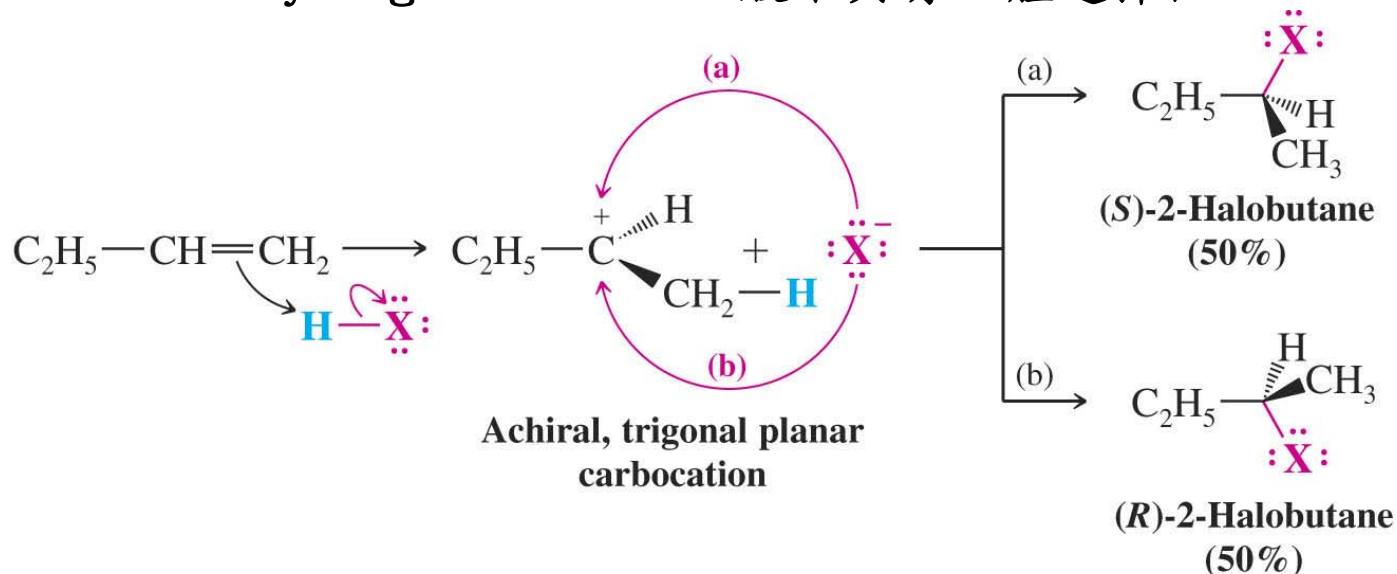
認真做課堂練習，page 335: 給出反應之major product:



regioselectivity: 當反應理論上可以產生兩種以上不同的 constitutional isomers，而實際上只產生一種產物或某一種產物佔優勢時，此類反應被稱為具有區域選擇性。



Addition of hydrogen halides一般不具有立體選擇性:

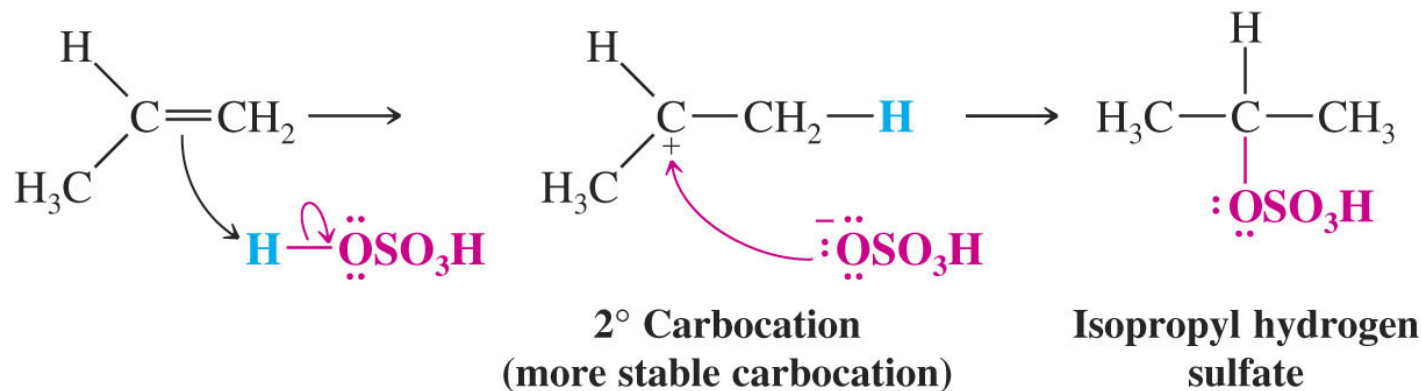


1-Butene donates a pair of electrons to the proton of HX to form an achiral carbocation.

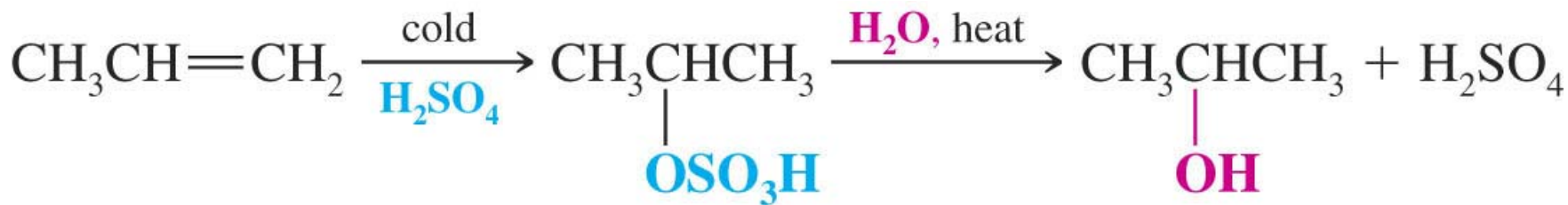
The carbocation reacts with the halide ion at equal rates by path (a) or (b) to form the enantiomers as a racemate.

3) Addition of H_2SO_4 : Markovnikov' rule

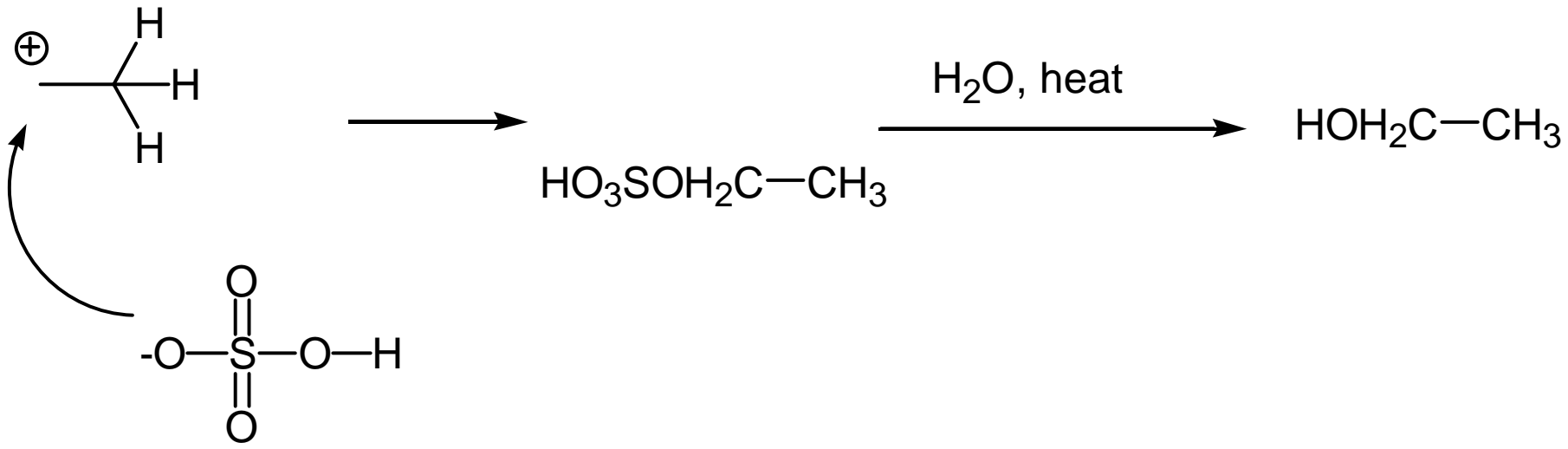
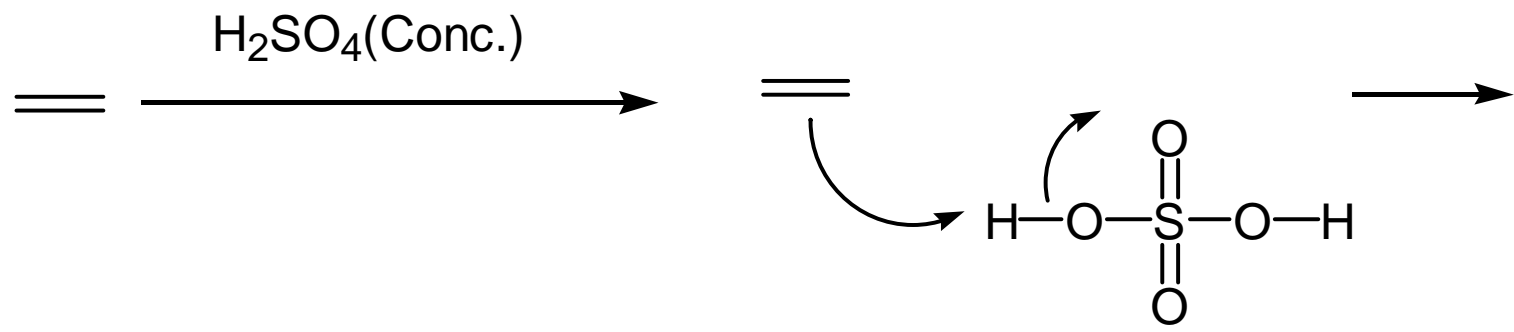
3)→6)均為由烯烴製備醇的方法:



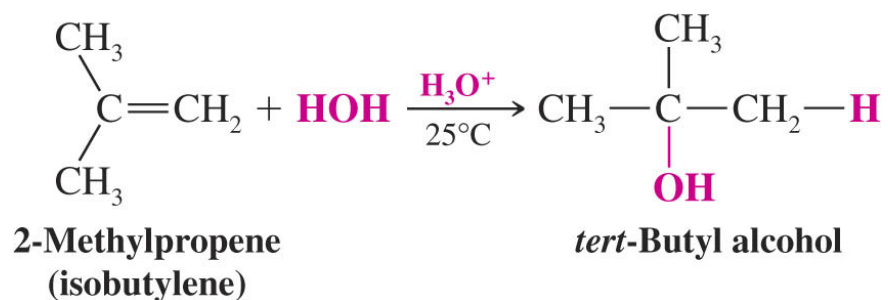
Sulfate 進一步水解成醇(第一種方法):



課堂練習，page 336 給出由 ethene 製備乙醇的機制

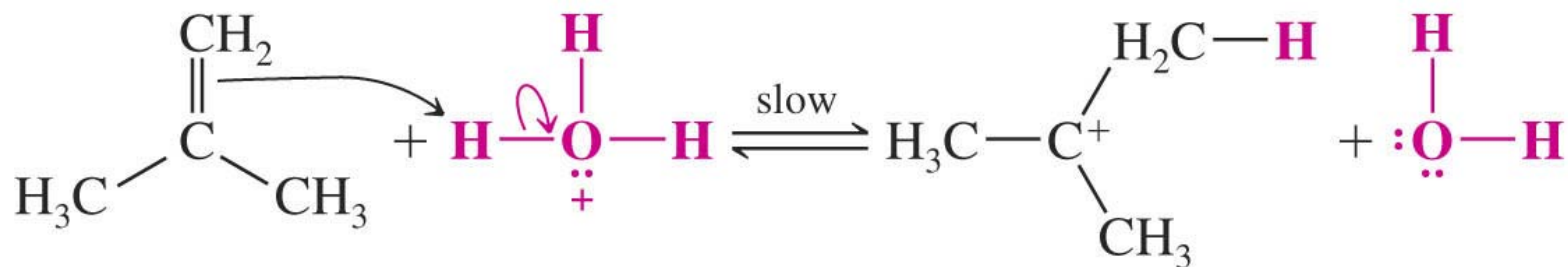


4) 製備alcohol的第二種方法：酸催化水解反應 Markovnikov' rule

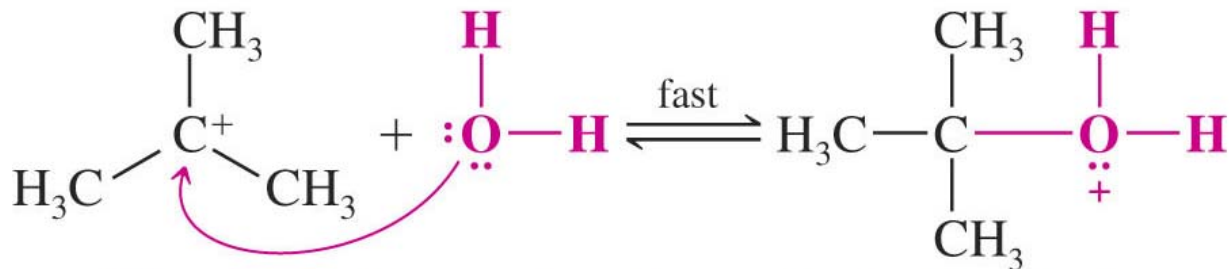


The H^+ must exist in the form of hydronium ion in water solution

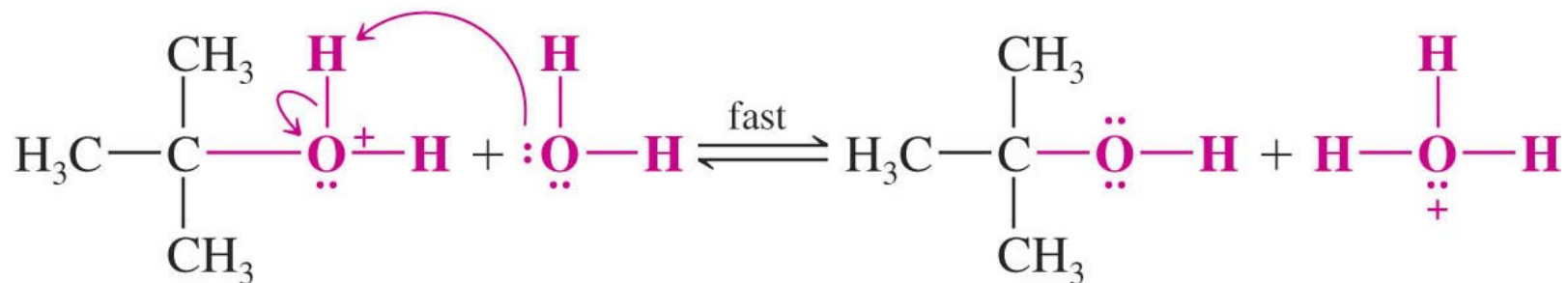
a) rate-determining step:



The alkene donates an electron pair to a proton to form the more stable 3° carbocation.



The carbocation reacts with a molecule of water to form a protonated alcohol.

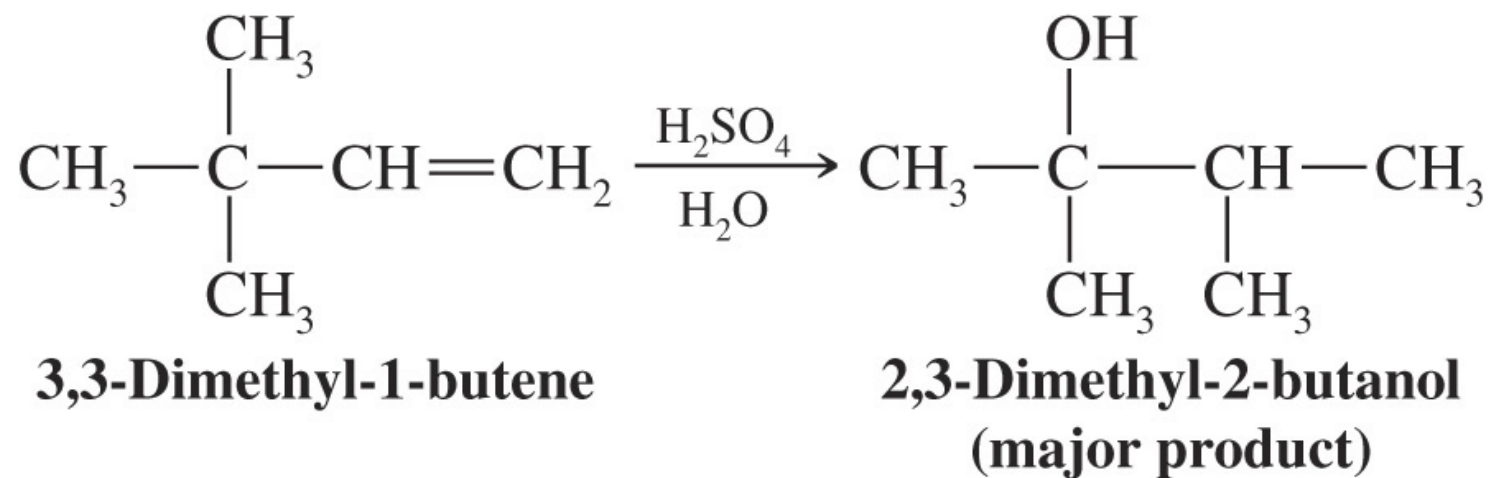


A transfer of a proton to a molecule of water leads to the product.

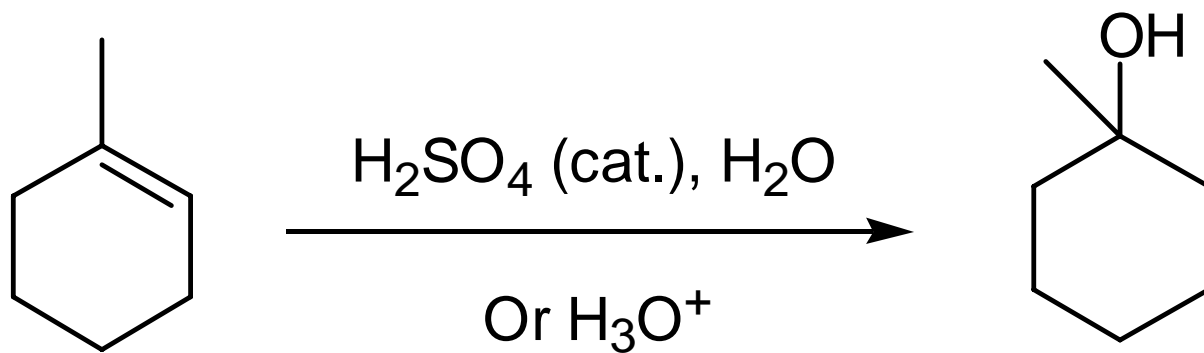
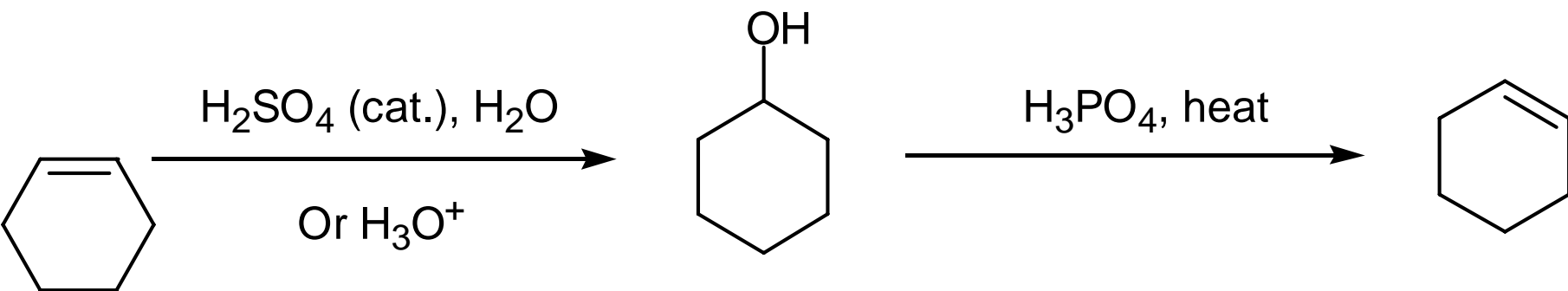
The mechanism is the reverse of that for dehydration of an alcohol

Hydration is favored by addition of a small amount of acid and a large amount of water

解釋此反應結果

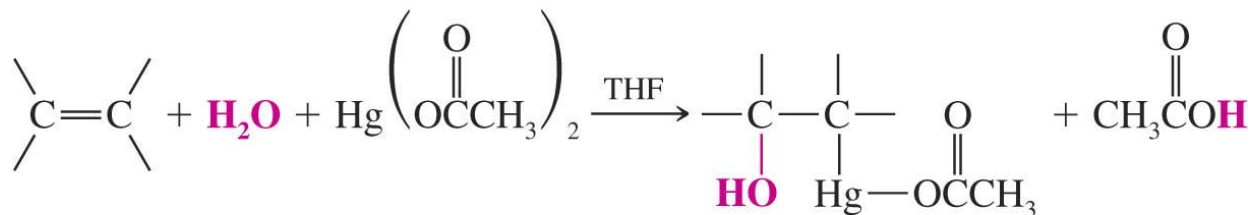


課堂練習，page 339-340: 給出反應之條件

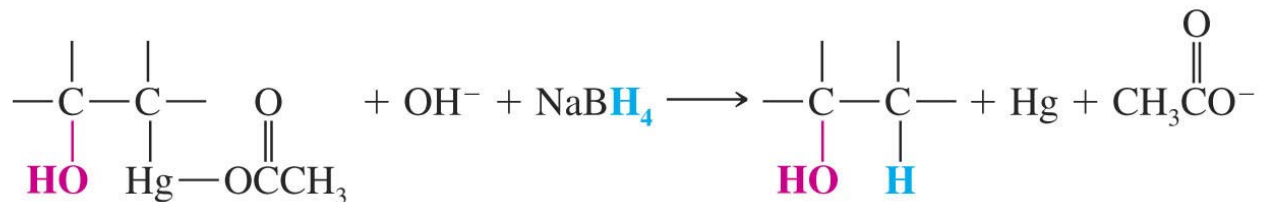


5) 製備alcohol的第三種方法：Oxymercuration of alkenes

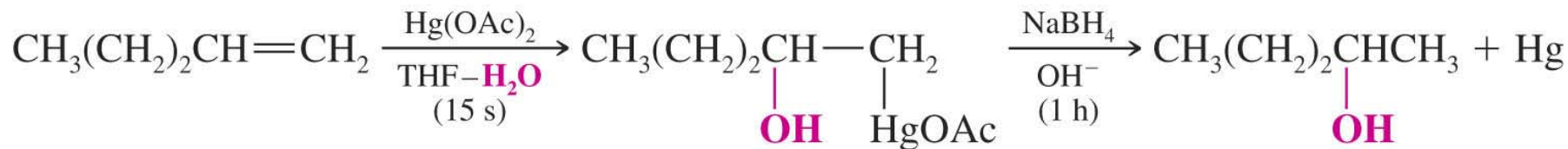
Step 1: Oxymercuration



Step 2: Demercuration



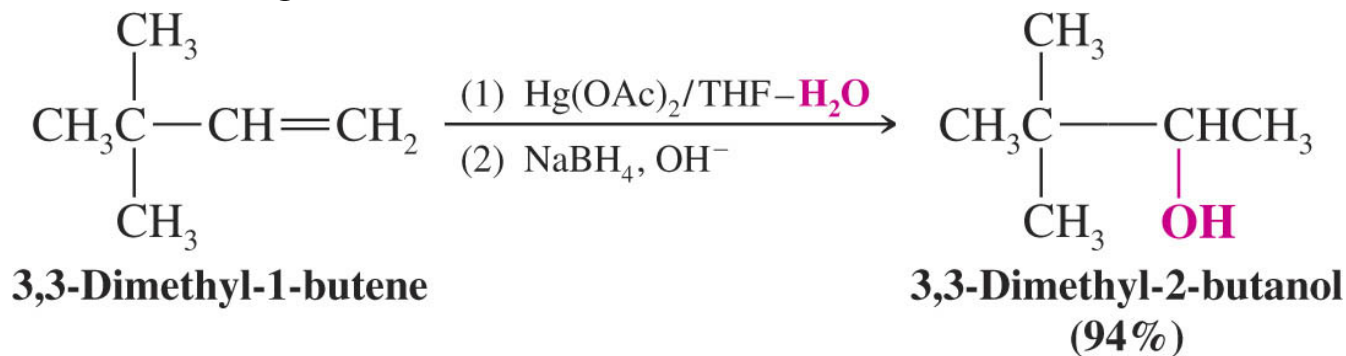
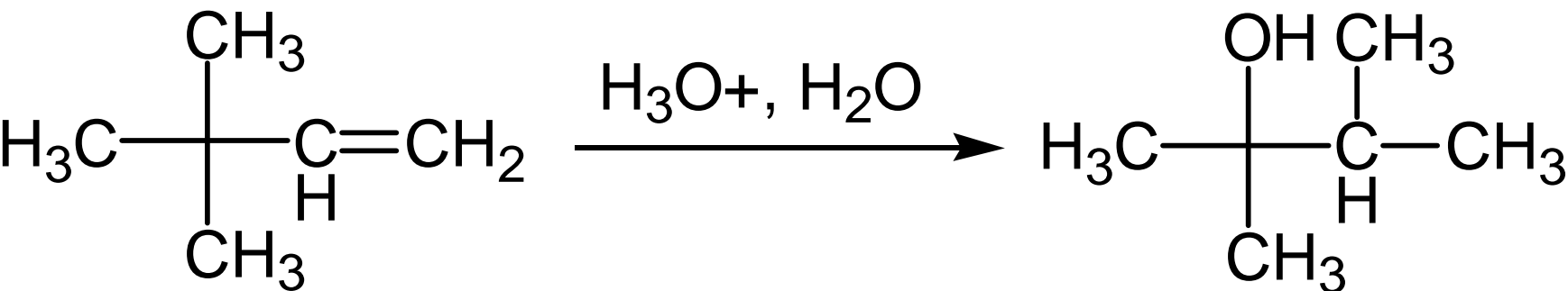
討論此反應的機制：



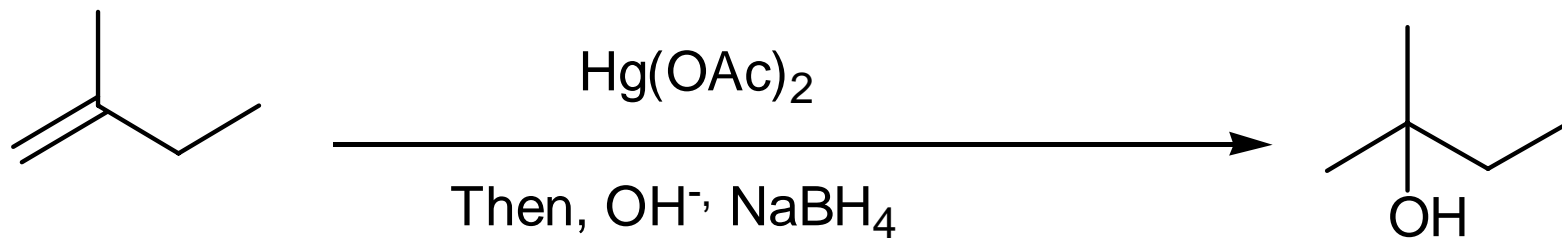
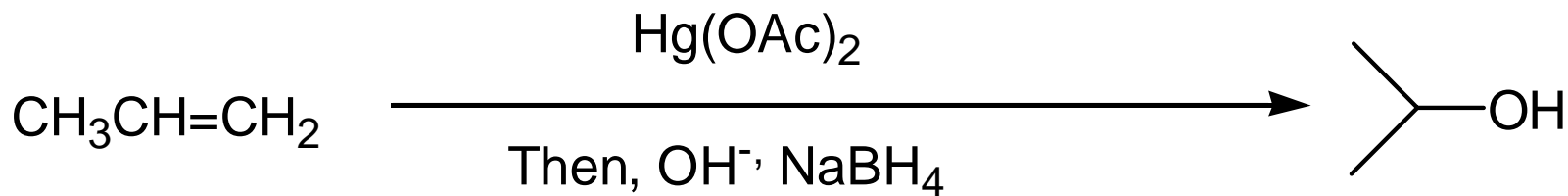
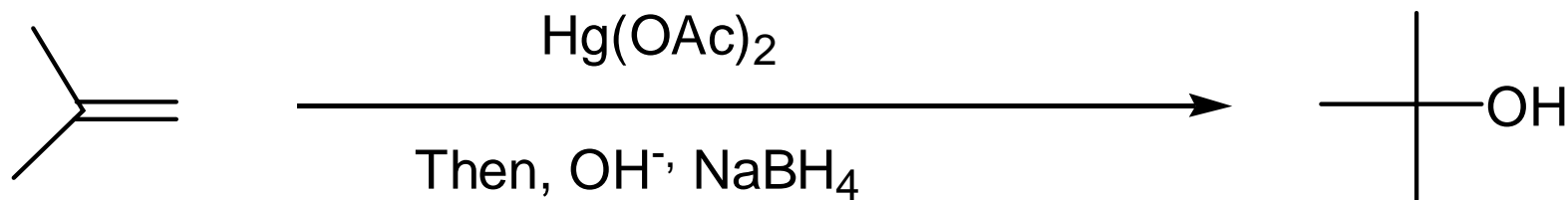
1-Pentene

2-Pentanol
(93%)

與方法四相比較，此方法不發生重排反應：

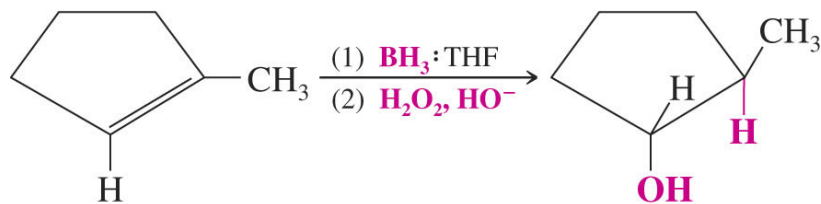


課堂練習，page 342:用Oxymercuration的方法製備下列醇

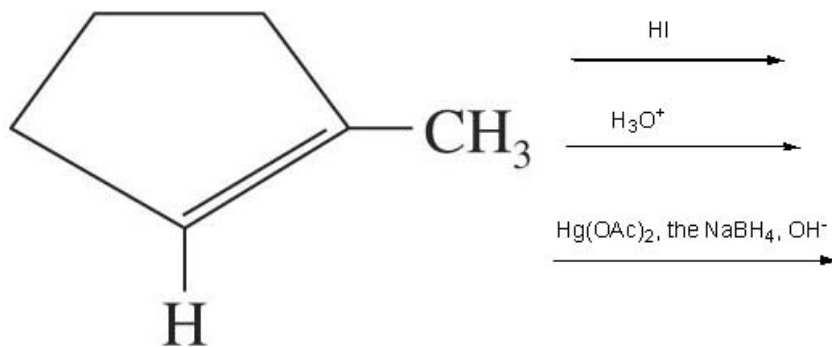


6) 製備alcohol的第四種方法：Hydroboration-Oxidation (硼氫化-氧化) — Anti-Markovnikov: 即產物中的氫原子是加在含氫較少的碳上。

Reagent: B_2H_6 or BH_3/THF



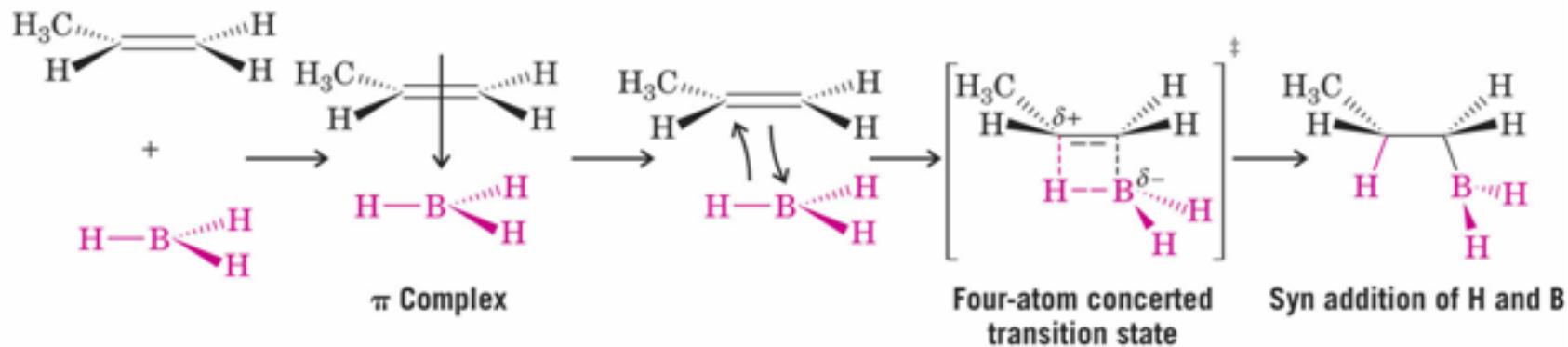
Stereoselectivity
And
regioselectivity



反應機制：

第一步：硼氫加成(Hydroboration)

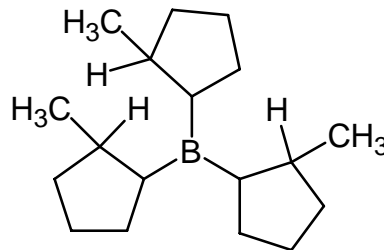
Hydroboration



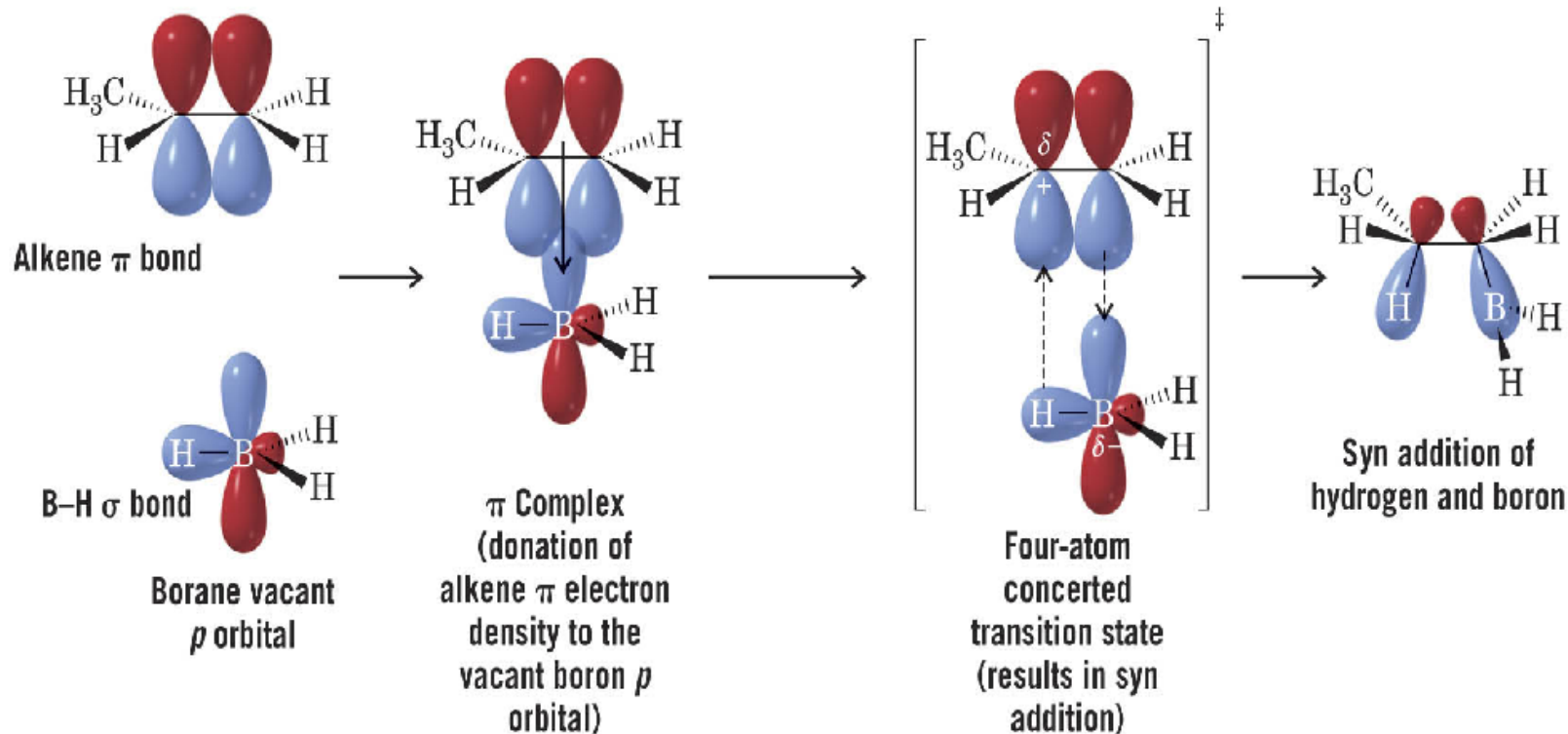
syn-addition (順式加成)

由於立體因素的影響，硼原子加在烷基取代少的碳原子上：Anti-Markovnikov;

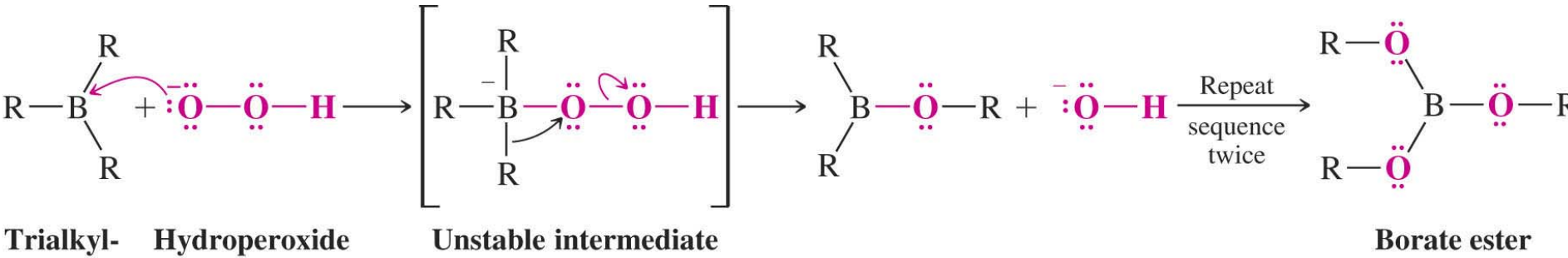
When the reaction is completed:



An orbital view of hydroboration



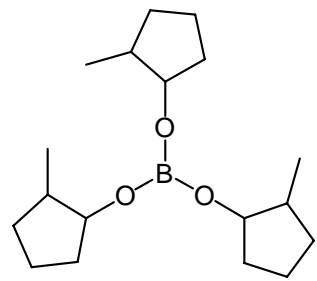
第二步：氧化反應：



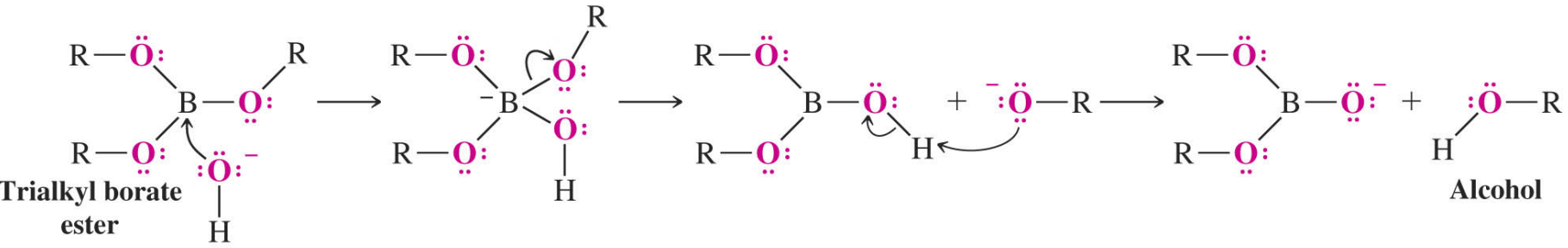
The boron atom accepts an electron pair from the hydroperoxide ion to form an unstable intermediate.

An alkyl group migrates from boron to the adjacent oxygen atom as a hydroxide ion departs. The configuration at the migrating carbon remains unchanged.

When the reaction is completed:



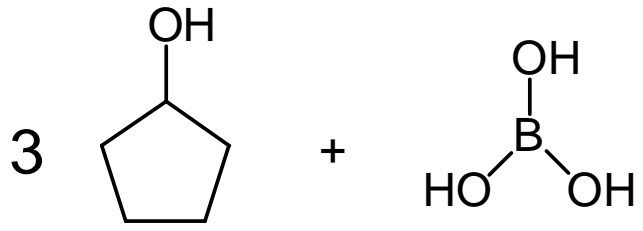
第三步：水解反應：



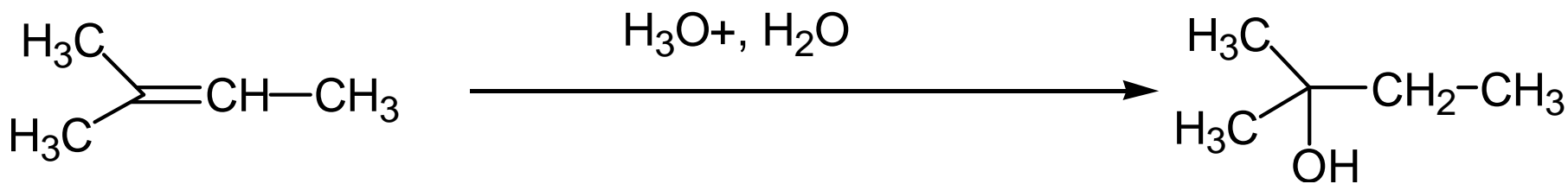
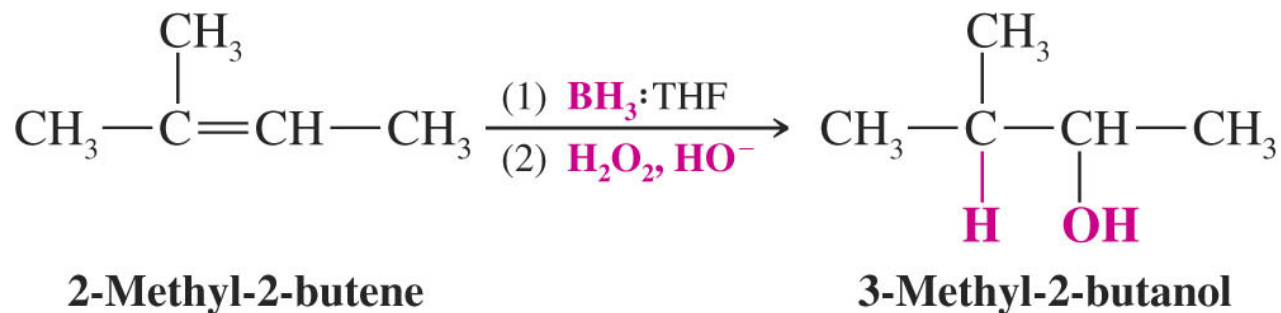
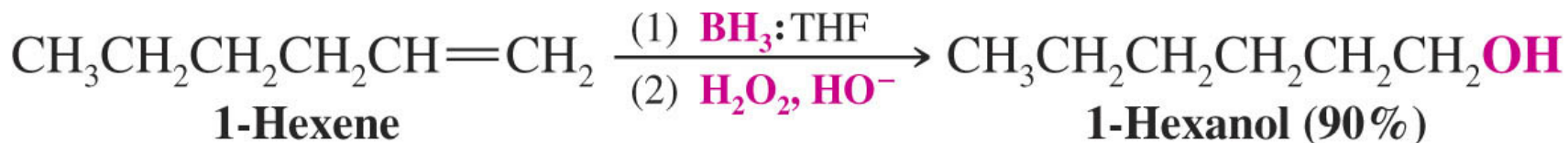
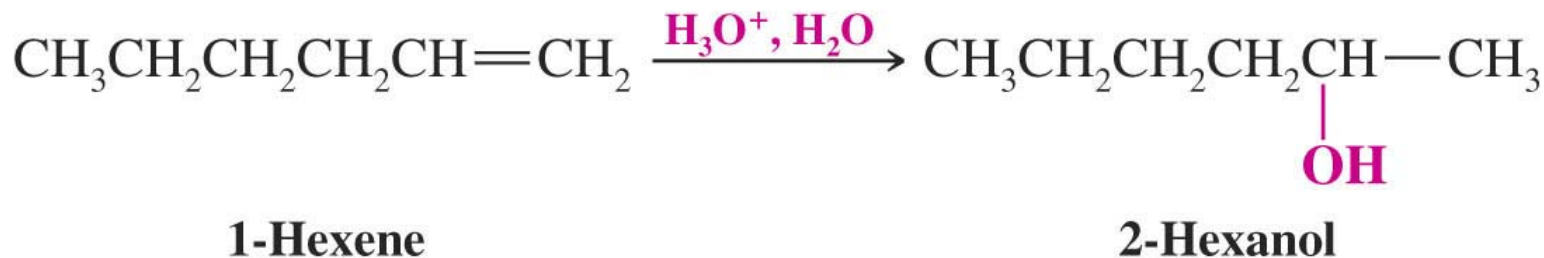
Hydroxide anion attacks the boron atom of the borate ester.

An alkoxide anion departs from the borate anion, reducing the formal charge on boron to zero.

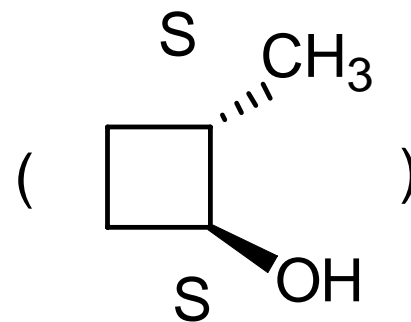
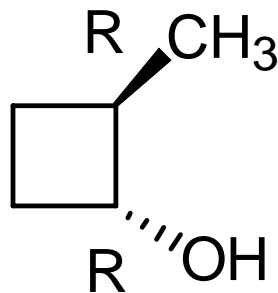
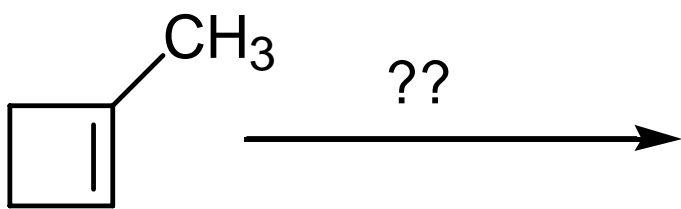
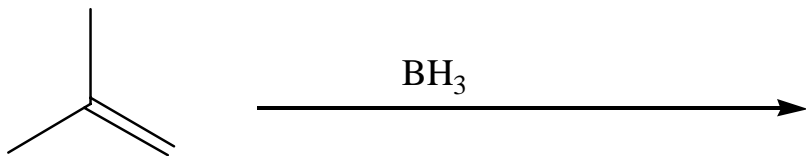
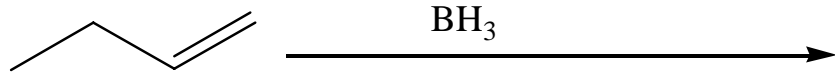
Proton transfer completes the formation of one alcohol molecule. The sequence repeats until all three alkoxy groups are released as alcohols and inorganic borate remains.



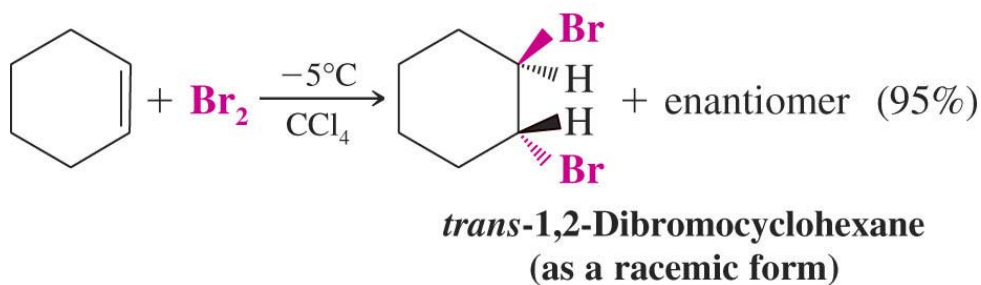
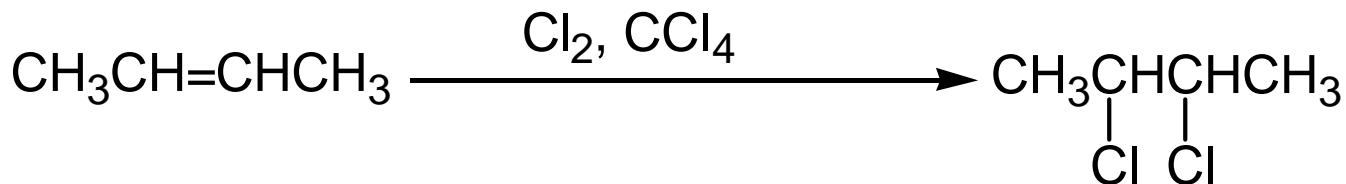
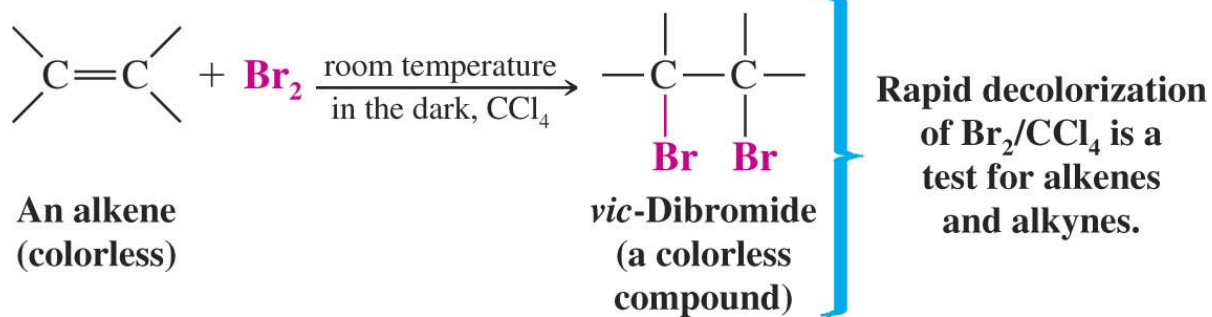
Regioselectivity: Comparing the following reactions:



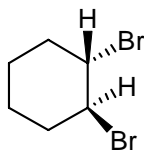
課堂練習，page 346-347: 以合適的烯烴合成tributylborane, triisobutylborane, tri-sec-butylborane



G) : Addition of bromine and chlorine:



(R,R)

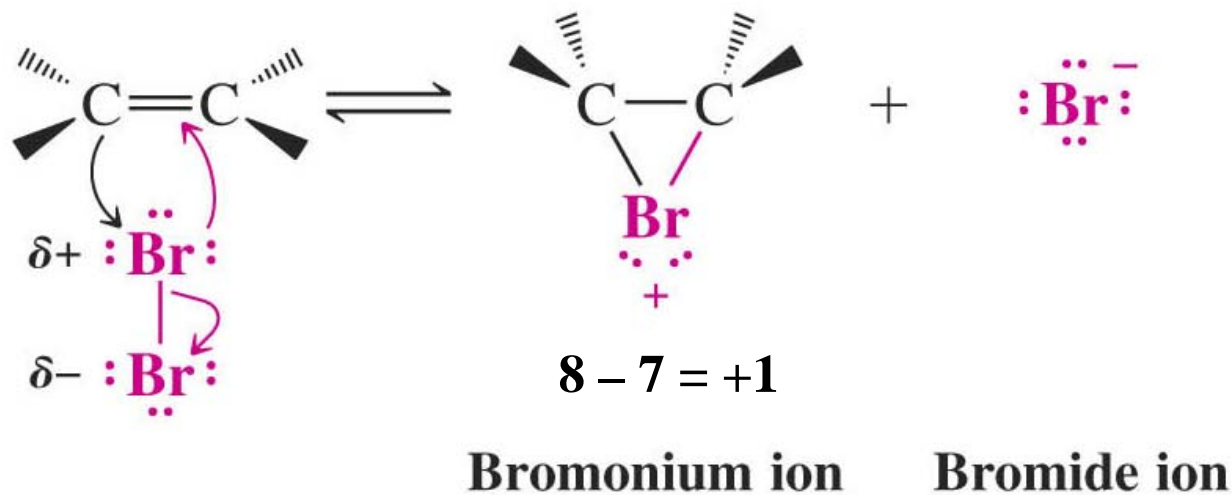


(S,S)

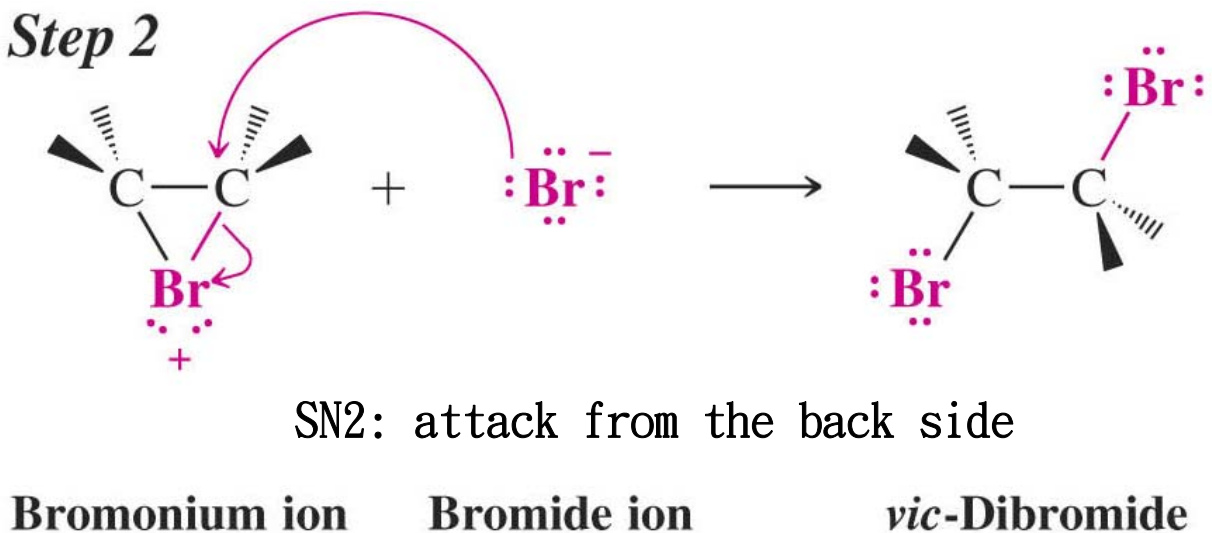
如何解釋生成反式的化合物

a) The mechanism of the halogenation:

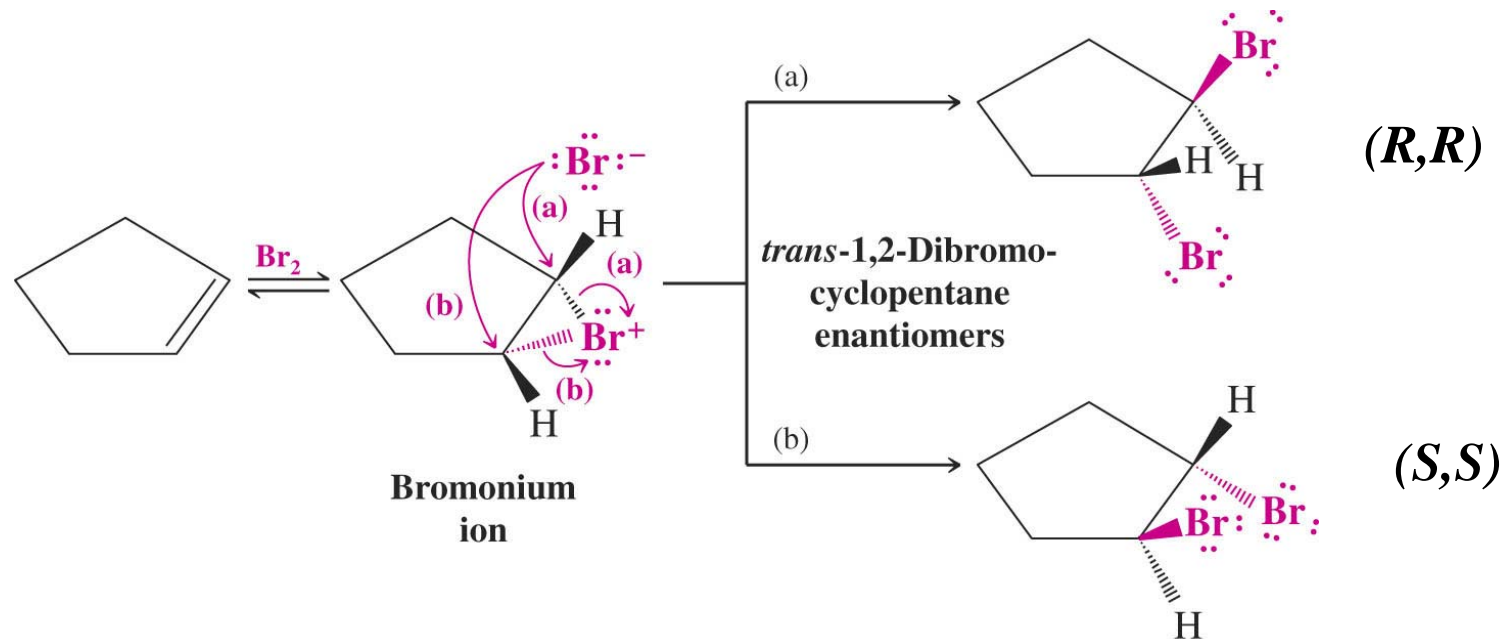
Step 1



Step 2



b) The stereochemistry of the addition of halogens to alkene



racemic mixture of *trans*-1,2-dibromocyclopentane enantiomers are formed

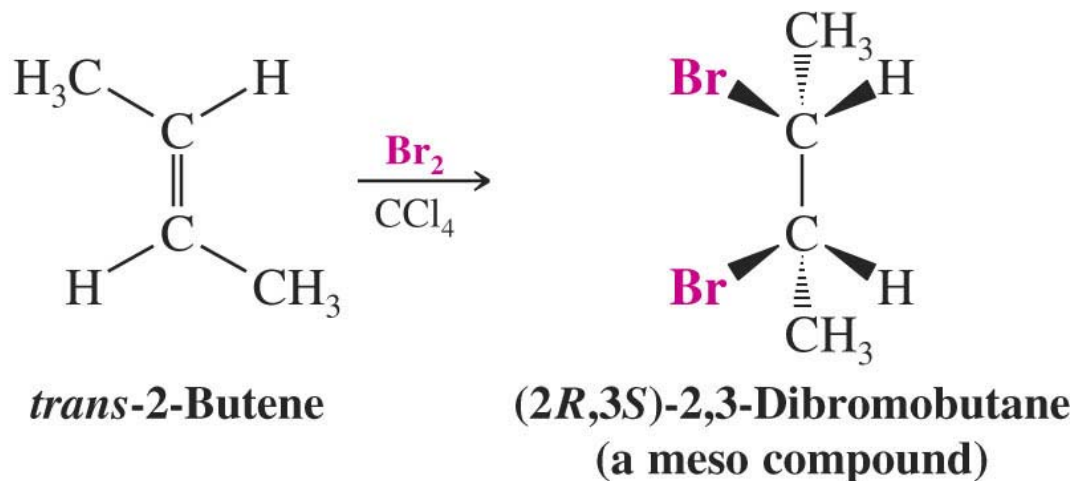
stereospecific reactions: 從一種特定的立體異構物的起始物得到 (exclusively) 特定的立體異構物的產物的反應。

Stereoselective: 反應起始物不一定為chiral, 經過反應後, 某一種立體異構物可以predominantly 或exclusively的生成。

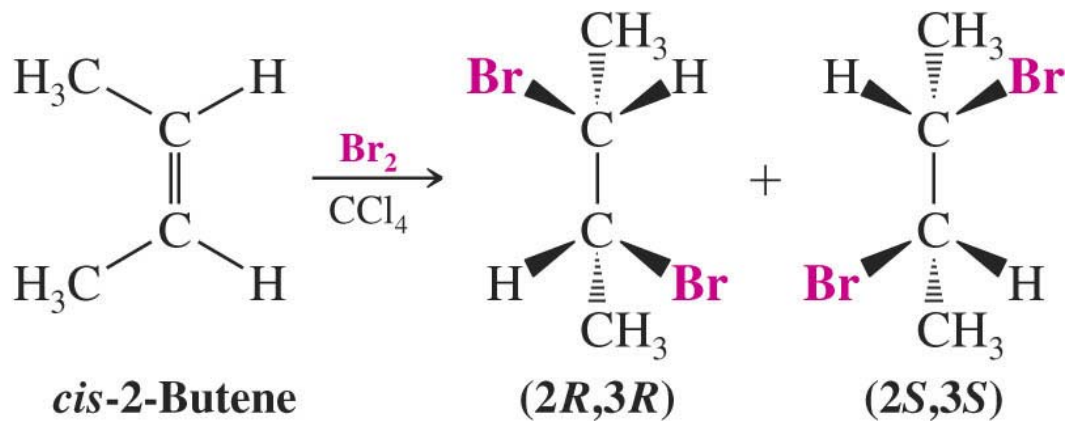
All stereospecific reactions are stereoselective, but the reverse is not necessary true

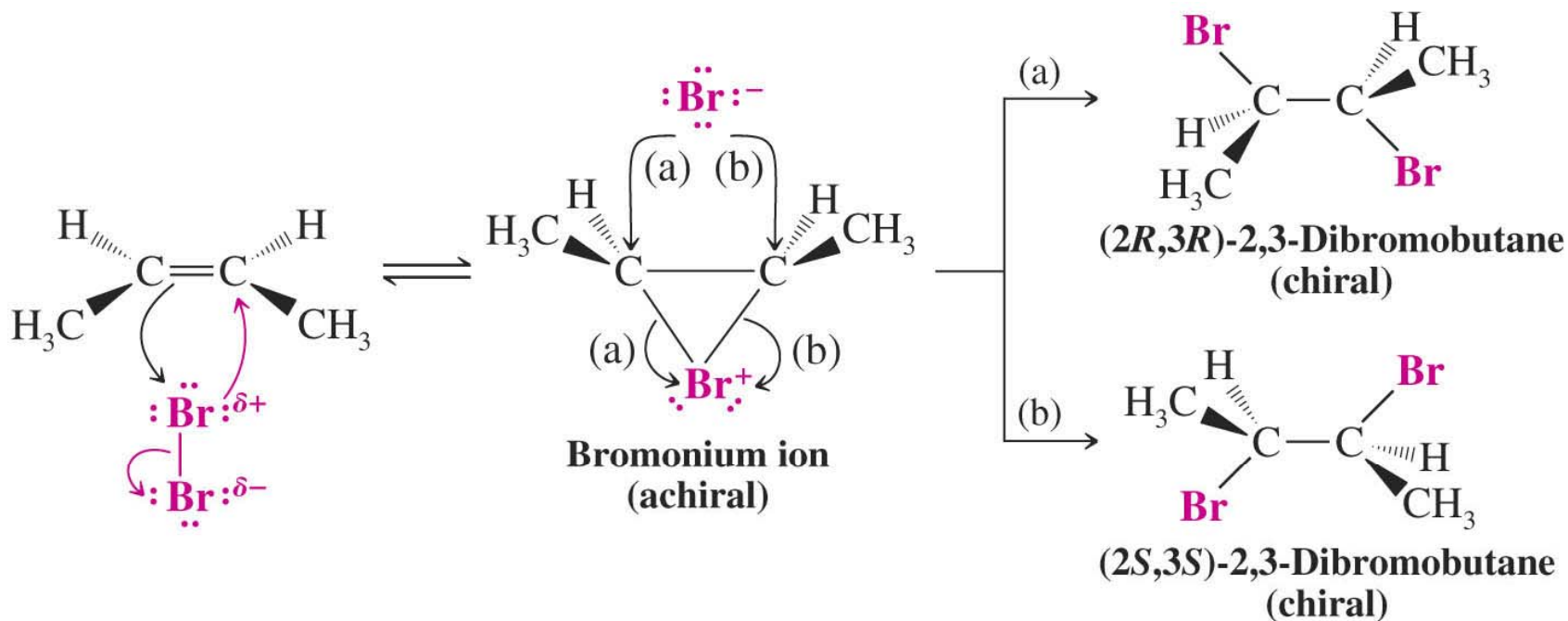
stereospecific reactions之實例

Reaction 1



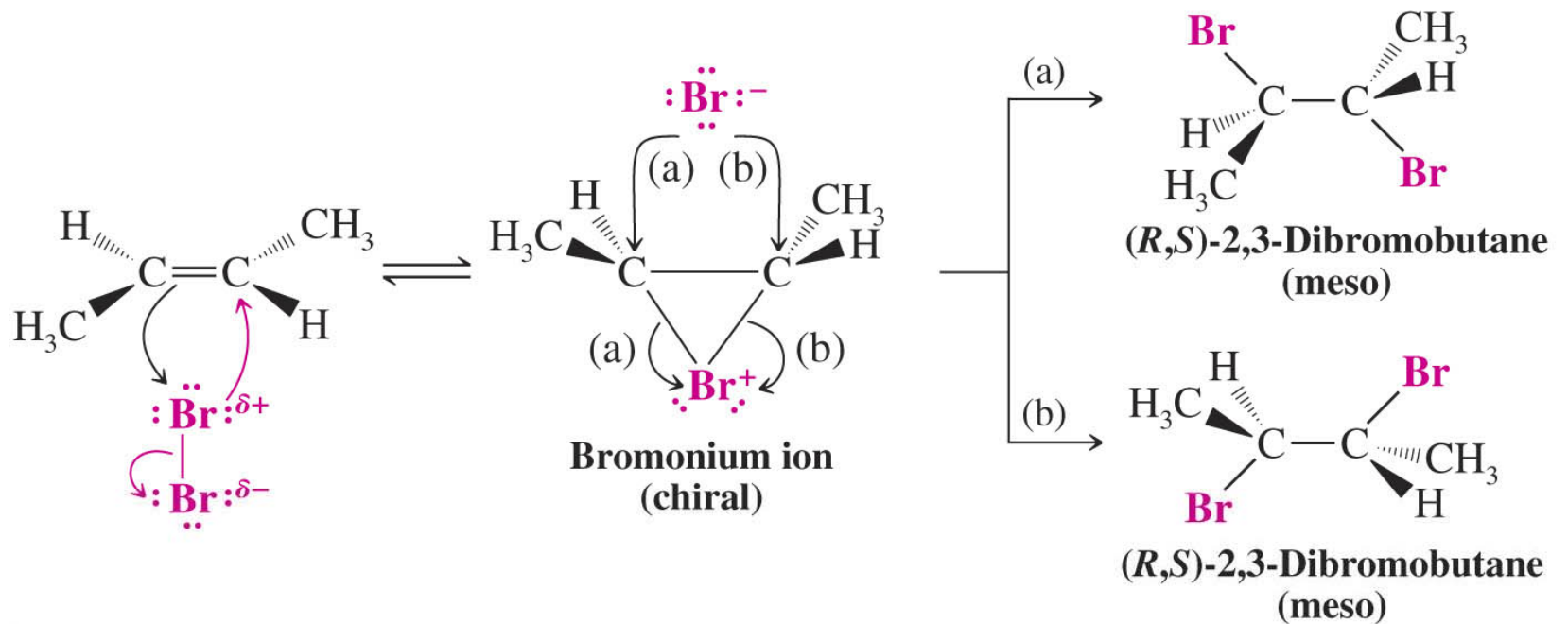
Reaction 2





cis-2-Butene reacts with bromine to yield an achiral bromonium ion and a bromide ion. [Reaction at the other face of the alkene (top) would yield the same bromonium ion.]

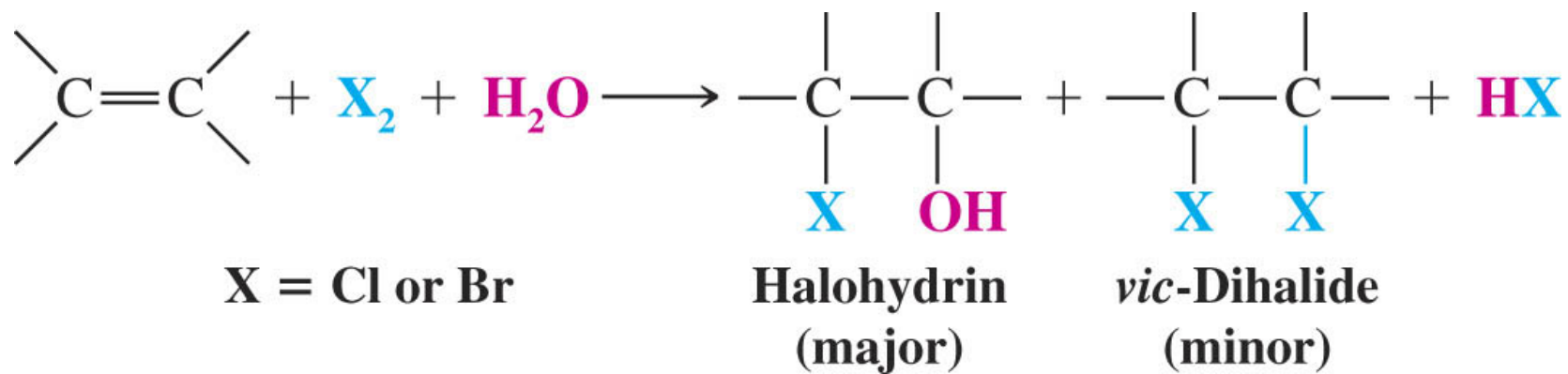
The bromonium ion reacts with the bromide ions at equal rates by paths (a) and (b) to yield the two enantiomers in equal amounts (i.e., as the racemic form).



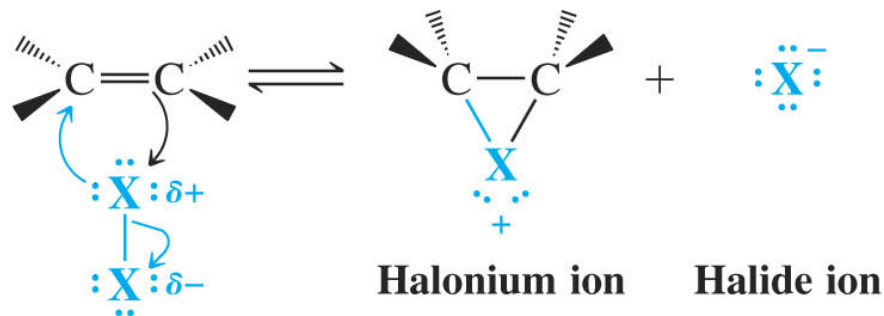
trans-2-Butene reacts with bromine to yield chiral bromonium ions and bromide ions. [Reaction at the other face (top) would yield the enantiomer of the bromonium ion as shown here.]

When the bromonium ions react by either path (a) or path (b), they yield the *same* achiral meso compound. [Reaction of the enantiomer of the intermediate bromonium ion would produce the same result.]

7) : Halohydrin formation:

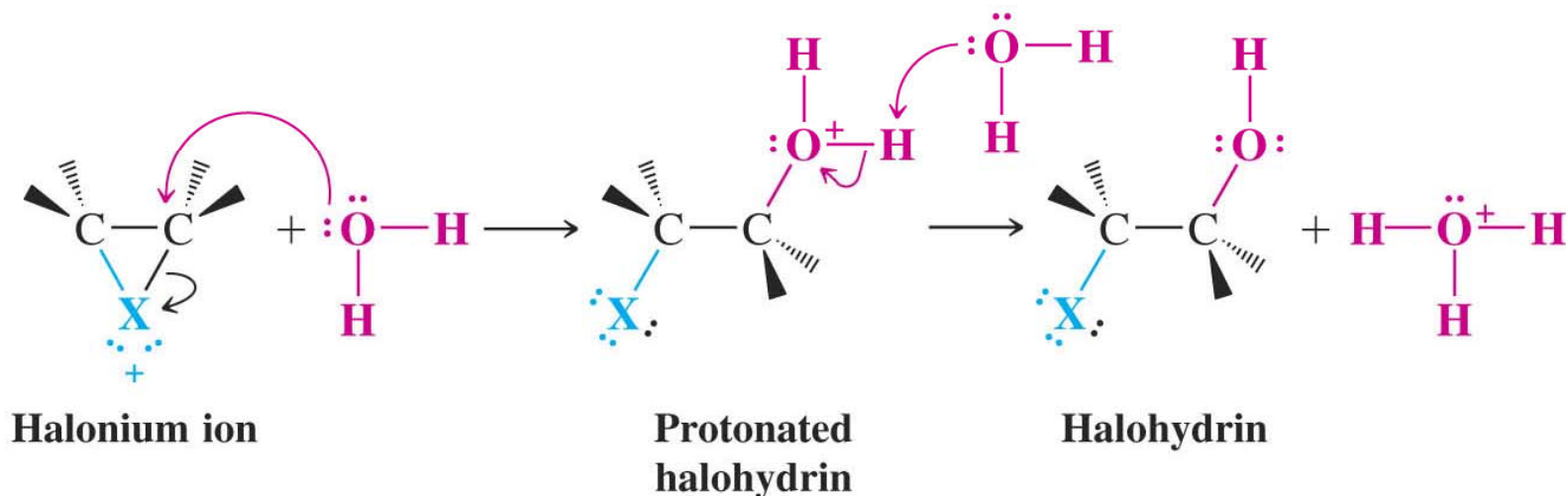


Step 1



This step is the same as for halogen addition to an alkene (see Section 8.12A).

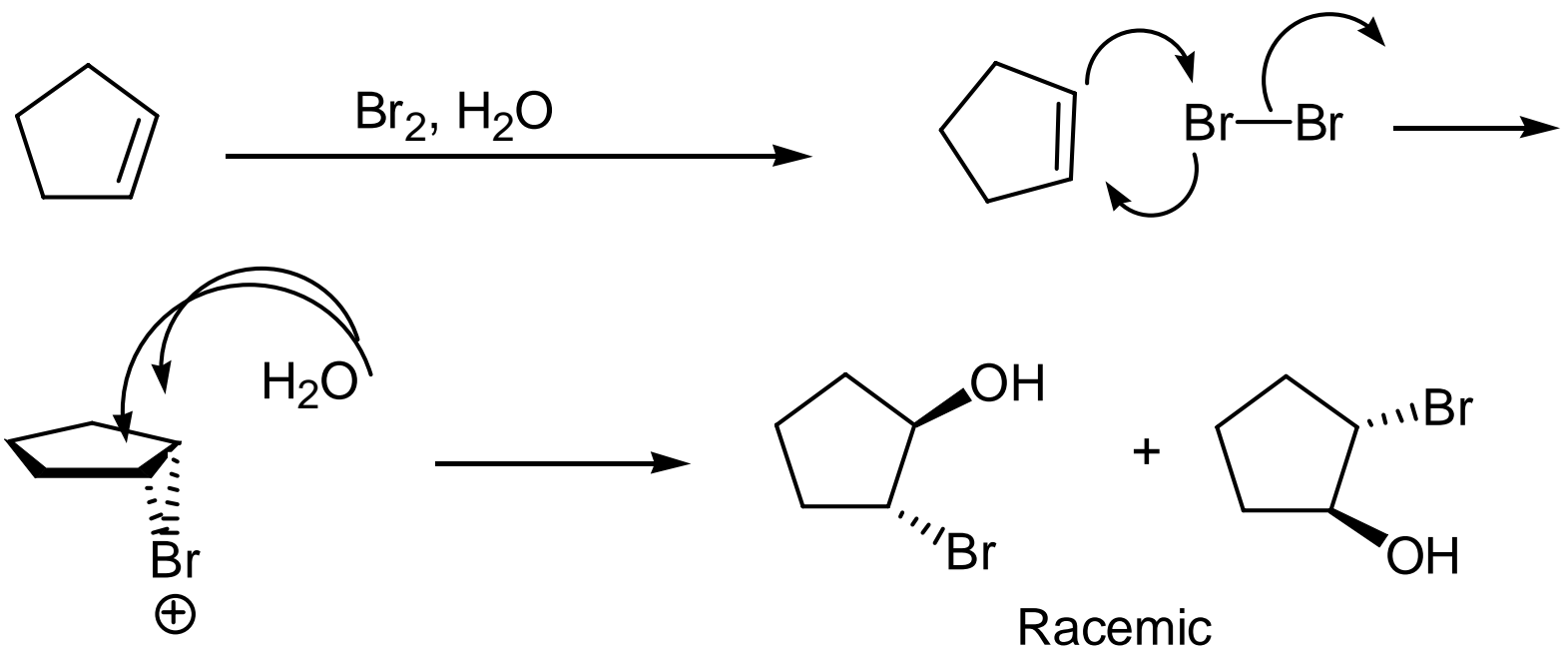
Steps 2 and 3



Here, however, a water molecule acts as the nucleophile and attacks a carbon of the ring, causing the formation of a protonated halohydrin.

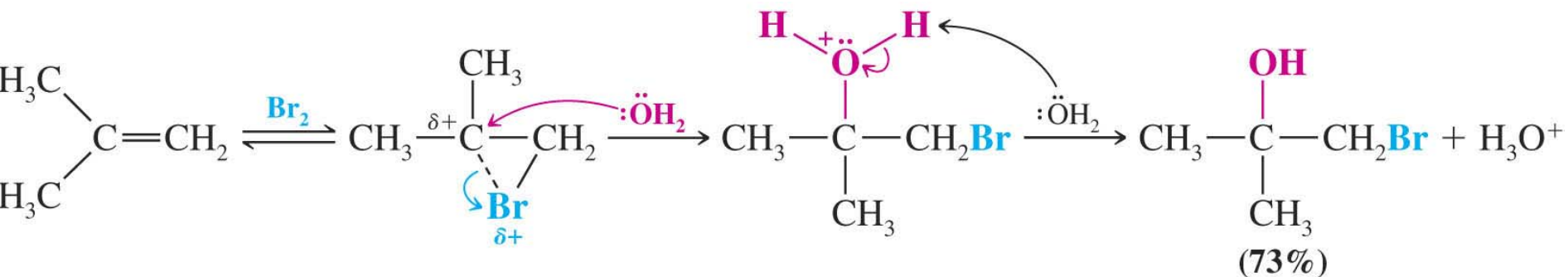
The protonated halohydrin loses a proton (it is transferred to a molecule of water). This step produces the halohydrin and hydronium ion.

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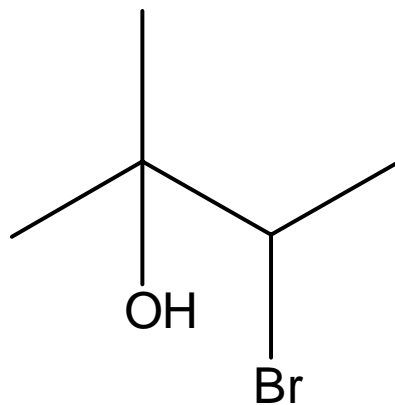
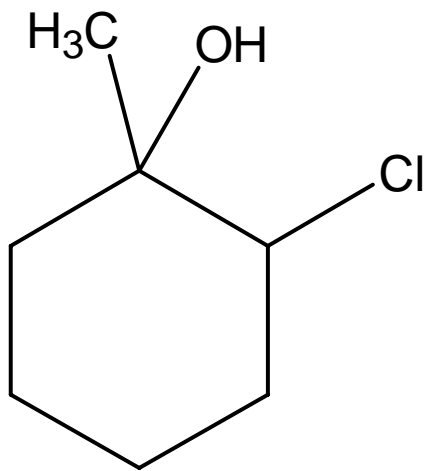


Symmetrical operation

反應中的regioselectivity:



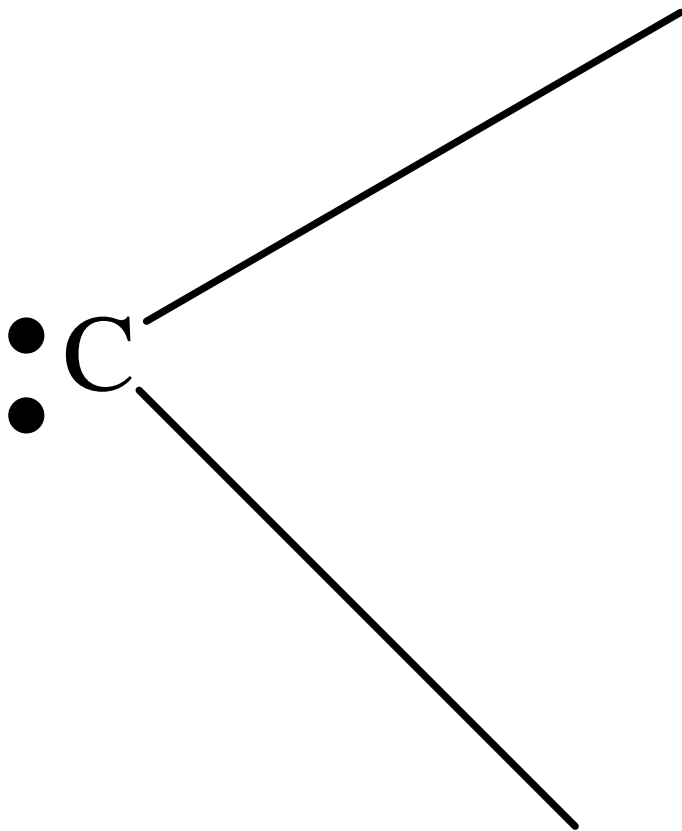
設計合成:



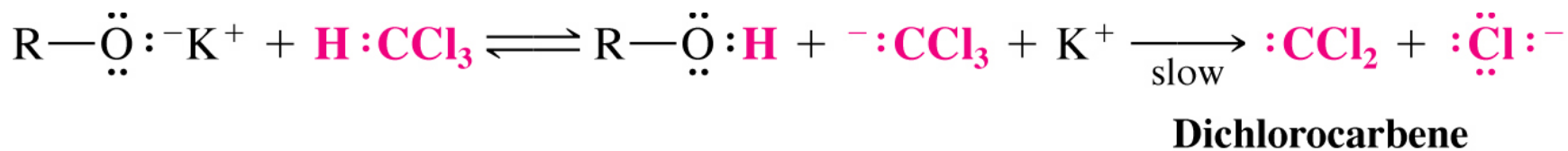
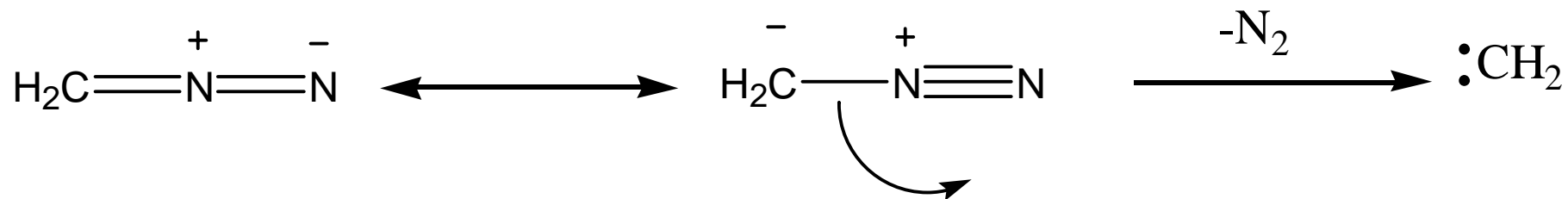
7)：烯烴其他類型的反應

a)與卡賓(carben)的加成反應

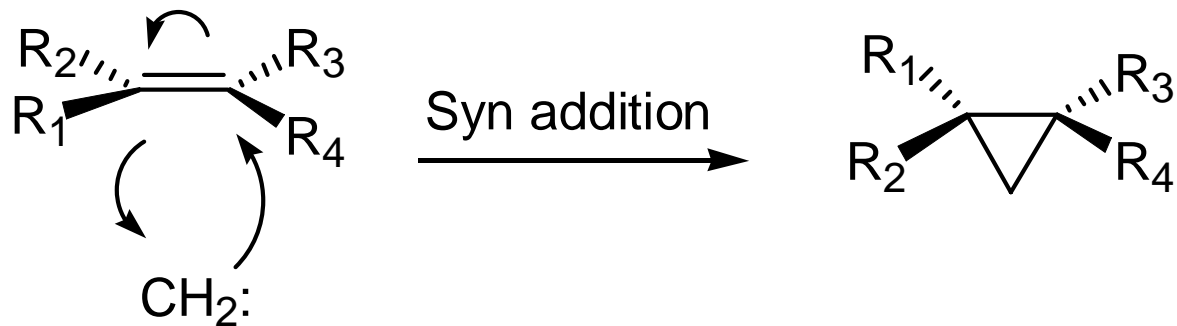
卡賓為有機化學中的一類高活性中間體：

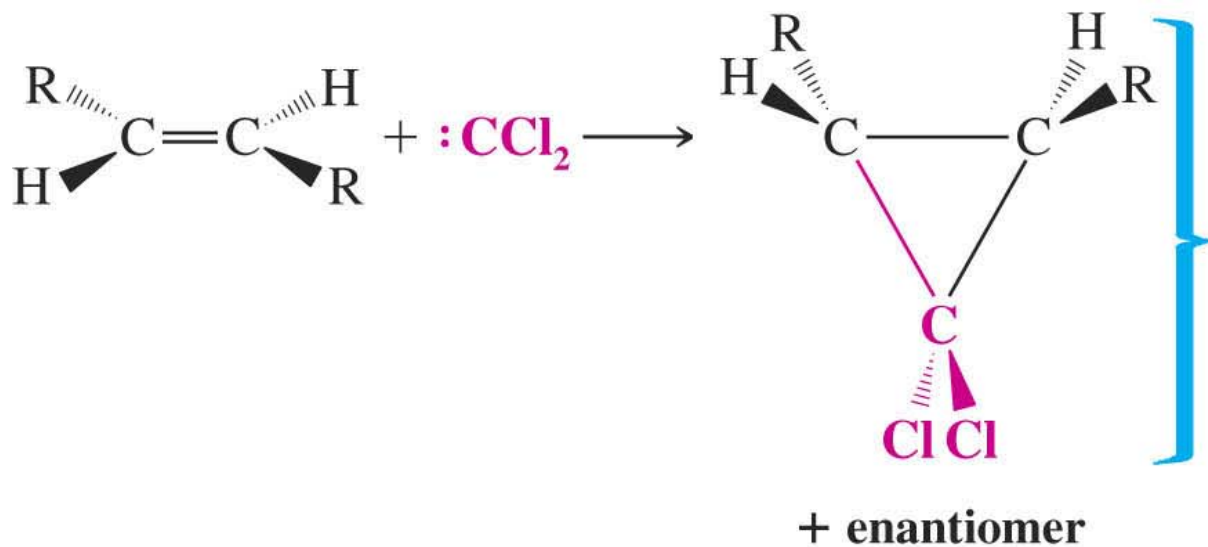


卡賓的生成：



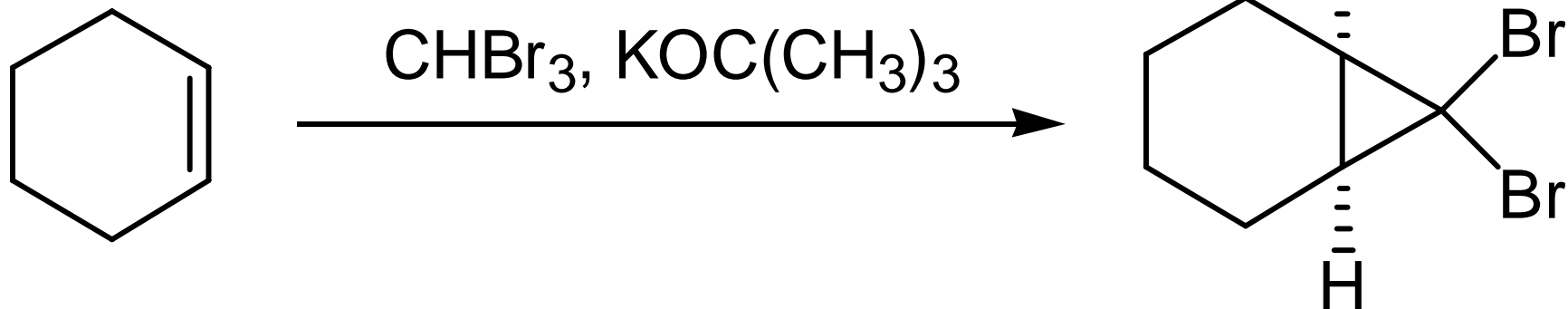
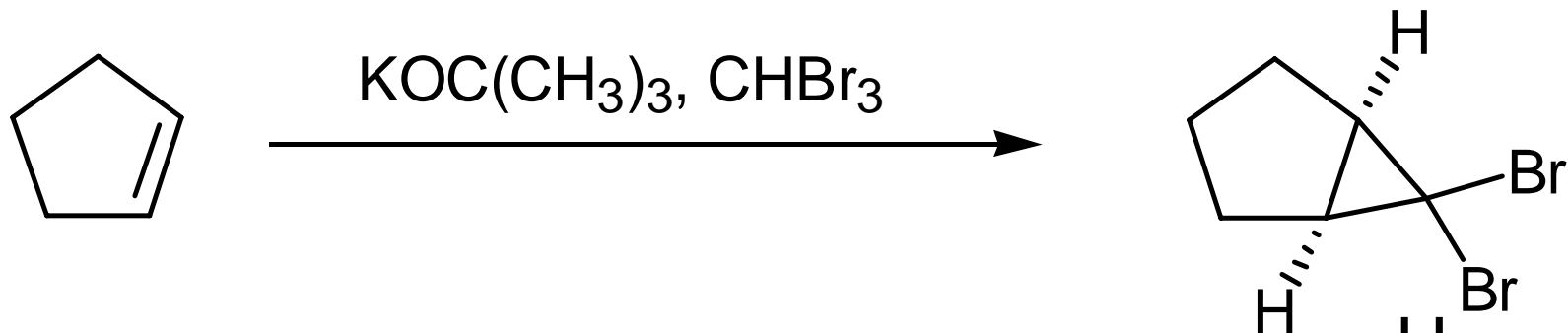
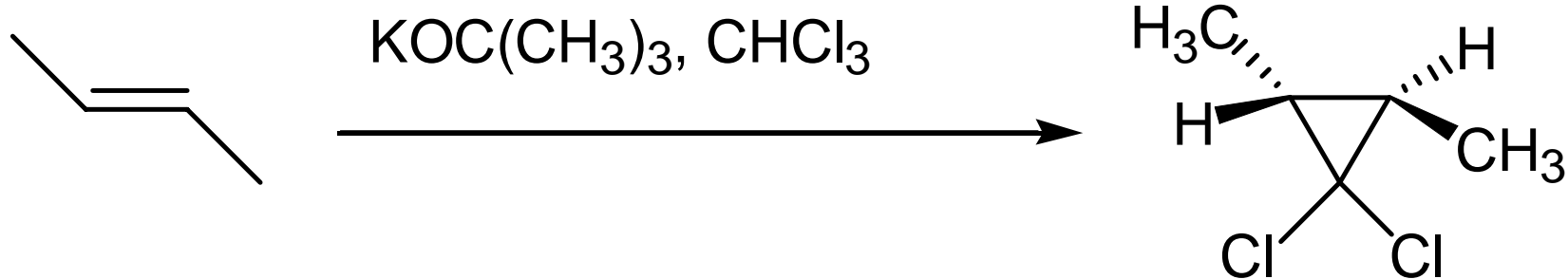
卡賓與烯烴的加成：



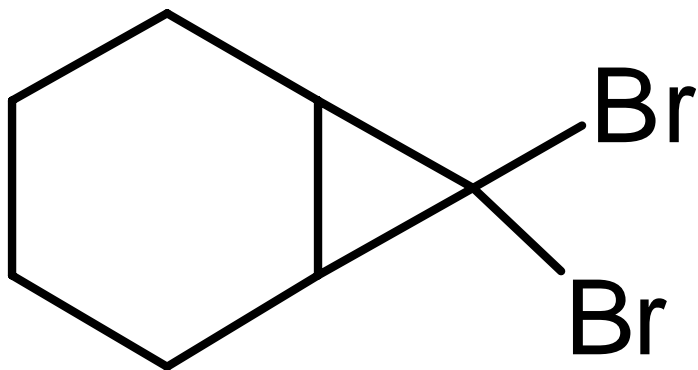


The addition of :CX_2 is stereospecific. If the R groups of the alkene are trans, they will be trans in the product. (If the R groups were initially cis, they would be cis in the product.)

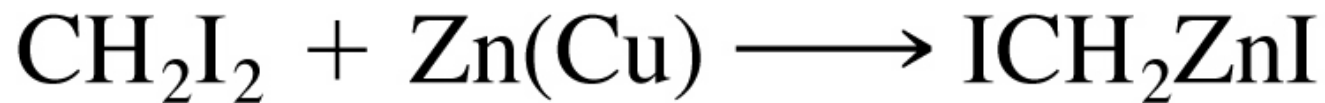
課堂練習，page 359



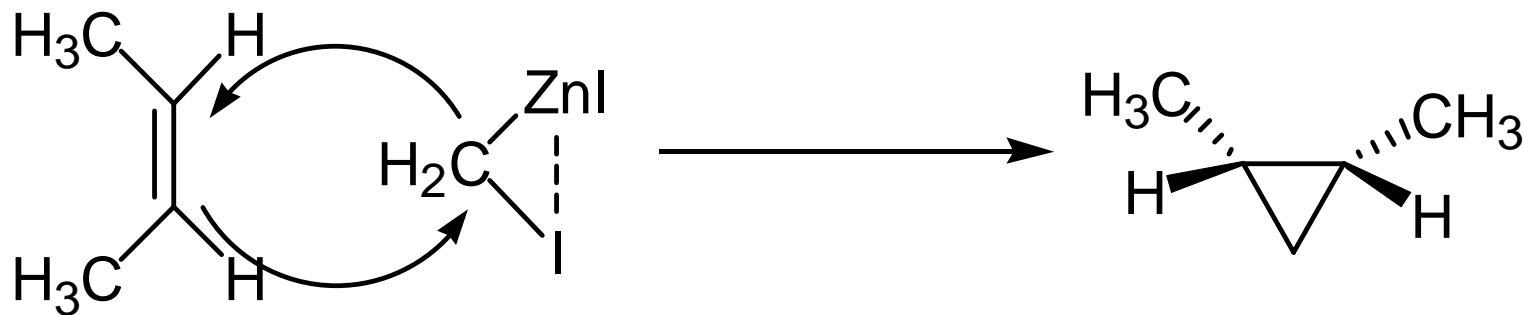
設計合成7，7-dibromobicyclo[4.1.0]heptane



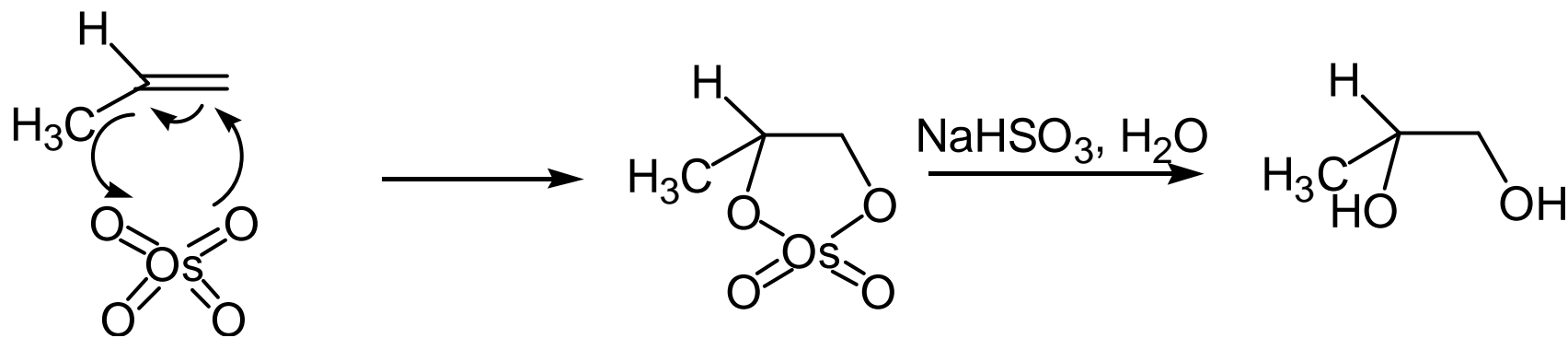
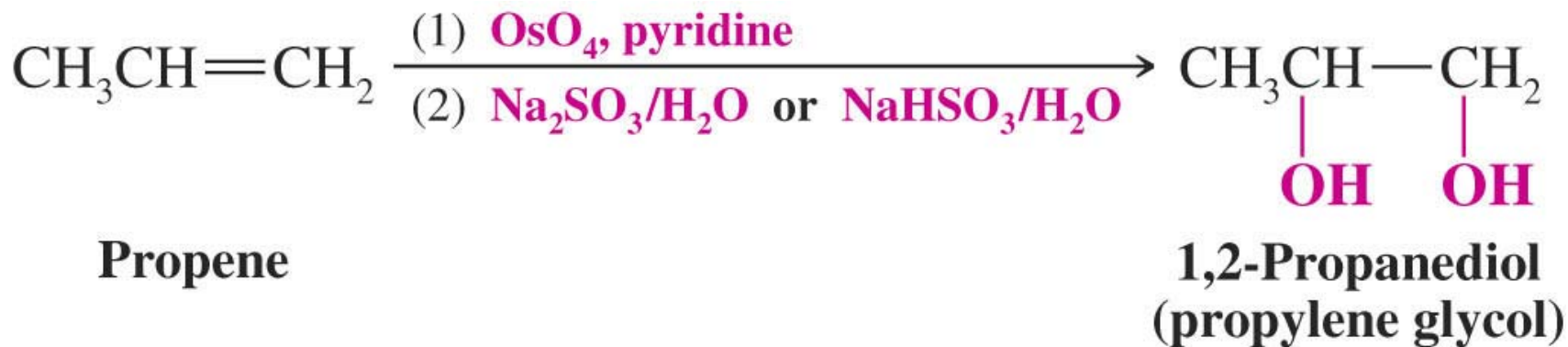
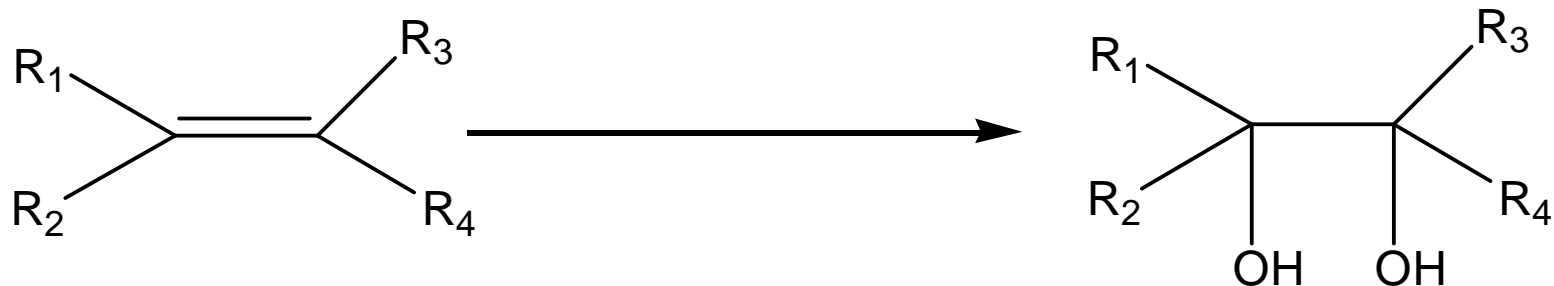
b) 與carbenoids的加成反應-Simmons-Smith reaction



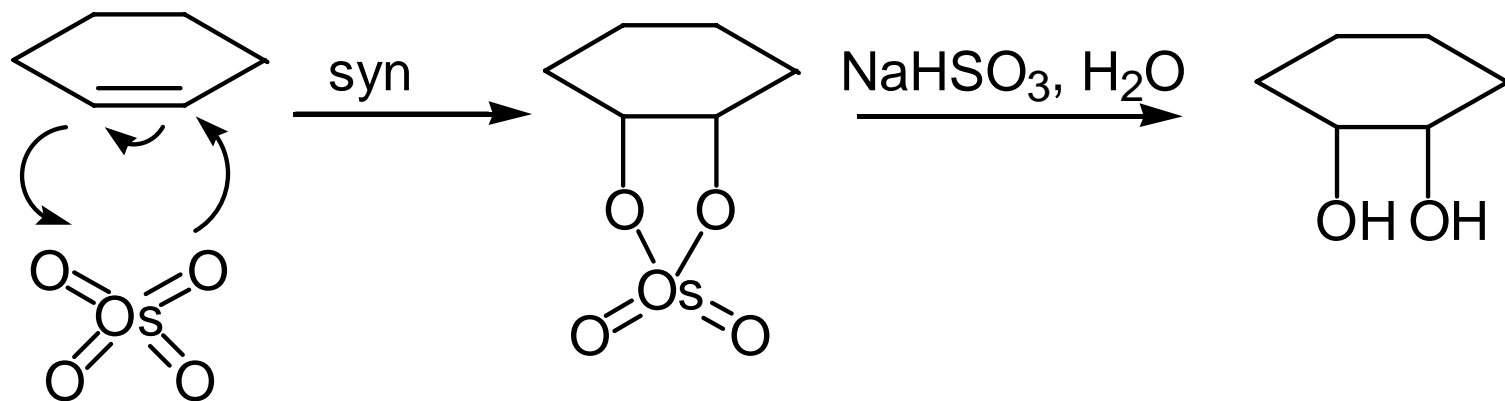
A carbenoid

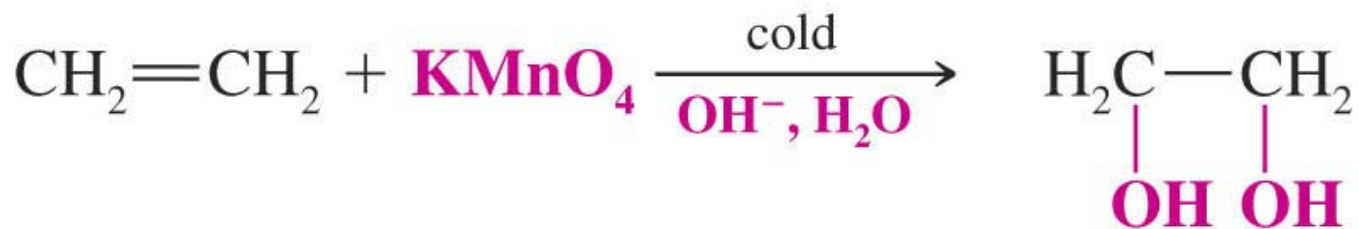


c) 烯烴的氧化及氧化斷裂反應



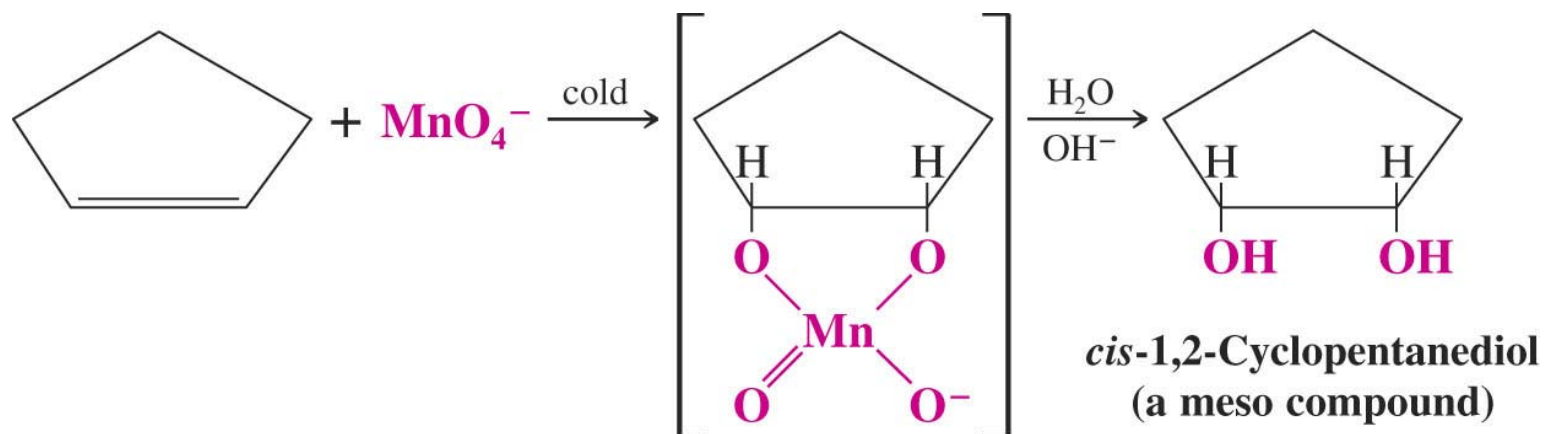
NMO is required





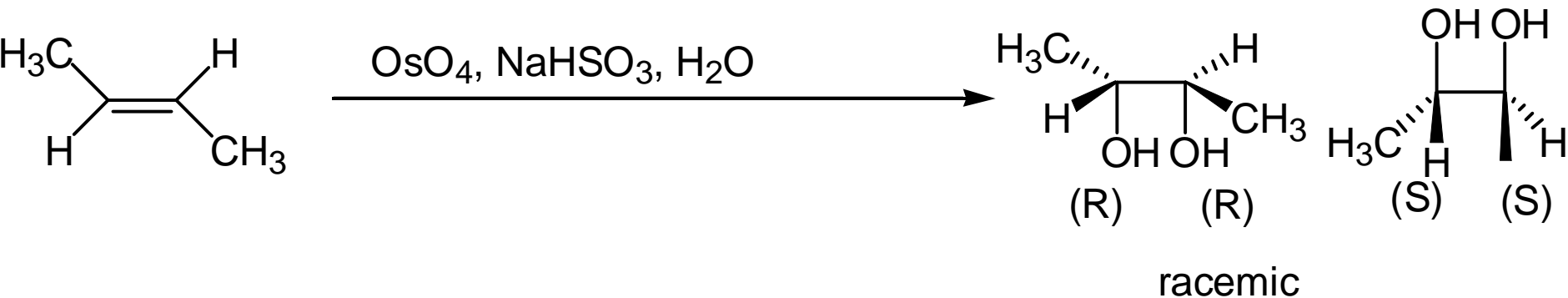
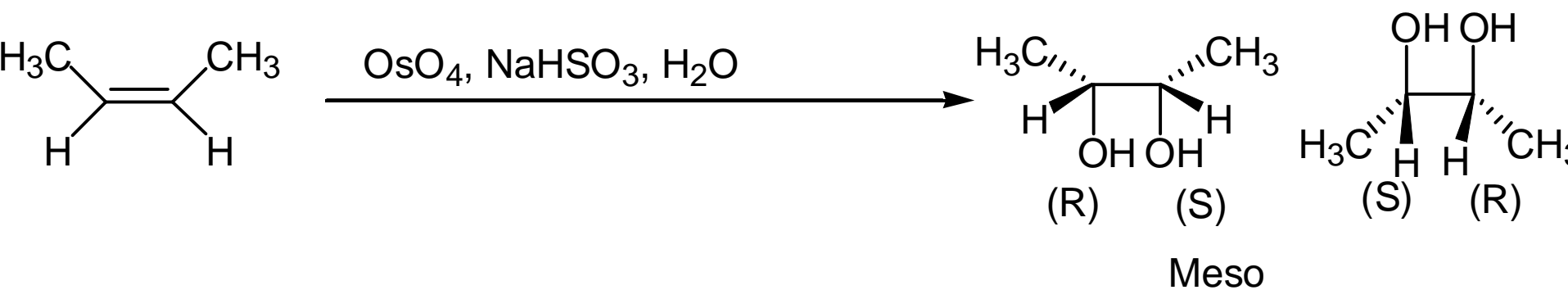
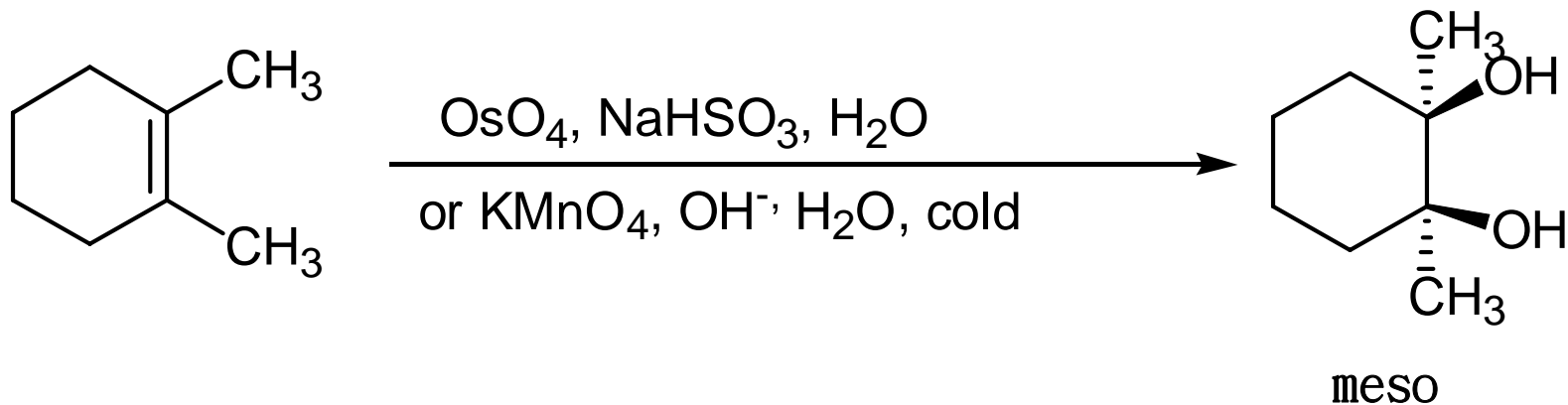
Ethene

1,2-Ethanediol
(ethylene glycol)

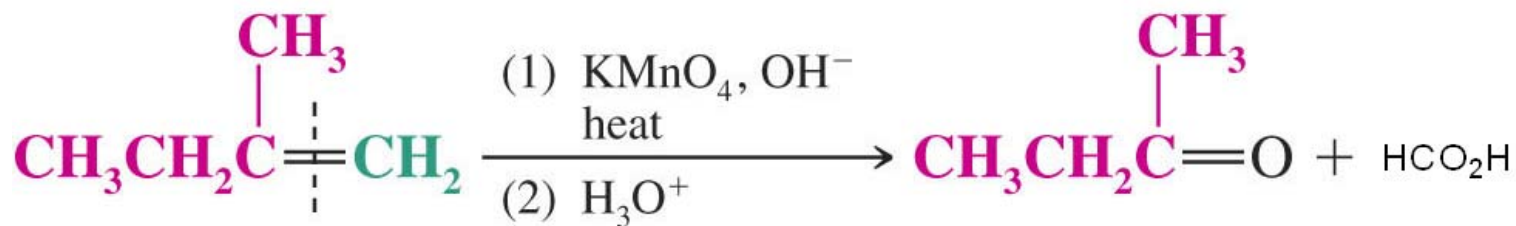
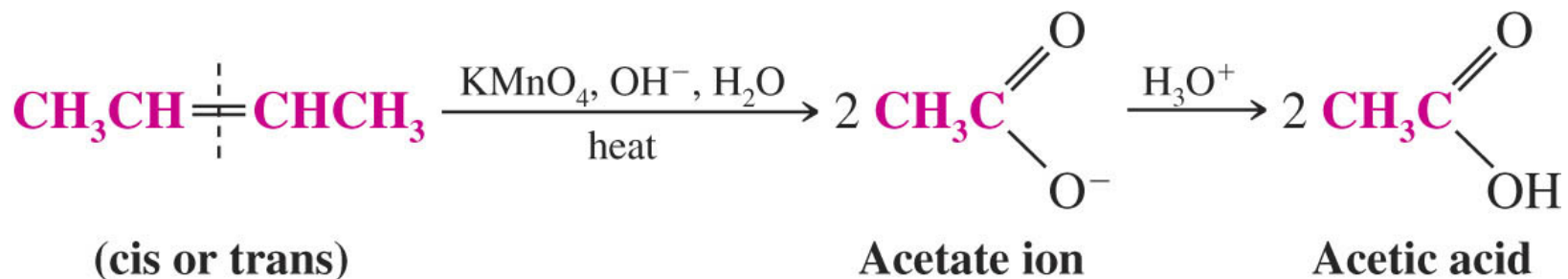


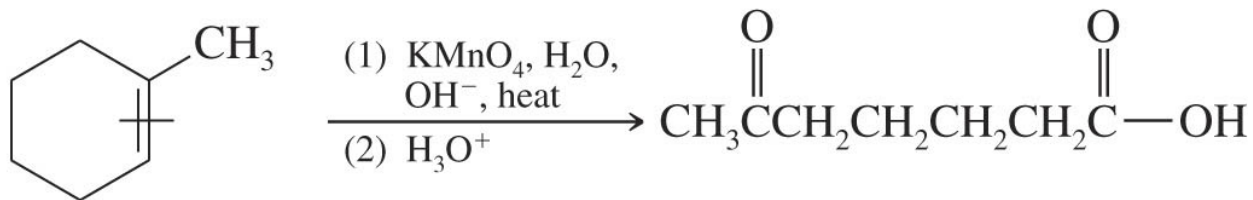
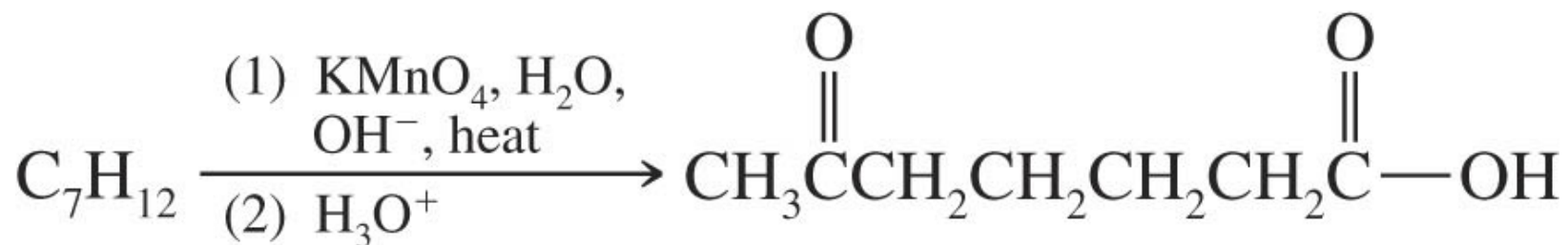
cis-1,2-Cyclopentanediol
(a meso compound)

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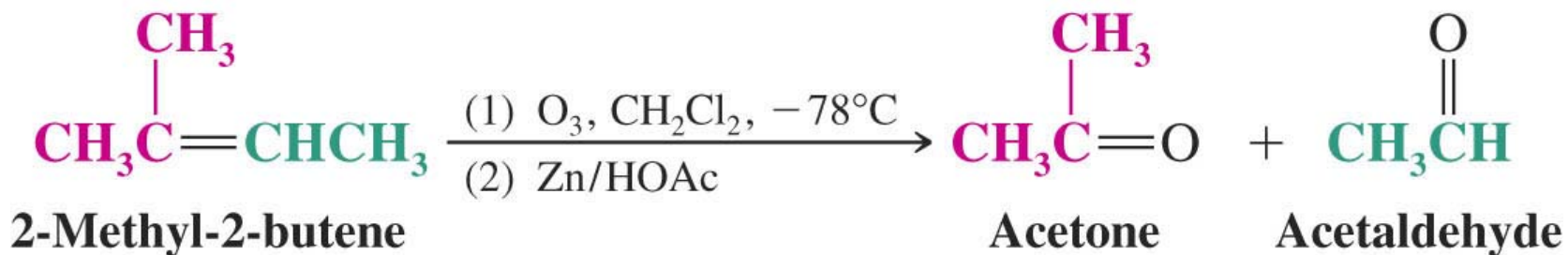


烯烴的Oxidative Cleavage of Alkenes

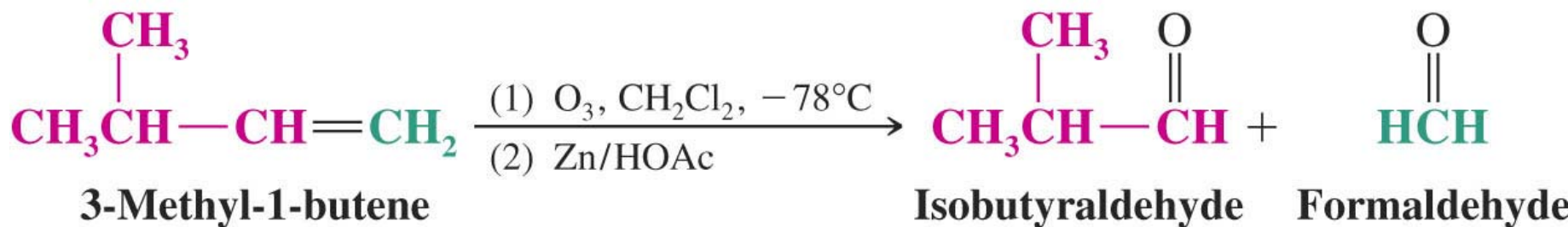




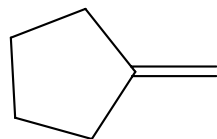
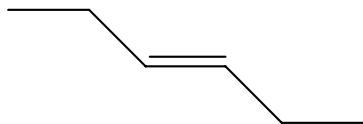
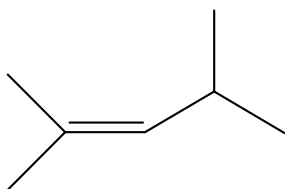
Unknown alkene
(1-methylcyclohexene)



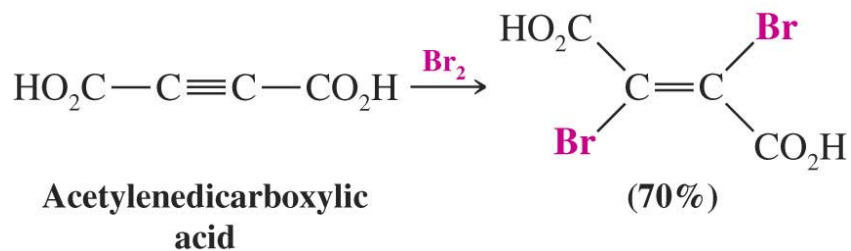
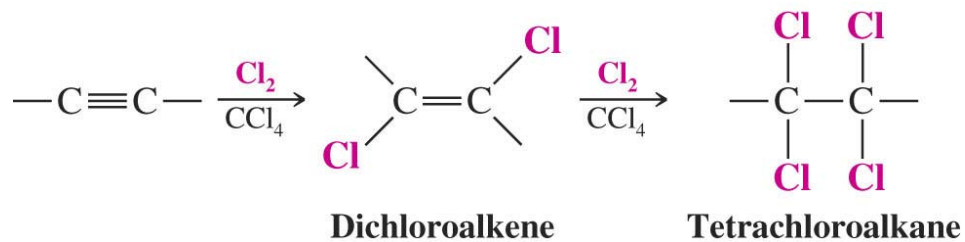
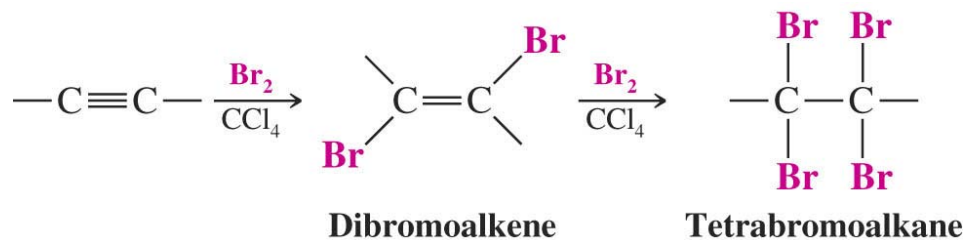
Ozonolysis

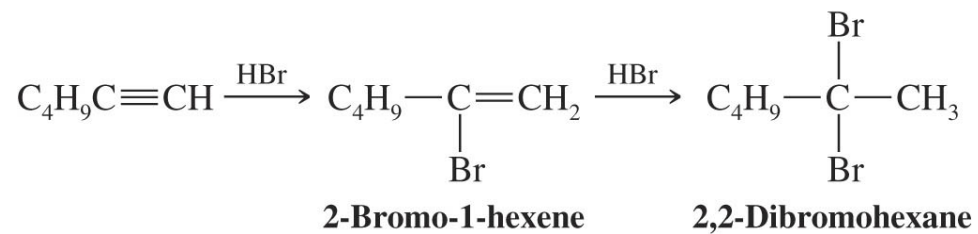


Exercise 365:



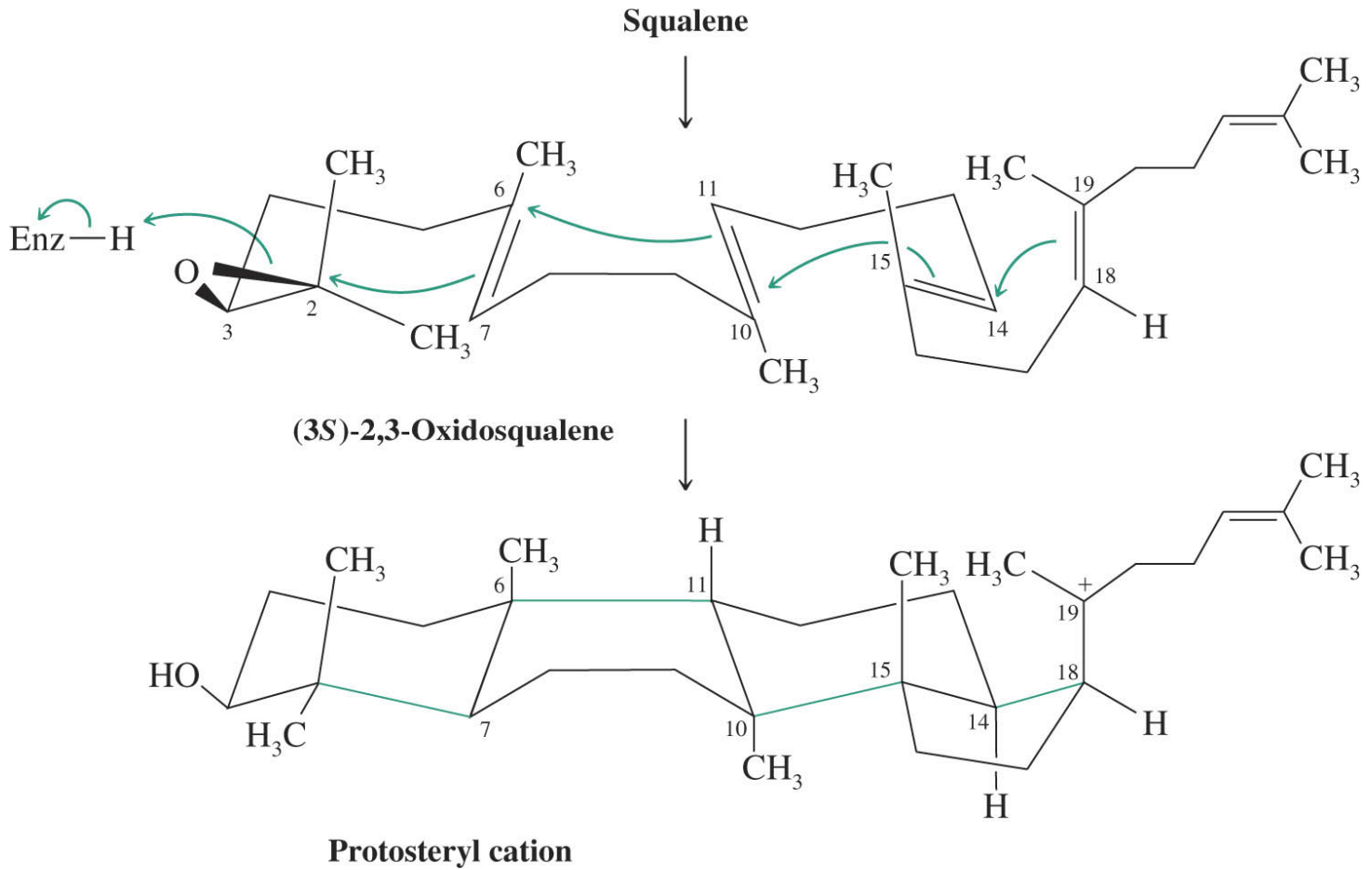
8) 炔烴的加成反應

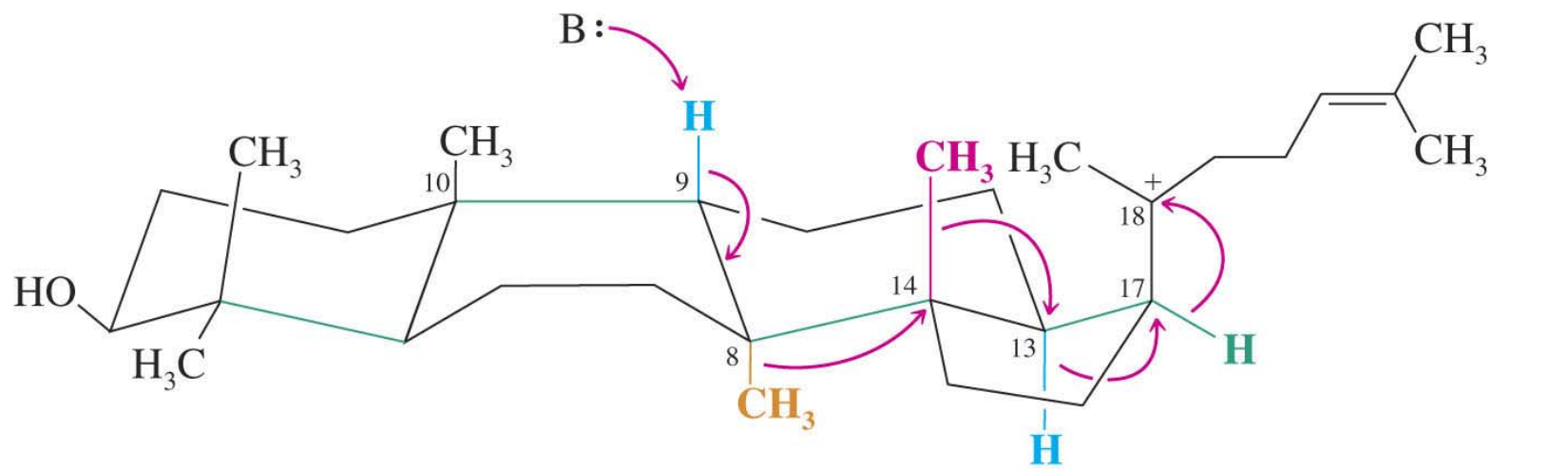




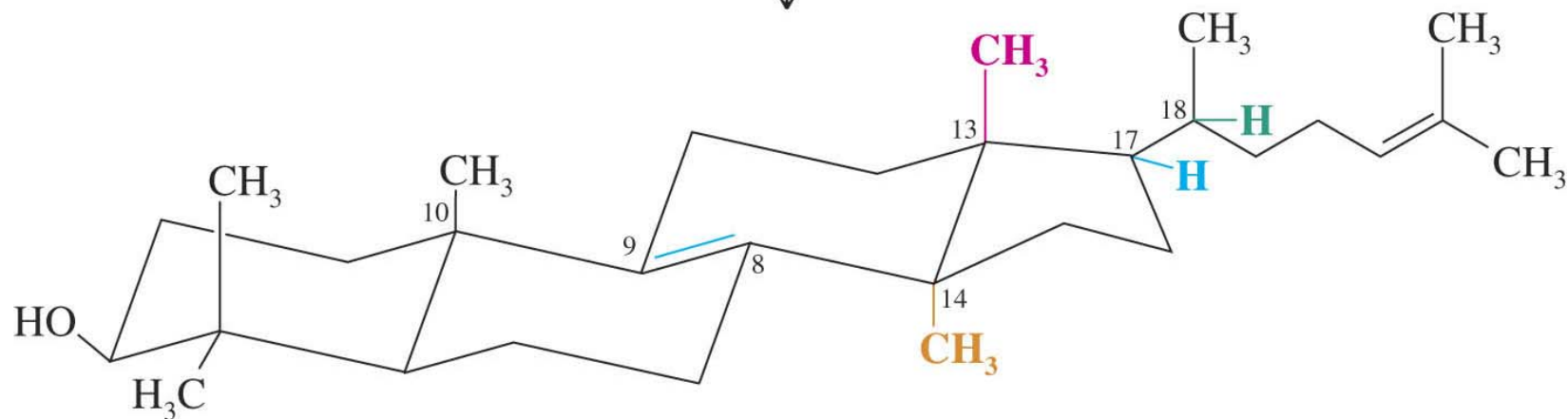
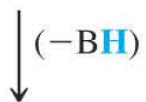
Markovnikov' rule

9) 烯烴的親核加成反應的生化反應實例



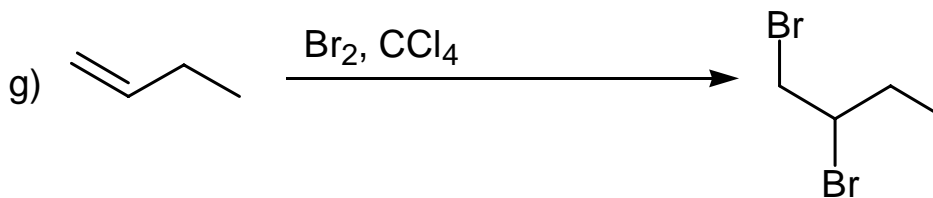
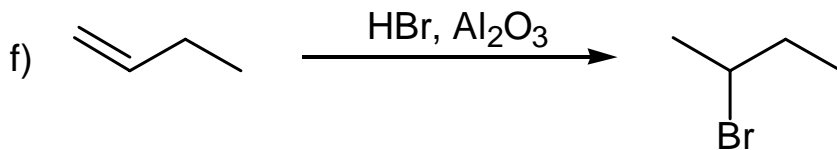
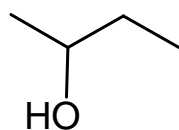
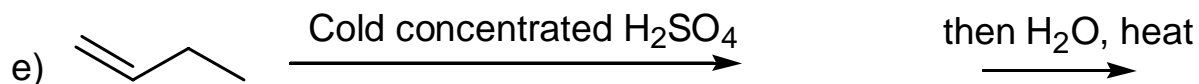
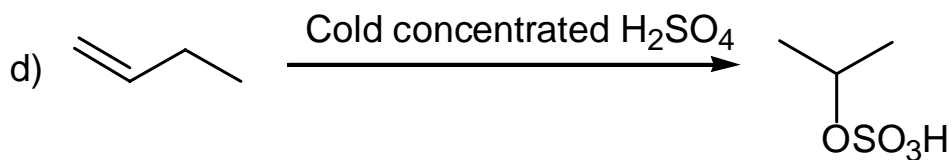
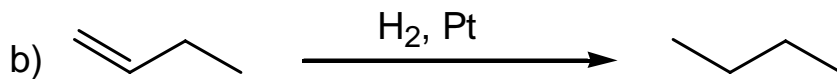
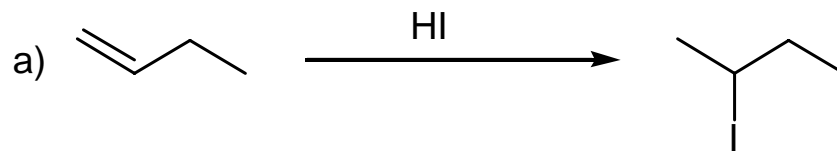


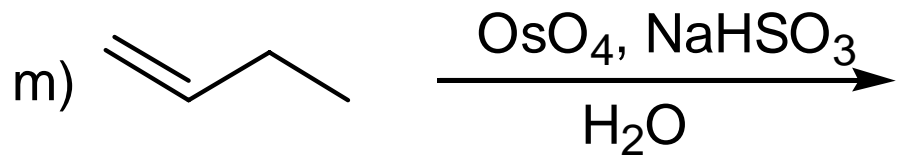
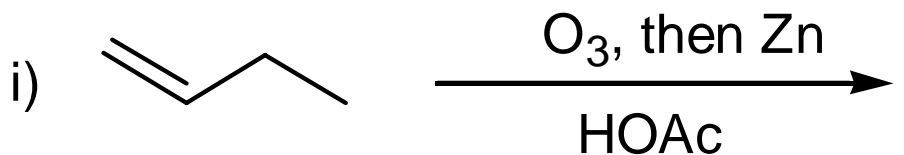
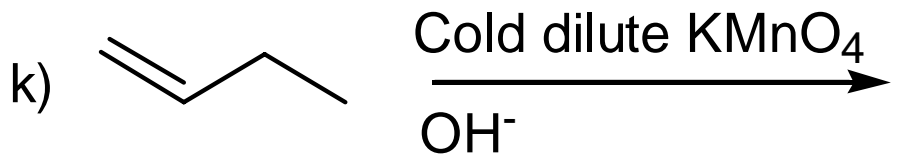
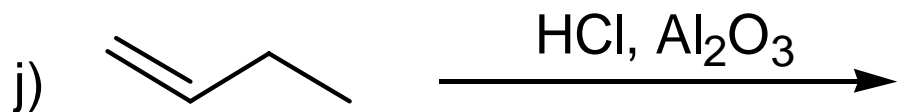
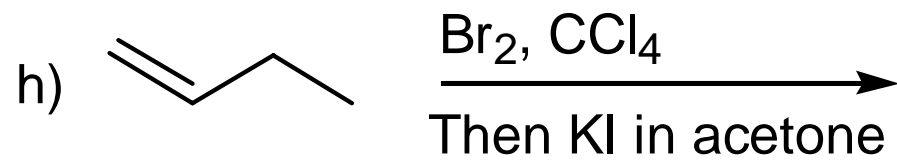
Protosteryl cation

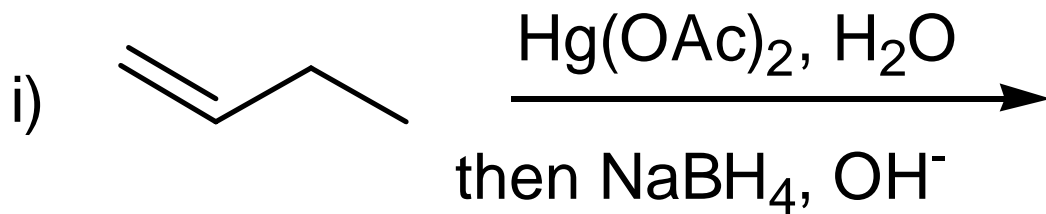
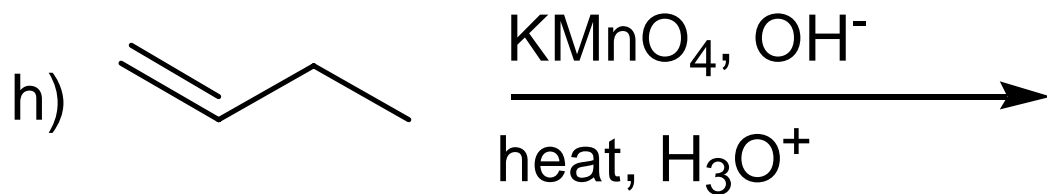


Lanosterol

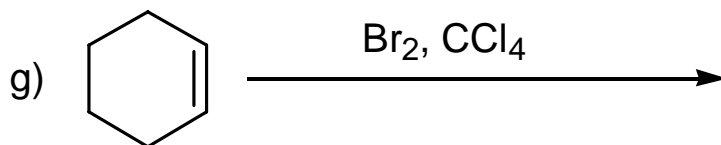
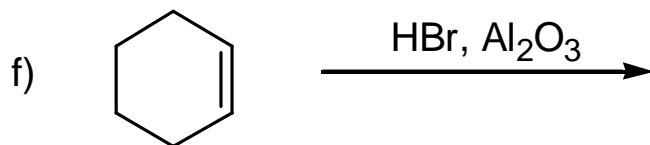
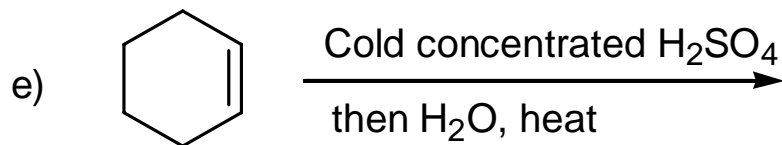
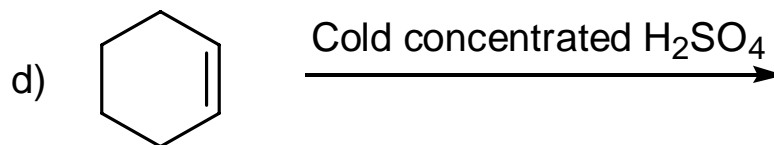
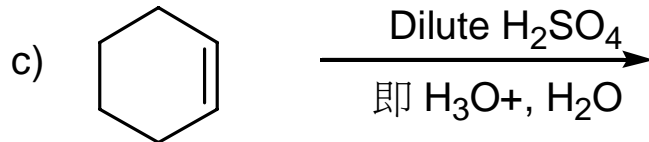
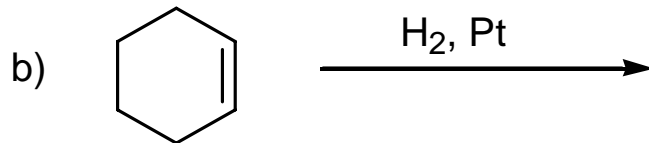
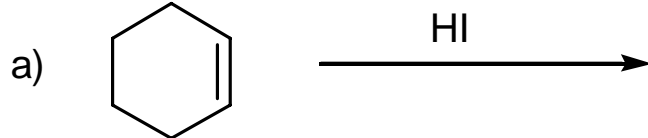
8.27 給出產物結構：

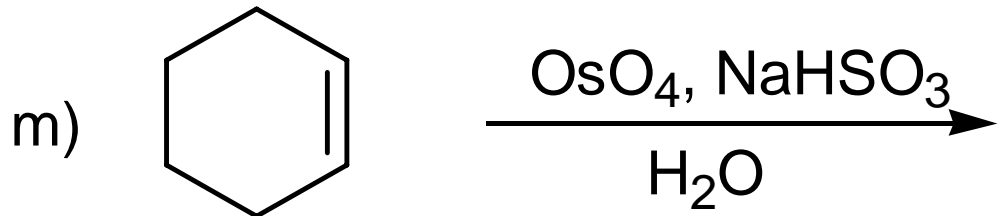
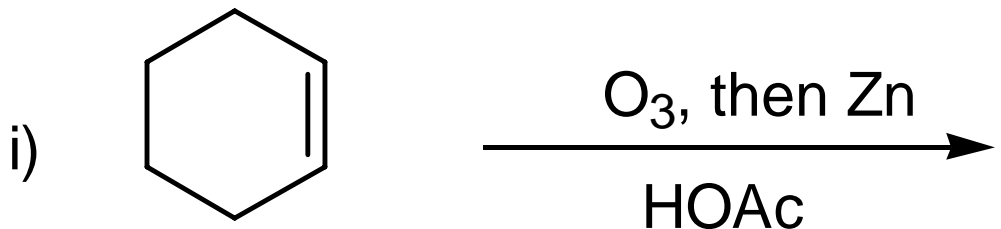
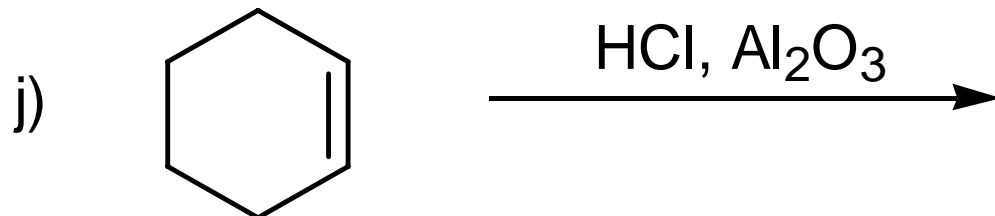
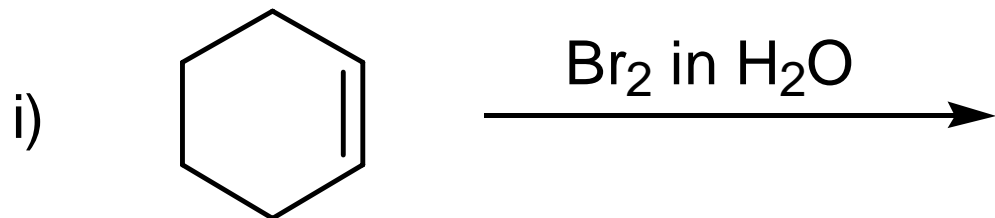


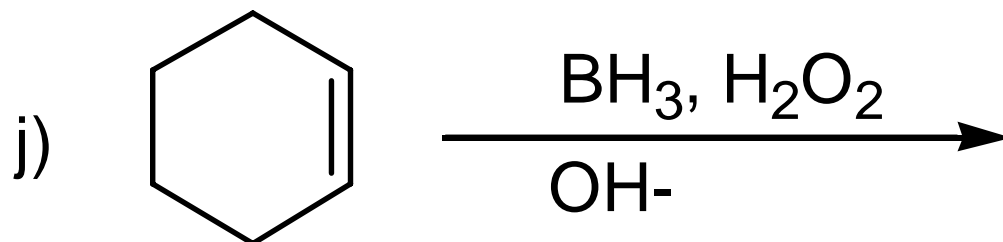
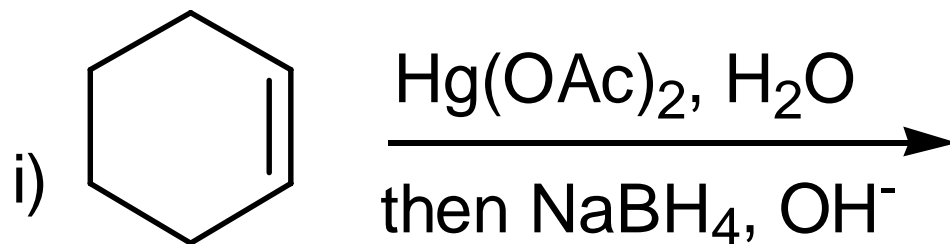
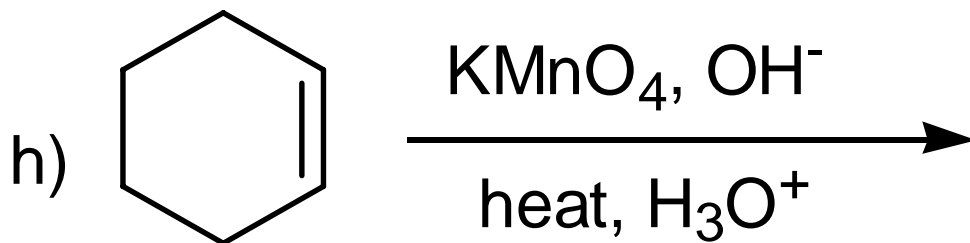




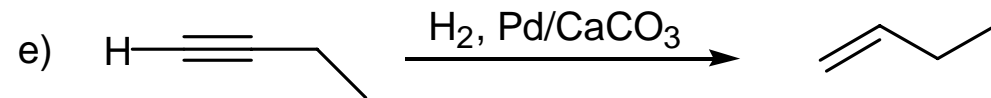
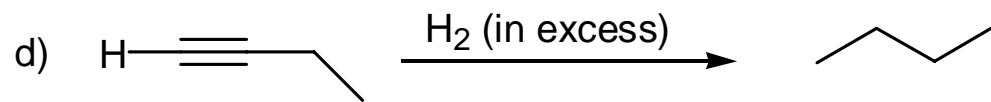
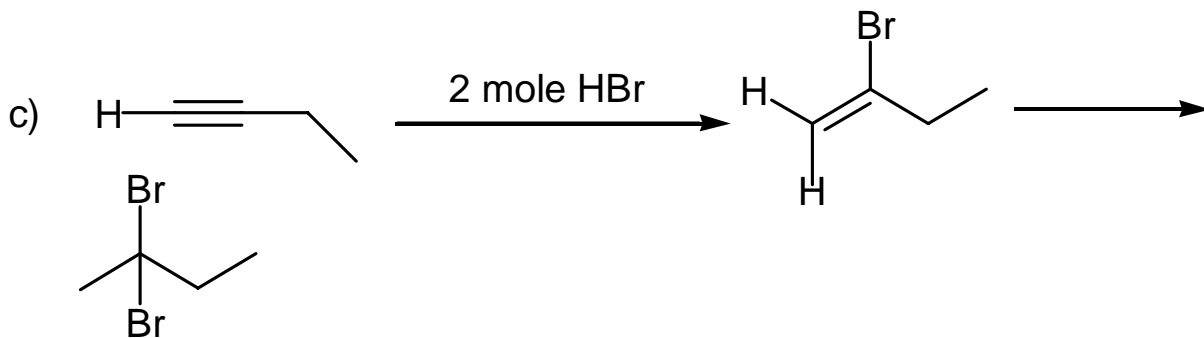
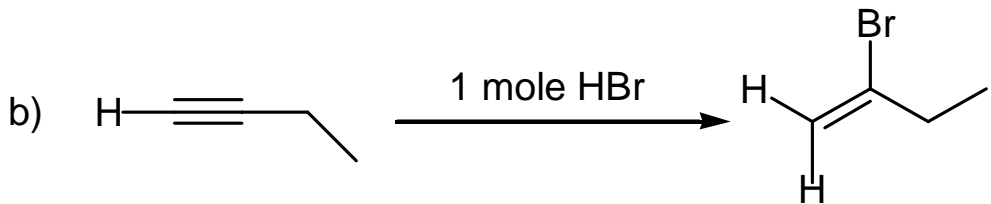
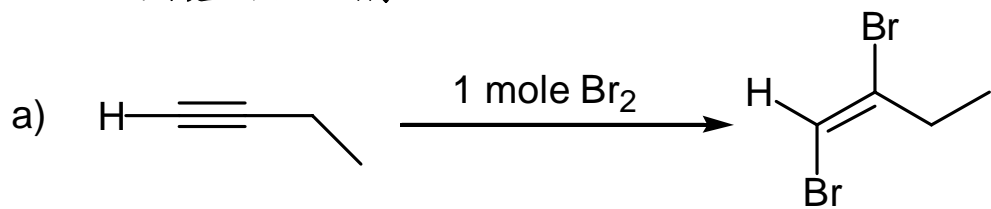
8.28 給出產物結構：

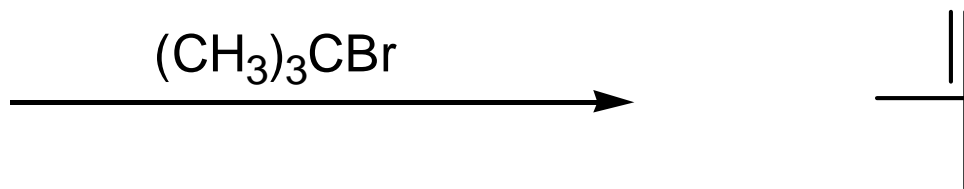
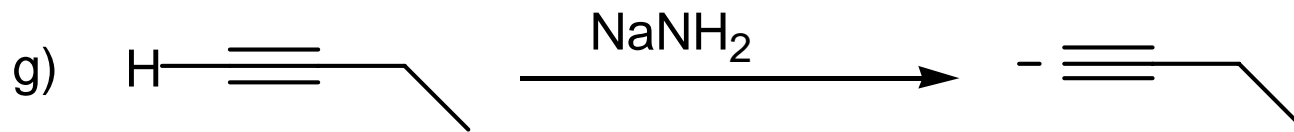
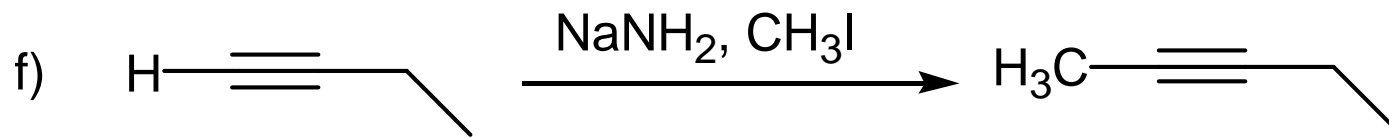




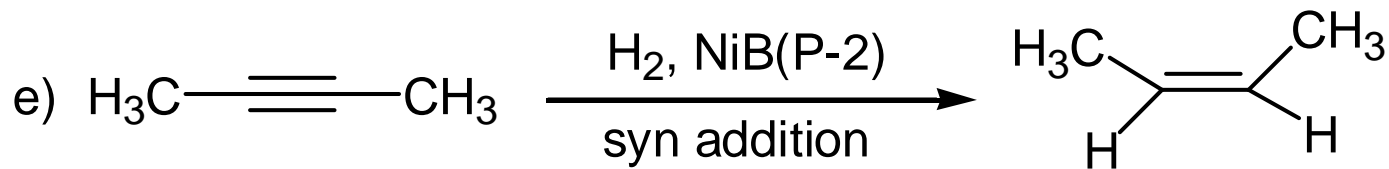
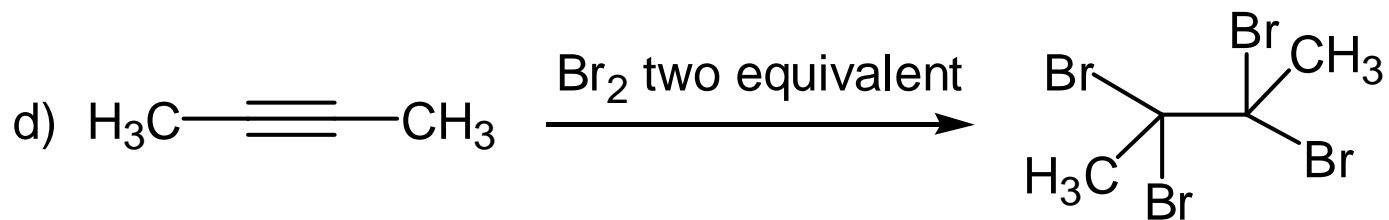
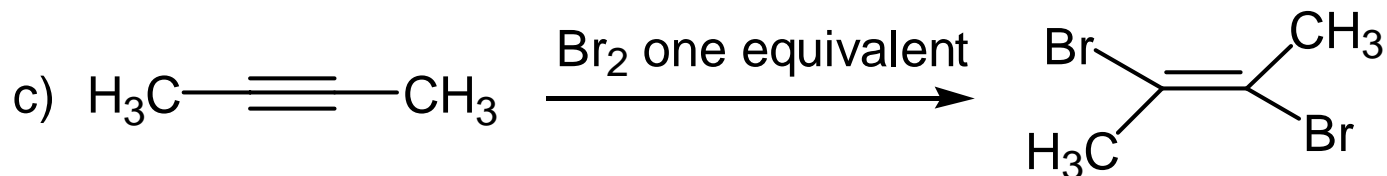
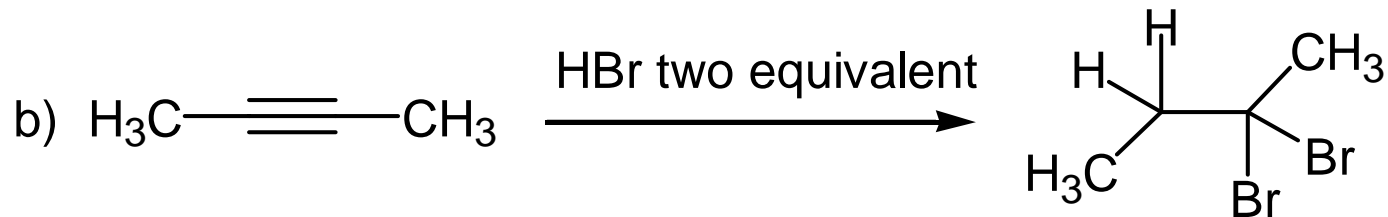
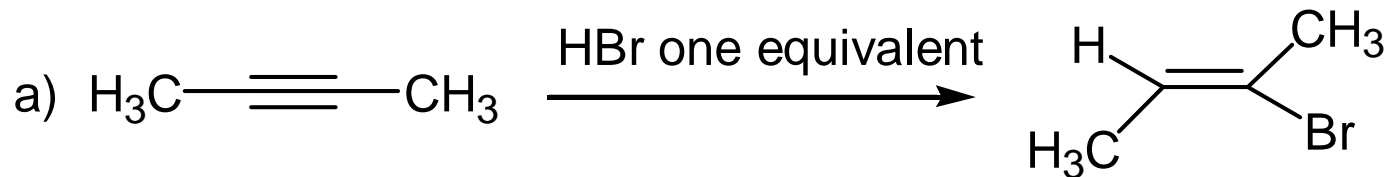


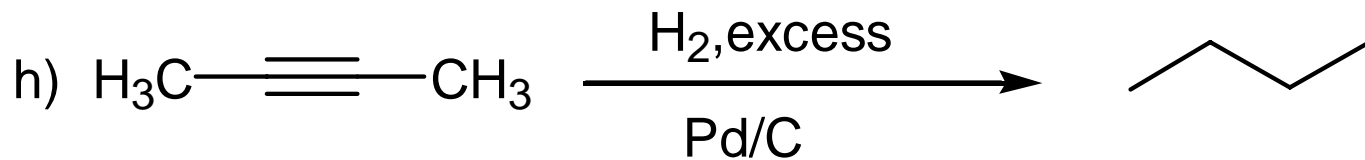
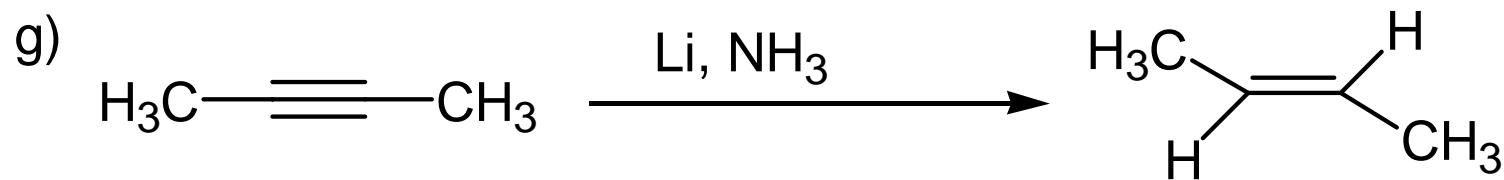
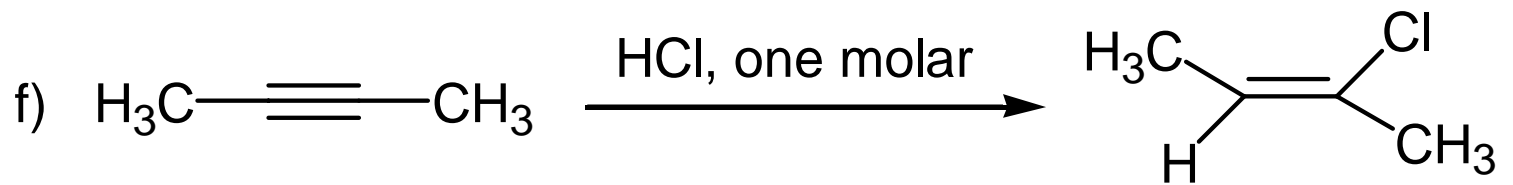
8.29 給出產物結構:



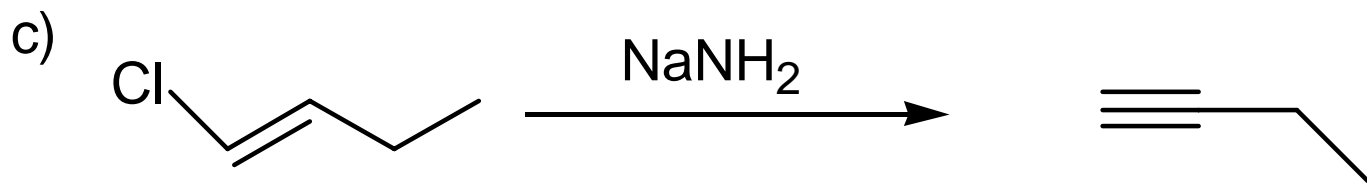
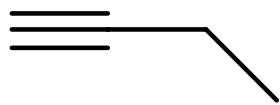
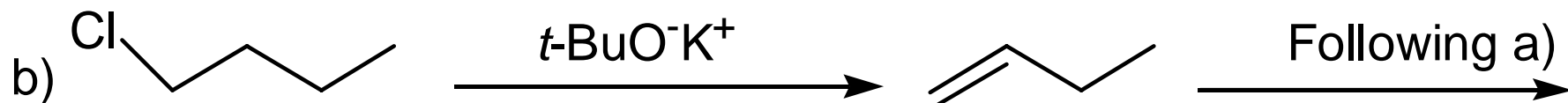
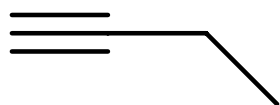
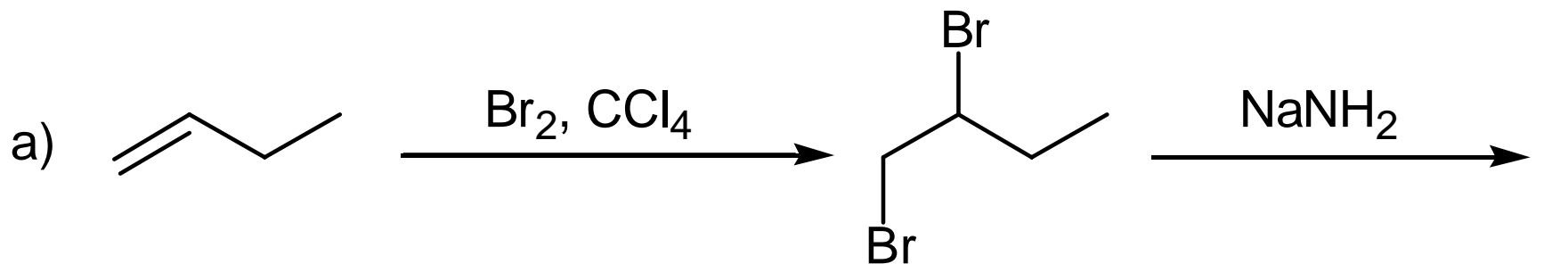


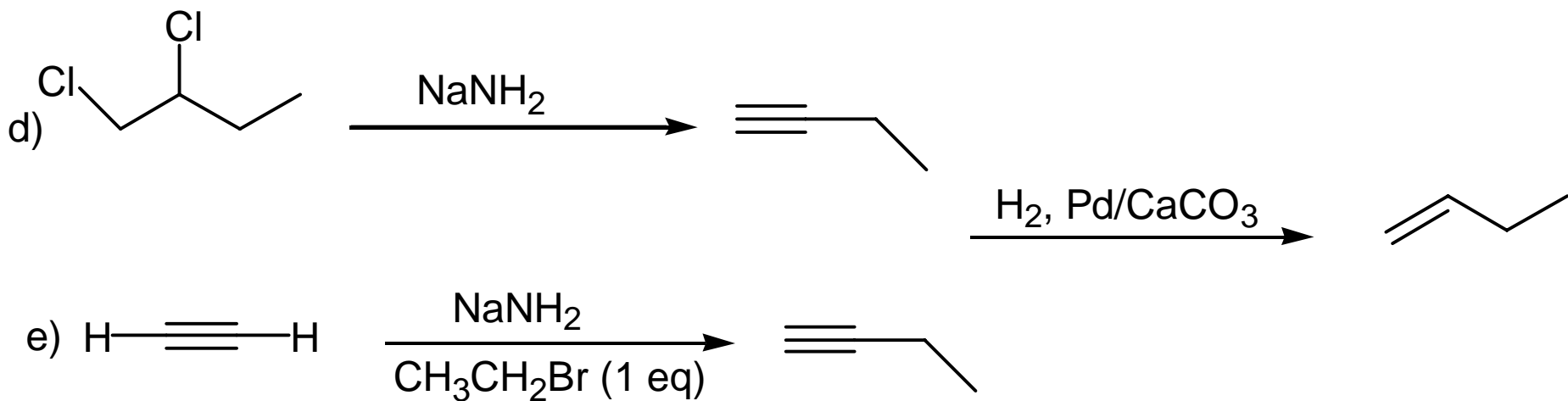
8.29 給出產物結構:



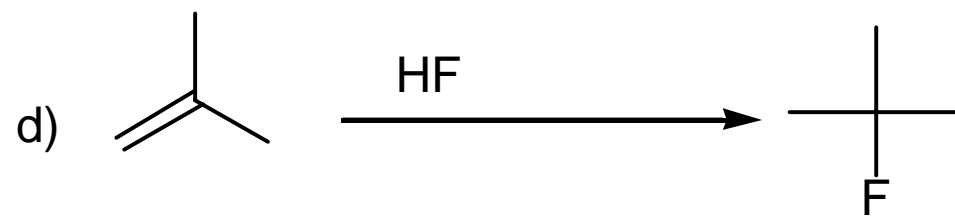
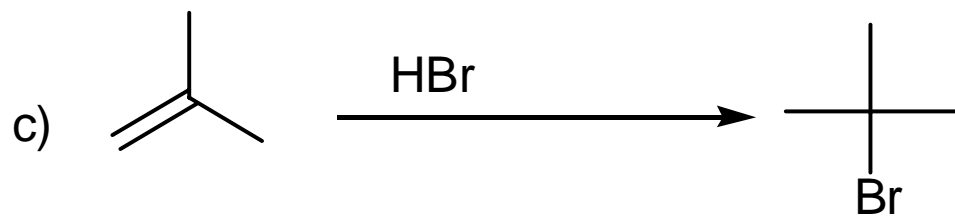
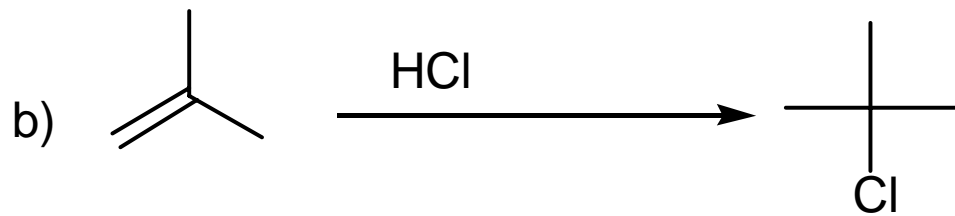
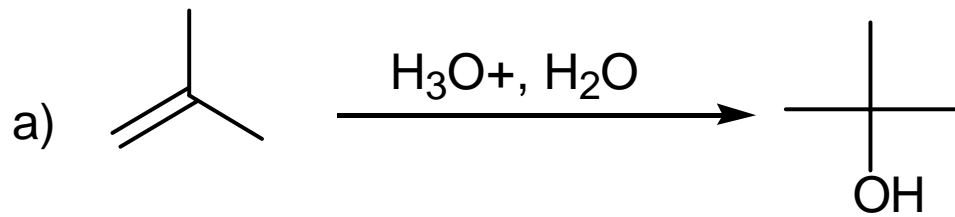


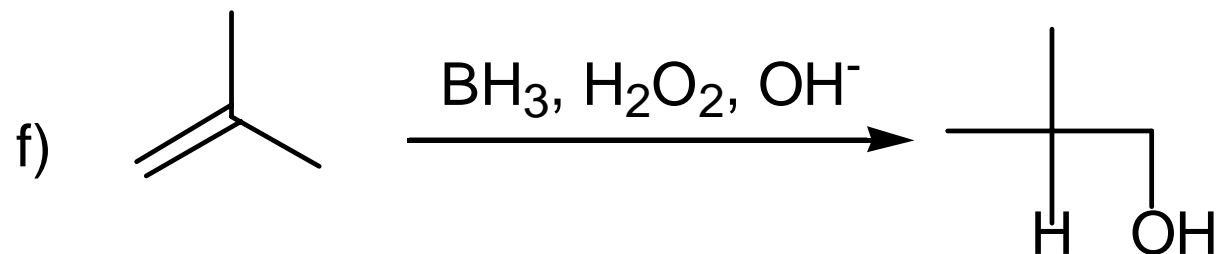
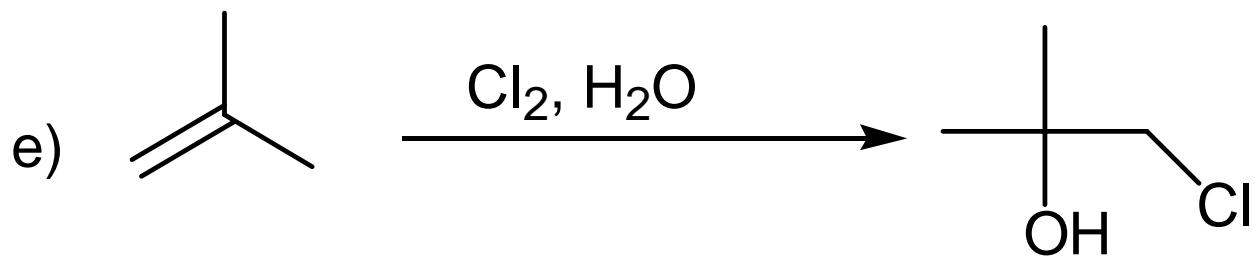
8.31 從下列化合物合成1-butyne



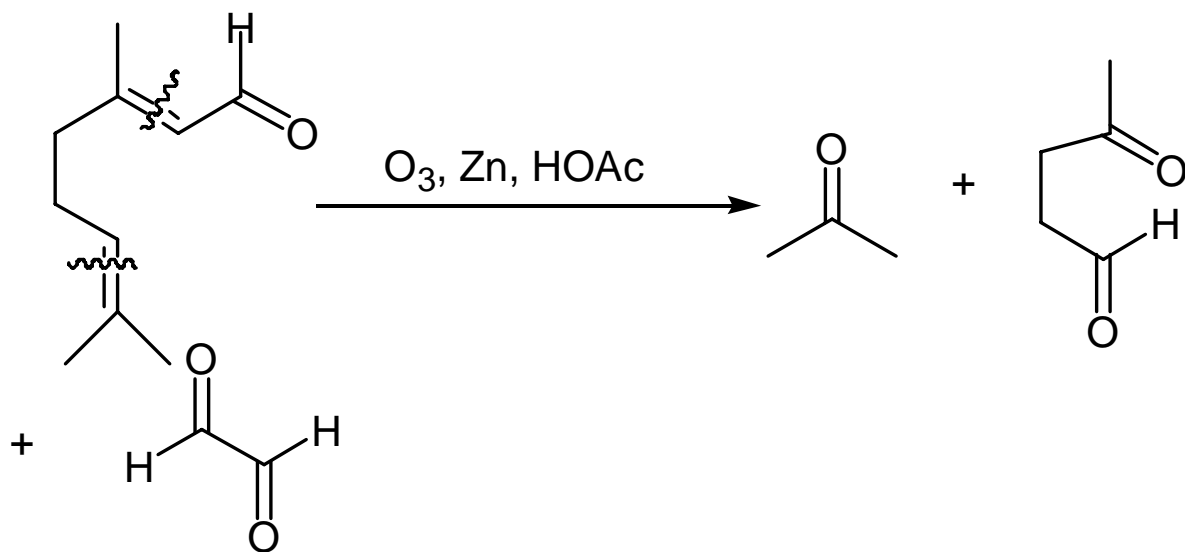


8.32 從2-methylpropene合成下列化合物





8. 38 給出產物結構:



8. 46 給出產物結構; 注明立體結構

