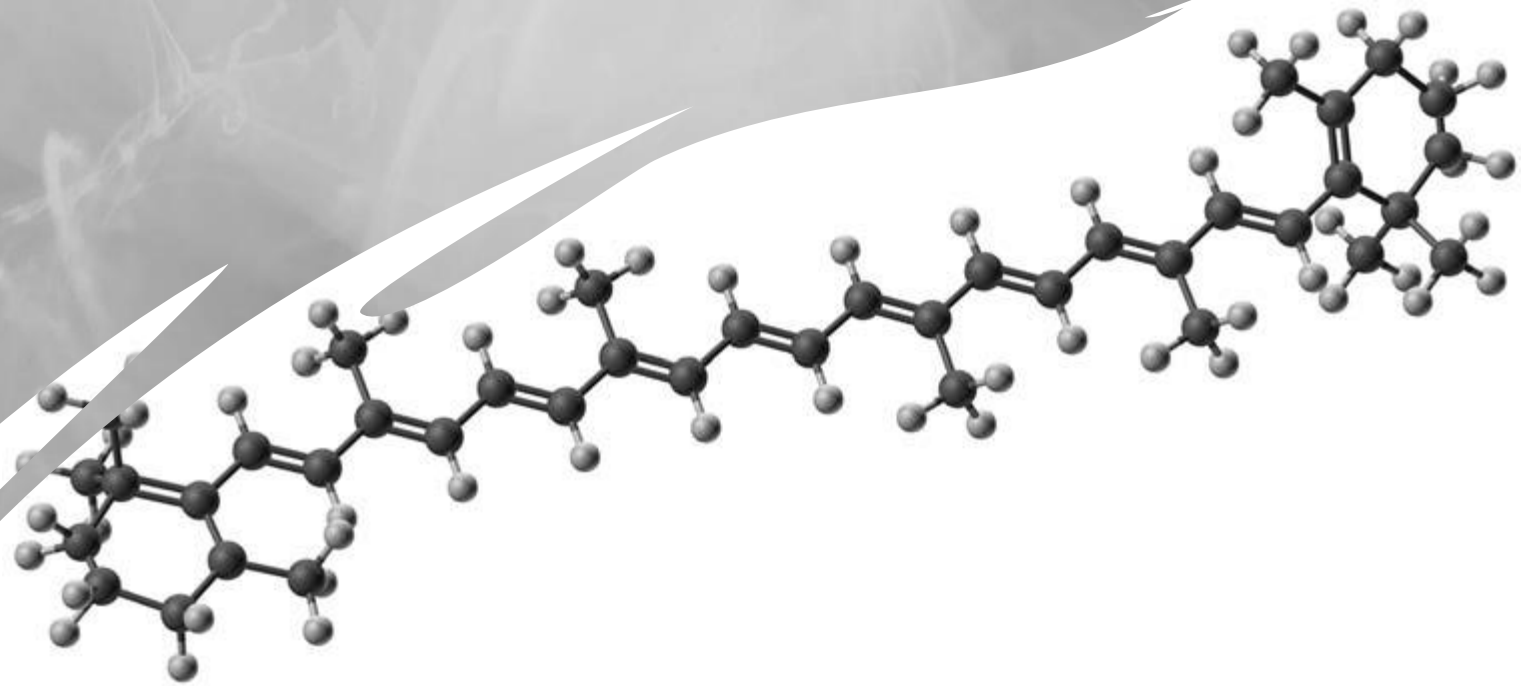
西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Chapter 4

Alkenes and Alkynes



KEY QUESTIONS

4.1 What Are the Structures and Shapes of Alkenes and Alkynes?

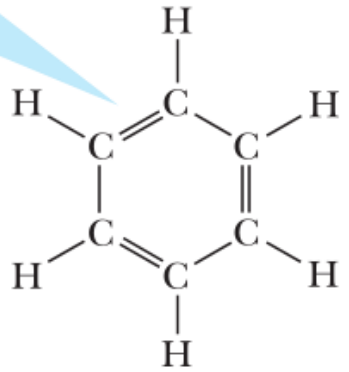
4.2 How Do We Name Alkenes and Alkynes?

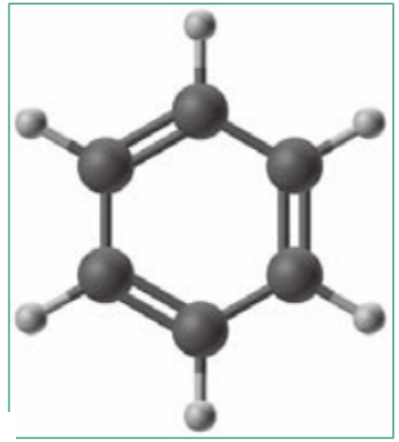
4.3 What Are the Physical Properties of Alkenes and Alkynes?

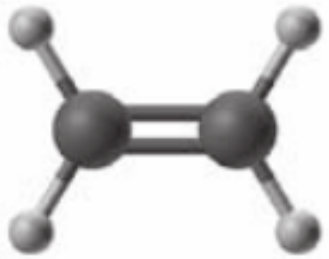
4.4 Why Are 1-Alkynes (Terminal Alkynes) Weak Acids?

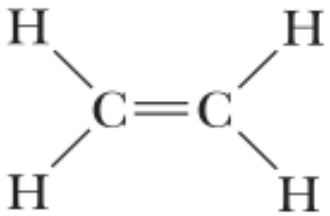
unsaturated hydrocarbons
（不饱和碳氢化合物）

although benzene and other arenes contain C–C double bonds, we must remember that their double bonds are not reactive in the ways we will describe in Chapters 5–8 (i.e., we will leave them unreacted in reactions that we cover in these chapters)









Ethene
(an alkene)

Ethyne
(an alkyne)

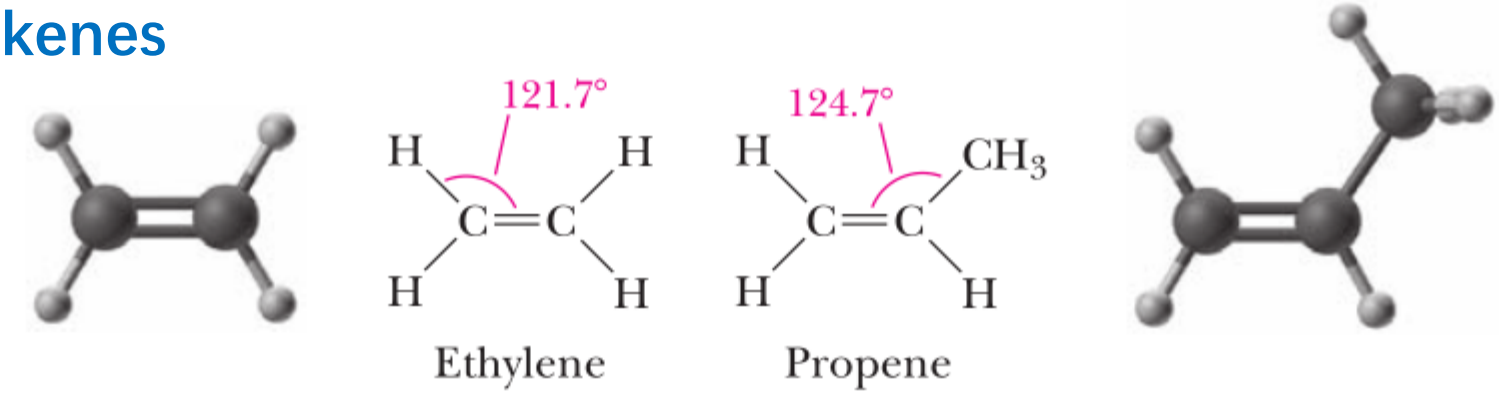
Alkene An unsaturated hydrocarbon that contains a carbon–carbon double bond.

Alkyne An unsaturated hydrocarbon that contains a carbon–carbon triple bond.

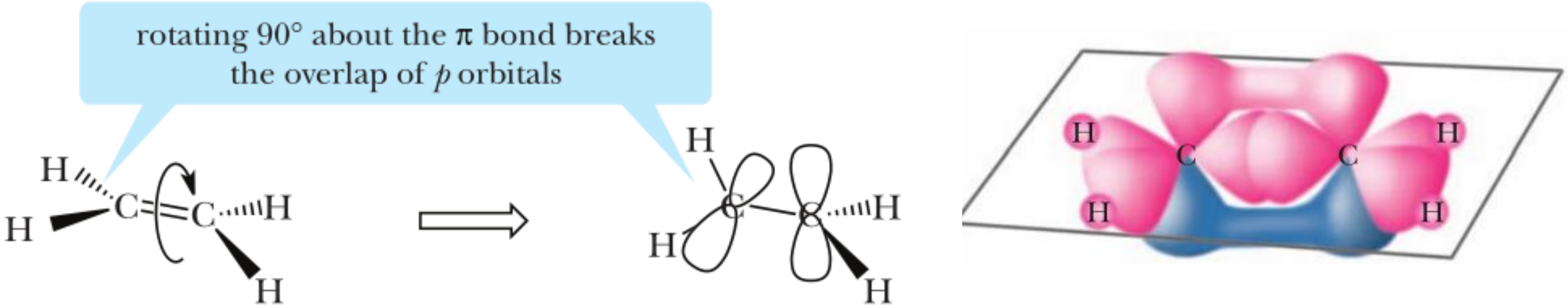
Arene A compoundcontaining one or morebenzene rings.

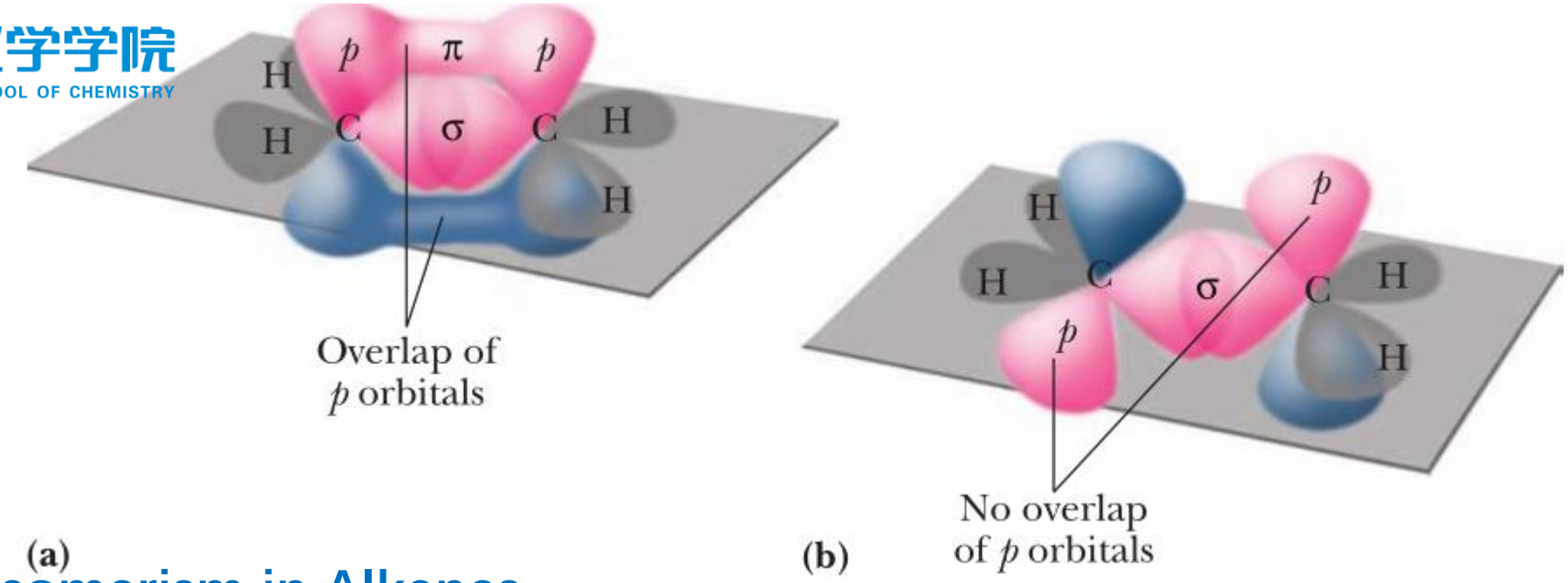
4.1 What Are the Structures and Shapes of Alkenes and Alkynes?

A. Shapes of Alkenes

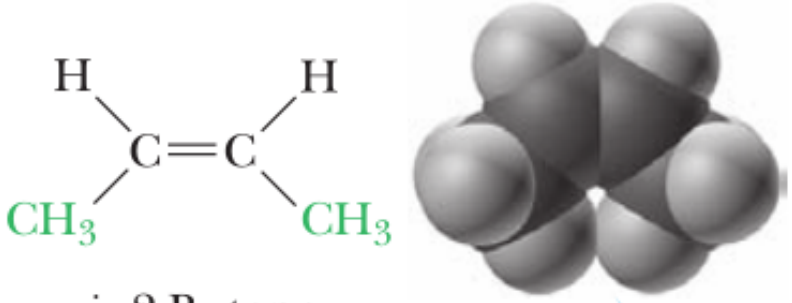


B. orbital overlap model of a Carbon–Carbon Double Bond

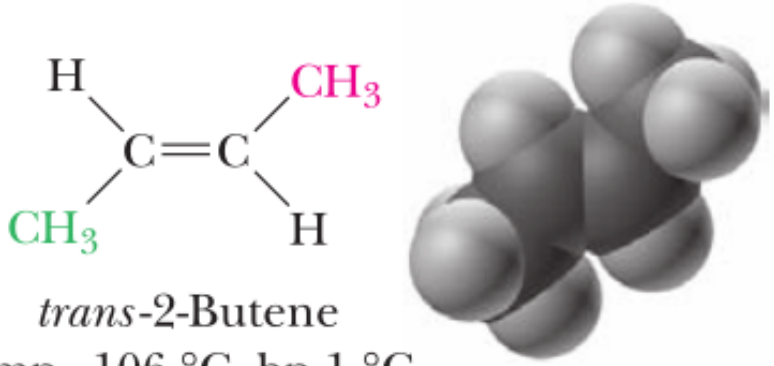




C. *Cis–Trans* isomerism in Alkenes



cis-2-Butene
mp –139 °C, bp 4 °C



trans-2-Butene
mp –106 °C, bp 1 °C

nonbonded interaction (steric) strain makes *cis*-2-butene less stable than *trans*-2-butene

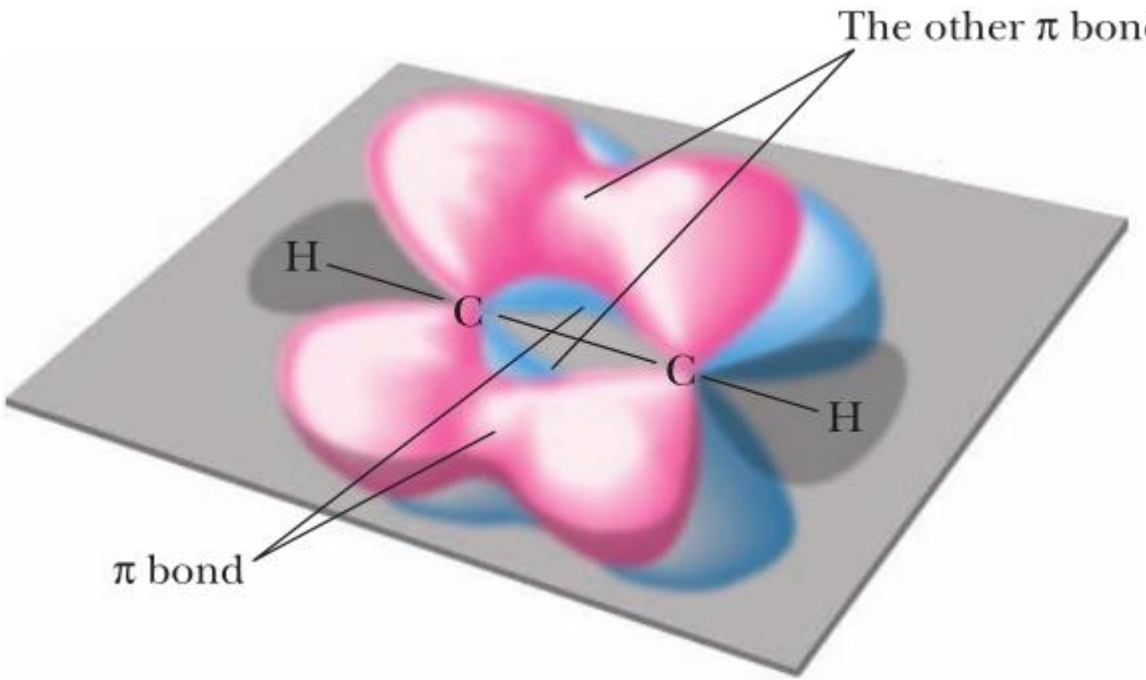
D. Structure of Alkynes

Acetylene

$$H-C\equiv C-H$$

Side view

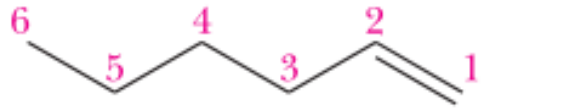
End view

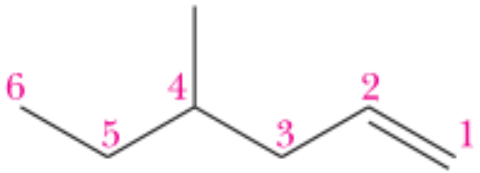


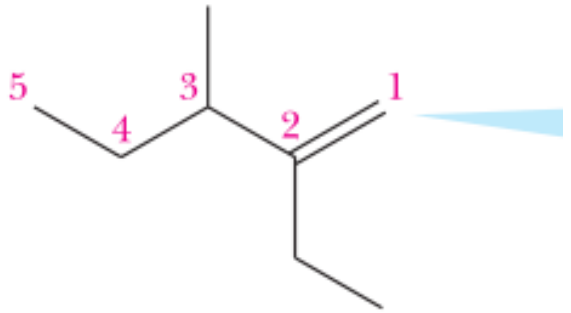
4.2 How Do We Name Alkenes and Alkynes?

A. IUPAC Names

IUPAC names of alkenes by changing the **-an-** infix of the parent alkane to **-en-**







$CH_3CH_2CH_2CH_2CH{=}CH_2$

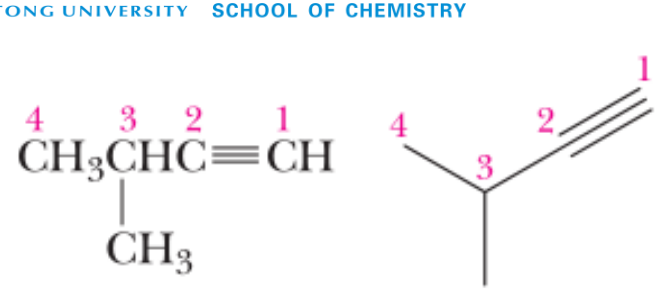
1-Hexene

$CH_3CH_2CH(CH_3)CH_2CH{=}CH_2$

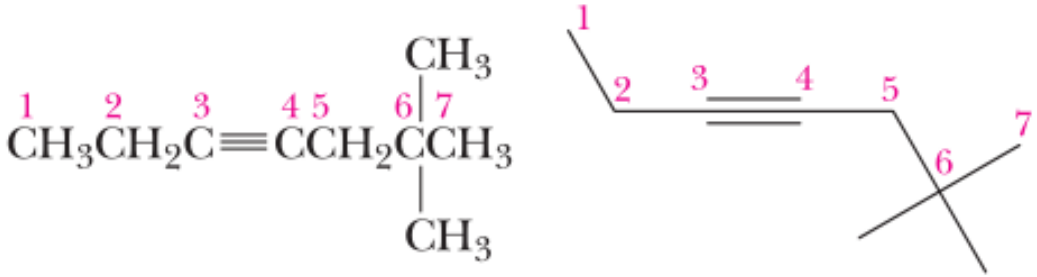
4-Methyl-1-hexene

$CH_3CH_2CH(CH_3)C{=}CH_2$, CH_2CH_3

2-Ethyl-3-methyl-1-pentene



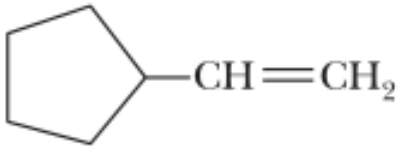
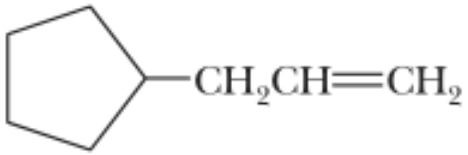
3-Methyl-1-butyne



6,6-Dimethyl-3-heptyne

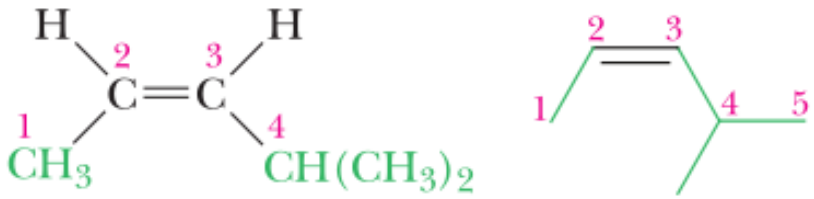
B. Common Names

	$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$CH_3C(CH_3){=}CH_2$
IUPAC name:	Ethene	Propene	2-Methylpropene
Common name:	Ethylene	Propylene	Isobutylene

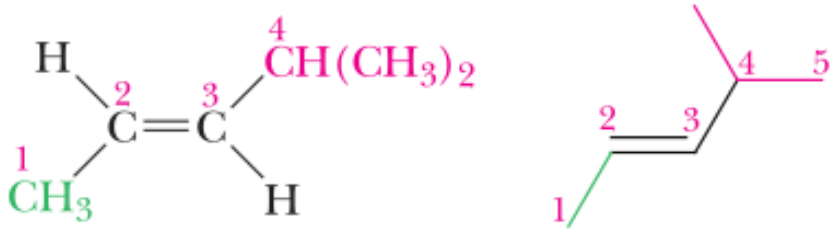
Alkenyl Group	Common Name	Example	Common Name
$CH_2{=}CH-$	Vinyl		Vinylcyclopentane
$CH_2{=}CHCH_2-$	Allyl		Allylcyclopentane

C. Systems for Designating Configuration in alkenes

The *Cis–Trans* System

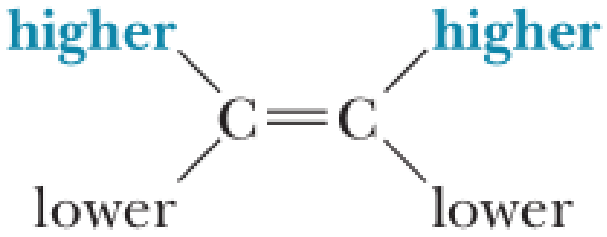


cis-4-Methyl-2-pentene

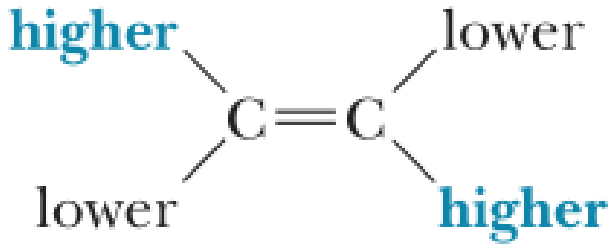


trans-4-Methyl-2-pentene

The E,Z System



Z (*zusammen*)



E (*entgegen*)

Z From the German zusammen, meaning
; specifies that groups of higher priority on the carbons of a double bond are on the same side.

E From the German entgegen, meaning opposite; specifies that groups of higher priority on the carbons of a double bond are on opposite sides.

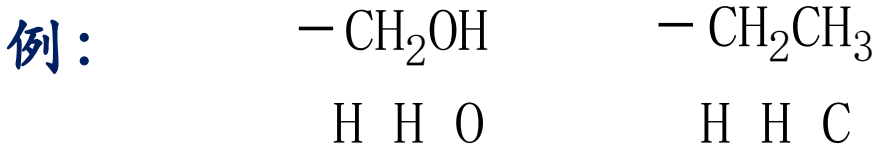
Priority Rules(次序规则)

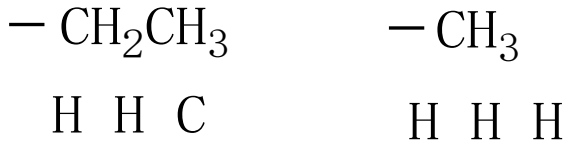
✓ 游离价所在原子，按原子序数排列，原子序数大为较优基团，同位素原子按原子量排列，原子量大为较优基团。

例：　$-OH$　　$-NH_2$　　$-CH_3$

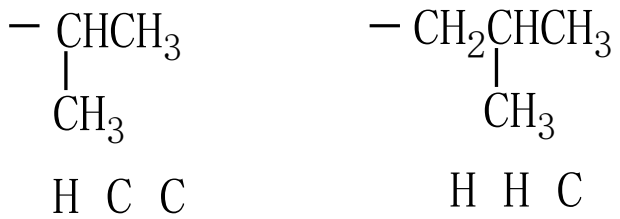
✓ 若游离价所连的原子比较不出来，次序无法确定则要外推。

例：



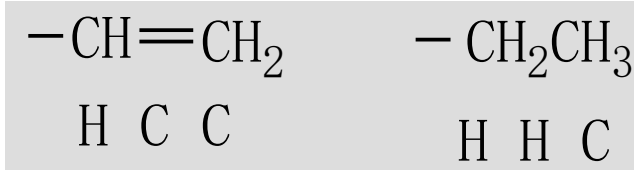


较优基团

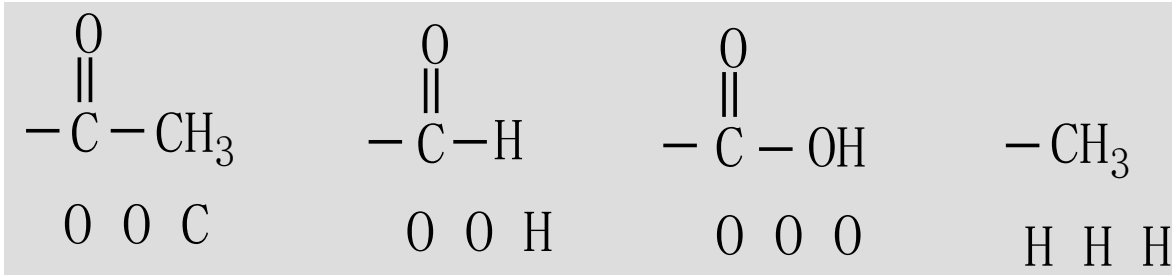


较优基团

✓ 若游离价所连碳上连有双键或叁键时，将双键或叁键当作单键。



较优基团



第二较优　　第三较优　　第一较优

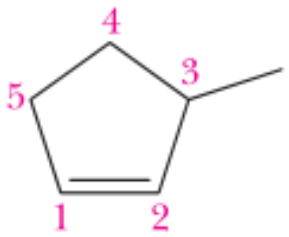
较优基团

-I > -Br > -Cl > -SO_3H > -F > -OCOR > -OR > -OH > -NO_2 > -NR_2 > -NRH > -CCl_3 >

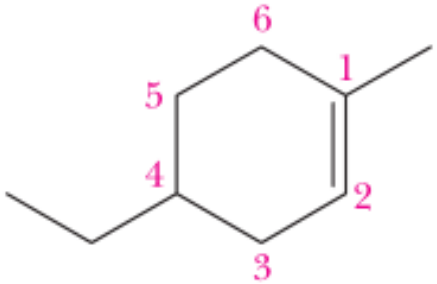
-COCl > CH_2Cl > -COOR > -COOH > -$CONH_2$ > -COR > -CHO > -CR_2OH > -CROH ……

D. Naming Cycloalkenes

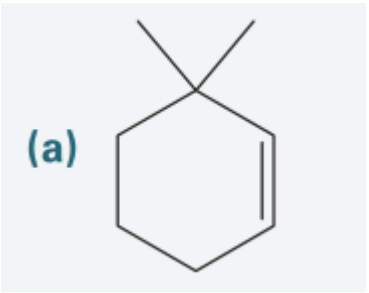
编号从双键碳原子开始，首先保证官能团位次最小，其次使取代基位次最小。



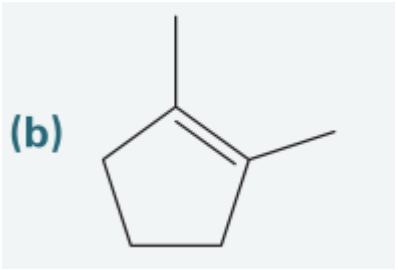
3-Methylcyclopentene
(not 5-methylcyclopentene)



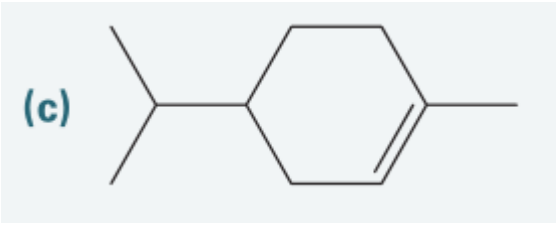
4-Ethyl-1-methylcyclohexene
(not 5-ethyl-2-methylcyclohexene)



3,3-Dimethylcyclohexene

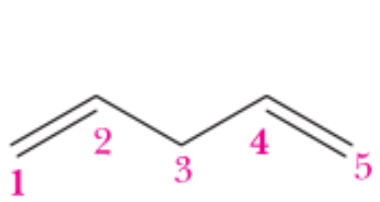


1,2-Dimethylcyclopentene



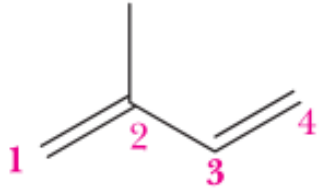
4-Isopropyl-1-Methylcyclohexene

E. Dienes, Trienes, and Polyenes



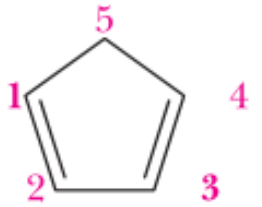
$CH_2{=}CHCH_2CH{=}CH_2$

1,4-Pentadiene



$CH_2{=}C(CH_3){-}CH{=}CH_2$

2-Methyl-1,3-butadiene
(Isoprene)

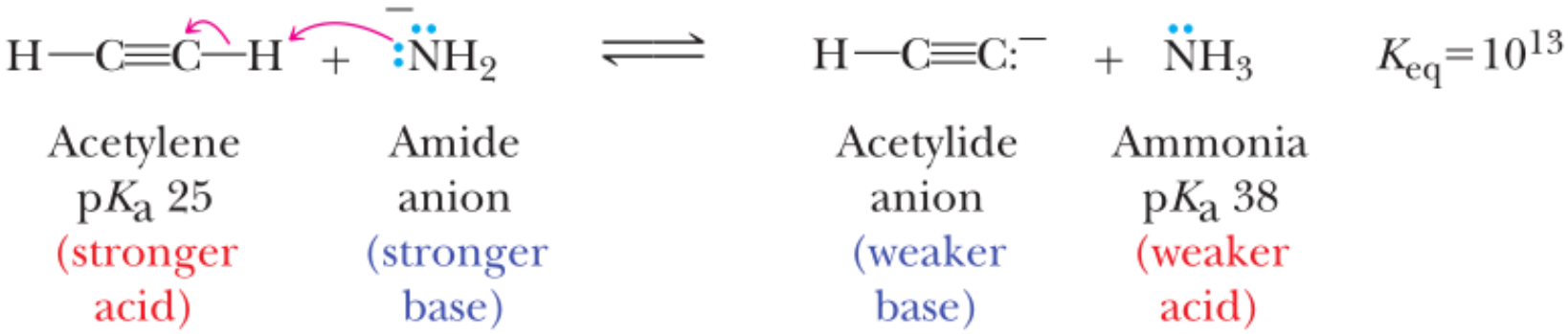


1,3-Cyclopentadiene

4.3 What Are the Physical Properties of Alkenes and Alkynes?

- Alkenes and alkynes are nonpolar compounds, and the only attractive forces between their molecules are dispersion forces（色散力）。
- their physical properties are similar to those of alkanes with the same carbon skeletons.

4.4 Why Are 1-Alkynes (Terminal Alkynes) Weak Acids?



these hydrogens are much lower in acidity and are not deprotonated by $NaNH_2$

$CH_3—CH_2—CH_2—C\equiv C—H$

only this hydrogen is acidic enough to be deprotonated by $NaNH_2$

炔氢的酸性：

TABLE 4.1 Acidity of Alkanes, Alkenes, and Alkynes

Weak Acid		Conjugate Base	pK_a
Water	HO—H	HO^-	15.7
Alkyne	HC≡C—H	HC≡C	25
Alkene	CH_2=CH—H	CH_2=CH^-	44
Alkane	CH_3CH_2—H	$CH_3CH_2^-$	51

Increasing acidity

乙炔中的碳为SP杂化，轨道中S成分较大，核对电子的束缚能力强，电子云靠近碳原子，使乙炔分子中的C－H键极性增加：

$\overset{\delta^- \quad \delta^+}{HC\equiv C-H}$

炔氢具有酸性。

炔化物的生成

- 乙炔或 $RC\equiv C-H$ 可和Na、$NaNH_2$等反应

$$HC\equiv C-H \xrightarrow{Na} HC\equiv CNa \xrightarrow{Na} NaC\equiv CNa$$

$$RC\equiv C-H + NaNH_2 \xrightarrow{液氨} RC\equiv CNa + NH_3$$

亲核试剂

在合成上可将炔基引入产物中——炔基的烷基化

$$CH_3C\equiv CH \xrightarrow{NaNH_2} CH_3C\equiv CNa \xrightarrow{CH_3CH_2Br} CH_3C\equiv CCH_2CH_3$$

亲核试剂

注意：
- 是一种增长碳链的方法
- 一般用伯卤代烷

- 炔氢的反应

$$HC{\equiv}CH + 2Ag(NH_3)_2NO_3 \longrightarrow AgC{\equiv}CAg\downarrow + 2NH_4NO_3 + 2NH_3$$

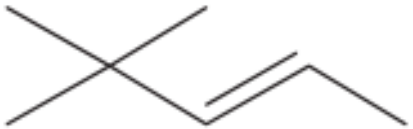
乙炔银（白色）

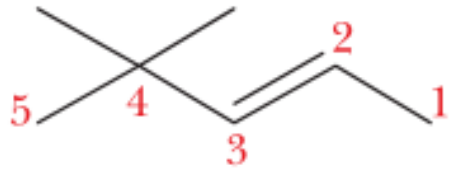
$$HC{\equiv}CH + 2Cu(NH_3)_2Cl \longrightarrow CuC{\equiv}CCu\downarrow + 2NH_4Cl + 2NH_3$$

乙炔亚铜（红色）

应用：鉴别乙炔或 $RC{\equiv}CH$

例：





***trans*-4,4-Dimethyl-2-pentene**

or

***trans*-4,4-Dimethylpent-2-ene**

or

***(E)*-4,4-Dimethyl-2-pentene**

作 业

4. 10、4.18、4.23、27