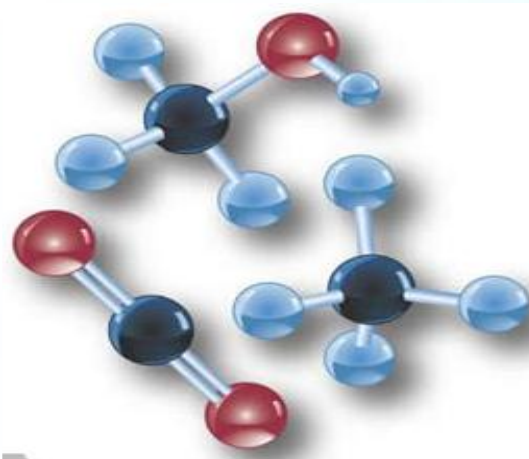
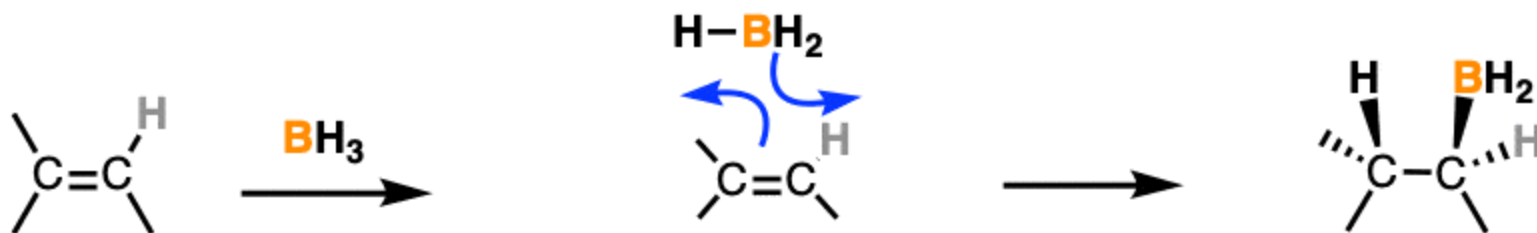


Organic Chemistry



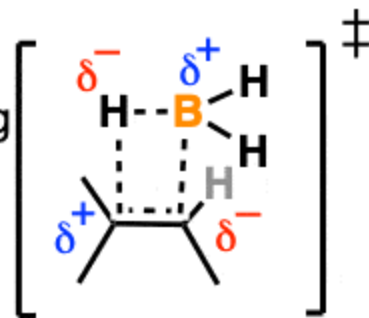


The Hydroboration Mechanism



- **concerted** transition state (all bonds forming and breaking at the same time)

- **syn** addition of B-H across the alkene

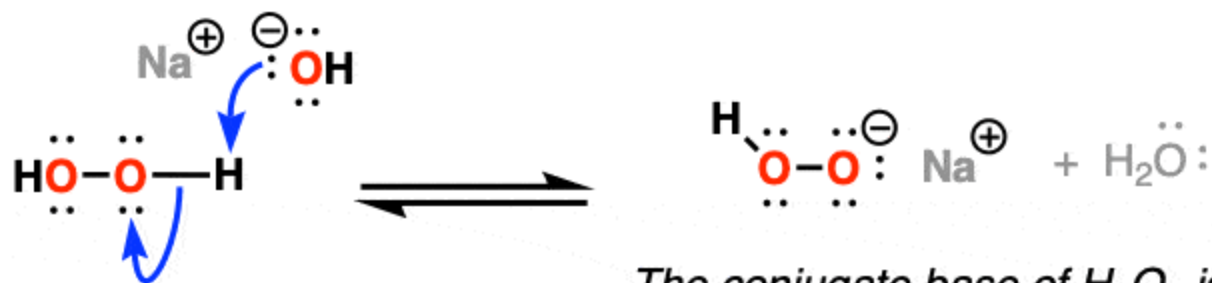


Transition state

- **hydrogen** (2.2) is more electronegative than **boron** (2.0)
- in the transition state, the **H** (δ^-) lines up with the carbon best able to stabilize **positive** charge (i.e. the *most substituted* carbon)

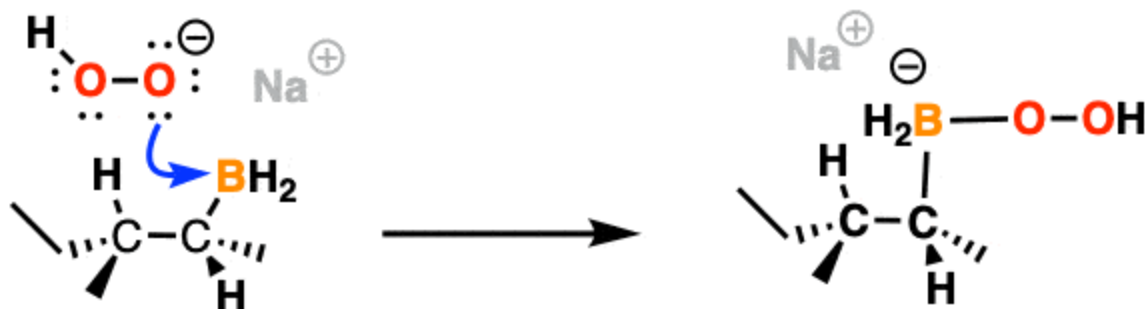


Step 1: Deprotonation of H_2O_2



The conjugate base of H_2O_2 is a better nucleophile than H_2O_2 itself

Step 2: Attack of peroxide on boron

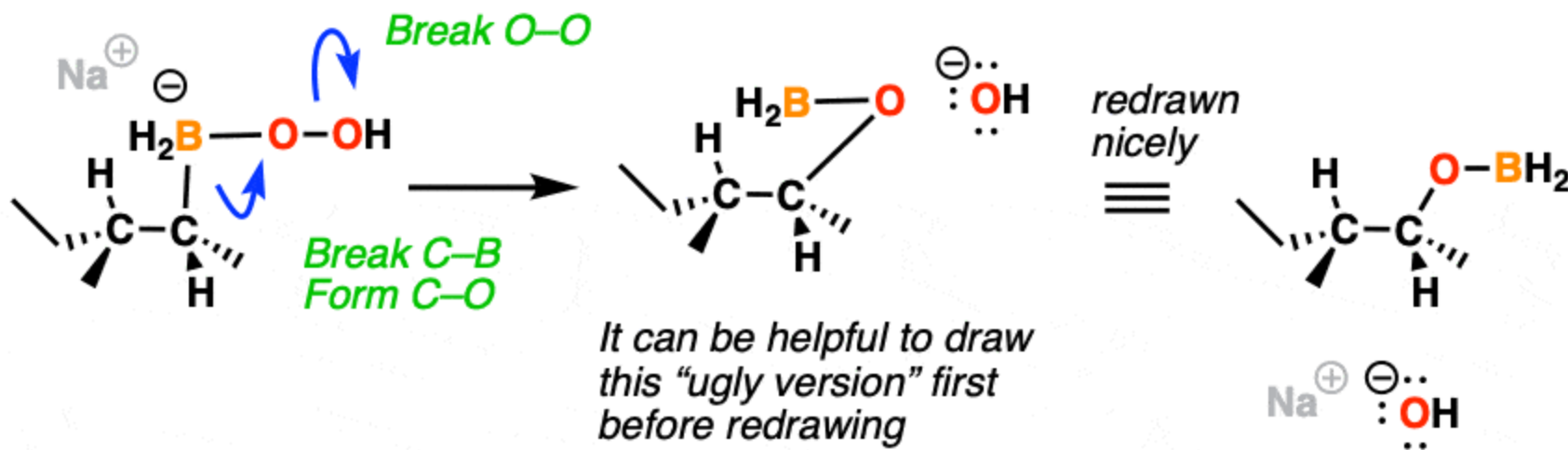




Mechanism of the key rearrangement step

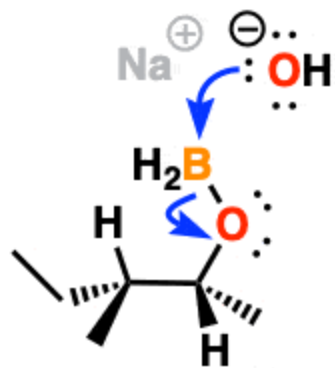
Step 3: Rearrangement

In this step the pair of electrons in the C-B bond attack oxygen, breaking the weak O-O bond of peroxide, and a new C-O bond is formed:

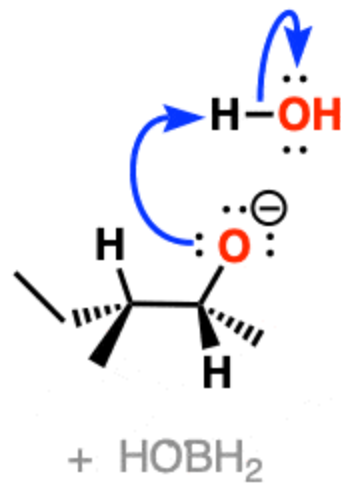
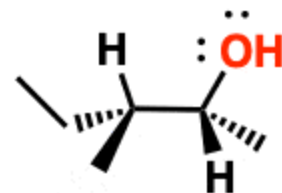




Step 4: Hydrolysis of B–O bond



Step 5: Protonation

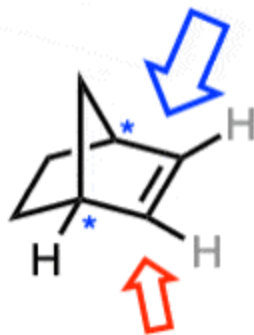




Hydroboration will favor the less hindered face of the alkene

If the alkene is on a molecule with pre-existing chiral centers, one face of the alkene may be more accessible to reagents than the other, leading to diastereomers

top face
approach - **avored**
(less hindered)



bottom face
approach
(more hindered)

* denotes chiral center

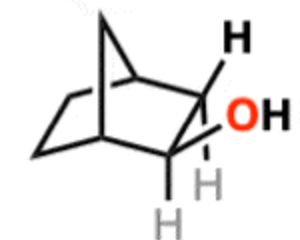
BH_3



H_2O_2

NaOH

Note that oxidation
occurs with
complete retention
of stereochemistry

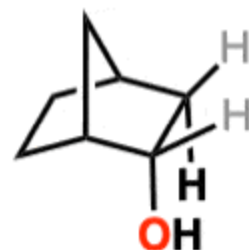


(+ enantiomer)

> 99 %

major
diastereomer

+



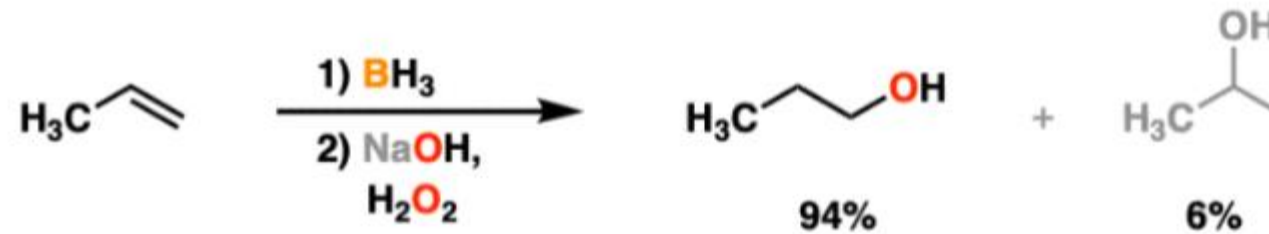
(+ enantiomer)

< 1%

minor
diastereomer



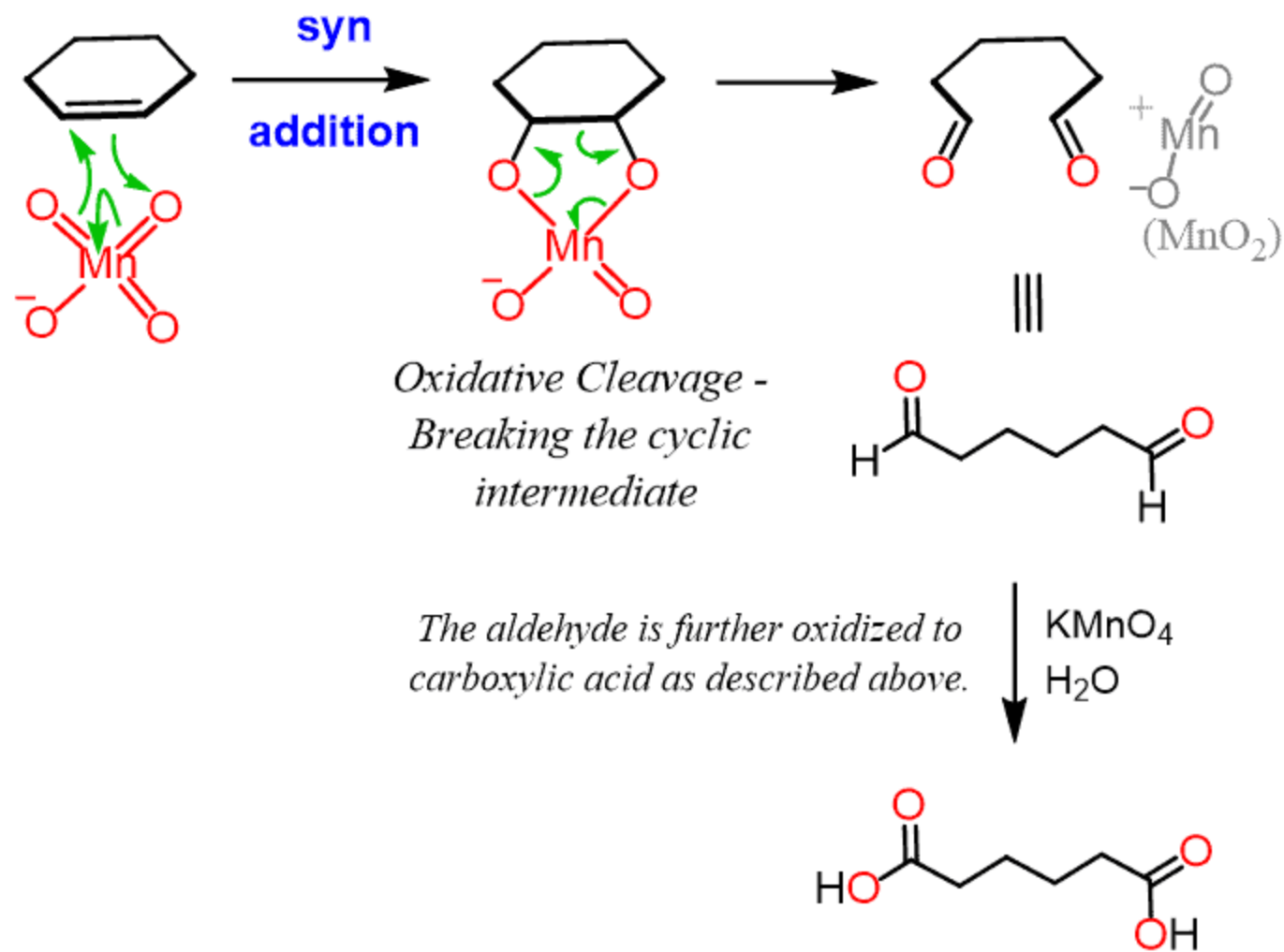
When hydroboration is performed on **propene**, the result is a 94:6 ratio of anti-Markovnikov to Markovnikov alcohols **A** and **B**



What do you predict will happen to anti-Markovnikov selectivity on **trifluoromethyl propene**?

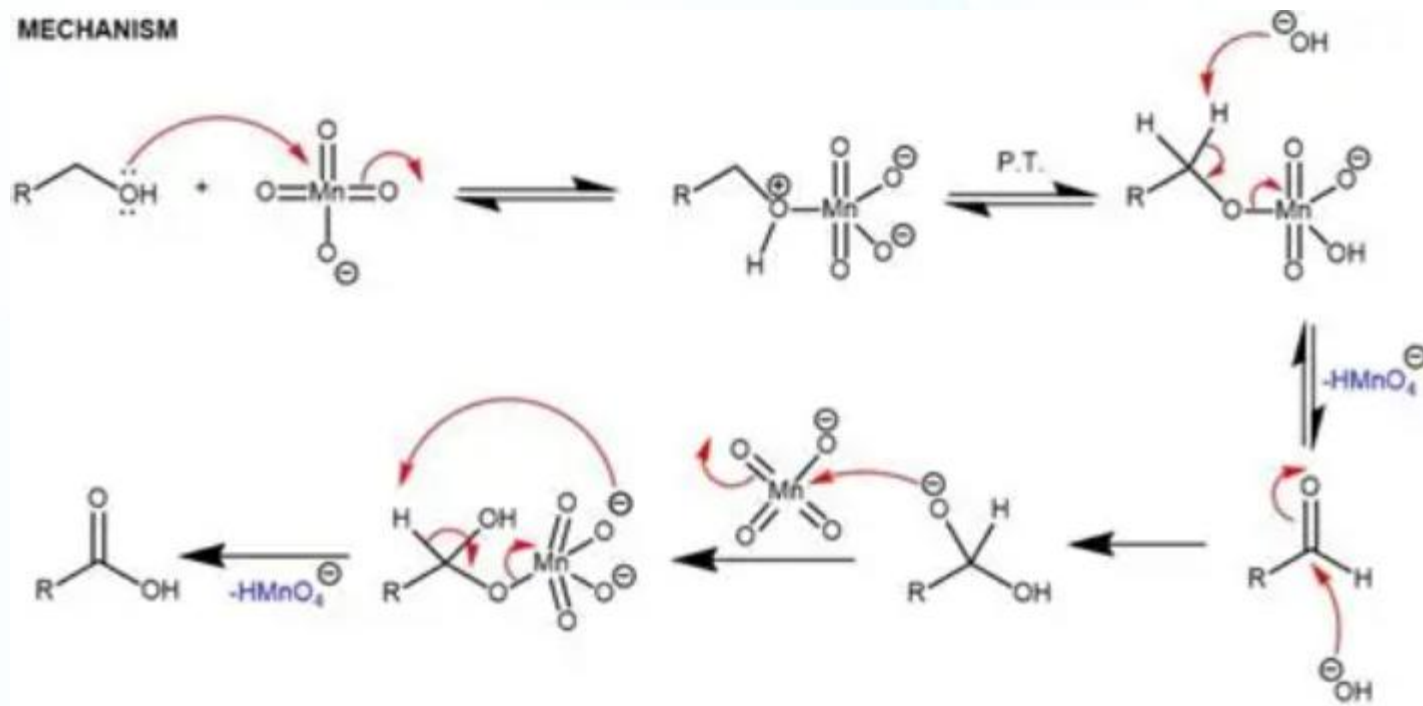


- A) Higher anti-Markovnikov selectivity (more A, less B)
- B) Lower anti-Markovnikov selectivity (less A, more B)
- C) About the same (+/- 2%)





MECHANISM





Chapter 6

Organic Compounds

—Alkyne and Conjugated Dienes

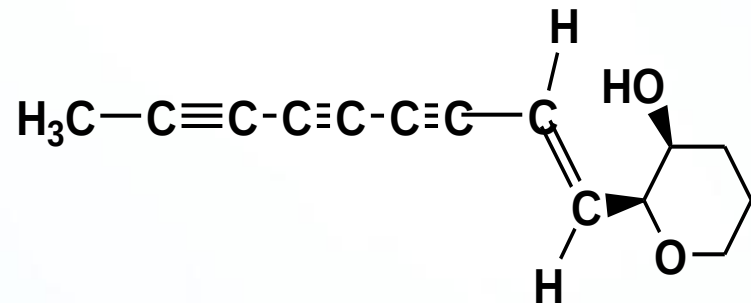


Outline:

- 1. How do we name alkynes?**
- 2. What are the structures and shapes of Alkynes?**
- 3. What is the electrophilic additions to alkenes?**
- 4. Why are 1-Alkynes (Terminal alkynes) weak acids?**
- 5. How can an acetylide anion be used to create a new carbon-carbon bond?**
- 6. How can alkynes be reduced to alkenes and alkanes?**
- 7. What are the structures and shapes of conjugated Dienes?**
- 8. What are the characteristic reaction of conjugated Dienes?**

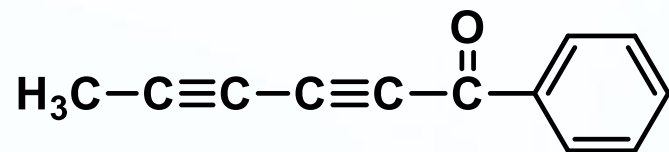


Alkynes



Ichthyothereol

(convulsant used by Amazon Indians for poisoned arrowheads)



Capillin

(Active against skin fungi)



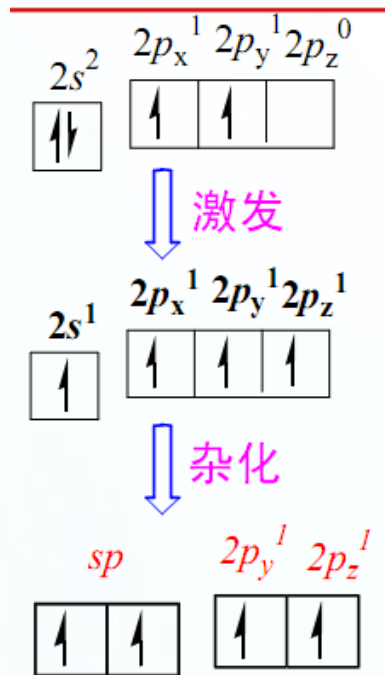
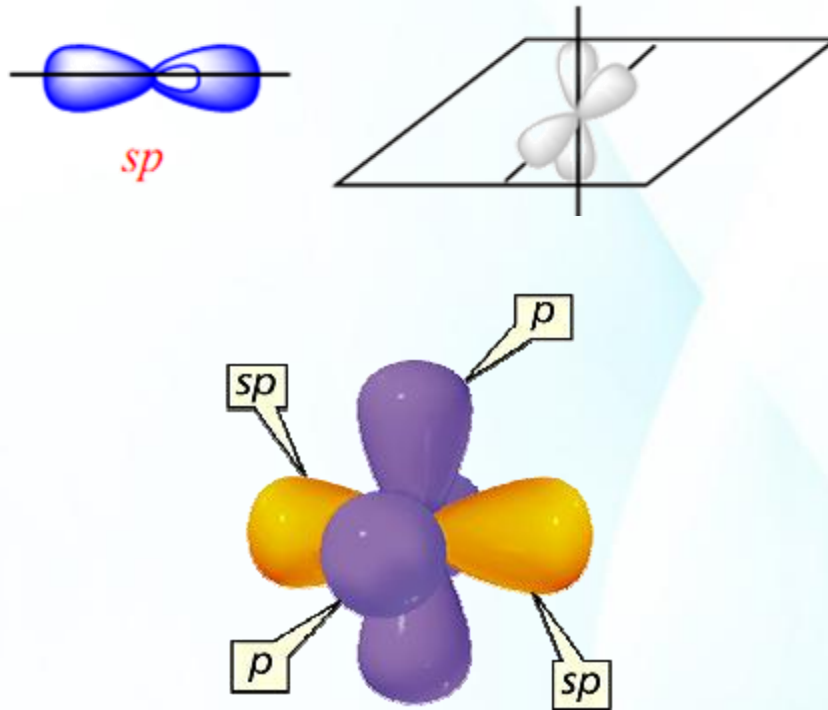
Hydrocarbons that contain a $\text{-C}\equiv\text{C-}$ bond are called alkynes.

General formula: $\text{C}_n\text{H}_{2n-2}$

n is the number of carbons in the chain.

Ethyne	C_2H_2	$\text{CH}\equiv\text{CH}$
Propyne	C_3H_4	$\text{CH}\equiv\text{CCH}_3$
1-Butyne	C_4H_6	$\text{CH}\equiv\text{CCH}_2\text{CH}_3$
2-Butyne	C_4H_6	$\text{CH}_3\text{C}\equiv\text{CCH}_3$
1-Pentyne	C_5H_8	$\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$
2-Pentyne	C_5H_8	$\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$
3-methyl-1-Butyne	C_5H_8	$\begin{array}{c} \text{HC}\equiv\text{CCHCH}_3 \\ \\ \text{CH}_3 \end{array}$

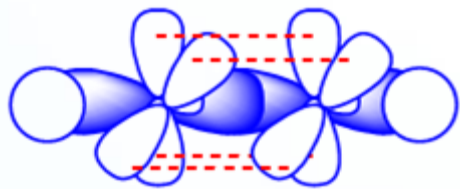
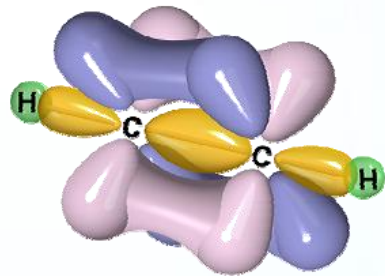
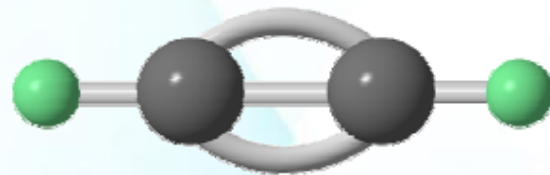
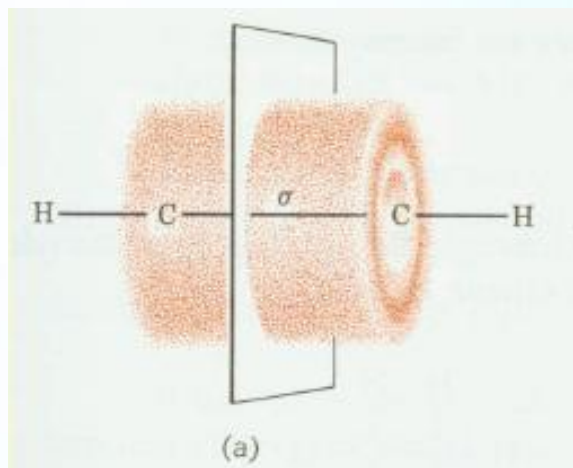
炔烃的结构



sp杂化，两个sp杂化轨道在一直线上，杂化轨道中s轨道和p轨道的成分各占一半



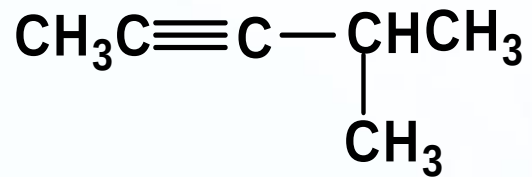
乙炔的结构



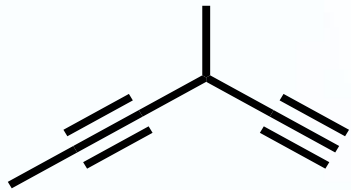
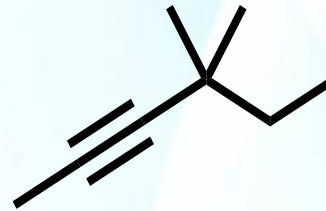
1. Nomenclature

- ① 要选择含有 $C\equiv C$ 的最长碳链为主链；
- ② 编号从最距离三键最近的一端开始，并用阿位伯数字表示双键的位置。

Similar to the Nomenclature for alkenes, only the suffix –ene in alkenes is replaced by –yne.



4-Methyl-2-pentyne

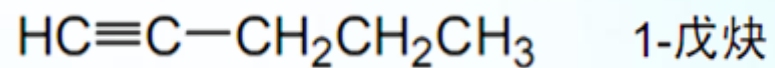


4,4-dimethyl-2-hexyne
4,4-dimethylhex-2-yne

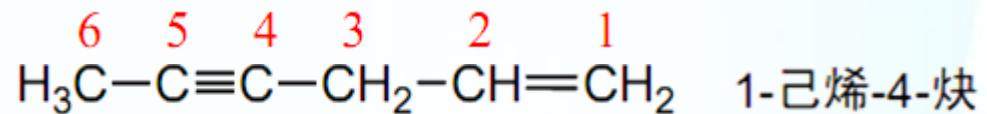
3-methyl-1,4-hex-di-yne
3-methylhex-1,4-diyne



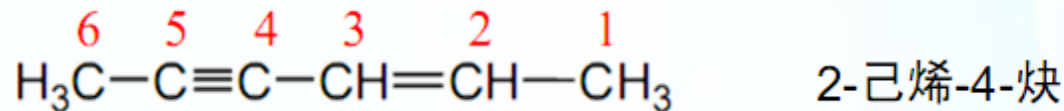
- 选含叁键的最长链为主链
- 使叁键的编号最小
- 按编号规则编号
- 同时有叁键和双键，并可以选择时，使双键的编号最小



Pent-1-yne



Hex-1-ene-4-yne

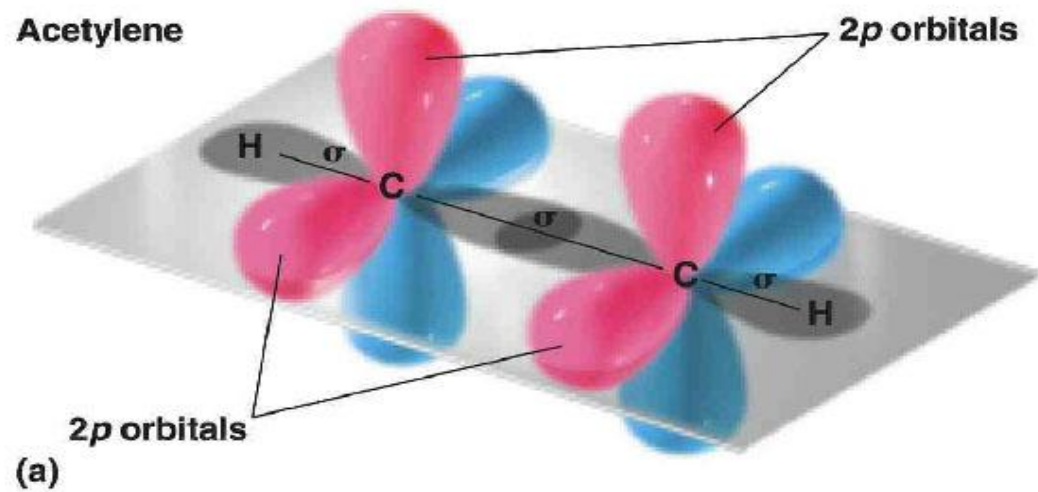
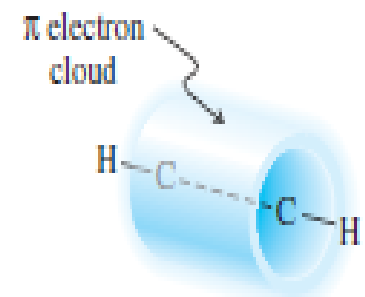
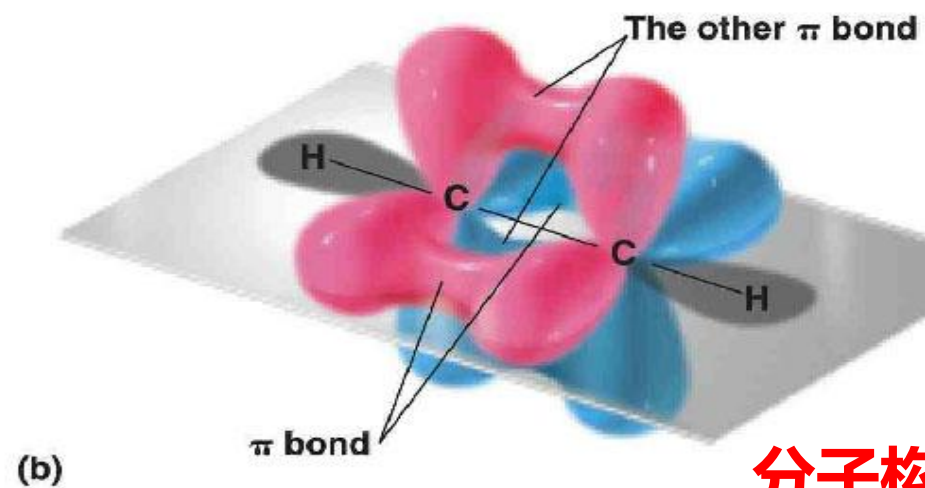
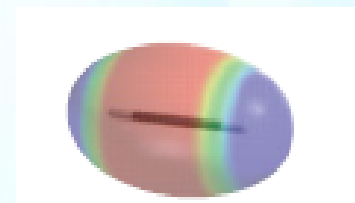


Hex-2-ene-4-yne



2. Structure

Acetylene



分子构型：线型

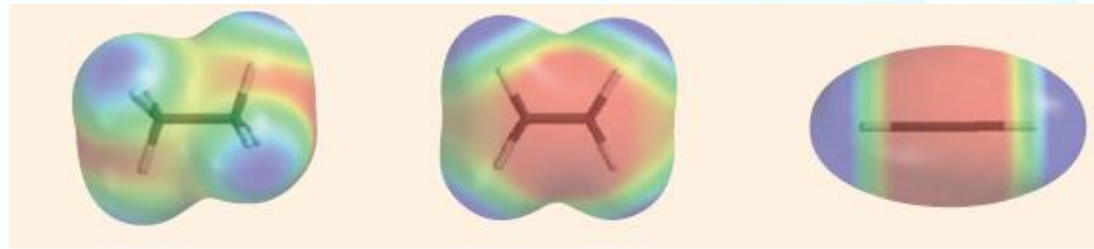


炔烃的物理性质

- 无色物质；常温常压下，2 - 4个碳气体；5 - 17个碳液体18个碳以上固体
- 炔烃的沸点随着分子中碳原子数的增大而升高
- 炔烃随碳原子数增加而增大,但都小于1
- 不溶于水，易溶于有机溶剂，相似相溶的规律

炔烃的结构特点:

- ① - $\text{C}\equiv\text{C}$ - 中碳原子为 sp 杂化;
- ② - $\text{C}\equiv\text{C}$ - 中有一个 σ 键、2个相互垂直的 π 键; sp 杂化轨道中的 s 成份多 (s 电子的特点就是离核近, 即 s 电子云更靠近原子核)。

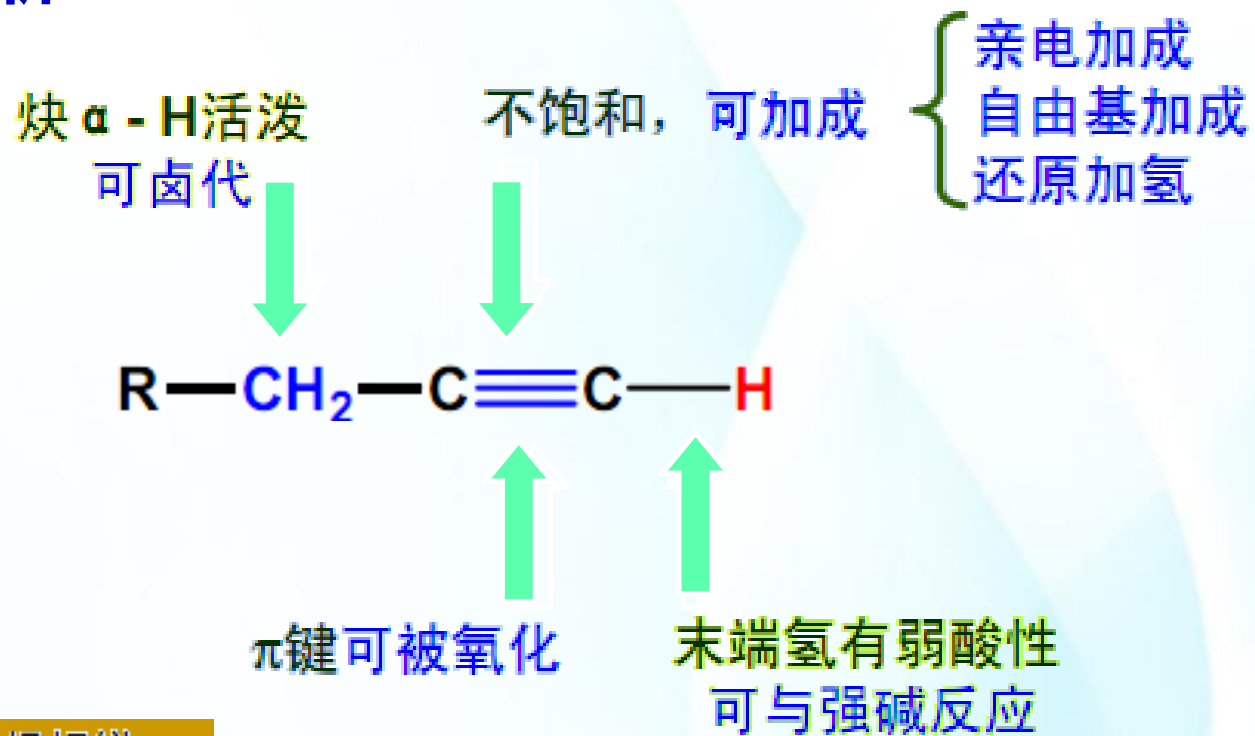


问题: 根据炔烃的结构, 它应具有怎样的化学性质?



3. Chemical Properties

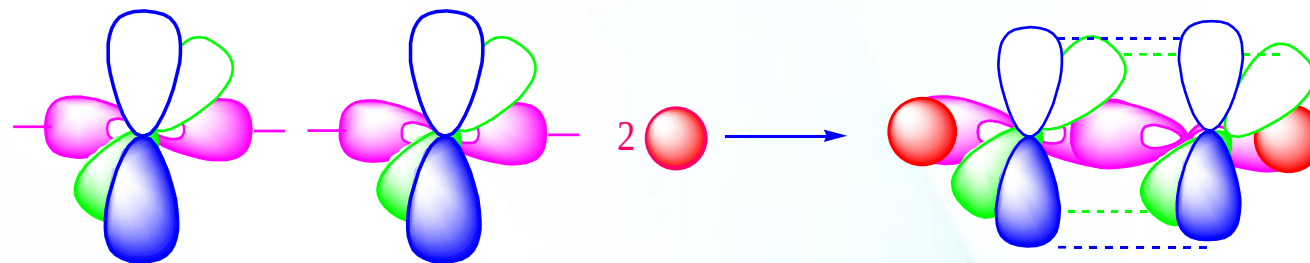
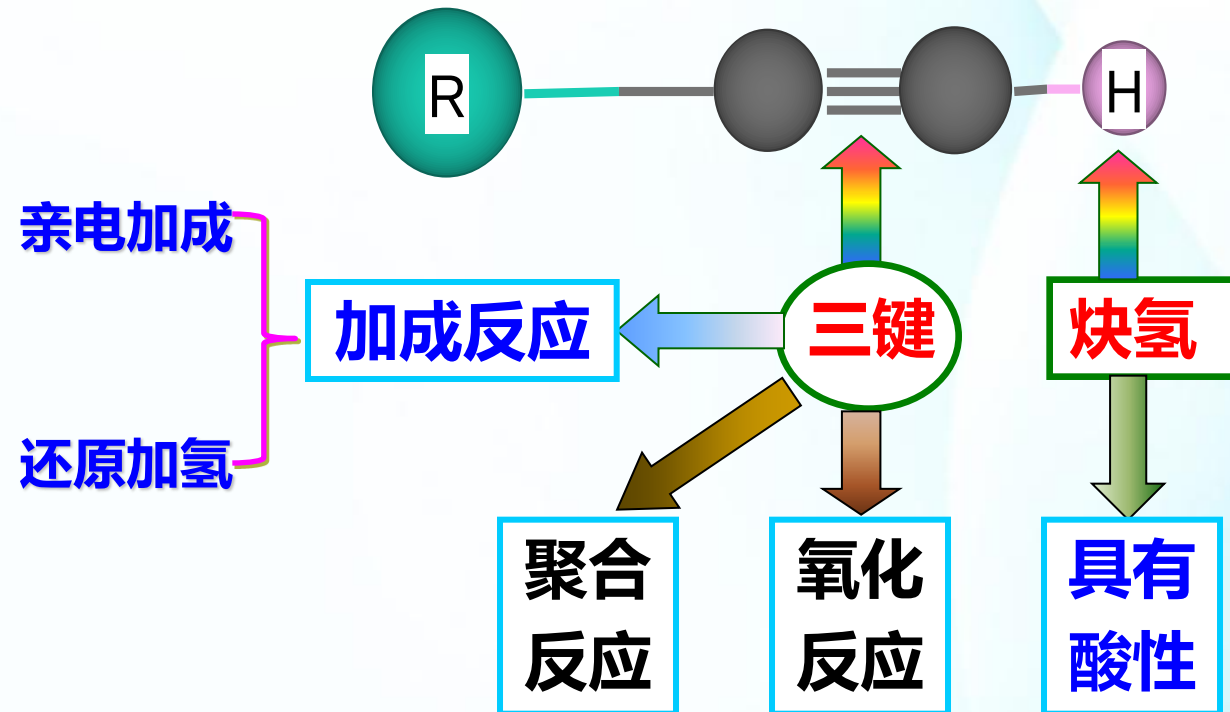
炔烃的性质分析



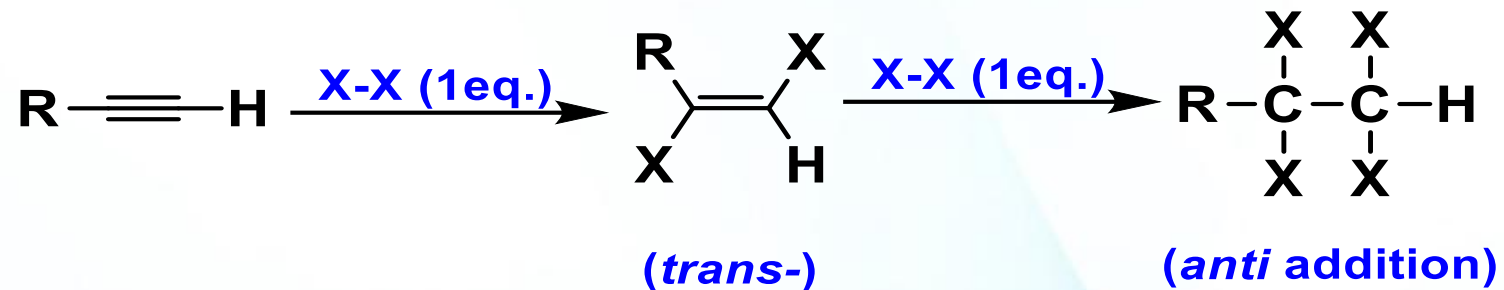
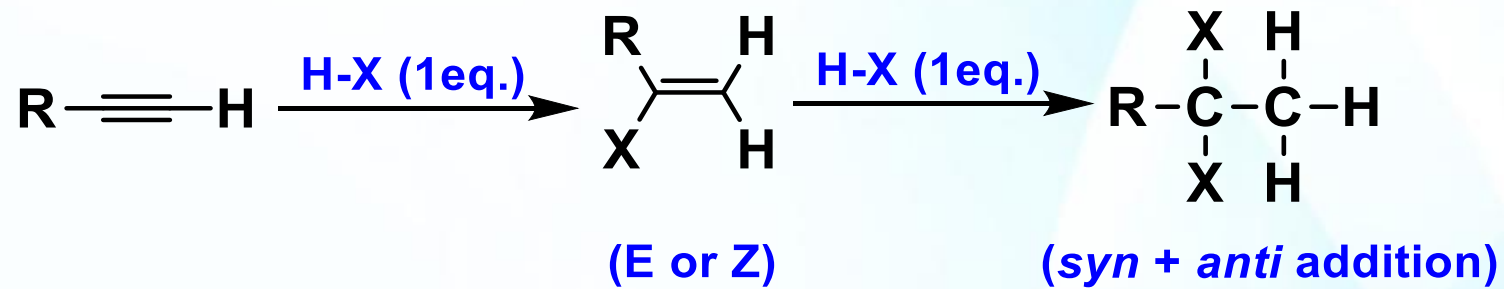
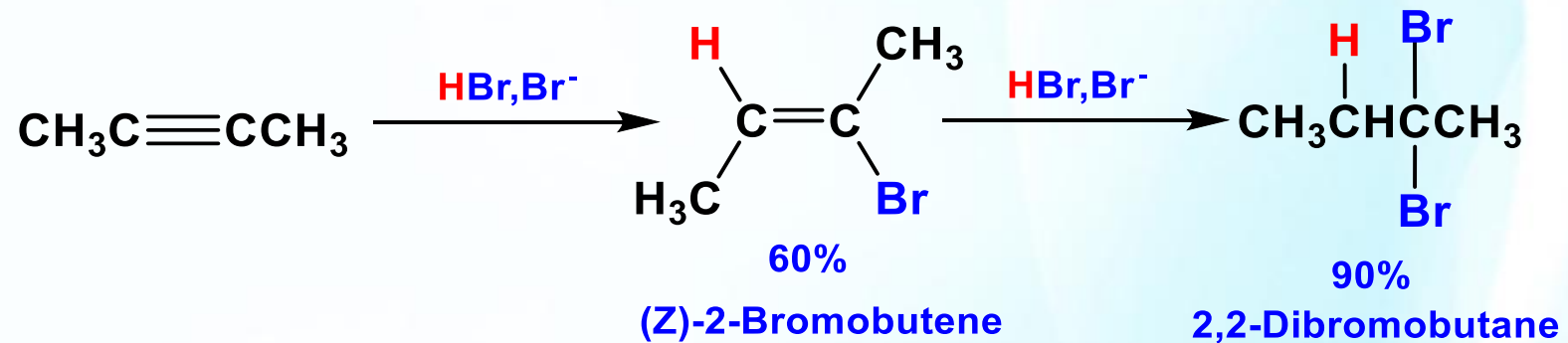
- 炔烃的性质与烯烃相似
- 问题: 两者有何不同之处?
炔烃有何特殊性质?



3. Chemical Properties



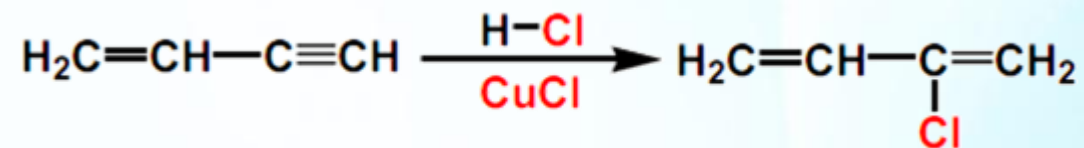
(1) Electrophilic Additions to Alkynes

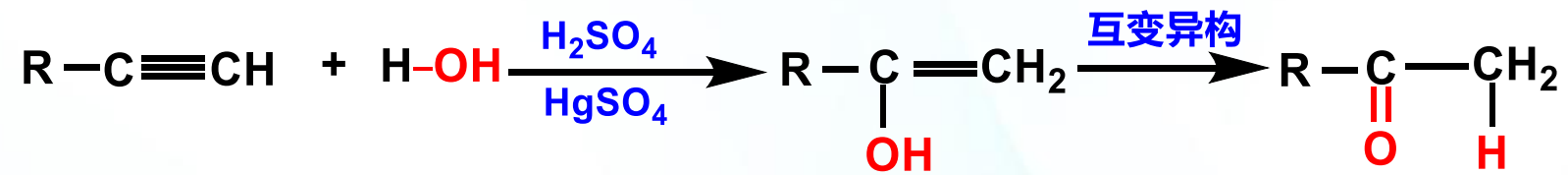
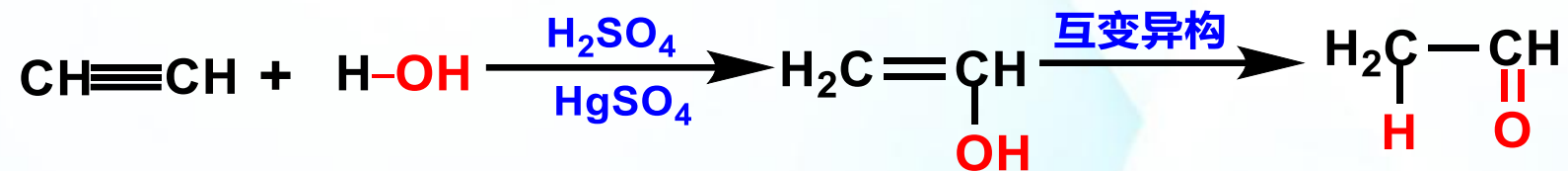
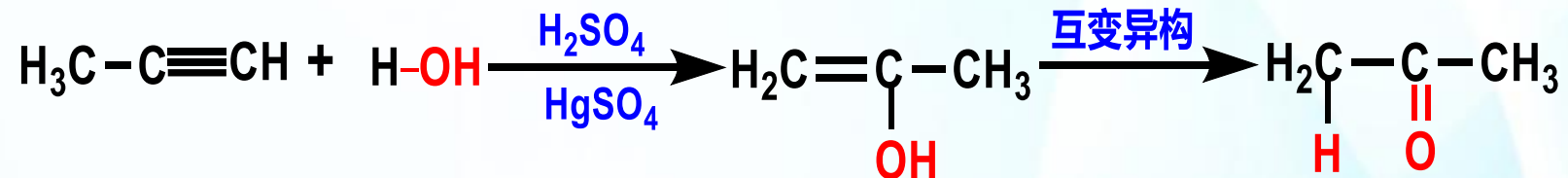




- 分步加成，可控制在第一步。
- 炔烃的加成遵循马氏规则且为反式加成
- 合成上应用：（1）制烯基卤代物（2）制偕二卤代物

催化剂（Hg盐或Cu盐）存在时，叁键比双键易加成



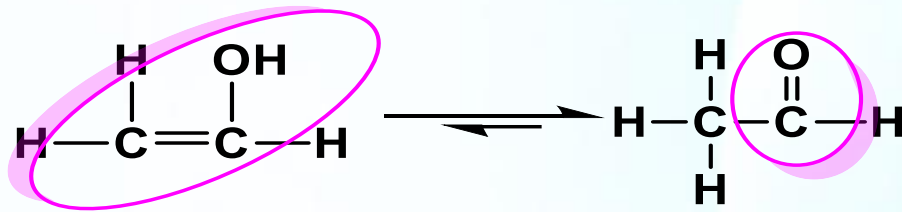


The intermediate undergoes acid-catalyzed rearrangement to give a ketone instead. This process is known as a keto-enol tautomerism.

Tautomerism

室温下，两个构造异构体间能迅速地自行相互转变，达到动态平衡的现象，叫互变异构现象。

互变异构体：分子中因某一原子的位置转移而产生的官能团异构体。

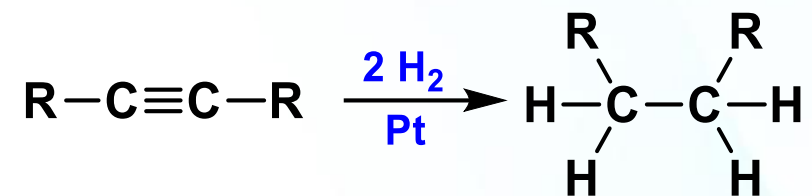


总键能 2678KJ/mol
1%

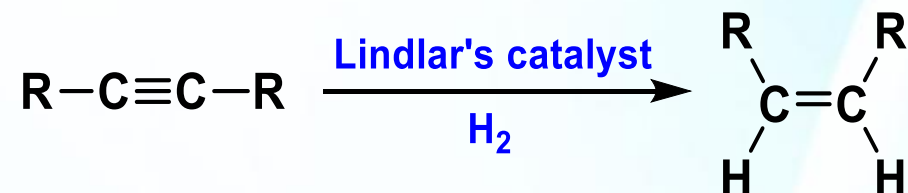
2741KJ/mol 更稳定!
99%



(2) Hydrogenation



The reaction can be stopped at the alkene stage if a less active or 'poisoned' catalyst is used.

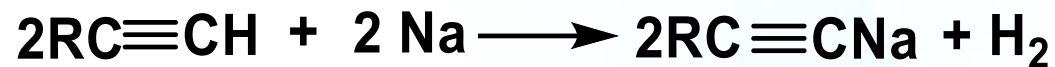
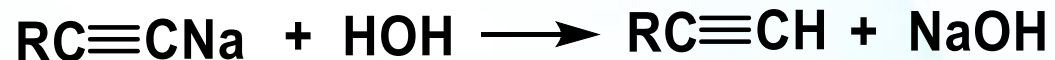
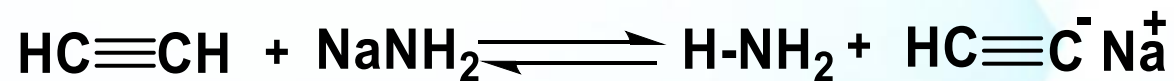


Lindlar's catalyst consists of metallic palladium deposited on calcium carbonate which is then treated with lead acetate and quinoline. (钯-碳酸钙-醋酸铅)

The stereochemistry of the alkene from such a reaction is **Z** since both hydrogen atoms are added to the same side of the alkyne.

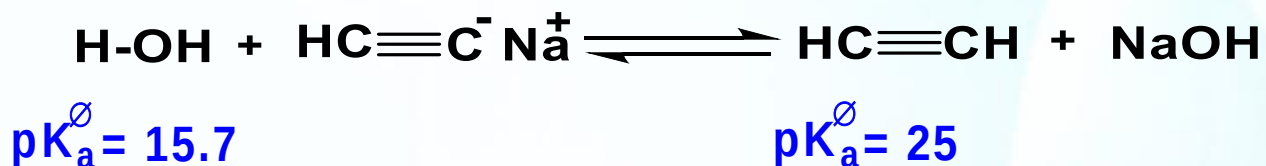


(3) Weak Acidity of terminal alkynes



$$pK_a^\ominus = 25$$

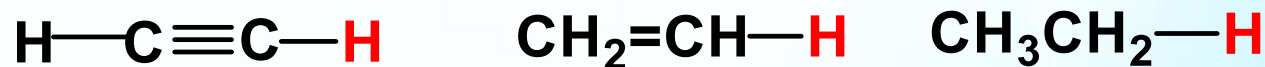
$$pK_a^\ominus = 35$$



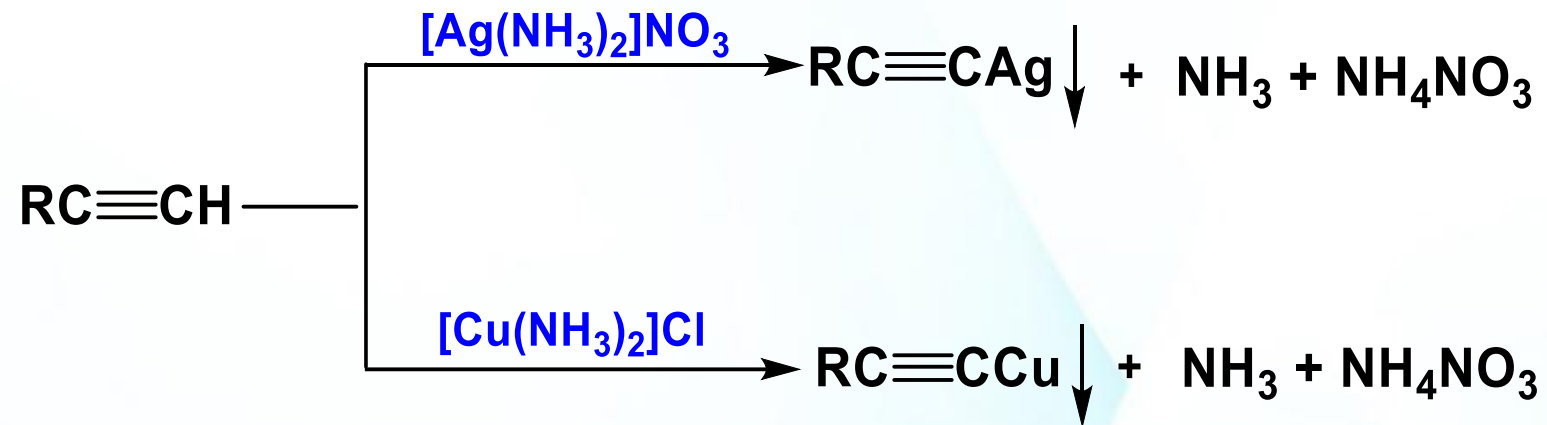
$$pK_a^\ominus = 15.7$$

$$pK_a^\ominus = 25$$

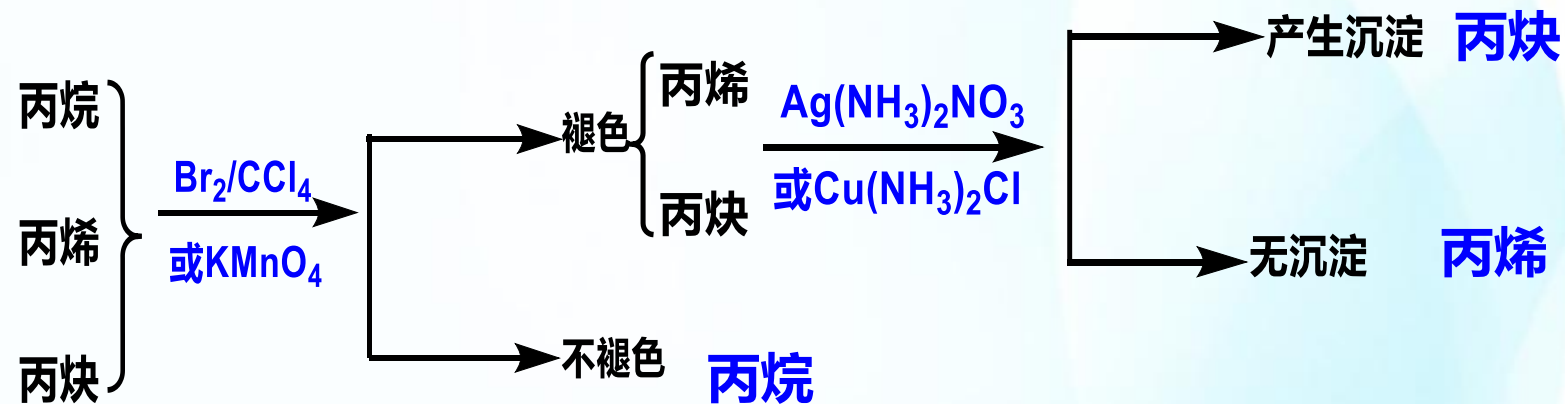
Acidity: $\text{H}_2\text{O} > \text{ROH} > \text{HC}\equiv\text{CH} > \text{NH}_3 > \text{RH}$



S成分越多，负离子越稳定，酸性越强。



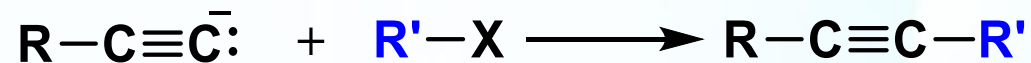
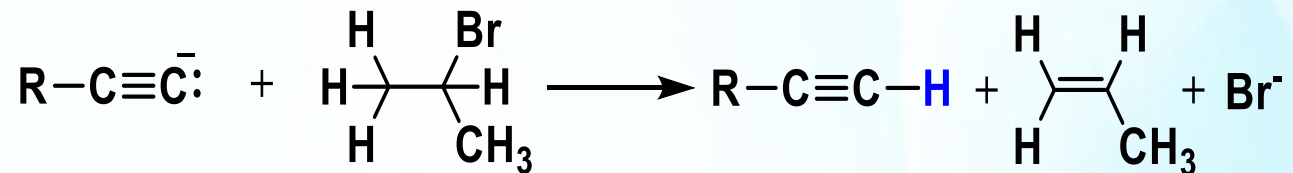
思考：如何用简单的化学方法鉴别丙烷，丙烯和丙炔



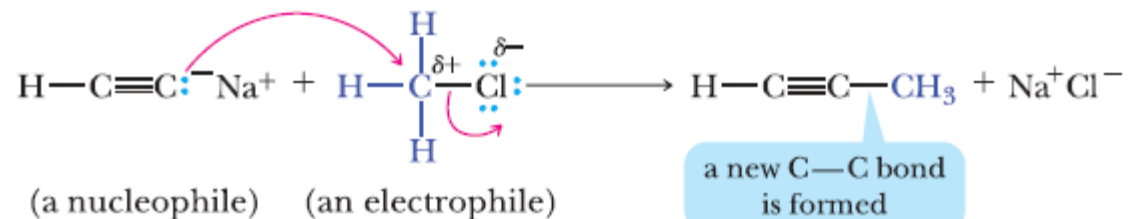
(4) Alkylation of Terminal Alkynes

The hydrogen of a terminal alkyne is weakly acidic and can be removed with a strong base such as sodium amide (NaNH_2) to produce an alkynide ion.

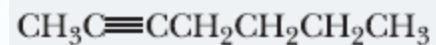
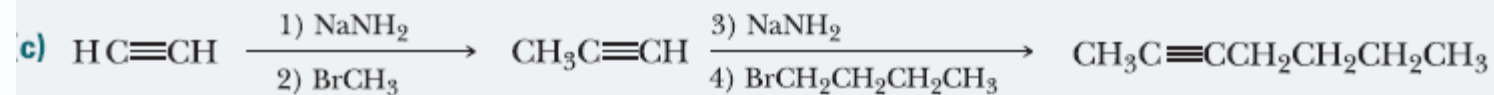
The alkynide ion can be treated with a primary alkyl halide to produce a disubstituted alkyne.



This reaction works best with primary alkyl halides.

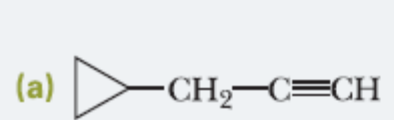
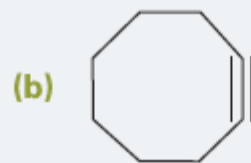


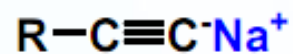
Propose a synthesis for each alkyne starting with acetylene and any necessary organic and inorganic reagents.





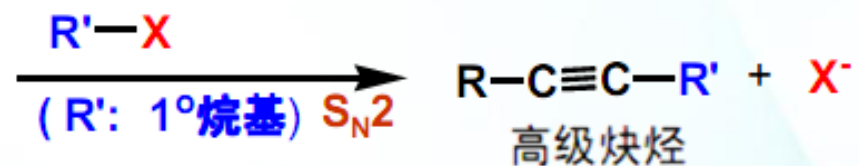
Propose a synthesis for each alkyne starting with acetylene and any necessary organic and inorganic reagents.





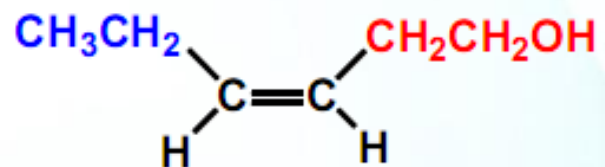
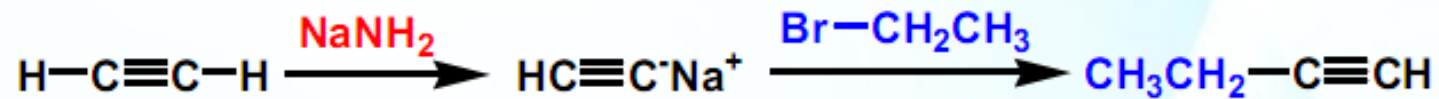
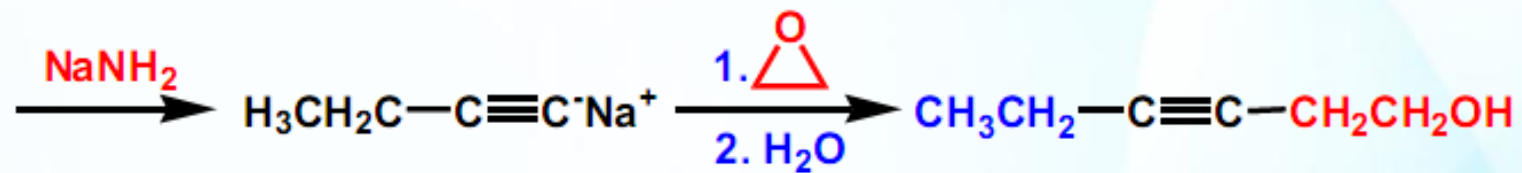
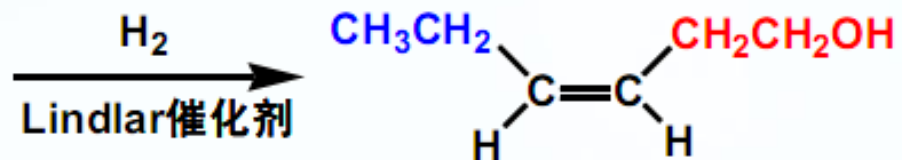
炔基负离子

亲核试剂





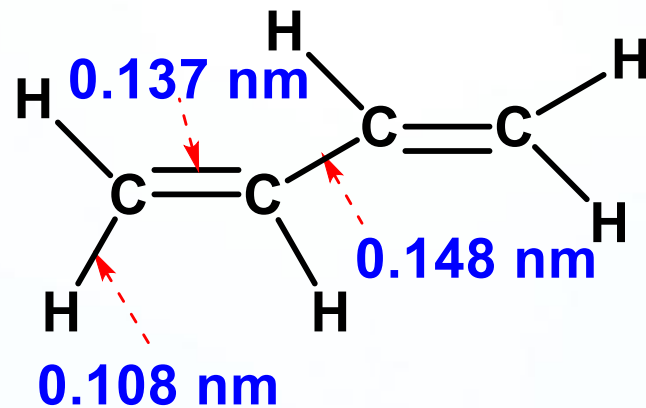
叶醇的合成



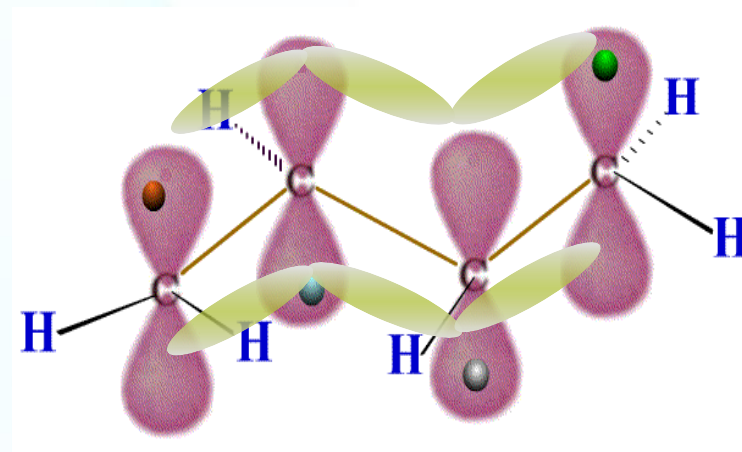


4. Conjugated Dienes

A conjugated diene consists of two alkene units separated by a single bond.



1,3-丁二烯



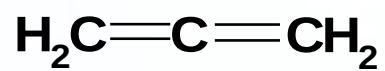
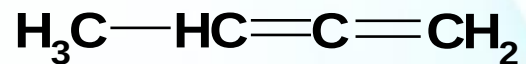
共轭体系结构特性:

- 1) 键长平均化; 2) 吸收光谱向长波方向移动;
- 3) 趋于稳定-氢化热降低;
- 4) 共轭体系可以发生共轭加成。

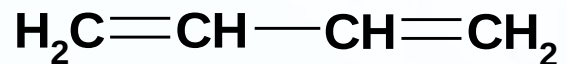
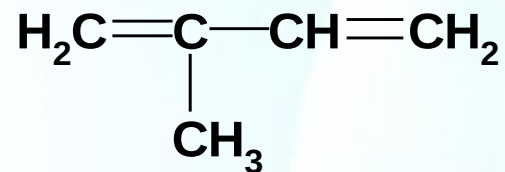


分类

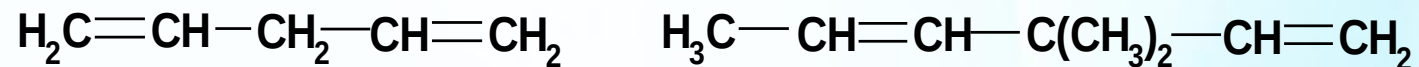
- 累积二烯烃：两个双键连在同一个碳原子上。



- 共轭二烯烃：两个双键被一个单键隔开。



- 隔离二烯烃：两个双键被多个单键隔开。

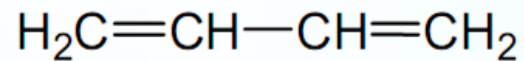
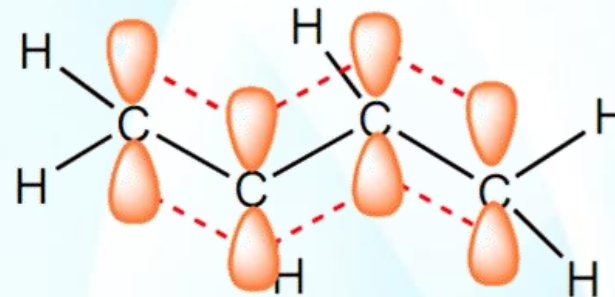




共轭效应: 由于共轭双键的存在, 而使分子中原子间发生相互影响, 以致引起键长的平均化, 体系稳定性增强的作用

共轭效应的类型

- π - π 共轭
- p - π 共轭



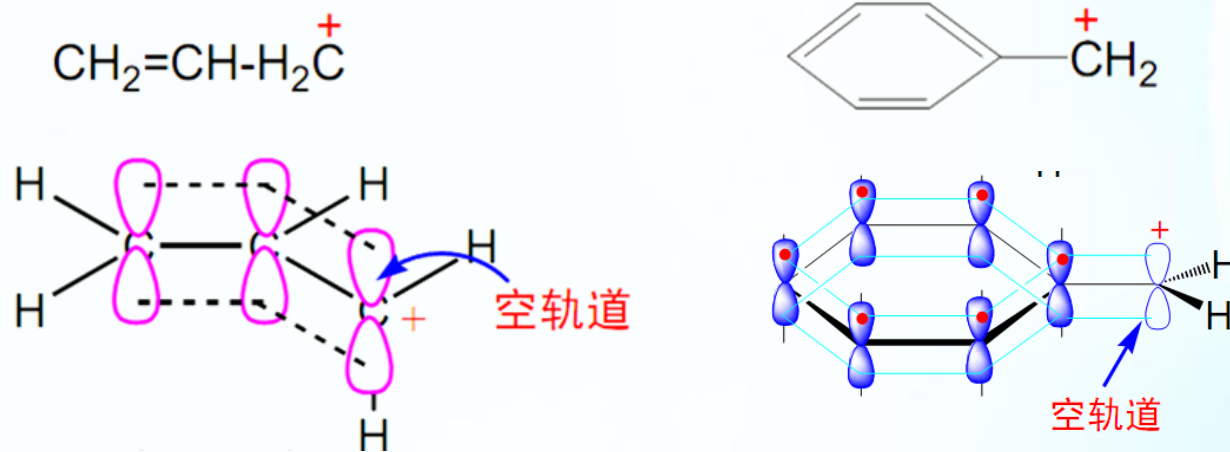
这种 π 轨道和 π 轨道参与的共轭, 叫 π - π 共轭

p- π 共轲：由原子p轨道与 π 键形成的共轲体系

- **多电子共轲 π 键(p- π 共轲)**：电子数大于原子数，双键或三键碳原子上连接的原子带有孤对电子。由p轨道和 π 轨道参与的共轲

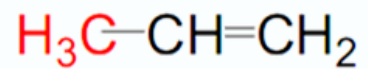
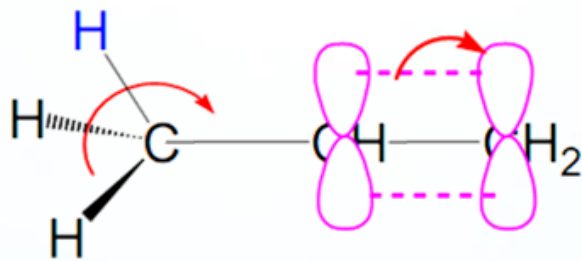
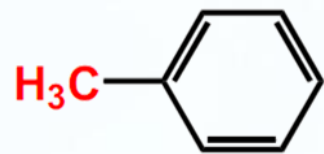
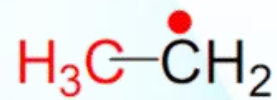
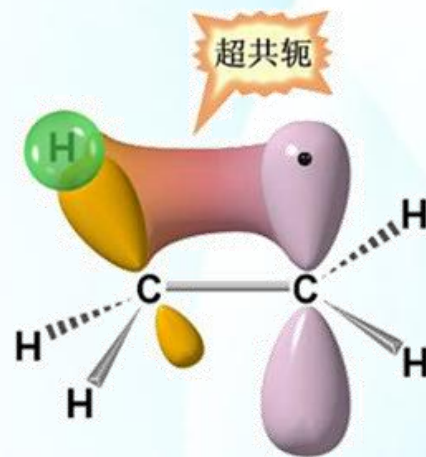
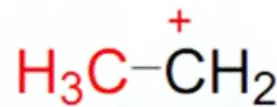
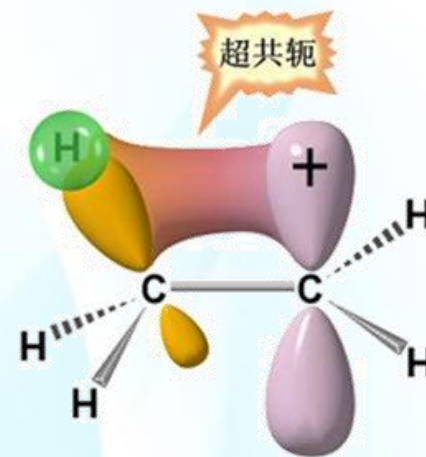


- **缺电子共轲 π 键(p- π 共轲)**：电子数小于原子数，双键或三键碳原子上连接的原子带有空的p轨道,如烯丙基正离子。也由p轨道和 π 轨道参与共轲

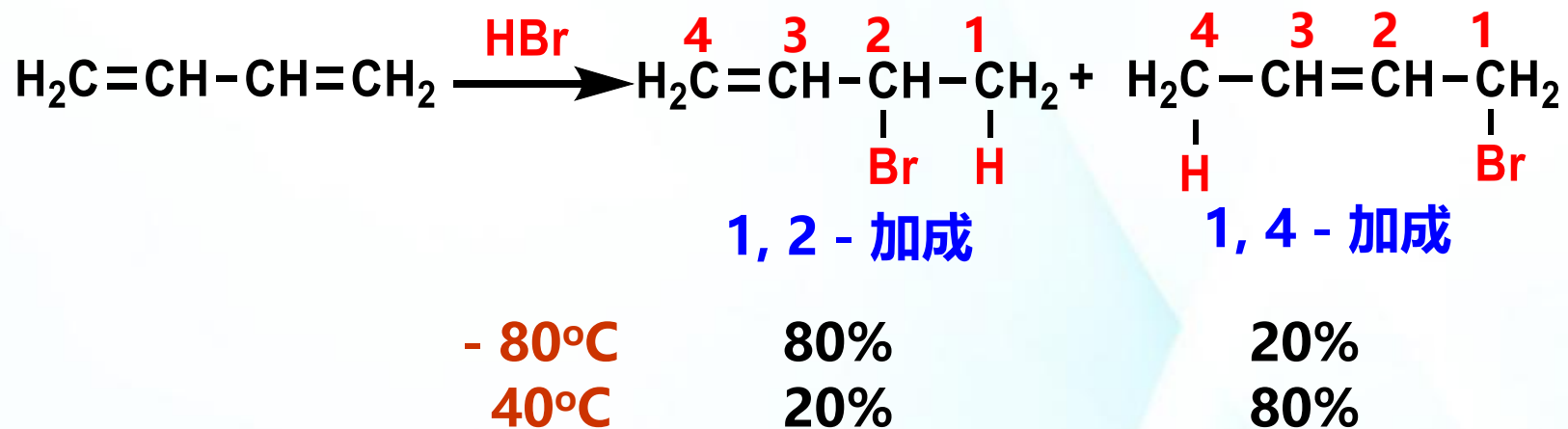




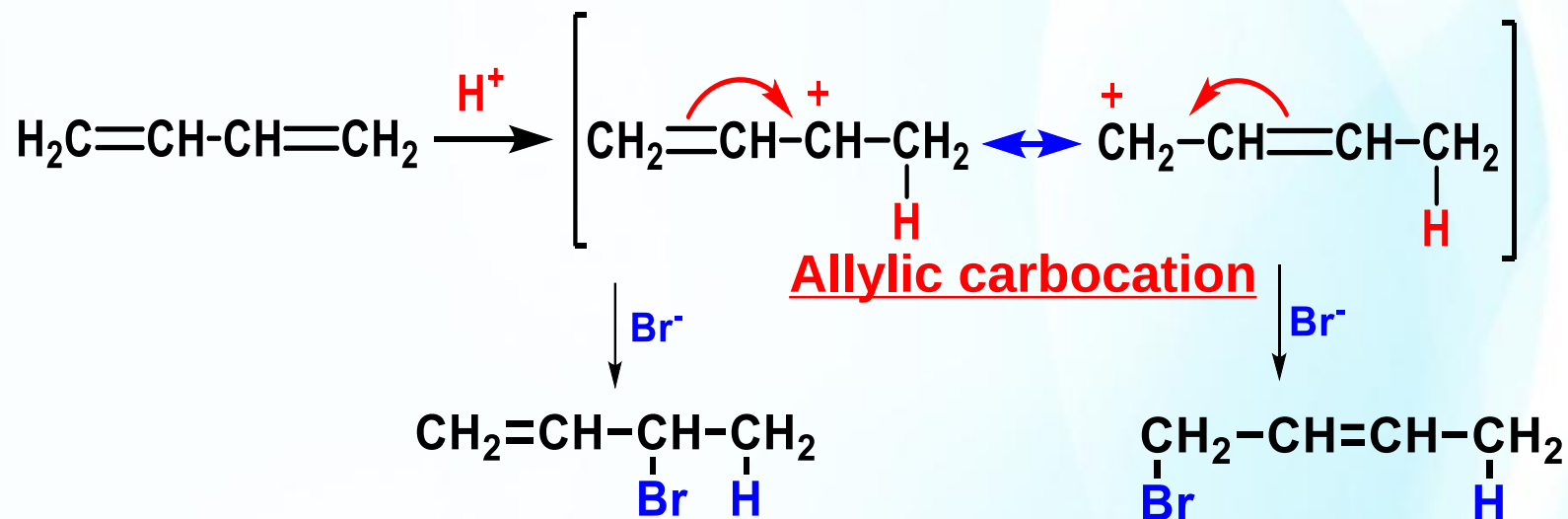
➤ σ - π 超共轭



Electrophilic Additions of conjugated Dienes



高温有利于1,4-加成，低温有利于1,2-加成。



Summary

1. 炔烃的命名;

2. 炔烃的结构;

3. 炔烃的化学性质

亲电加成反应 (烯醇式-酮式互变异构)

催化氢化反应

末端炔烃的酸性

末端炔烃的烷基化

4. 共轭二烯烃的结构与亲电加成反应。

作业：

P161: 5.15, 5.19, 5.33, 5.43



也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!