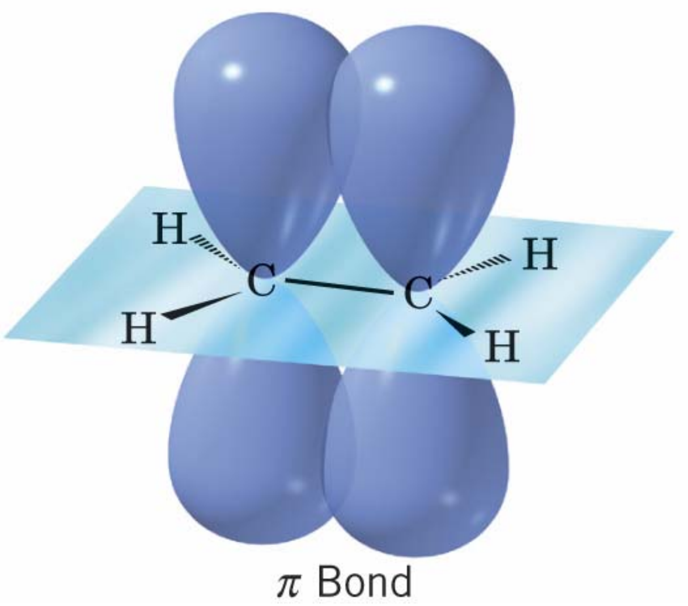
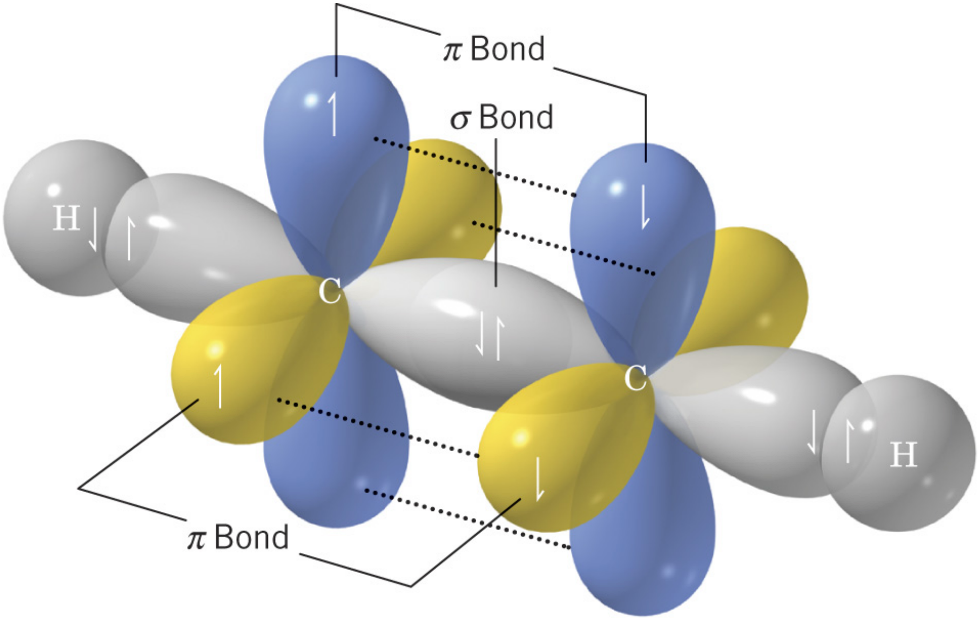
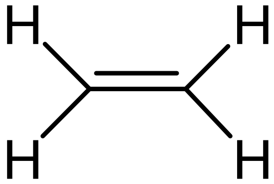
第7章 烯烴(alkenes)和炔烴(Alkynes)的性質，命名及主要合成方法



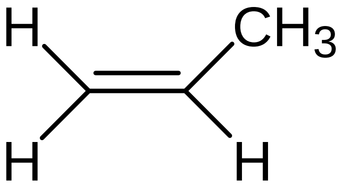


sp^2

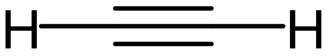
sp



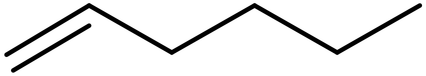
Ethene



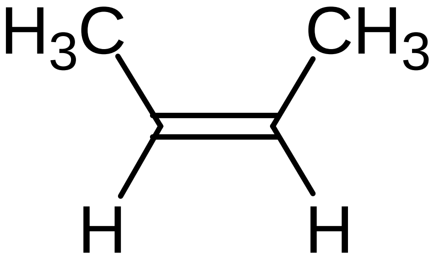
Propene



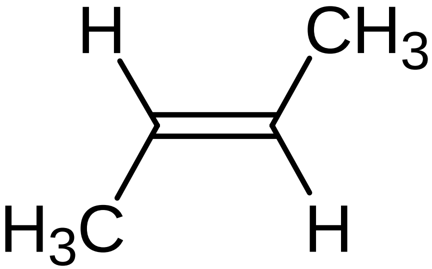
Ethyne



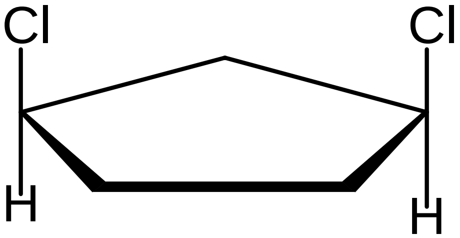
1-hexene



cis-2-butene



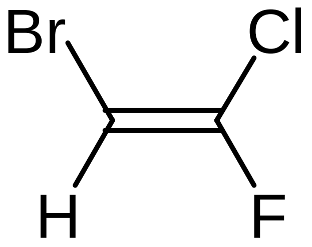
trans-2-butene



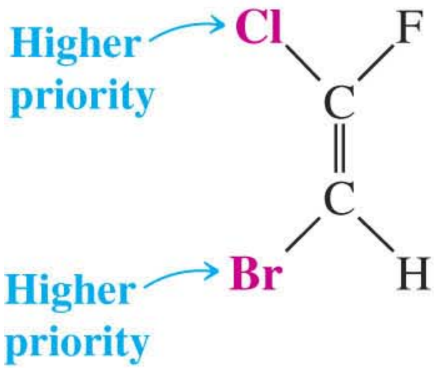
cis-1,5-dichlorocyclopentane

1）烯烴的*E*, *Z*-命名法

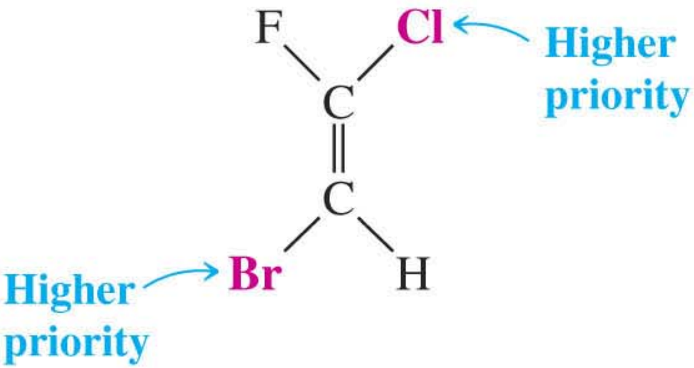
cis- *trans*- 系統對某些烯烴類化合物，不能給予明確的命名，例如：



在（E）-, （Z), 命名系統中，先確立雙鍵同一碳上基團的優先順序，再比較兩個雙鍵碳原子上的基團，優先基團在同側為*Z*, 反向為*E*:



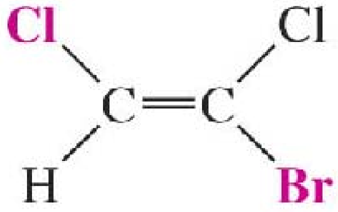
(*Z*)-2-Bromo-1-chloro-1-fluoroethene



(*E*)-2-Bromo-1-chloro-1-fluoroethene

Cl > F

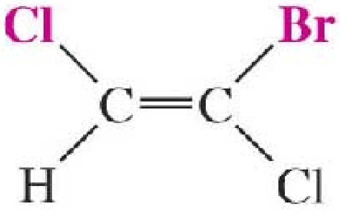
Br > H



(*E*)-1-Bromo-1,2-dichloroethene

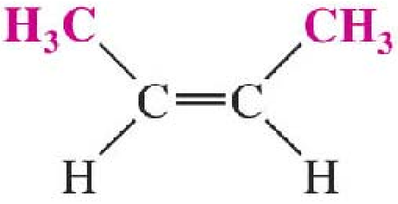
Cl > H

Br > Cl



(*Z*)-1-Bromo-1,2-dichloroethene

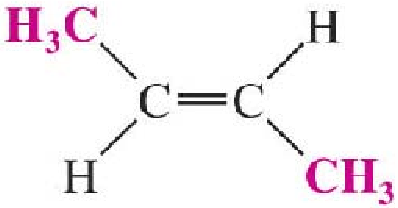
*cis*或*trans*類的烯烴亦可以*Z, E*系統來命名：



(*Z*)-2-Butene or (*Z*)-but-2-ene

(*cis*-2-butene)

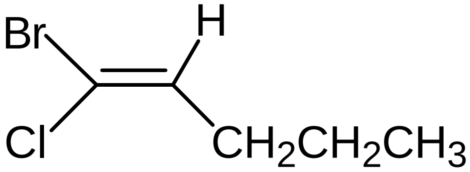
$CH_3 > H$



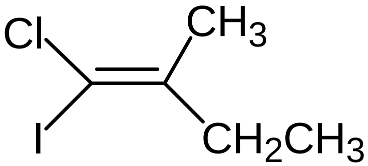
(*E*)-2-Butene or (*E*)-but-2-ene

(*trans*-2-butene)

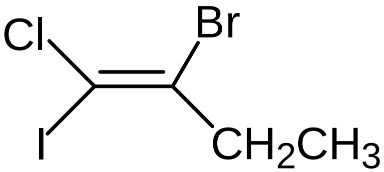
課堂練習，page 289:



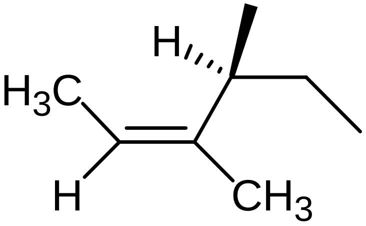
(*Z*)-1-bromo-1-chloro-1-pentene



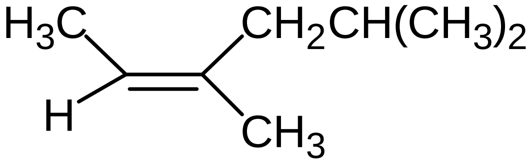
(*Z*)-1-1-chloro-1-iodo-2-methylbutene



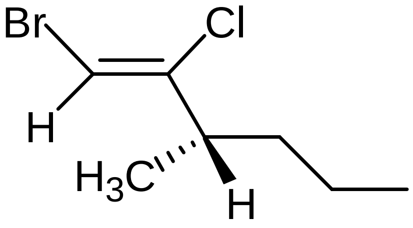
(*E*)-1-chloro-1-iodo-2-bromobutene



(*Z*),(S)-3,4-Dimethyl-2-hexene



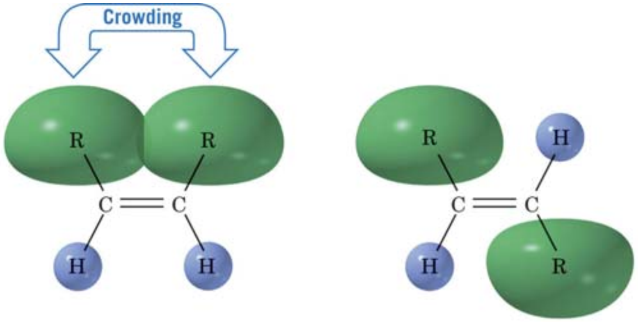
(*Z*)-3,5-Dimethyl-2-hexene



(*Z*),(S)-1-bromo-2-chloro-3-methyl-1-hexene

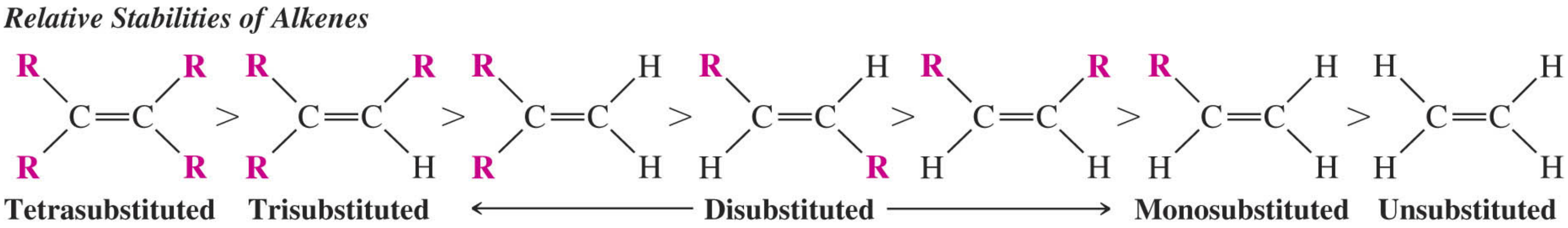
2）烯烴的相對穩定性

1）*cis* 與 *trans*的立體異構物相比較

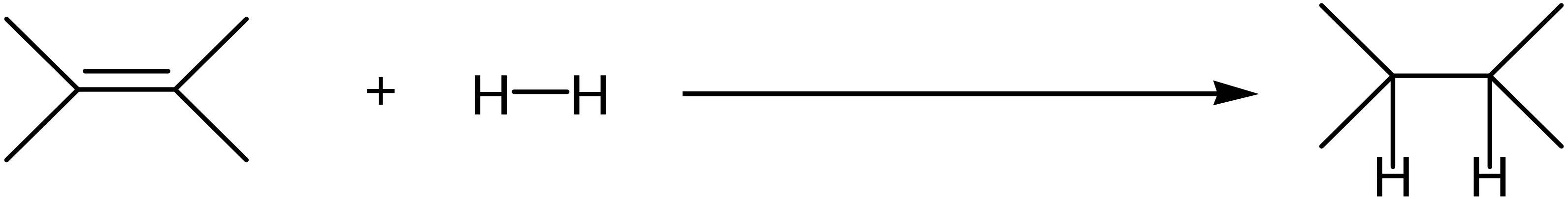


由於*cis*異構物有較大的crowing，故較*trans*異構物不穩定

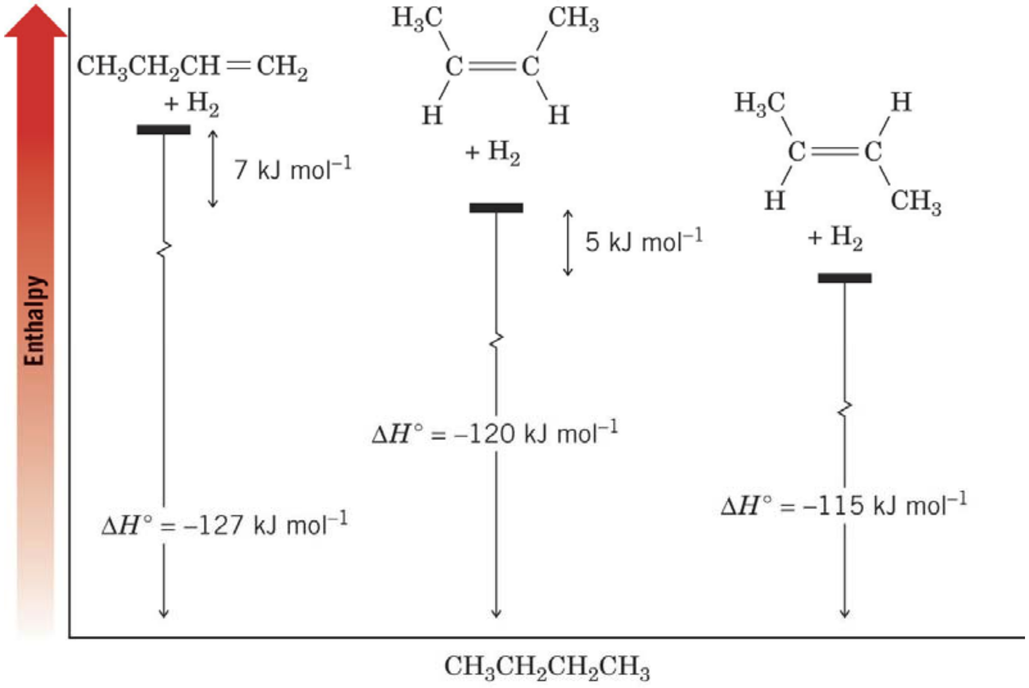
2）烯烴的穩定性:烯烴雙鍵上的烷基取代越多，烯烴的穩定性就越大。



烯烴穩定性的測量：heat of reaction

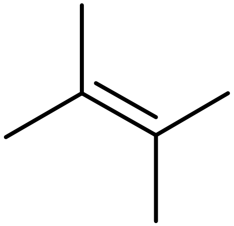


烯烴與氫的加成反應為放熱反應，放出的熱量越多，烯烴就越不穩定

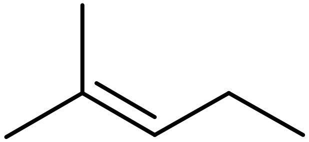


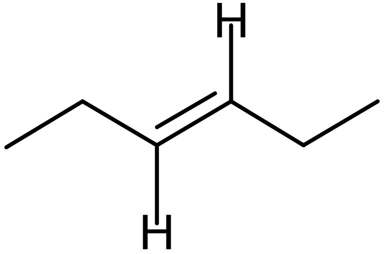
3）環烯烴的穩定性：小於五個碳的環烯烴只能以*cis*的形式存在。

課堂練習，page 291:比較烯烴的穩定性

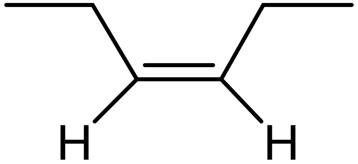


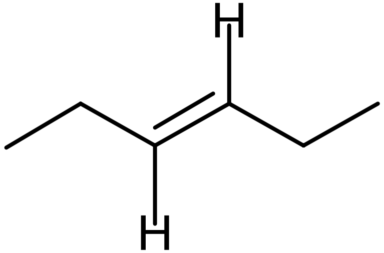
>



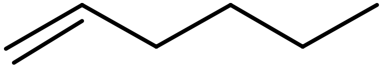


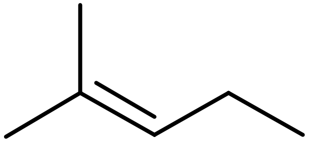
>



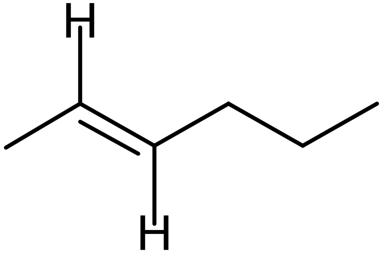


>



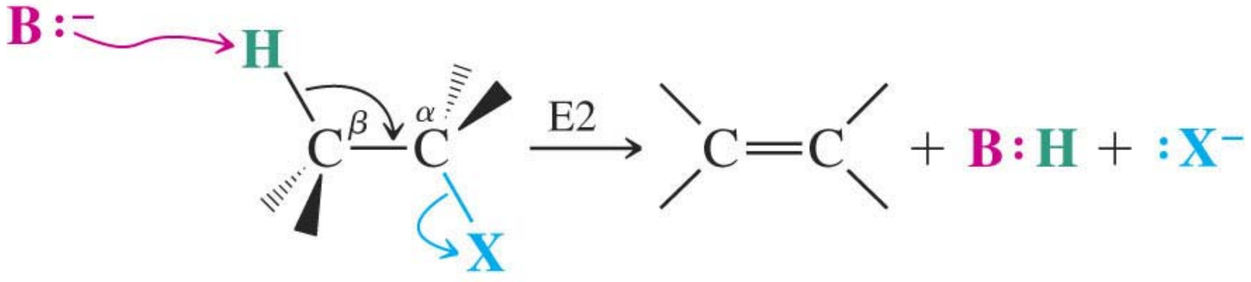


>

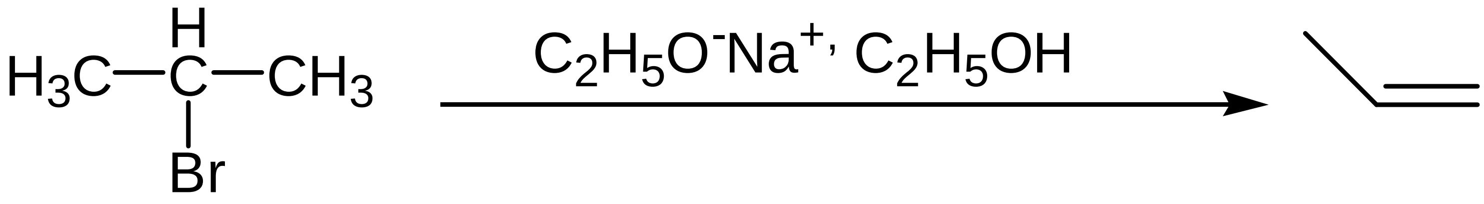


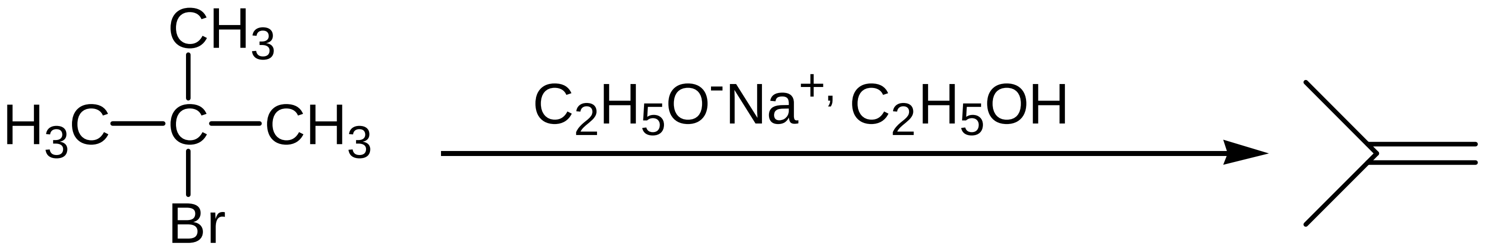
3）烯烴的製備

a）鹵代烷烴的E2消除反應

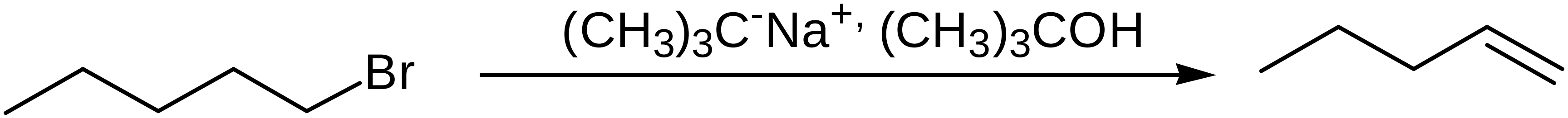


secondary and tertiary halides 一般來說比較適用於雙分子消除反應(E2)反應。$C_2H_5O^-Na^+/C_2H_5OH$為適合的反應條件

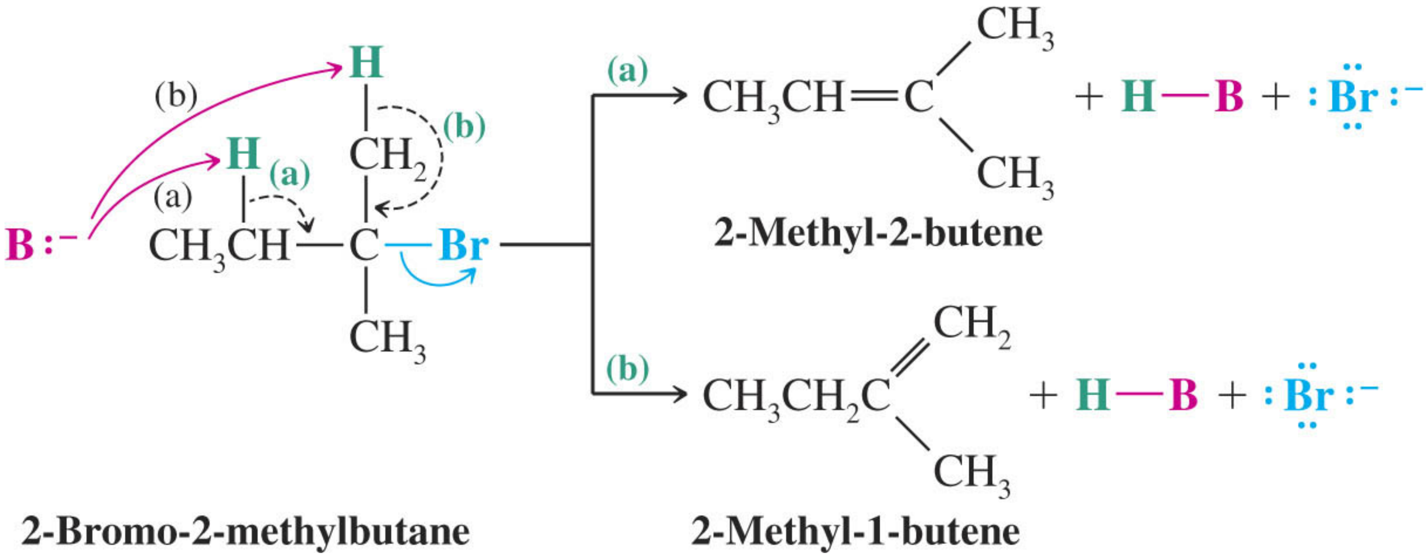




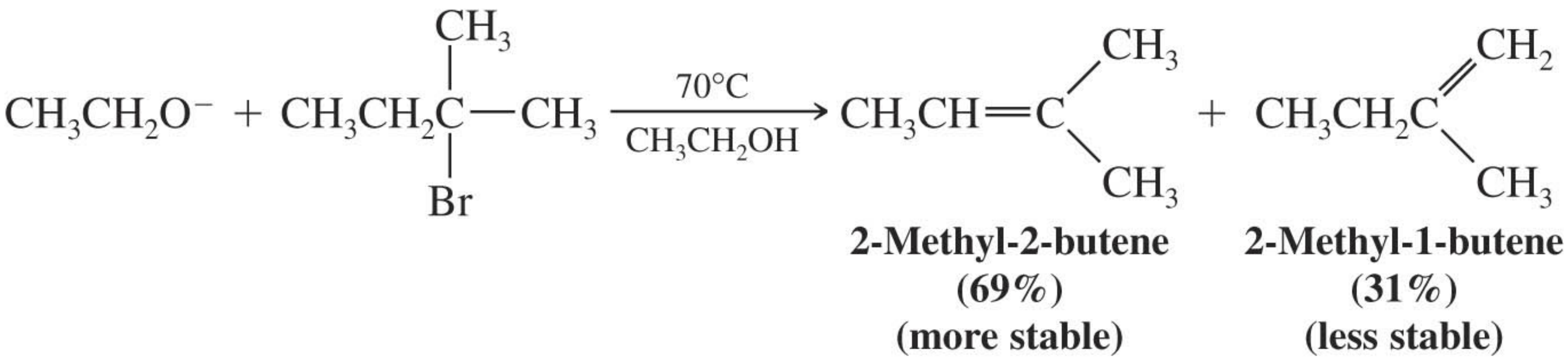
若反應物為一級鹵代烷烴，為了減小SN2反應的發生，需用大體積的鹼。（*t*-BuONa/*t*-BuOH）。

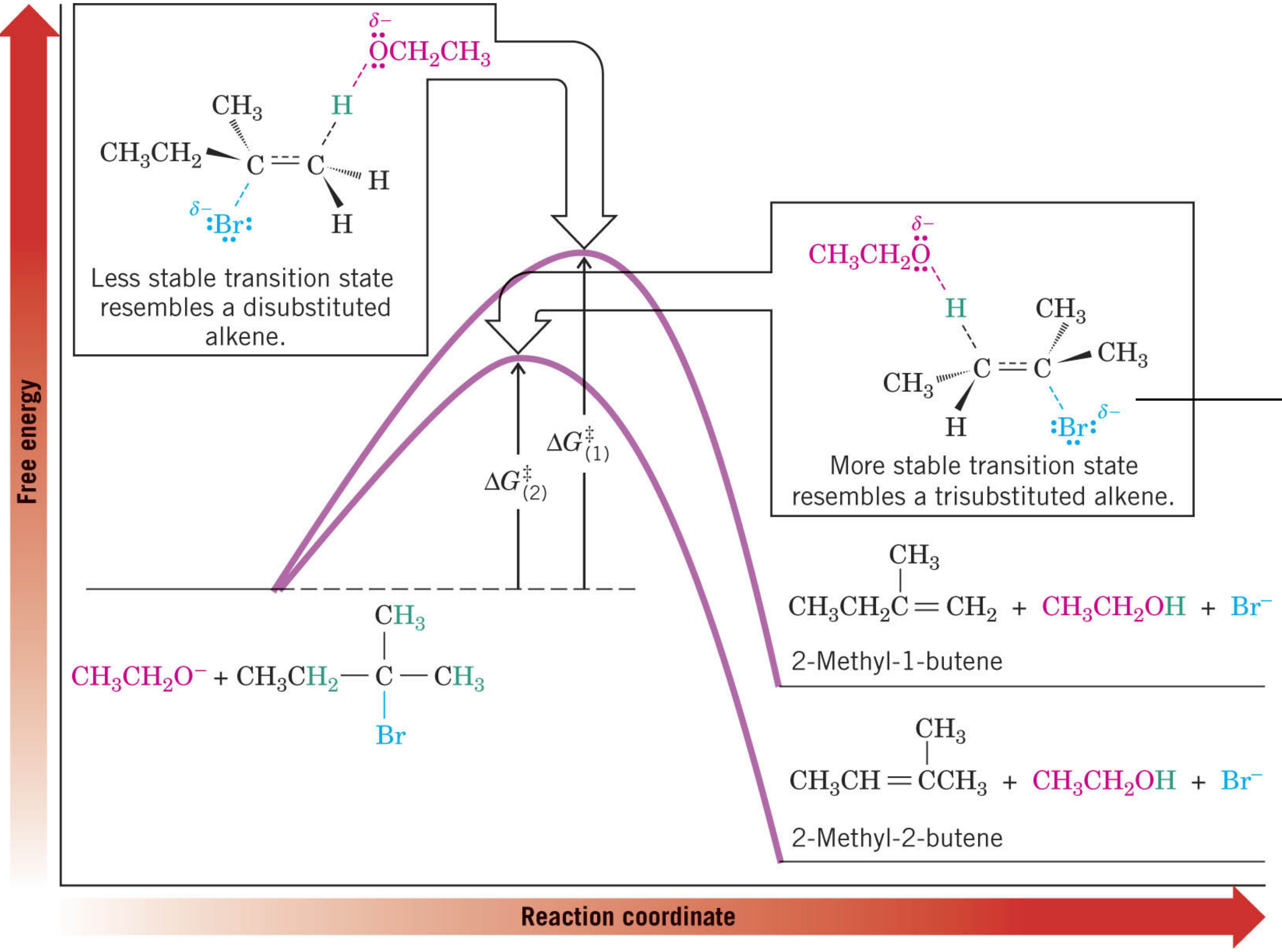


E2消除反應的Zaitsev’s rule:



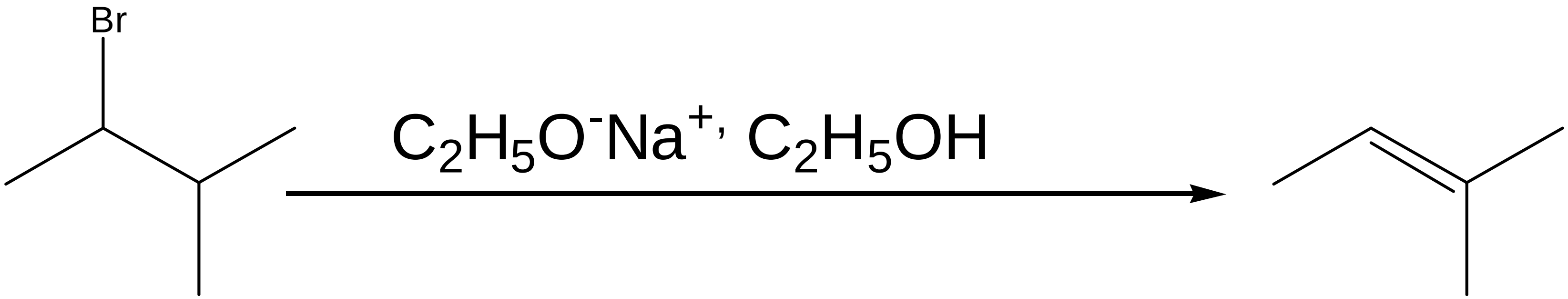
當在消除反應中有兩個可能的烯烴產物時，在用以小體積鹼的情況下；有較多烷基取代的烯烴的形成佔優勢。



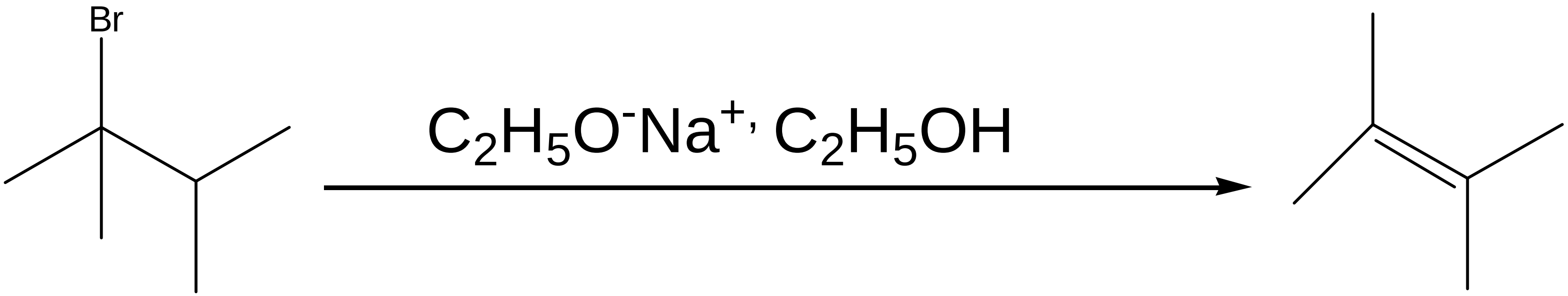


過渡態的能量較低，有較低的activation energy.

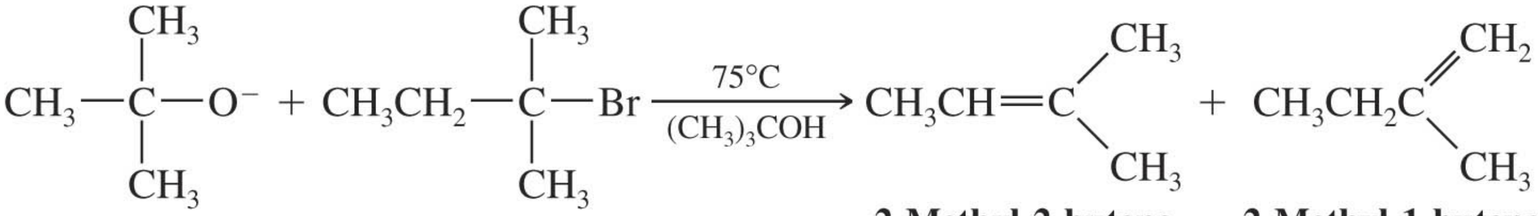
課堂練習，page 295:以判定主產物之結構：



$C_2H_5O^-Na^+, C_2H_5OH$



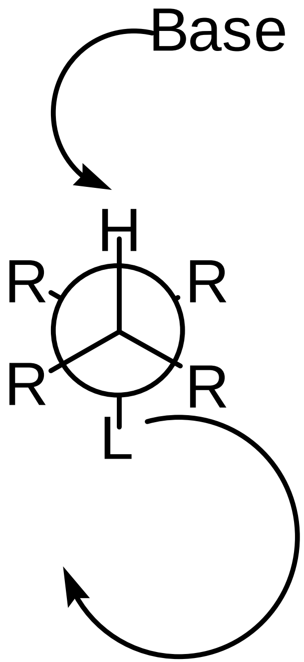
$C_2H_5O^-Na^+, C_2H_5OH$

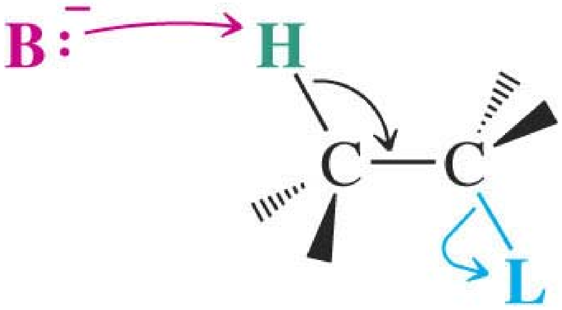


2-Methyl-2-butene
(27.5%)
(more substituted)

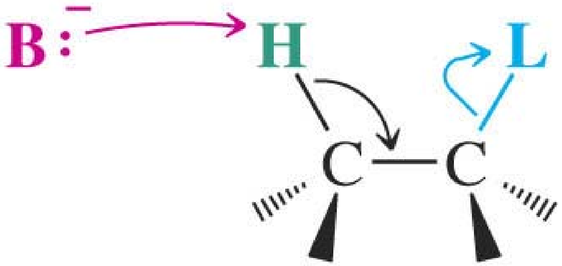
2-Methyl-1-butene
(72.5%)
(less substituted)

E2反應中的立體化學:四個原子(H-C-C-L)必須在同一平面上;被稱為coplanarity.
其中，anti coplanar比syn coplanar更佔優勢:



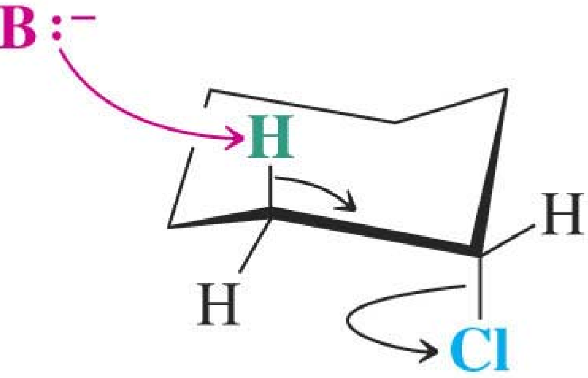


**Anti coplanar
transition state
(preferred)**

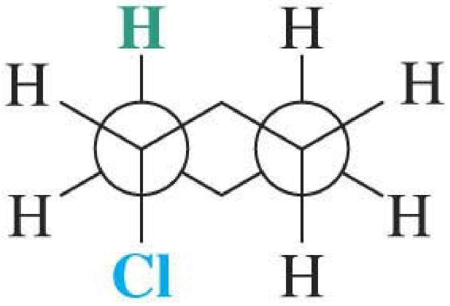


**Syn coplanar
transition state
(only with certain
rigid molecules)**

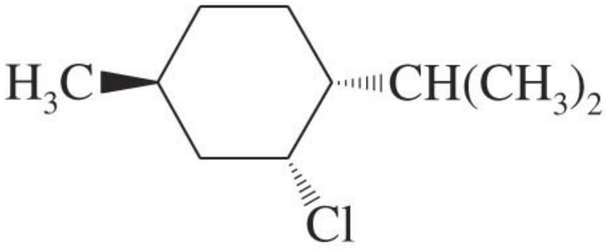
在環狀halides中，離去基團，被鹼所攻擊的氫必須處在diaxial的位置:



Here the β-hydrogen and the chlorine are both axial. This allows an anti coplanar transition state.

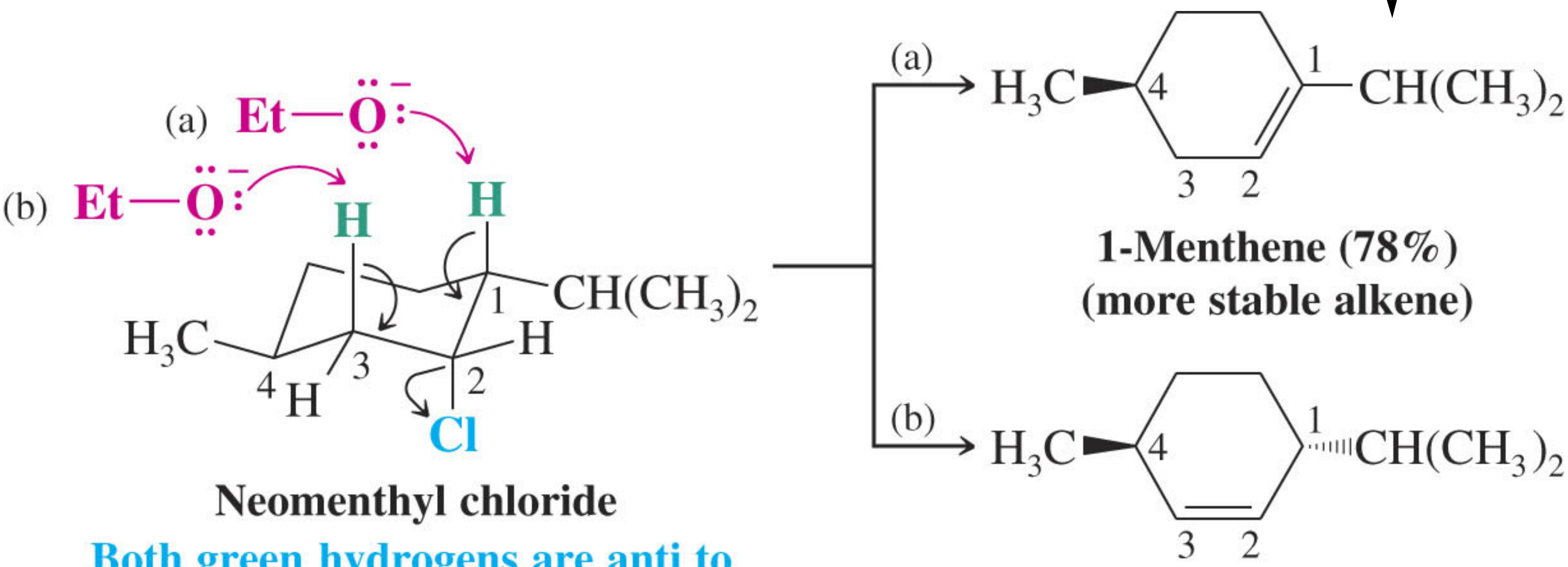


A Newman projection formula shows that the β hydrogen and the chlorine are anti coplanar when they are both axial.



Neomenthyl chloride

符合Zaitsev’s rule

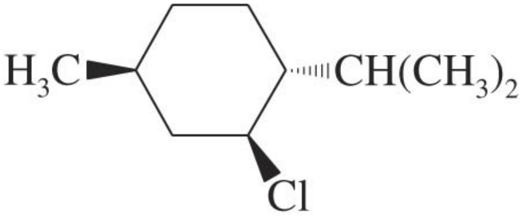


Neomenthyl chloride

Both green hydrogens are anti to the chlorine in this the more stable conformation. Elimination by path (a) leads to 1-menthene; by path (b) to 2-menthene.

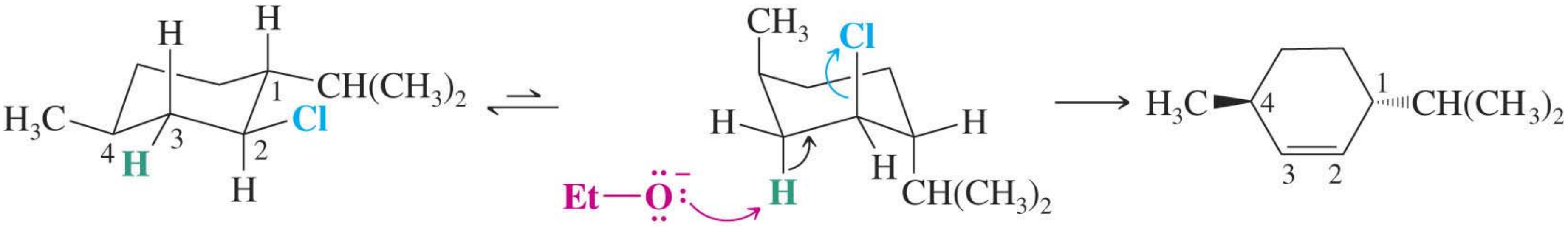
1-Menthene (78%)
(more stable alkene)

2-Menthene (22%)
(less stable alkene)



Menthyl chloride

反應較上一個化合物慢很多



Menthyl chloride
(*more stable conformation*)

Elimination is not possible for this conformation because no hydrogen is anti to the leaving group.

Menthyl chloride
(*less stable conformation*)

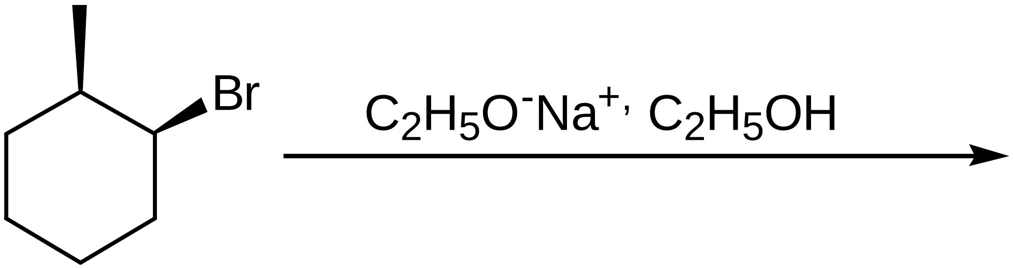
Elimination is possible from this conformation because the green hydrogen is anti to the chlorine.

2-Menthene (100%)

Higher activation energy

課堂練習，page 298:解釋在E2消除反應中，cis-1-bromo-4-tertbutylcyclohexane比其trans的立體異構物快很多。

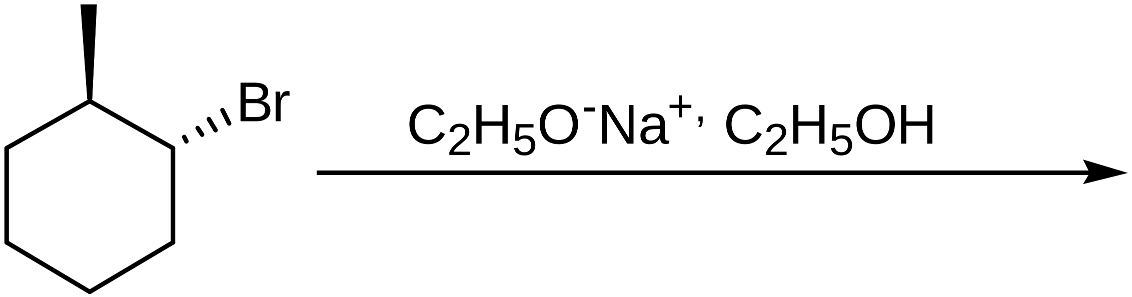
給出生成物之結構



$C_2H_5O^-Na^+$, C_2H_5OH

Major

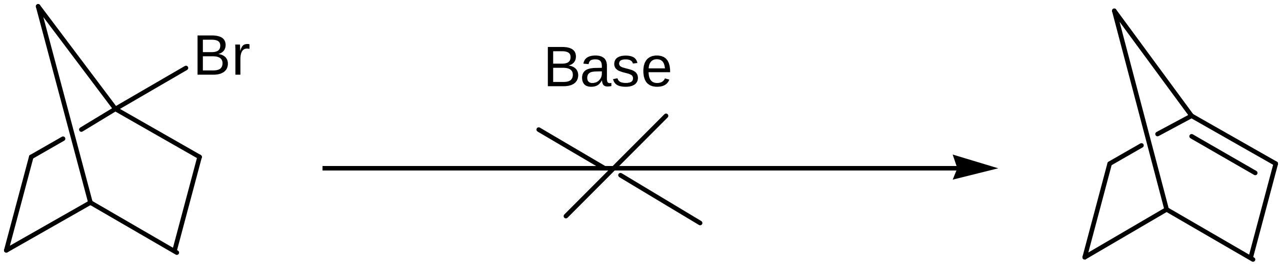
minor



$C_2H_5O^-Na^+$, C_2H_5OH

Only one product

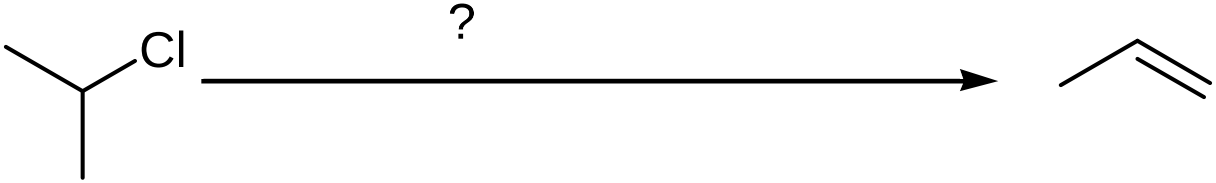
解釋下面的反應為什麼不能發生



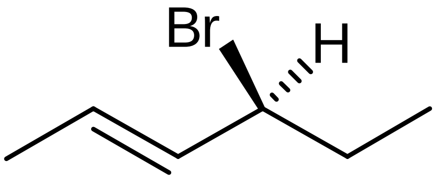
給出反應試劑

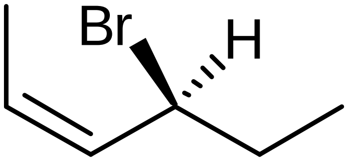
a)

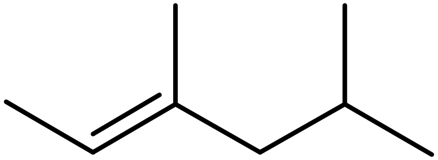
b)

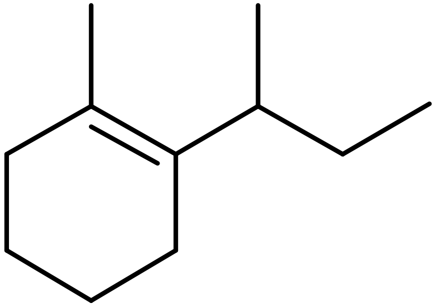


命名下列化合物





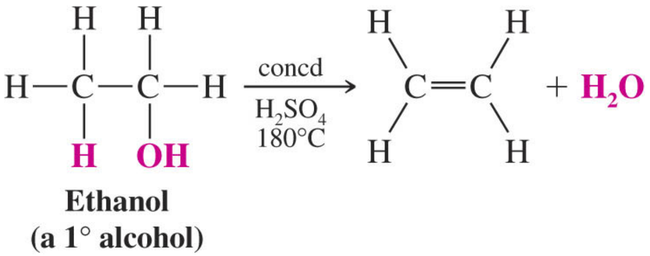




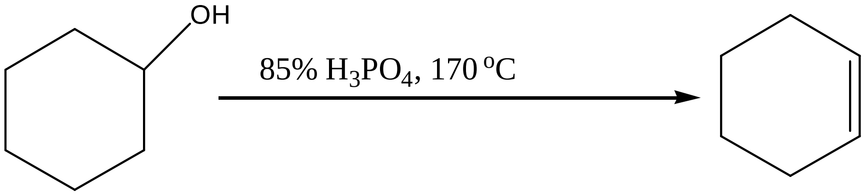
b）烯烴的第二種製備方法：醇的酸催化脫水反應

此類反應所需的酸的濃度以及溫度同常取決於alcohol底物的結構：

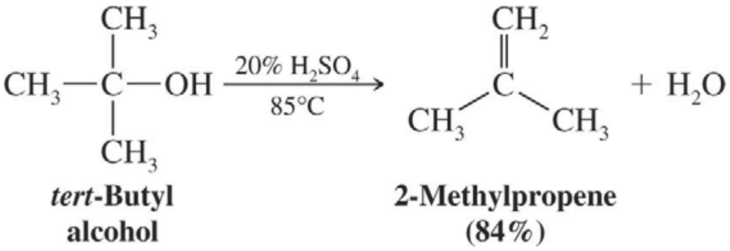
a)1°alcohol:最不容易發生反應；通常需要強酸高熱條件



b)2°alcohol:比1級醇容易一些

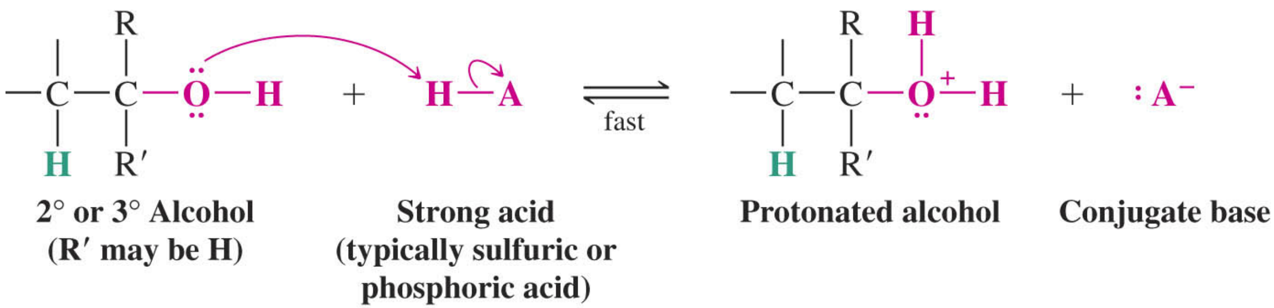


c)3°alcohol:最容易發生酸催化脫水反應



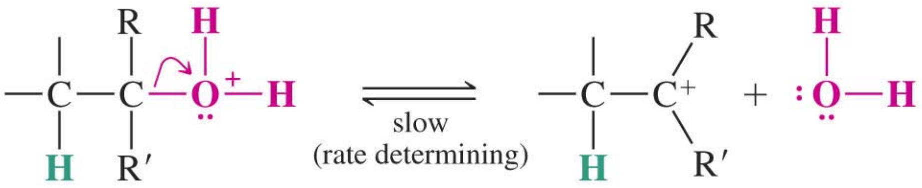
2°，3°alcohols脫水反應的反應機制:E1

Step 1



The alcohol accepts a proton from the acid in a fast step.

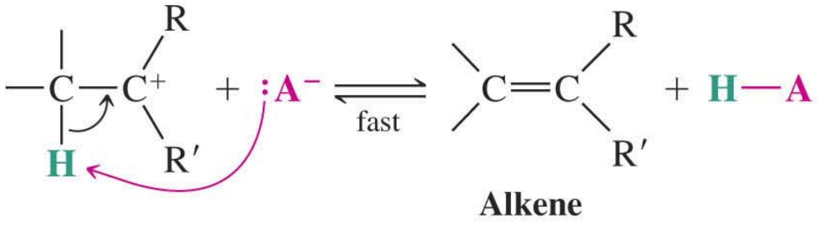
Step 2



Rate-determining ste

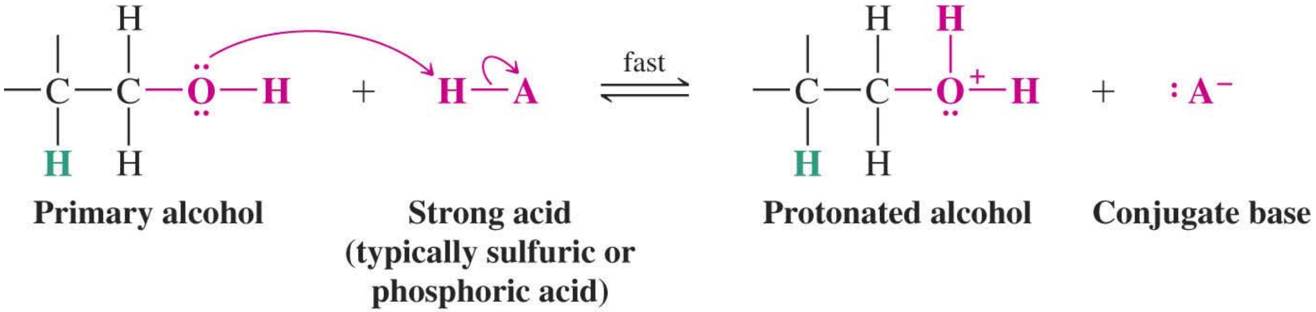
The protonated alcohol loses a molecule of water to become a carbocation. This step is slow and rate determining.

Step 3

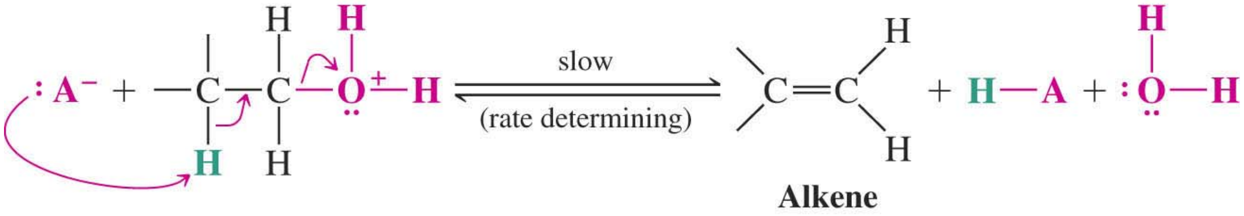


The carbocation loses a proton to a base. In this step, the base may be another molecule of the alcohol, water, or the conjugate base of the acid. The proton transfer results in the formation of the alkene. Note that the overall role of the acid is catalytic (it is used in the reaction and regenerated).

1°脫水反應的機制：E2

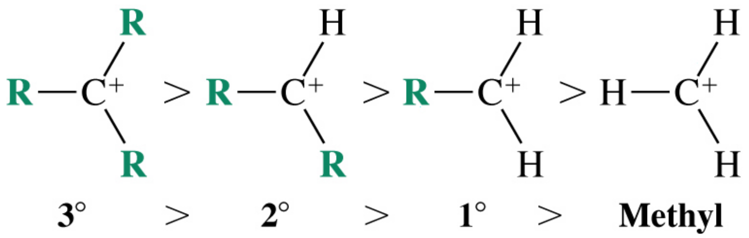


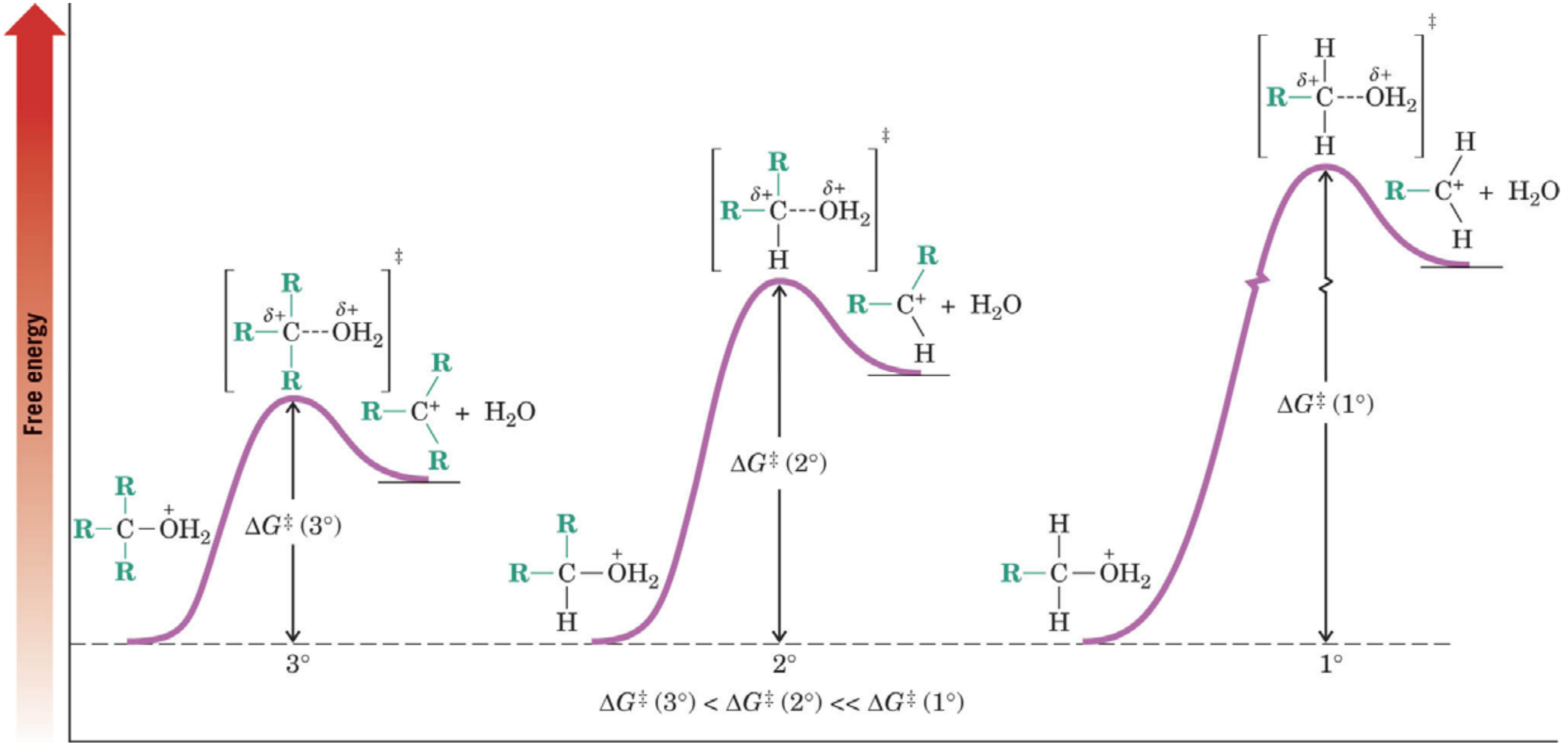
The alcohol accepts a proton from the acid in a fast step.



A base removes a hydrogen from the β carbon as the double bond forms and the protonated hydroxyl group departs. (The base may be another molecule of the alcohol or the conjugate base of the acid.)

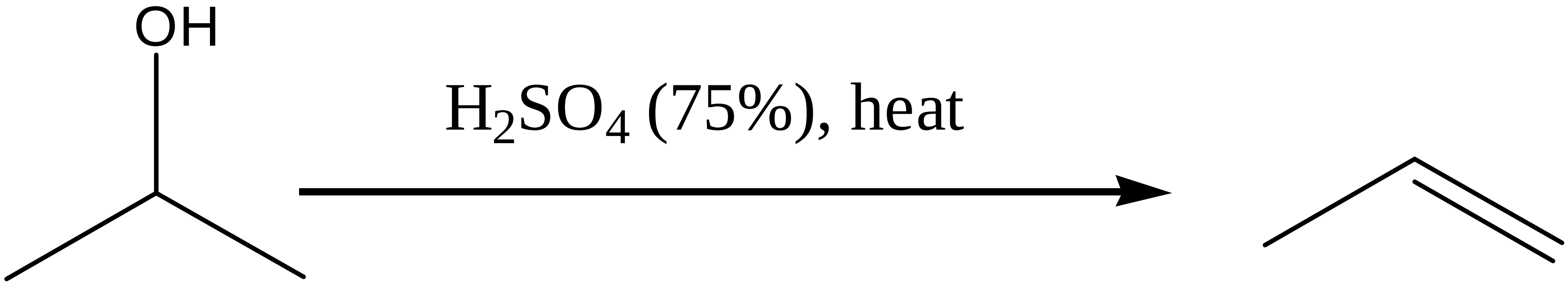
Rate-determining step



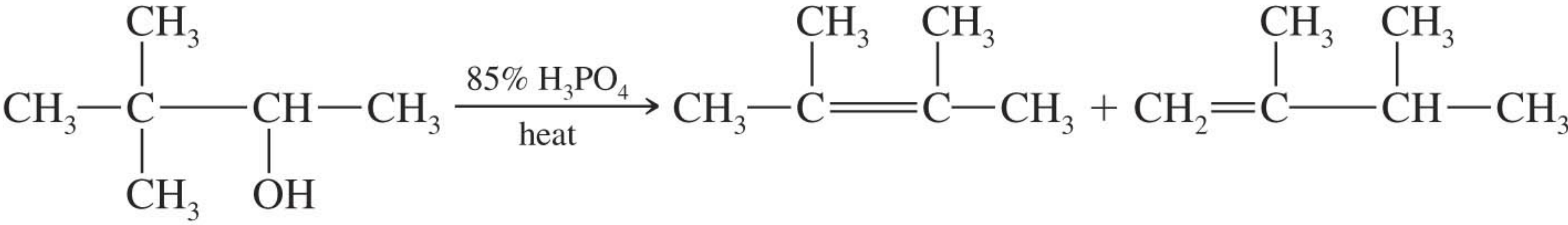


由於一級正碳離子的不穩定性，故一級醇不能發生額E1脫水反應

課堂練習，page 300:分步給出下列反應的反應機制



伴隨著某些二級, 一級alcohol酸催化脫水反應(E1)而發生的重排反應, 重排反應的條件是可以生成更穩定的正碳離子:

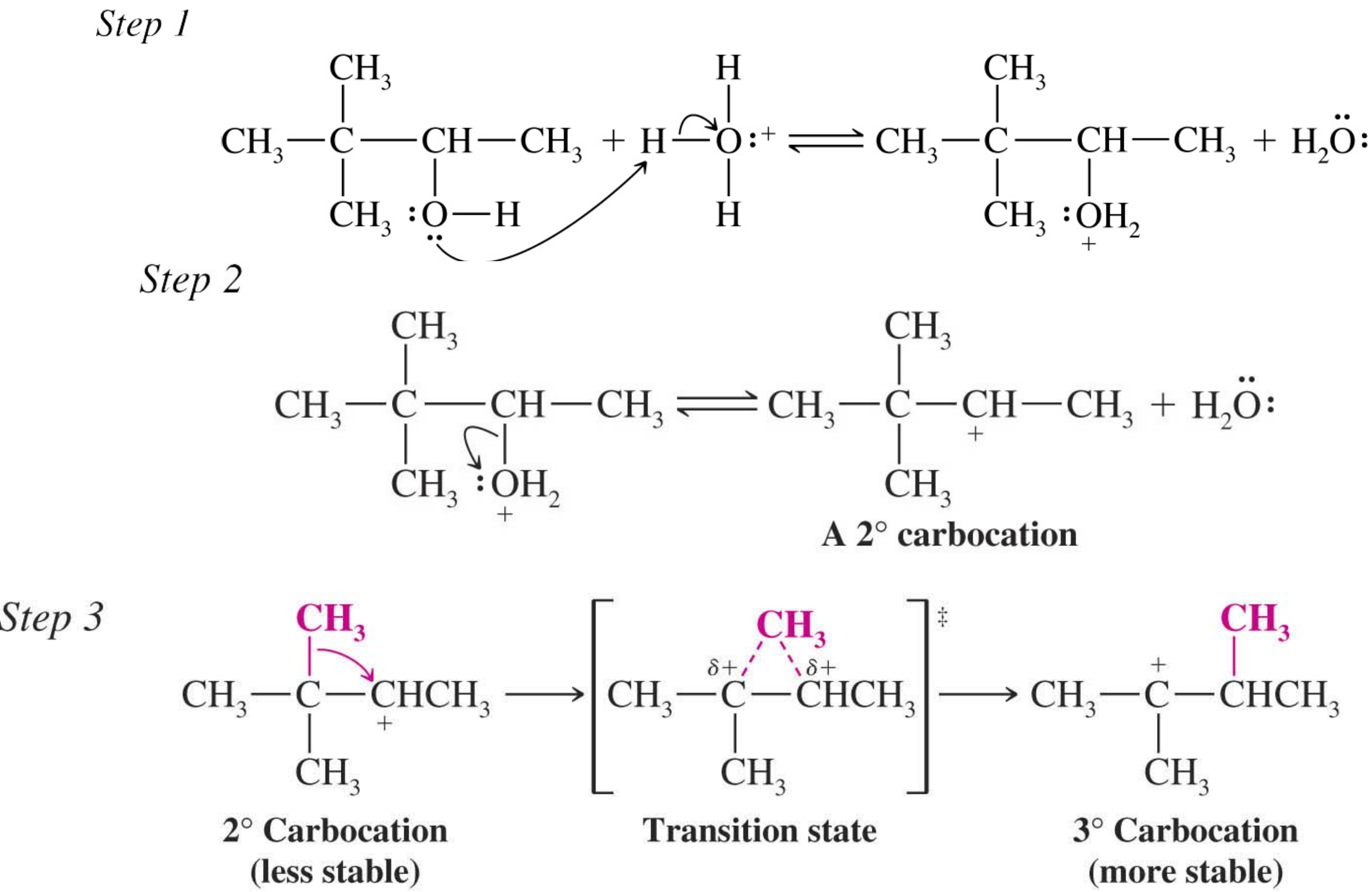


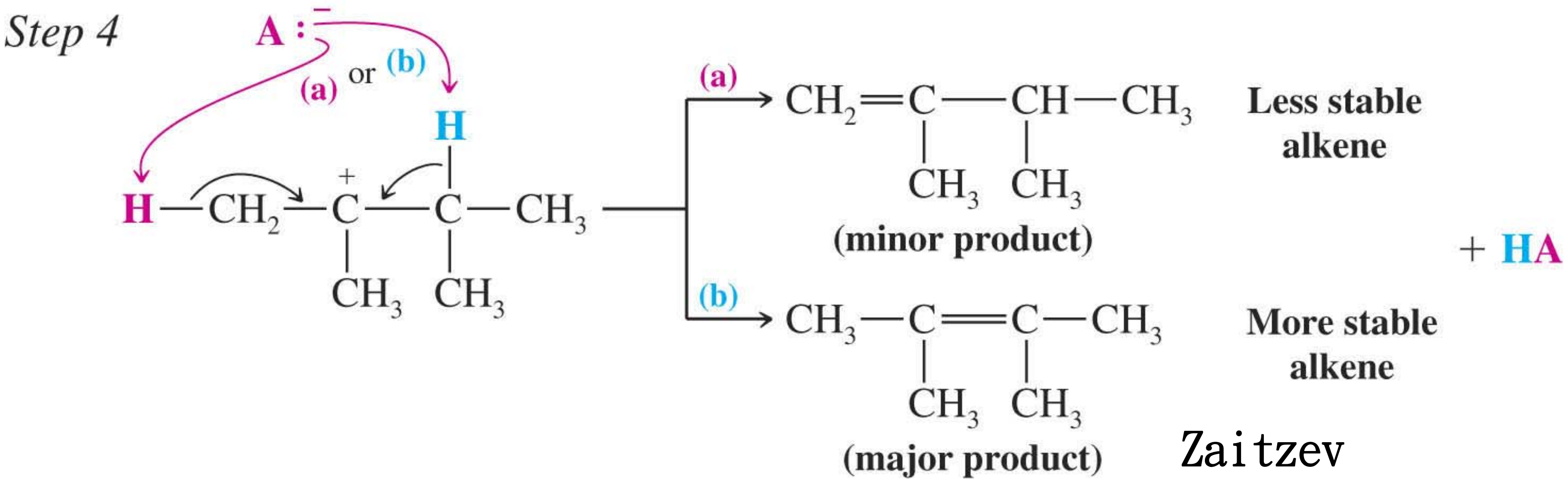
$$\mathrm{CH_3-C(CH_3)_2-CH(OH)-CH_3} \xrightarrow[\text{heat}]{85\%\ \mathrm{H_3PO_4}} \mathrm{CH_3-C(CH_3)=C(CH_3)-CH_3} + \mathrm{CH_2=C(CH_3)-CH(CH_3)-CH_3}$$

3,3-Dimethyl-2-butanol

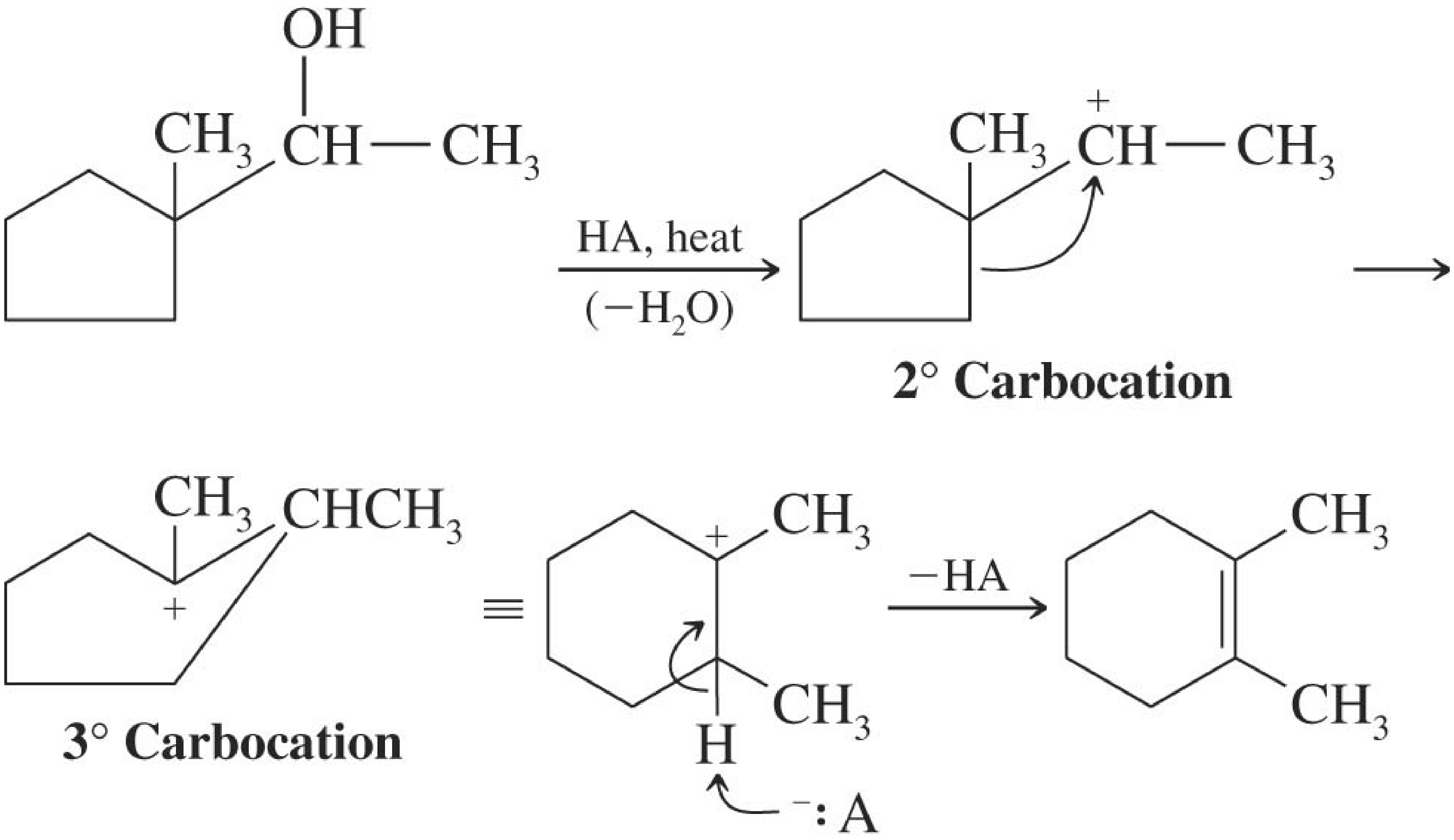
2,3-Dimethyl-2-butene
(major product)

2,3-Dimethyl-1-butene
(minor product)

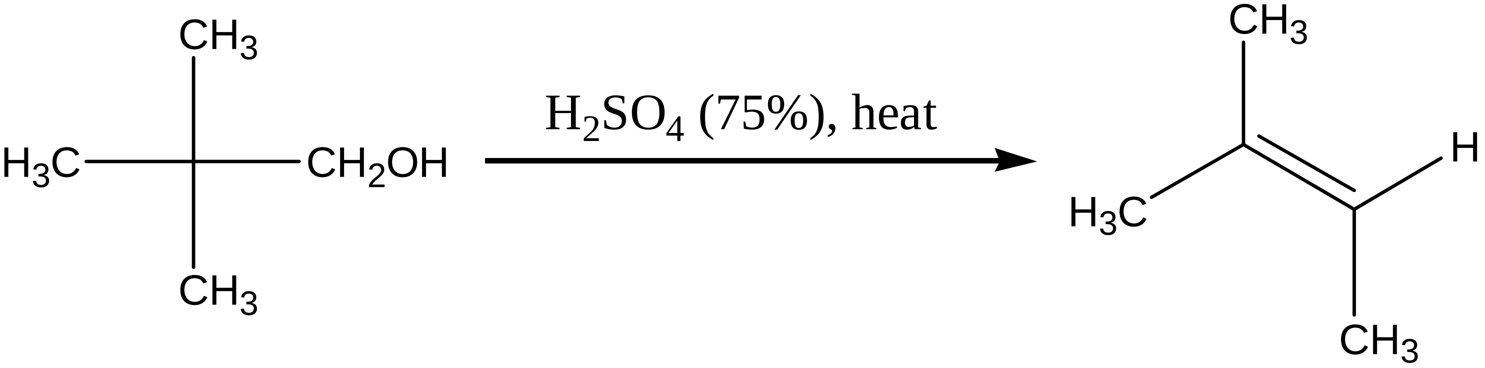

Step 1
Step 2
A 2° carbocation
Step 3
2° Carbocation (less stable)
Transition state
3° Carbocation (more stable)

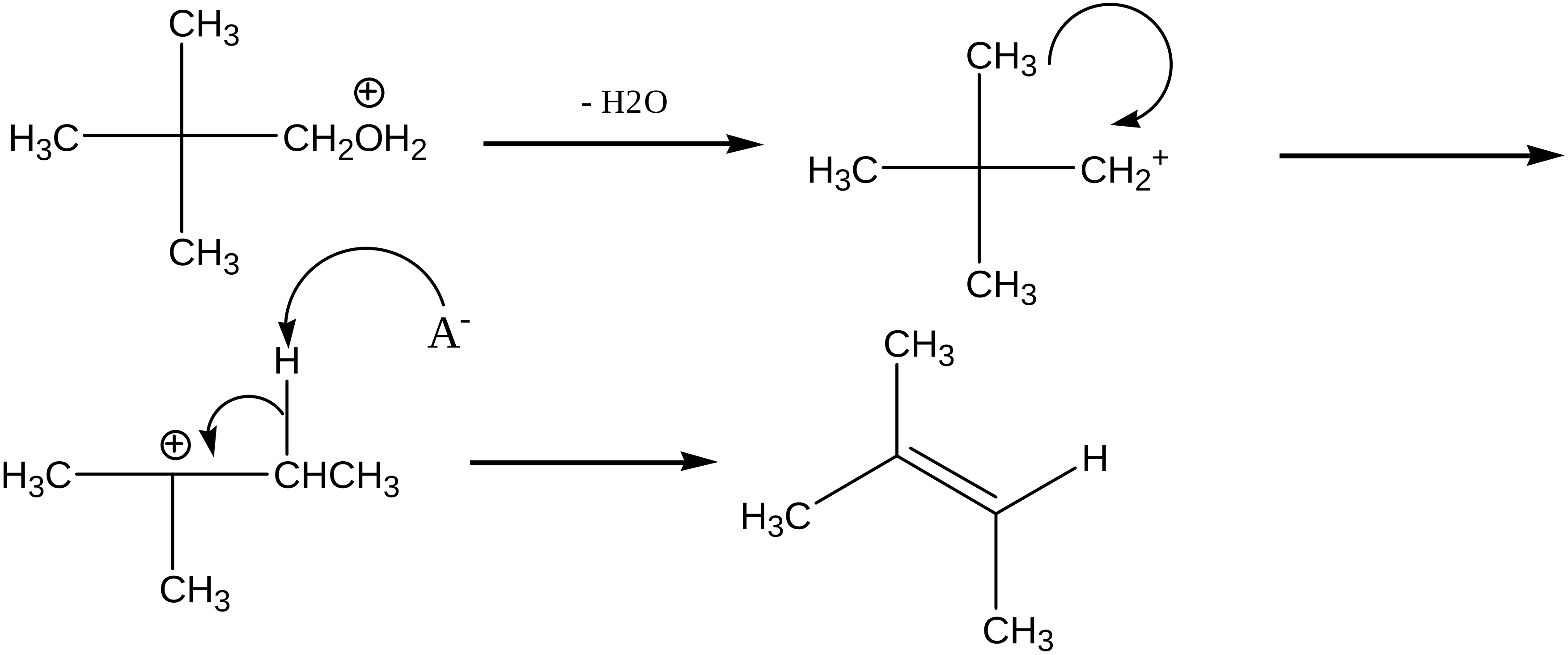

Step 4
A:⁻
(a)
or
(b)
H
H—CH₂—C⁺—C—CH₃
CH₃ CH₃
(a)
CH₂=C—CH—CH₃
CH₃ CH₃
(minor product)
Less stable alkene
(b)
CH₃—C=C—CH₃
CH₃ CH₃
(major product)
More stable alkene
+ HA

Zaitzev

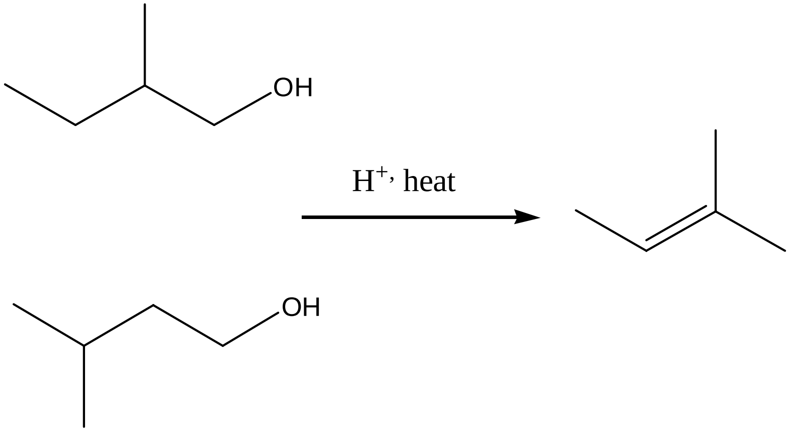

OH
CH3
CH
CH3
HA, heat
(−H2O)
CH3
CH
CH3
2° Carbocation
CH3
CHCH3
3° Carbocation
≡
CH3
CH3
H
⁻:A
−HA
CH3
CH3

課堂練習，page 305：分步給出下列反應的反應機制

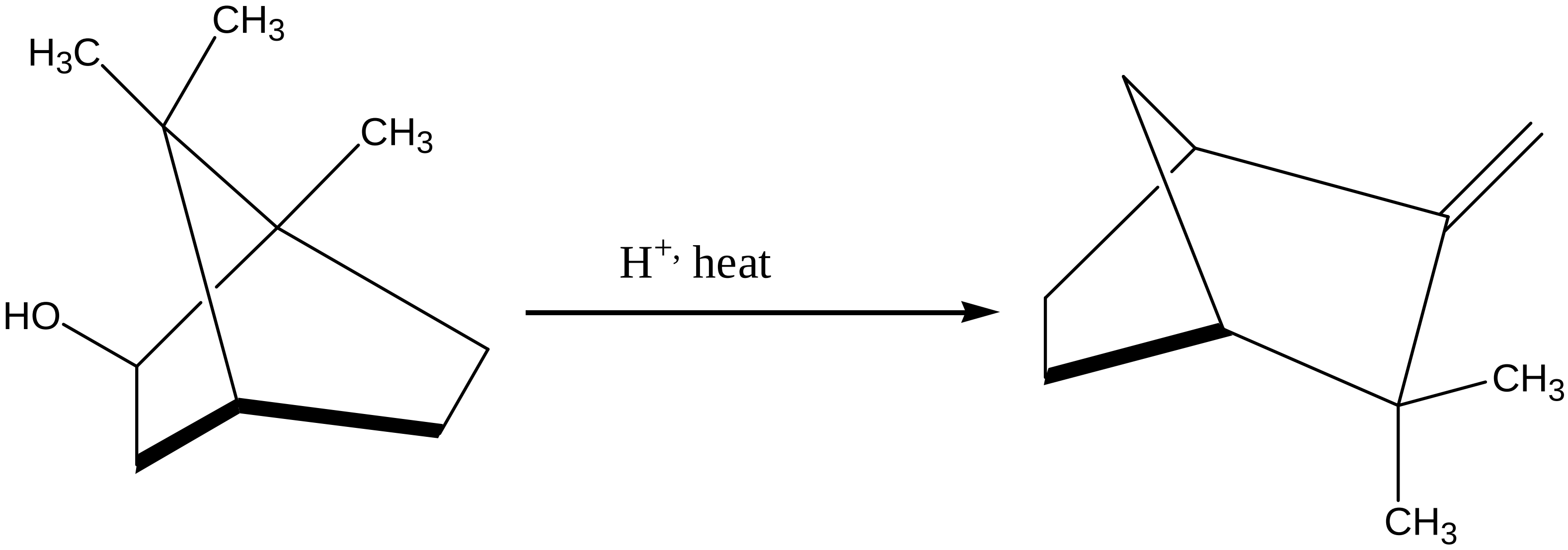




解釋下列反應為什麼得到同一種產物:



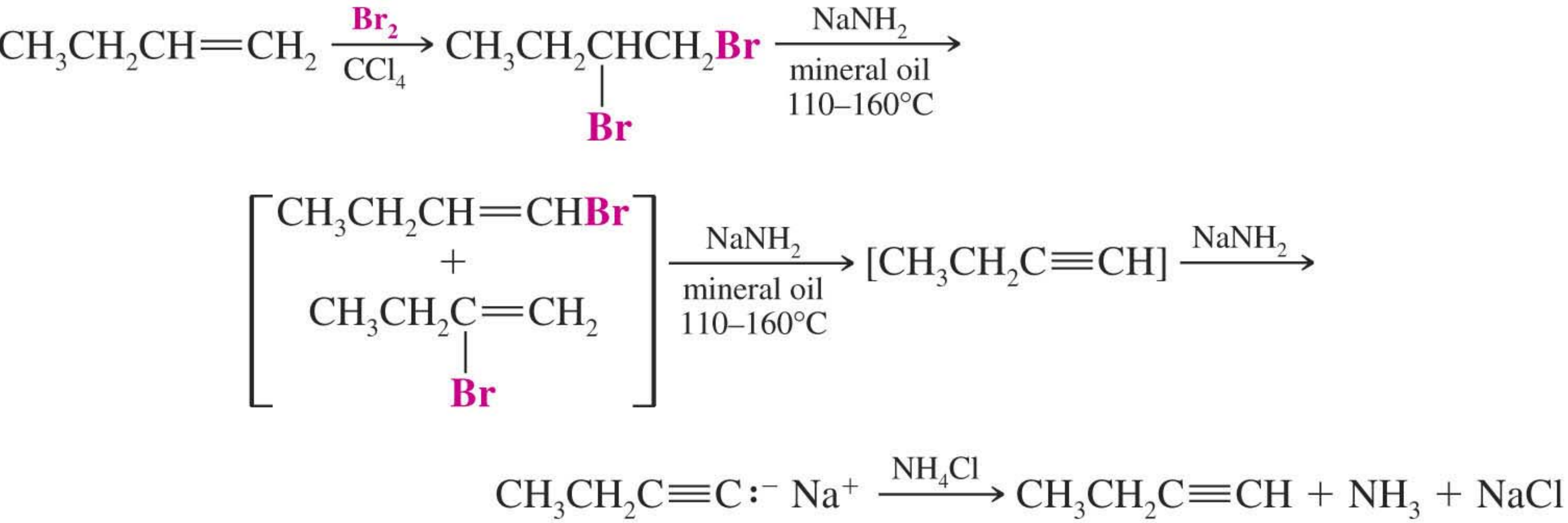
給出下列反應的反應機制:



c）烯烴的第三種製備方法：炔烴的氫化及還原反應

製備炔烴的幾種方法:

i）Dihydrohalogenation of vic-dibromides to form alkynes:

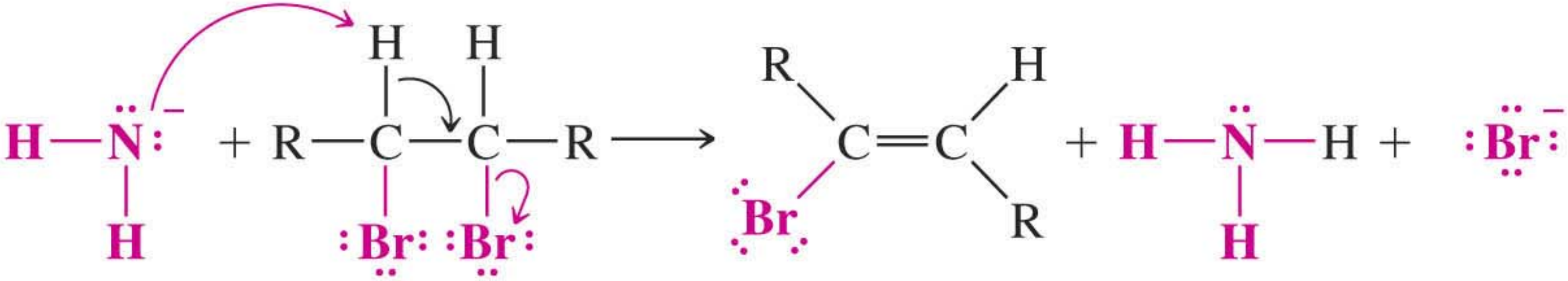


$$CH_3CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[\text{mineral oil } 110\text{–}160^\circ C]{NaNH_2}$$

$$\left[\begin{array}{c} CH_3CH_2CH{=}CHBr \\ + \\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2 \end{array}\right] \xrightarrow[\text{mineral oil } 110\text{–}160^\circ C]{NaNH_2} [CH_3CH_2C{\equiv}CH] \xrightarrow{NaNH_2}$$

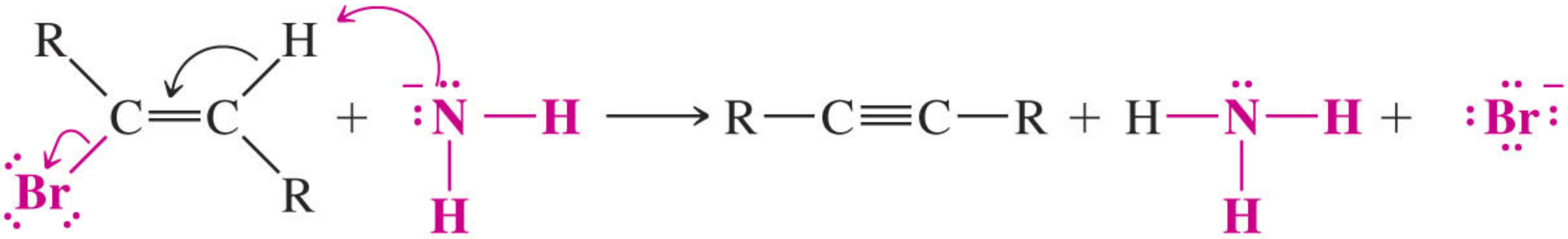
$$CH_3CH_2C{\equiv}C\!:^- \, Na^+ \xrightarrow{NH_4Cl} CH_3CH_2C{\equiv}CH + NH_3 + NaCl$$

Step 1

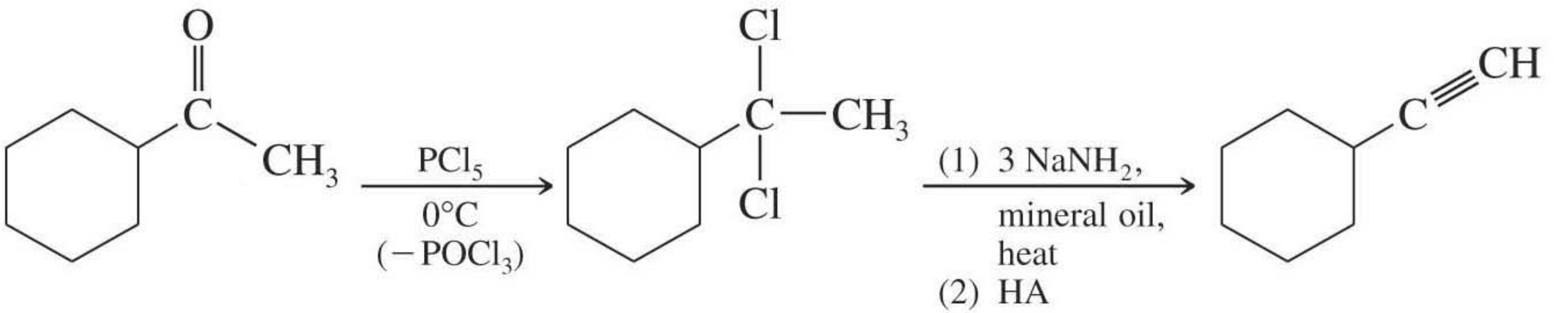


The strongly basic amide ion brings about an E2 reaction.

Step 2



A second E2 reaction produces the alkyne.

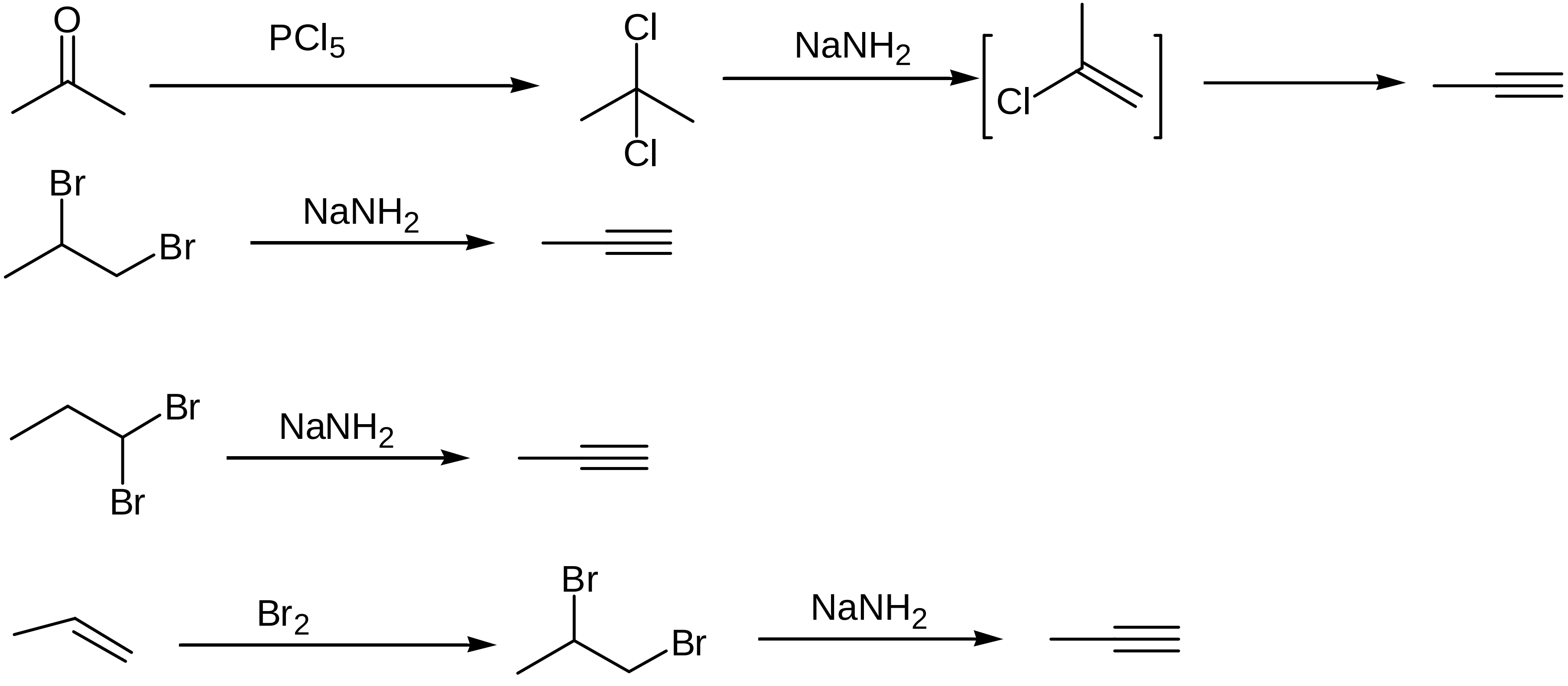


Cyclohexyl methyl ketone

A *gem*-dichloride (70–80%)

Cyclohexylacetylene (46%)

課堂練習，由下列起始物，在適當的條件下合成 propyne page 308:



ii) Replacement of the acetylene hydrogen atom of terminal alkynes:

此類反應適用於一級alkyl halides.對於2，3級alkyl halides 來講；E2反應佔優勢

$$CH_3C{\equiv}C{-}H + NaNH_2 \xrightarrow{\text{liq. } NH_3} CH_3C{\equiv}C{:}^{-}Na^{+} + NH_3$$

	$H{-}\ddot{\underset{\cdot\cdot}{O}}H$	>	$H{-}\ddot{\underset{\cdot\cdot}{O}}R$	>	$H{-}C{\equiv}CR$	>	$H{-}\ddot{N}H_2$	>	$H{-}CH{=}CH_2$	>	$H{-}CH_2CH_3$
pK_a	**15.7**		**16–17**		**25**		**38**		**44**		**50**

The relative acidity of acetylenic hydrogens in solution

課堂練習，page 309:判斷下列反應是否可以發生，並給出產物

$$\mathrm{CH_3CH{=}CH_2} \quad + \quad \mathrm{NaNH_2} \quad \xcancel{\xrightarrow{\qquad\qquad\qquad}}$$

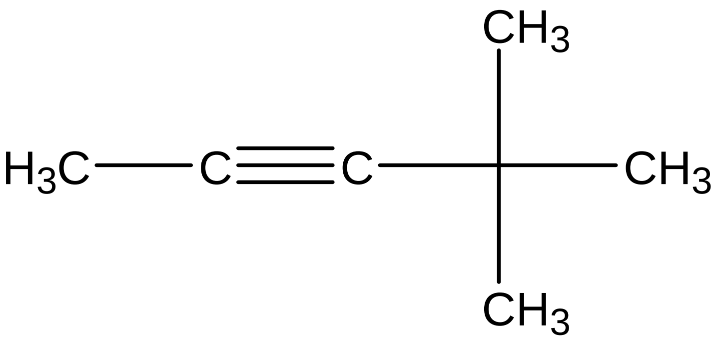
$$\mathrm{H_3CC{\equiv}CH} \quad + \quad \mathrm{NaNH_2} \quad \longrightarrow \quad \mathrm{H_3CC{\equiv}C^{-}Na^{+}}$$

$$\mathrm{CH_3CH_2CH_2} \quad + \quad \mathrm{NaNH_2} \quad \xcancel{\xrightarrow{\qquad\qquad\qquad}}$$

$$\mathrm{H_3CC{\equiv}C^{-}Na^{+}} \quad + \quad \mathrm{EtOH} \quad \longrightarrow \quad \mathrm{H_3CC{\equiv}CH}$$

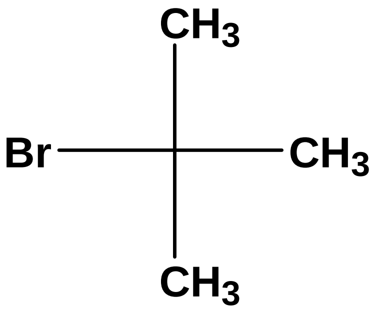
$$\mathrm{H_3CC{\equiv}C^{-}Na^{+}} \quad + \mathrm{NH_4Cl} \quad \longrightarrow \quad \mathrm{H_3CC{\equiv}CH}$$

課堂練習，page 310:從下列起始物中挑選合適的起始物來合成4,4-dimethyl-2-pentyne

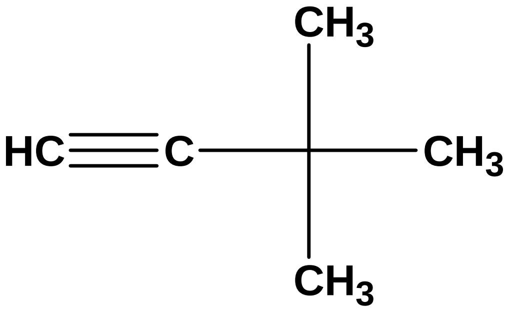


$$H_3C-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

$H_3C-C\equiv CH$



$$Br-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$



$$HC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

CH_3I

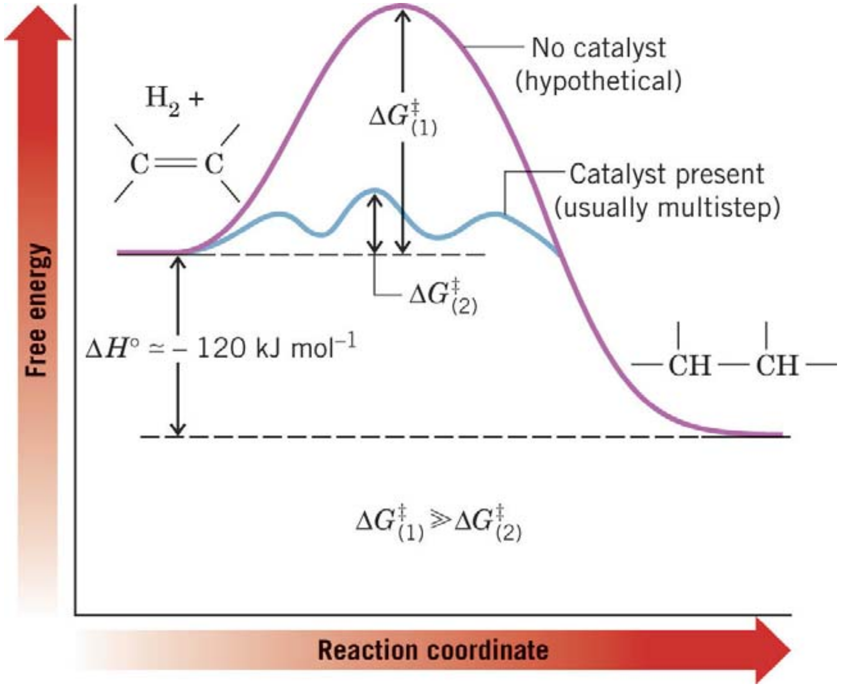
由炔烴轉化為烯烴的方法

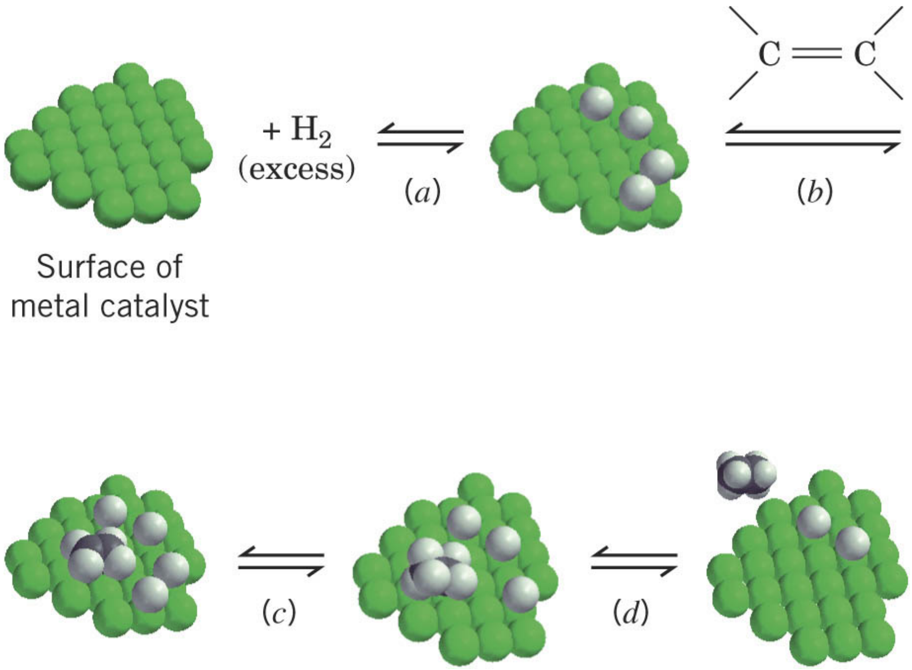
i)氫化加成反應

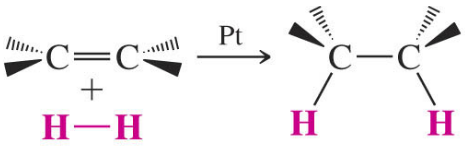
$$\mathrm{CH_2{=}CH_2 + H_2 \xrightarrow[\substack{\text{or Pt}\\ \text{25 C}}]{\text{Ni,Pd,}} CH_3{-}CH_3}$$

$$\mathrm{CH_3CH{=}CH_2 + H_2 \xrightarrow[\substack{\text{or Pt}\\ \text{25 C}}]{\text{Ni,Pd,}} CH_3CH_2{-}CH_3}$$

$$\mathrm{CH_3CH_2CH_2CH_2CH{=}CH_2 + H_2 \xrightarrow{Rh[(C_6H_5)_3P]_3Cl} CH_3CH_2CH_2CH_2CH_2CH_3}$$

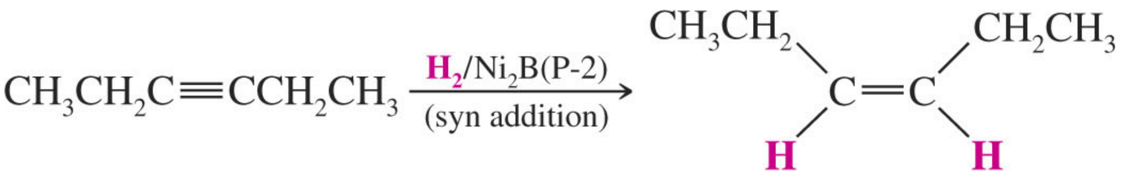






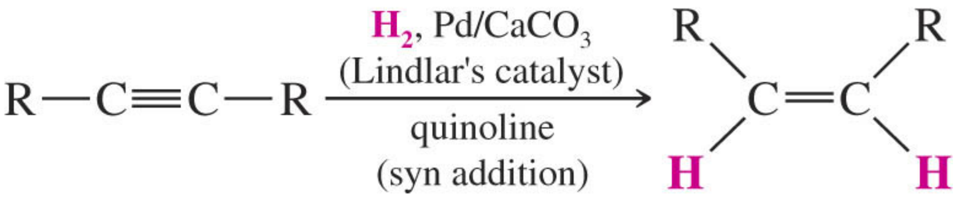
Catalytic hydrogenation is a syn addition.

$$CH_3C{\equiv}CCH_3 \xrightarrow[H_2]{Pt} [CH_3CH{=}CHCH_3] \xrightarrow[H_2]{Pt} CH_3CH_2CH_2CH_3$$



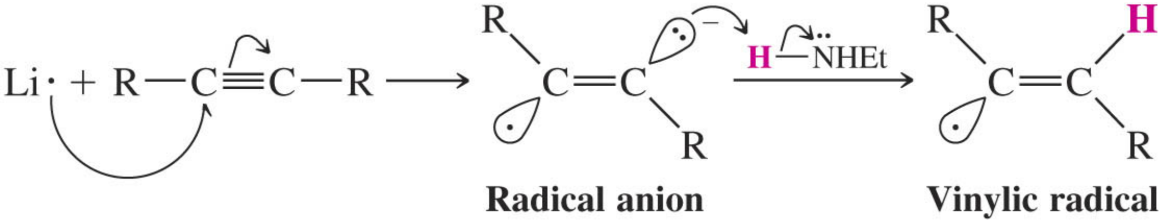
3-Hexyne

(*Z*)-3-Hexene
(*cis*-3-hexene)
(97%)



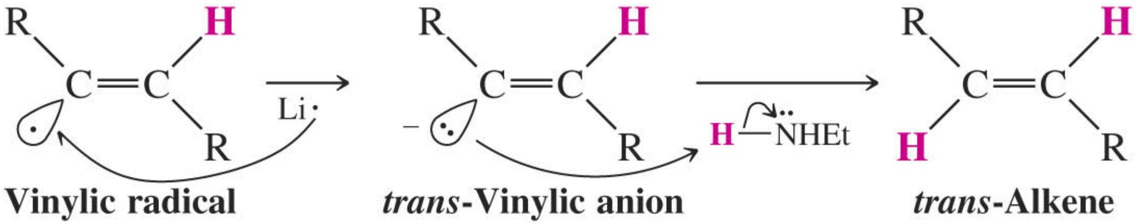
由於syn addition, 所得到的烯烴必定為Z-型

ii)由炔烴產生E-型烯烴的方法:Birch reduction



A lithium atom donates an electron to the *π* bond of the alkyne. An electron pair shifts to one carbon as the hybridization states change to *sp*^{2}.

The radical anion acts as a base and removes a proton from a molecule of the ethylamine.



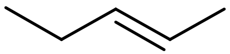
A second lithium atom donates an electron to the vinylic radical.

The anion acts as a base and removes a proton from a second molecule of ethylamine.

課後練習:Page 323

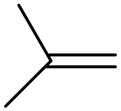
7.18:改正錯誤之命名

a)



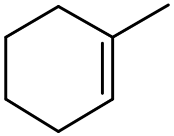
Change 3-trans-pentene into 2-trans-pentene

b)



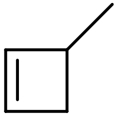
Change 1,1-dimethylethene into 2-methylpropene

c)



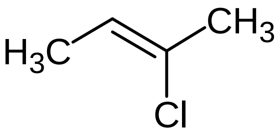
Change 2-methylcyclohexene into 1-methylcyclohexene

d)



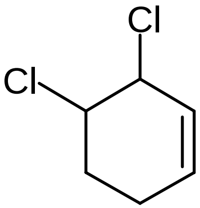
Change 4-methylcyclobutene 3-methylcyclobutene

e)



Change 3-Chloro-2-butene into 2-chloro-2-butene

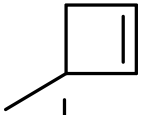
f)



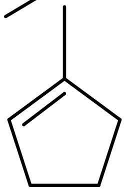
Change 5,6-Dichlorocyclohexene into 3,4-dichlorocyclohexene

7.19:依據化合物的名稱給出化合物的結構:

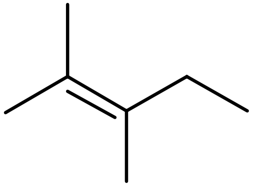
a)



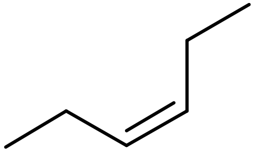
b)



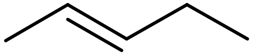
c)



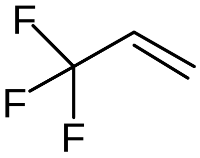
d)



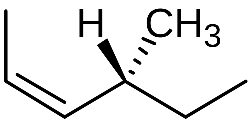
e)



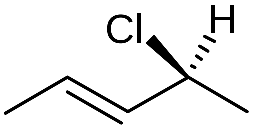
f)



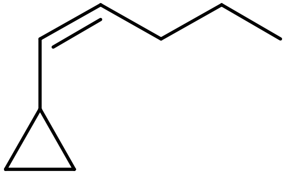
g)



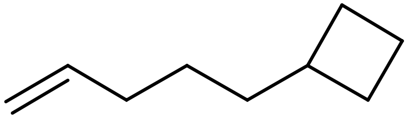
h)



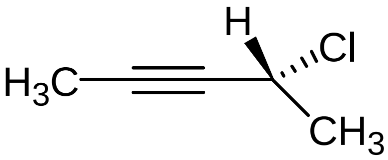
i)



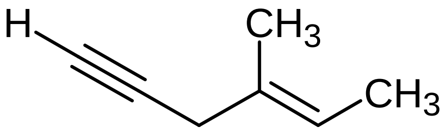
j)



k)

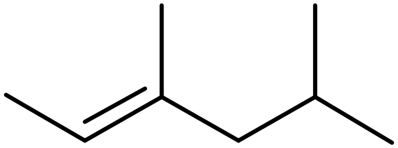


l)



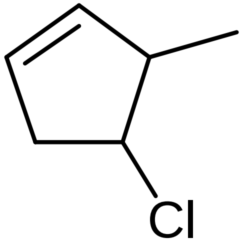
7.21: Give the IUPAC names:

a)



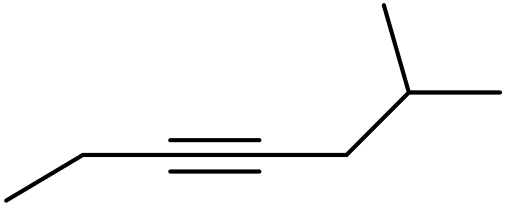
(*Z*)-3,5-Dimethyl-2-hexene

b)



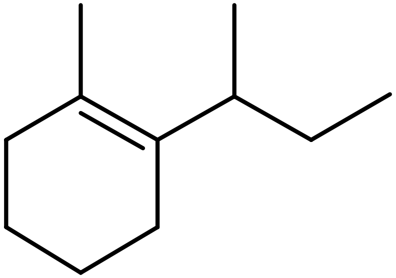
4-Chloro-3-methyl-1-cyclopentene

c)



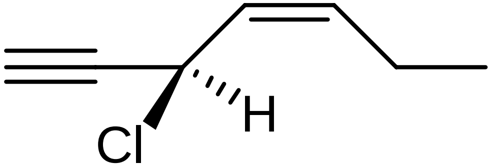
6-methyl-3-heptyne

d)



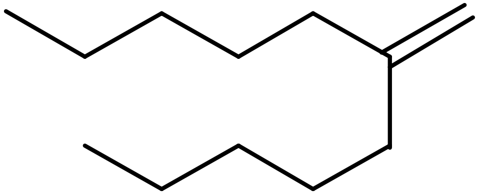
1-*sec*-Butyl-2-methylcyclohexene

e)



(*Z*,*R*)-3-chloro-hex-4-en-1-yne

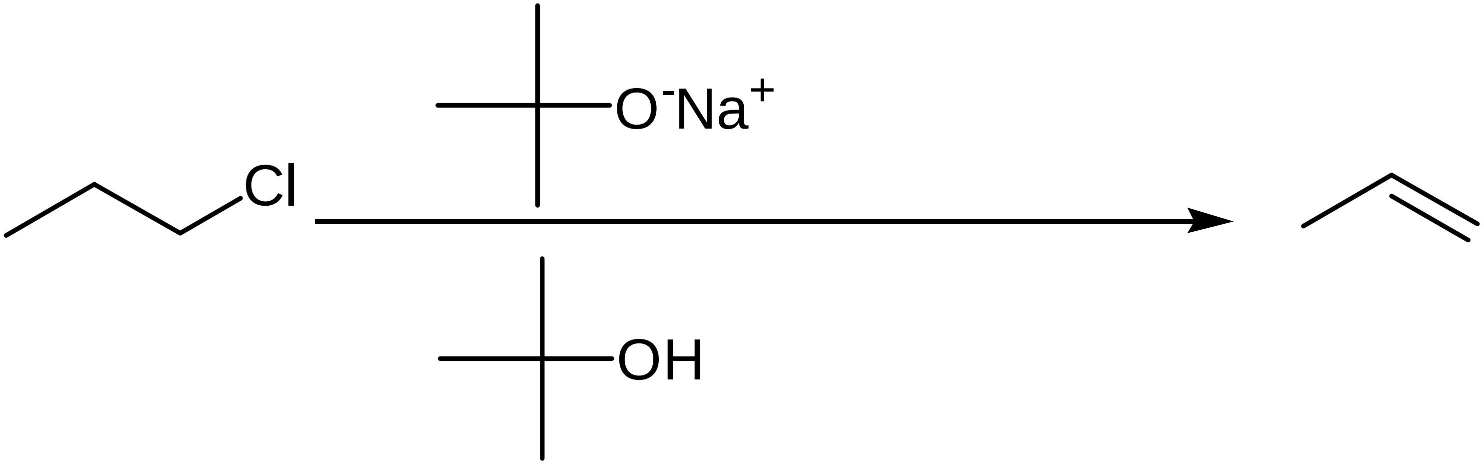
f)



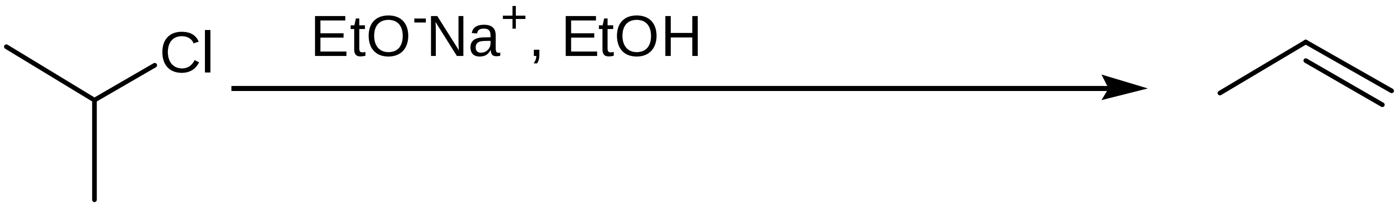
2-Pentyl-1-heptene

7.22:選用合適的反應條件來合成propene ：

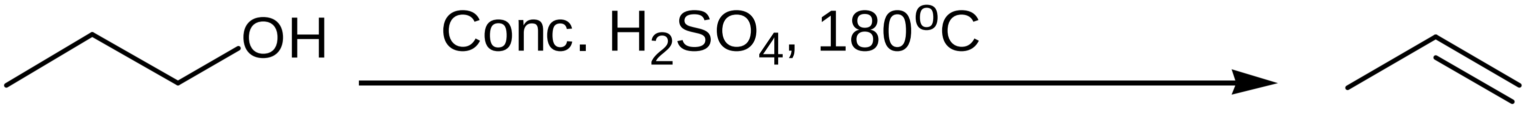
a)



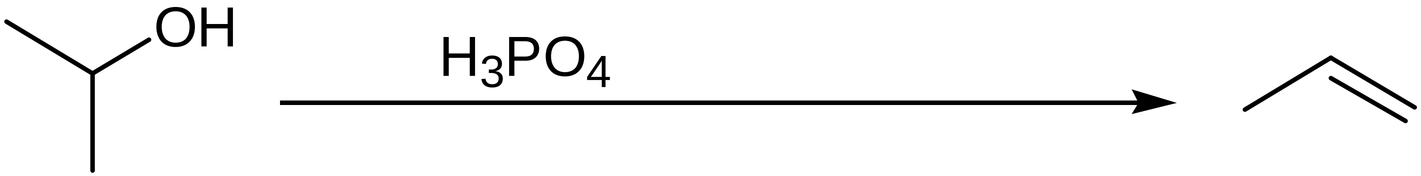
b)



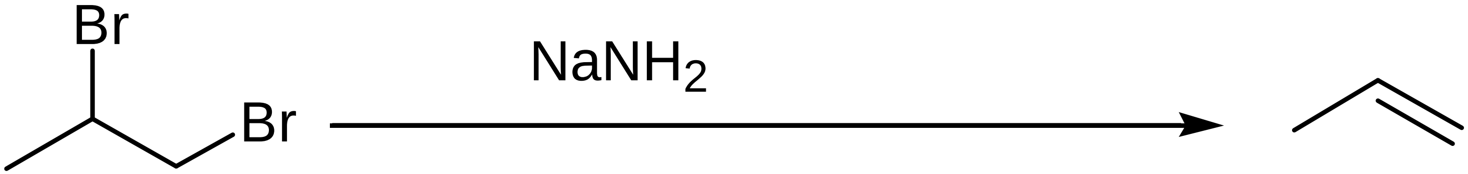
c)



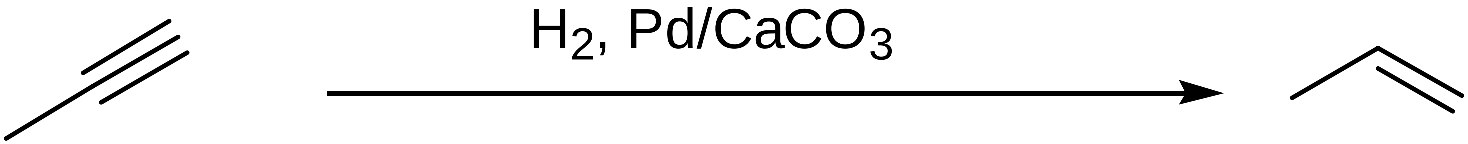
d)



e)

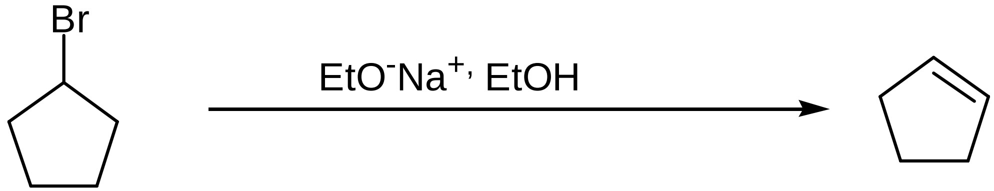


f)

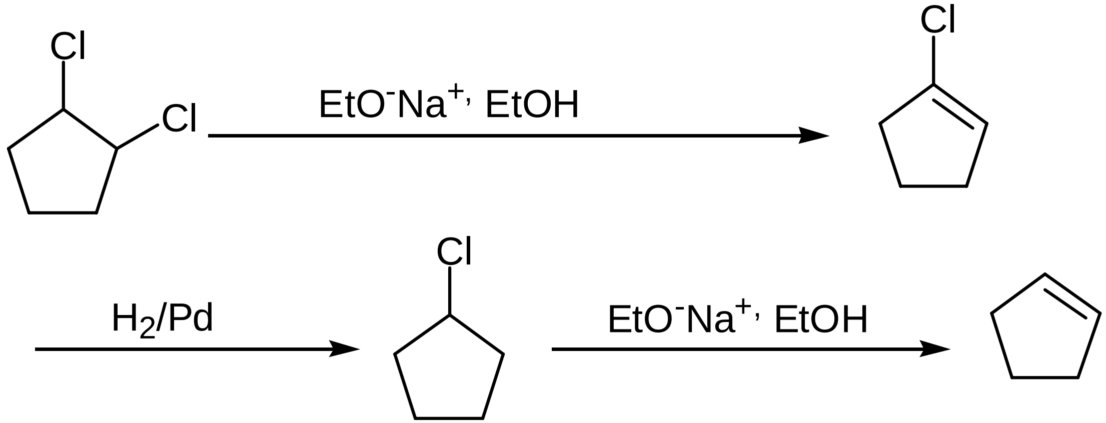


7.23:設計合成cyclopentene的途徑 ：

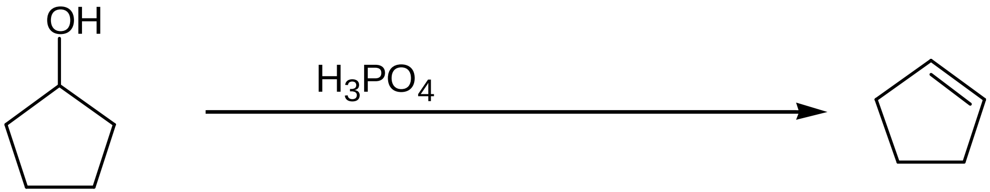
a)



b)

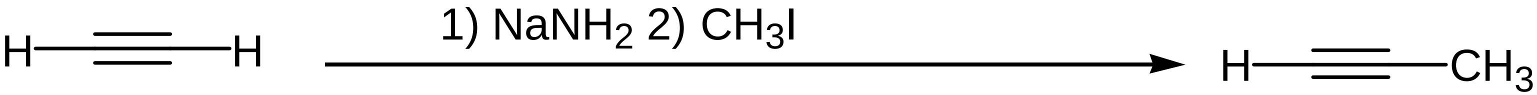


c)

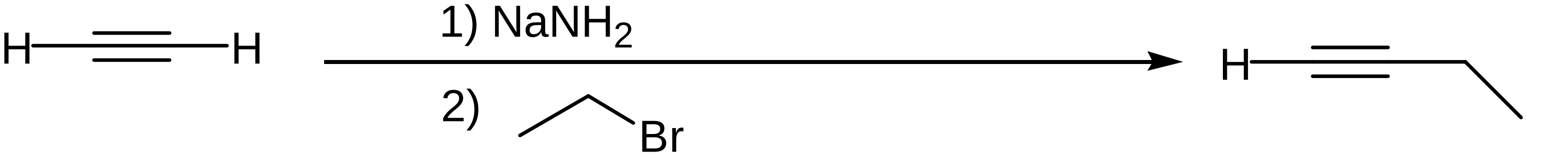


7.24: Starting with ethyne, outline the synthesis of each of the following:

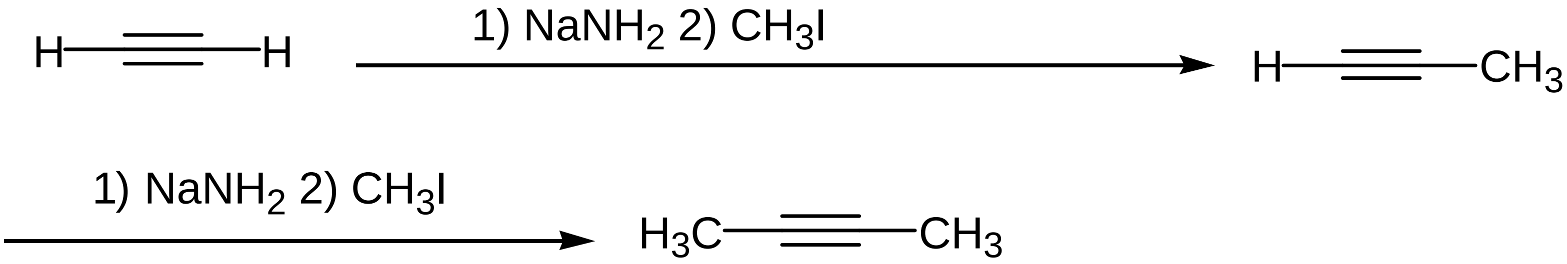
a)



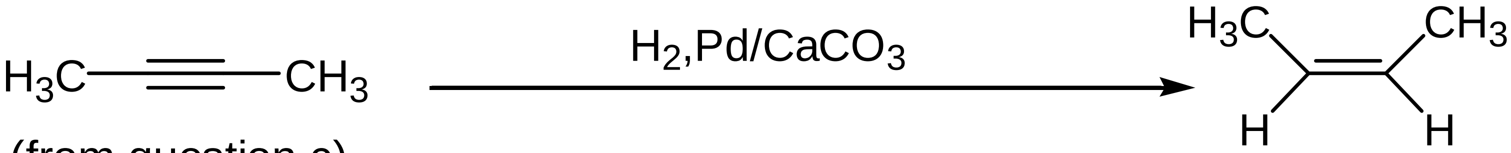
b)



c)

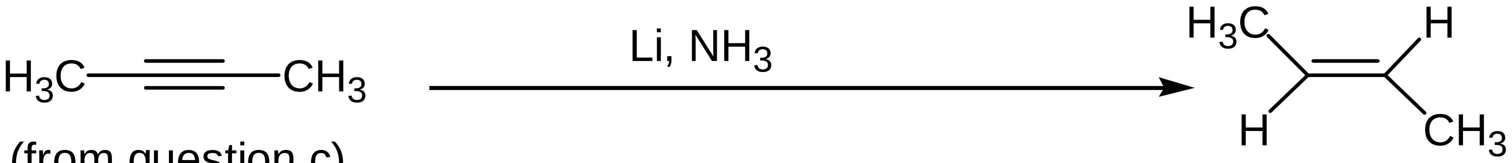


d)



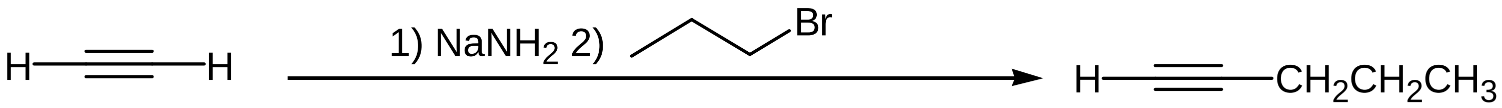
(from question c)

e)



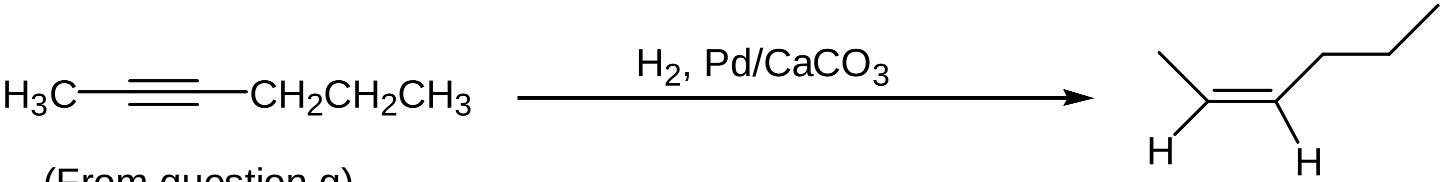
(from question c)

f)



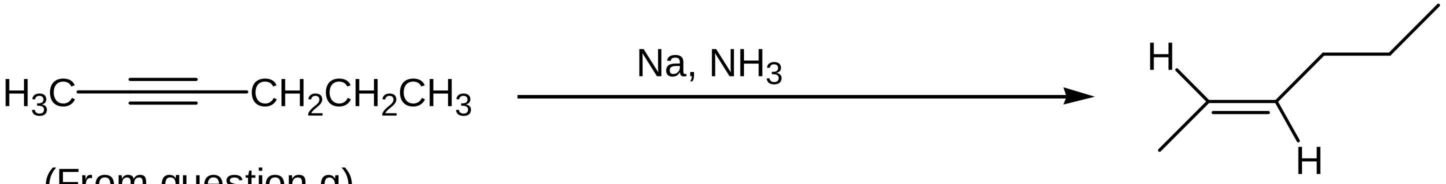
g) $H-C\equiv C-CH_2CH_2CH_3 \xrightarrow{1)\ NaNH_2\ 2)\ \ CH_3I} H_3C-C\equiv C-CH_2CH_2CH_3$

h)



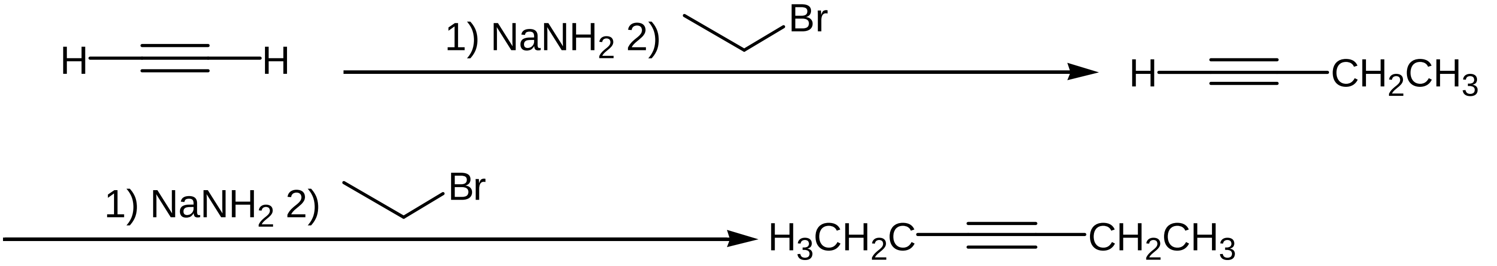
(From question g)

i)

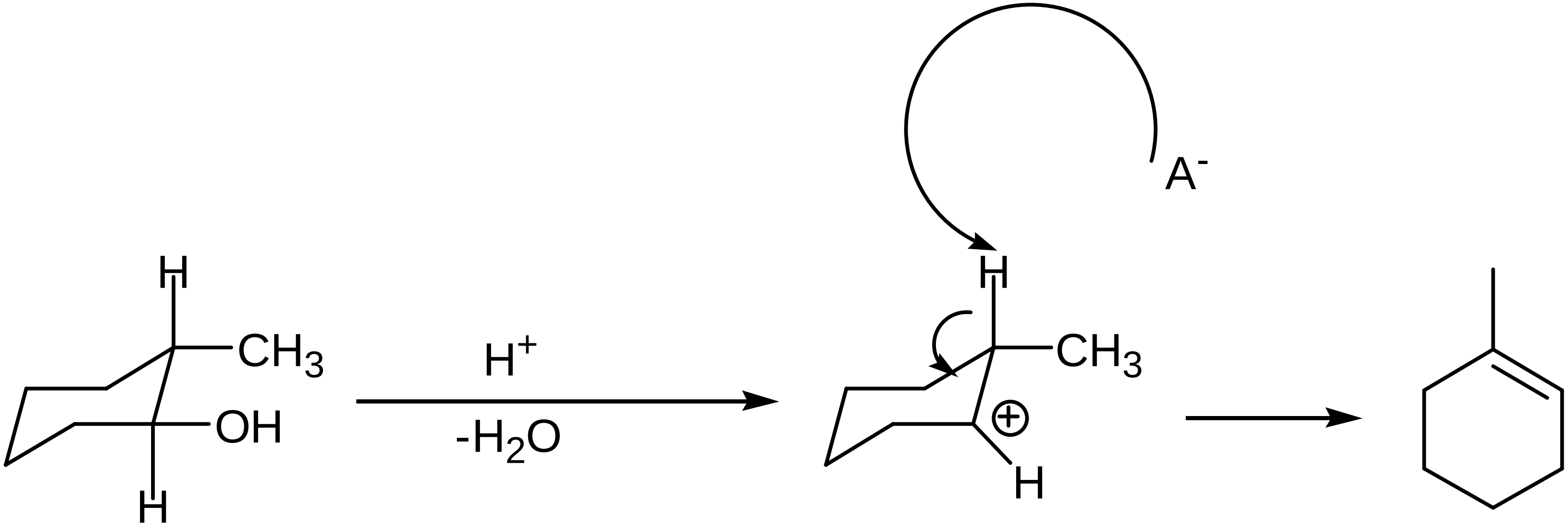


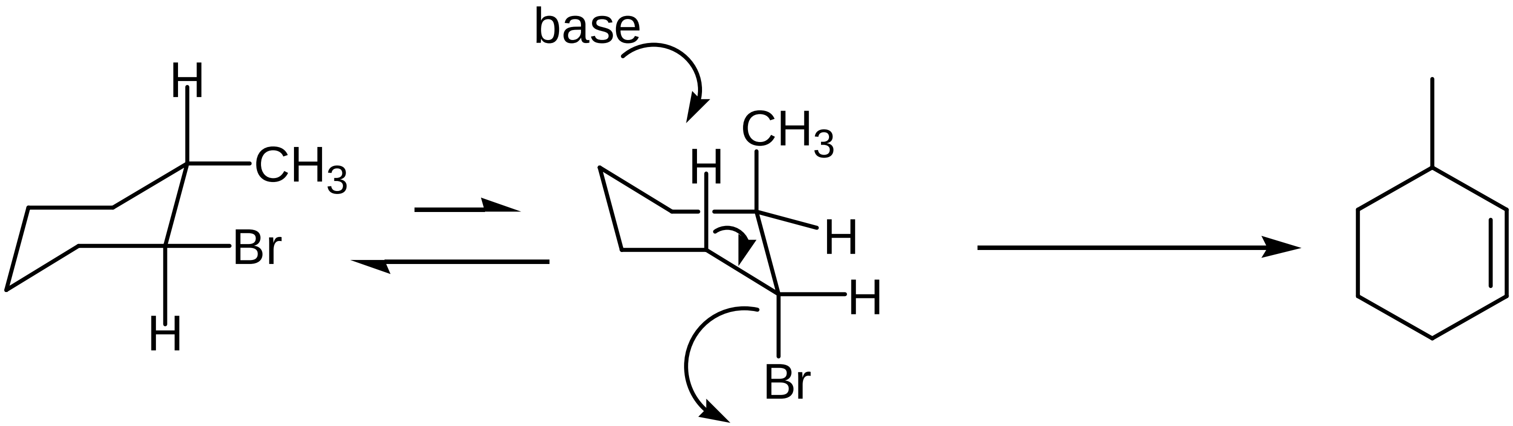
(From question g)

j)



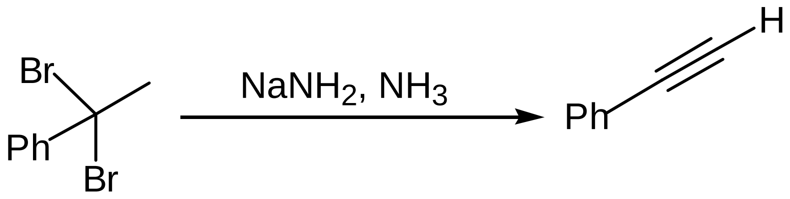
7.26: Explain:



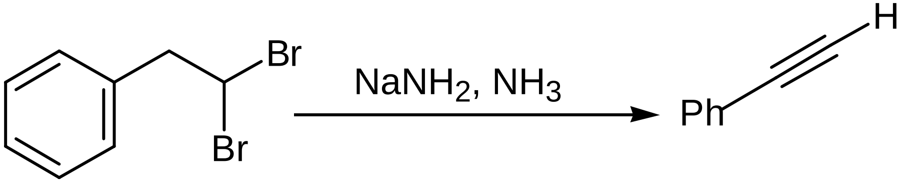


7.27: Outline the synthesis of phenylethyne form each of the following:

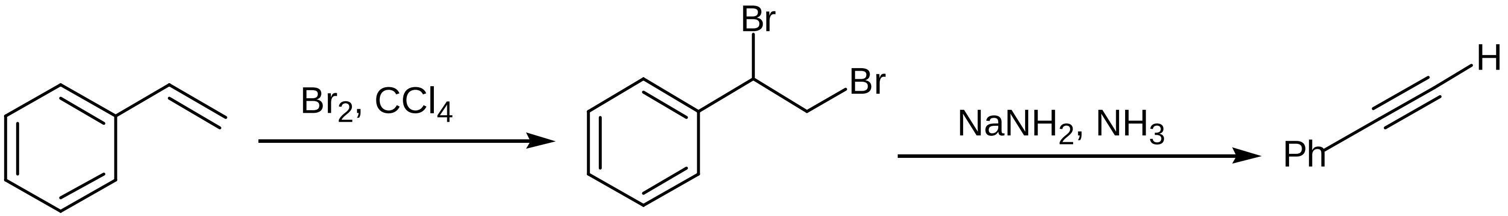
a)



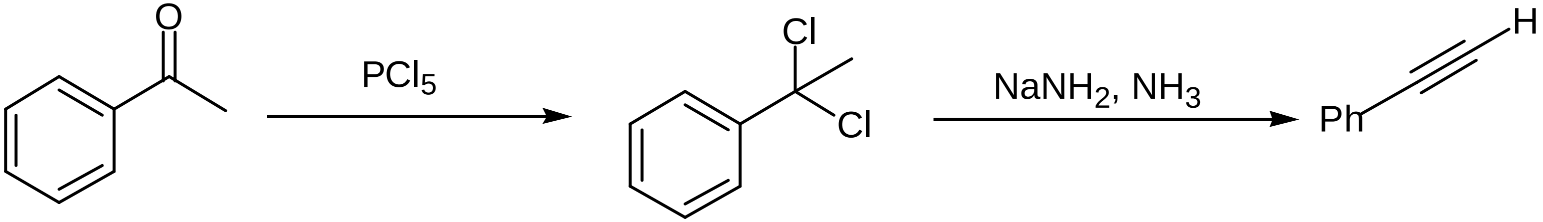
b)



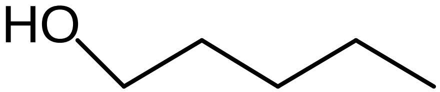
c)



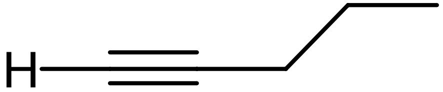
d)



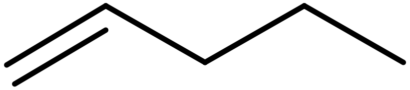
7.28: Arrange the acidity in decreasing order:



>



>



>