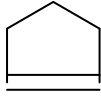


第四章 炔烃和二烯烃

通式: C_nH_{2n-2}

同分异构: $CH_3CH_2CH_2C\equiv CH$ $CH_3CH=CHCH=CH_2$  C_5H_8

一 炔烃的结构

1. C原子的SP杂化

键角 180° 直线型

2. $C\equiv C$ 的组成

$H-C\equiv C-H$

二 同分异构和命名

命名类似于烯烃

C_2H_2 $HC\equiv CH$

C_3H_4 $CH_3C\equiv CH$

C_4H_6 $CH_3-C\equiv C-CH_3$ 2-丁炔

C_5H_8 $\begin{array}{c} CH_3-CH-C\equiv CH \\ | \\ CH_3 \end{array}$ 3-甲基-1-丁炔

烯炔同时存在, 烯在前炔在后。双键先编号。主链碳数放在“烯”前面。

eg: $CH_2=CH-CH_2-C\equiv CH$ 1-戊烯-4-炔

$CH_3-C\equiv C-CH_2-\underset{\begin{array}{c} | \\ CH_3 \end{array}}{CH}-CH=CH_2$
3-甲基-1-庚烯-5-炔

若主链的编号有两种不同的系列时, 系用最低系列的原则:

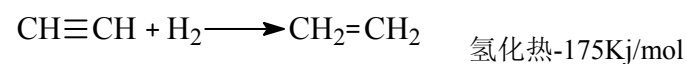
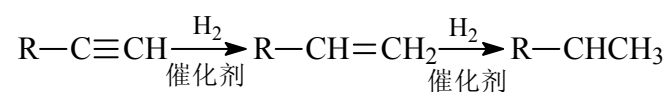
eg: $\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{C}\equiv\overset{1}{CH}$ 3-戊烯-1-炔 (不叫 2-戊烯-4-炔)

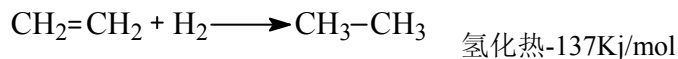
衍生物命名: $CH\equiv CH$ 为母体 (略)

三 炔烃的物性 (自阅)

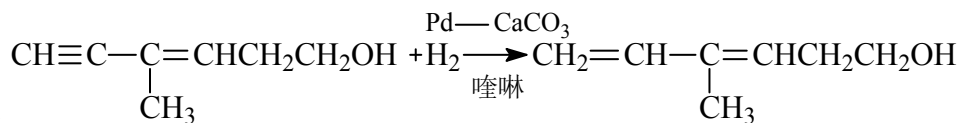
四 炔烃的化学性质

1、催化氢化



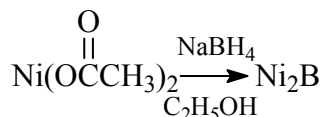


因为炔烃在催化表面的吸附作用较快



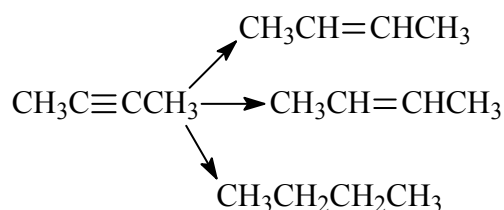
所以

(Lindlar 催化剂 Pd-CaCO₃, Pd-BaSO₄。加喹啉是为了降低活性)



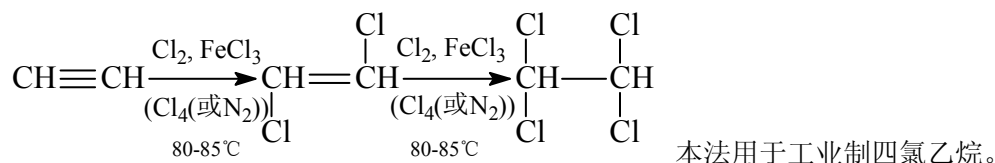
催化剂: Ni₂B

所以

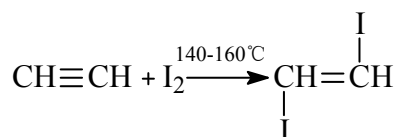


2、亲电加成:

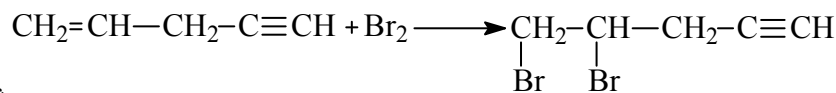
(1) 与 X₂



Br₂ 同样可以。

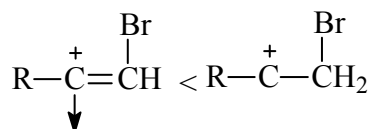


I₂ 较困难



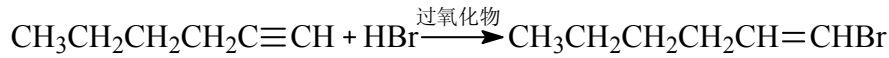
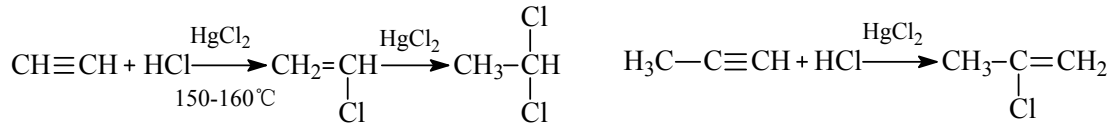
但双键比三键活泼

因为 1、三键键长短, P 轨道交叠程度大。2、SP 杂化 C 原子比 SP² 杂化碳原子对电子的吸附能力强。



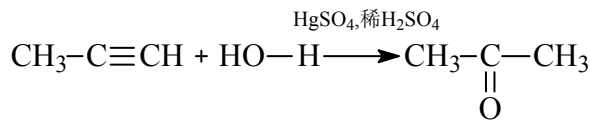
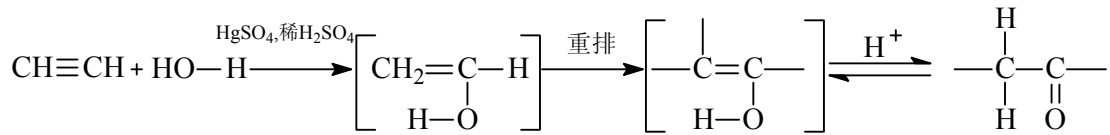
稳定性: SP 杂化

(2) 与 HX (难于烯炔) 服从马氏规则



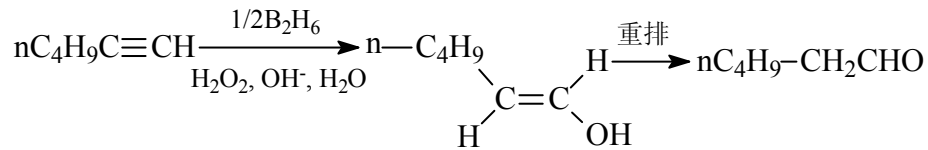
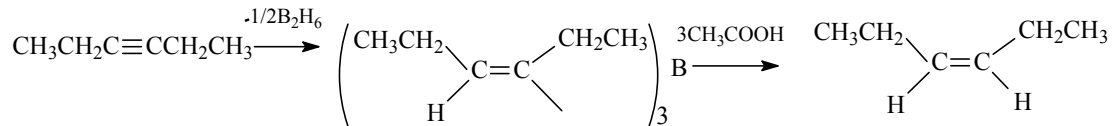
1-溴-1-己烯

(3) 与水合成 (Kucherov 反应) 工业制乙醛



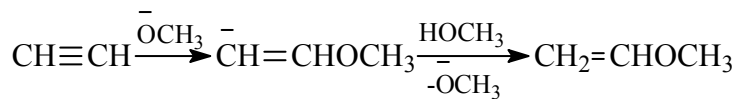
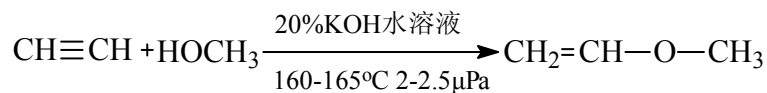
除了乙醛外，都得到乙酮

(4)、硼氢化反应

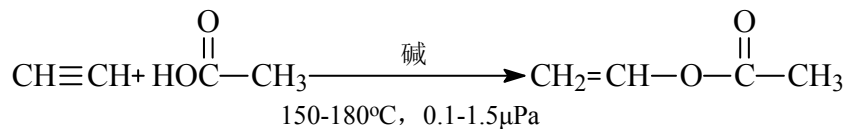


3 亲核加成 (与带有活泼氢的有机物反应)

(1) 与醇加成



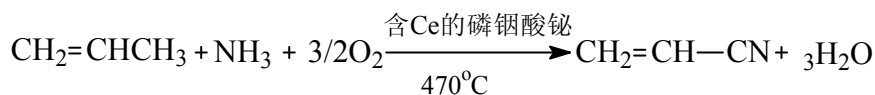
(2) 与 CH_3COOH



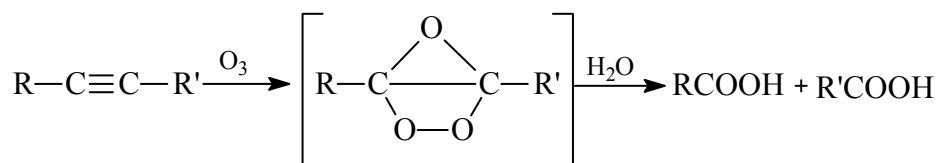
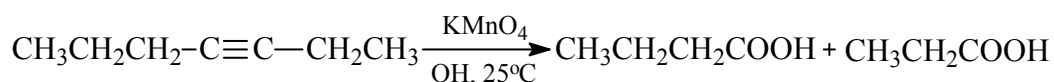
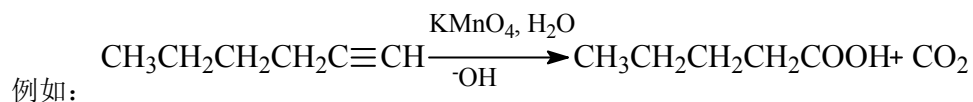
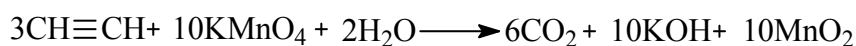
醋酸乙烯酯，是制备

维尼纶的主要原料。

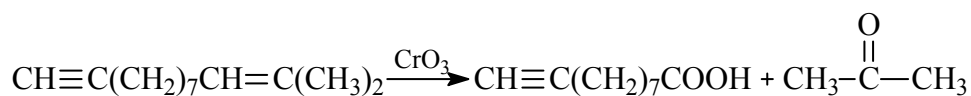
(3) 与 HCN



4、氧化反应——推测结构



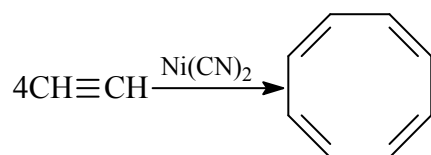
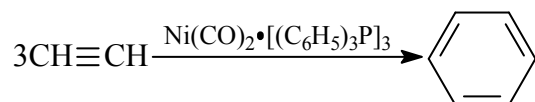
双键比三键易于氧化



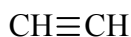
5、聚合反应：

形成二聚、三聚、四聚体，不易聚合为高聚物

例如：

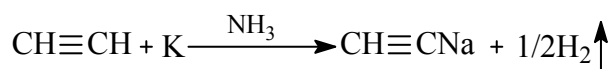
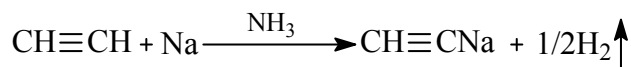


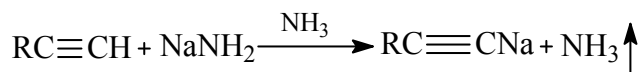
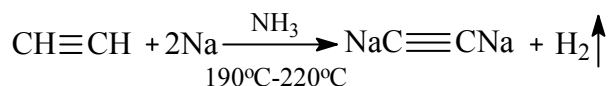
6、炔氢的活泼性



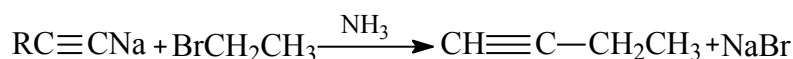
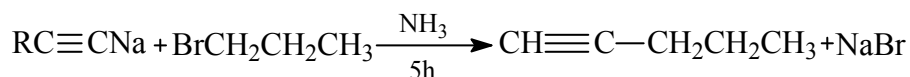
S 成分增多，电子云更偏向于 C，使 H 容易 $\rightarrow \text{H}^+$ ；同时 C-H 键比烷烃、烯烃短，离解能。使其不会发生均裂，而更趋于异裂，其酸性小于水而大于氢。

(1)、金属炔化合物的生成

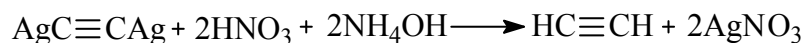
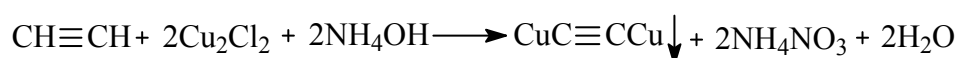
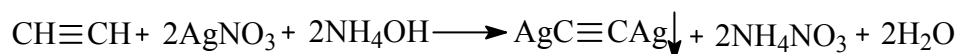




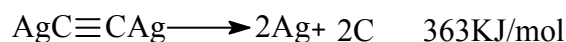
炔烃的烷基化



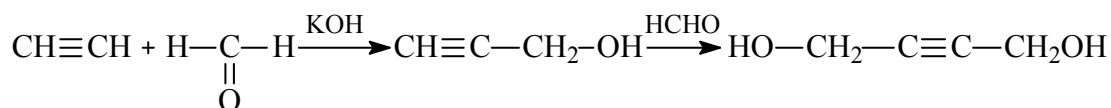
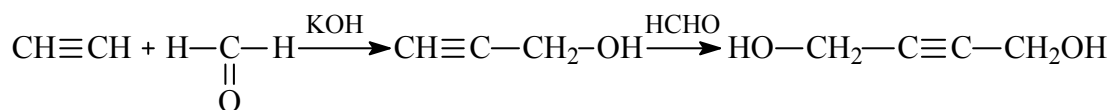
与重金属：鉴别炔烃（有活泼 H 的）



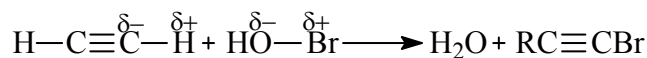
重金属炔化合物干燥时不安定，易于爆炸，所以要用 HNO_3 处理



(2) 与醛酮反应——炔醇

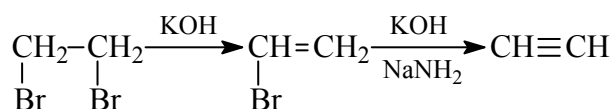


(3) 与 HOX

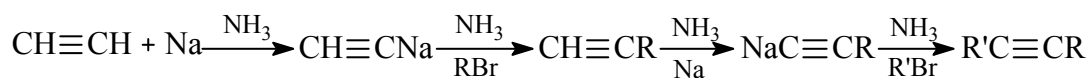


五、炔烃的制备

1、二卤代烷HX



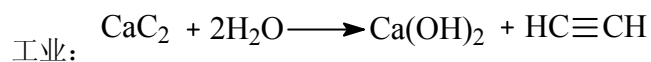
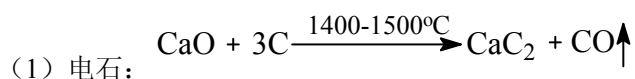
2、炔烃的烷基化：



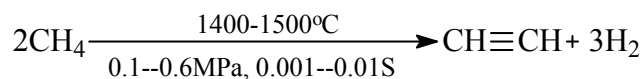
3、工业

六、乙炔的制备和用途

1、制备



(2) 甲烷部分氧化



(3) 石油裂解: 乙烯, 乙炔

2、应用:

(1) 维尼龙(丙烯腈)、聚氯乙烯、氯丁橡胶等的基本原料

(2) 高温电焊、切割 $>300^\circ\text{C}$, 爆炸范围大(3-81%)

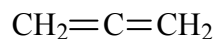
4. 4 共轭二烯烃的结构和特性

一、分类

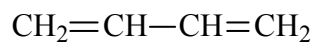
1、隔离二烯烃:



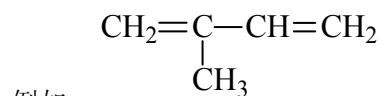
2、累积二烯烃:



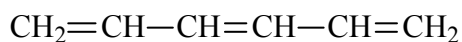
3、共轭二烯烃:



二、命名: 类似于烯烃, 主链应含两个双键在内

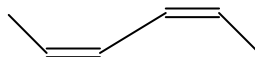
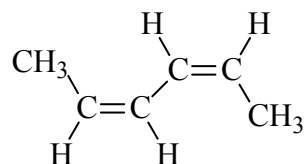


2-甲基-1, 3-丁二烯

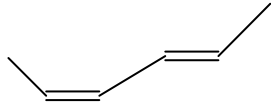
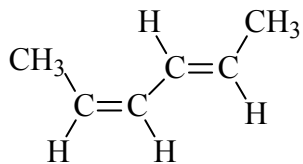


1, 3, 5-己二烯

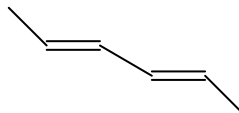
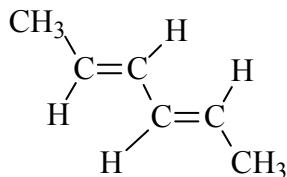
顺反异构



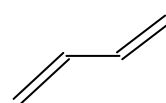
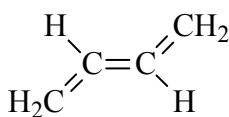
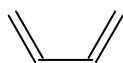
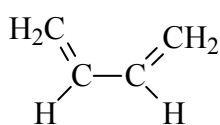
顺, 顺-2, 4-己二烯, (Z), (Z)-2,4-己二烯



顺, 反-2, 4-己二烯, (Z), (E)-2,4-己二烯



反, 反-2, 4-己二烯, (E), (E)-2,4-己二烯

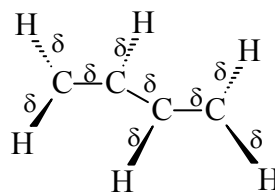
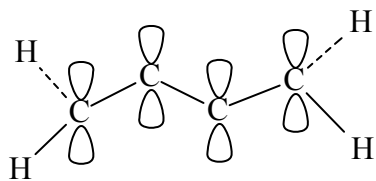


S-顺-1, 3-丁二烯

S-反-1, 3-丁二烯

二、共轭二烯烃的结构

C 原子: sp^2 杂化



特性:

1、键长平均化

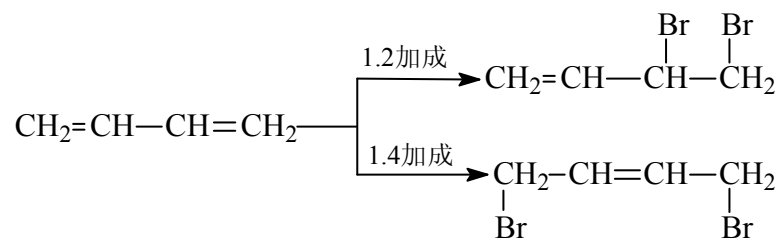
2、体系能量降低, 稳定性增加

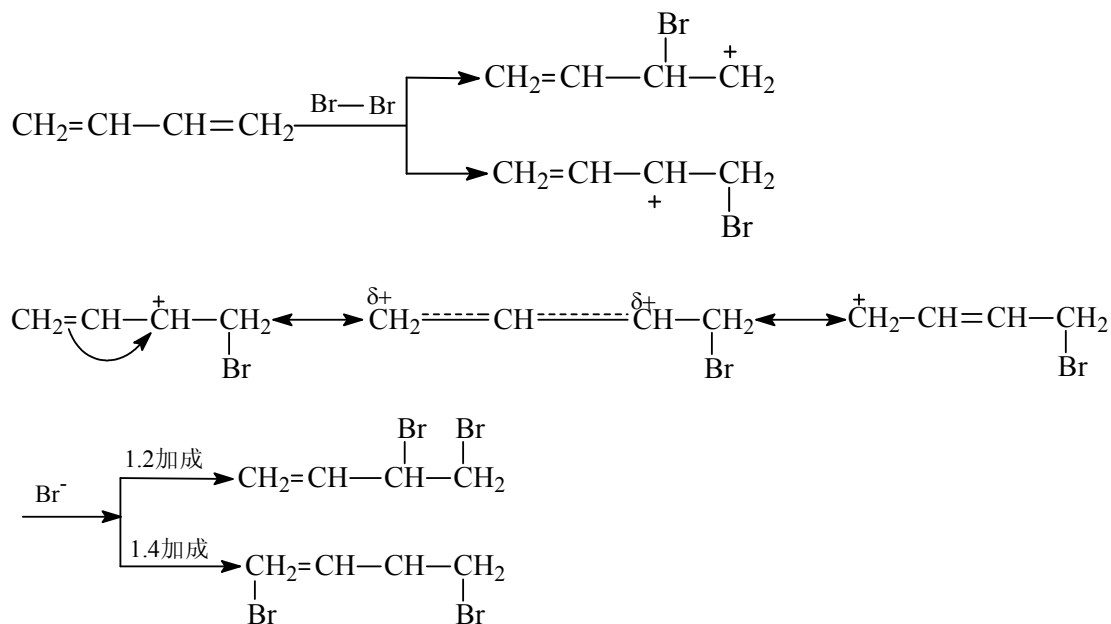
如乙烯分子中, 成键轨道的能量是 $\alpha + \beta$, $E_{总} = 4\alpha + 4\beta$

丁二烯: $E_{总} = 4\alpha + 2 \times 1.618\beta + 2 \times 0.618\beta = 4\alpha + 4.472\beta$

4.5 共轭二烯烃的性质

一、1,4 加成: (亲电)





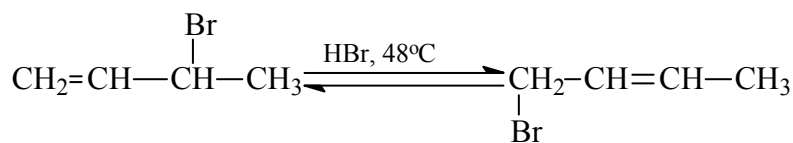
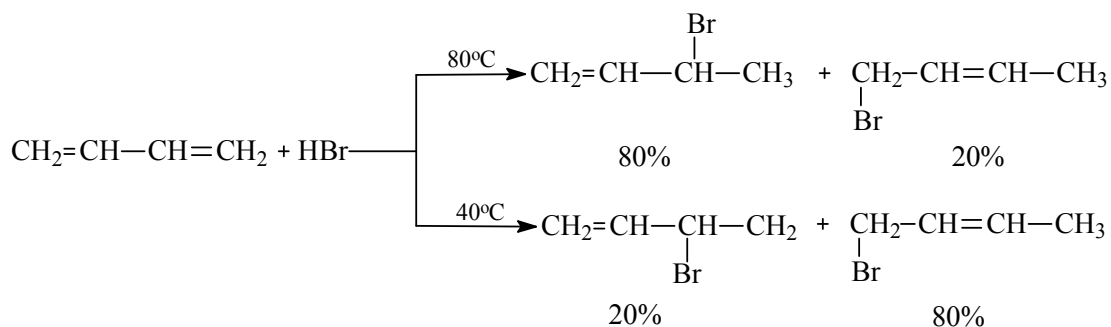
影响因素:

(1) 溶剂: 极性溶剂有利于 1.4 加成 (极性分散)

正己烷 38% (1.4)

氯仿 63% (1.4)

(2) T: 低温 1.2, 高温 1.4

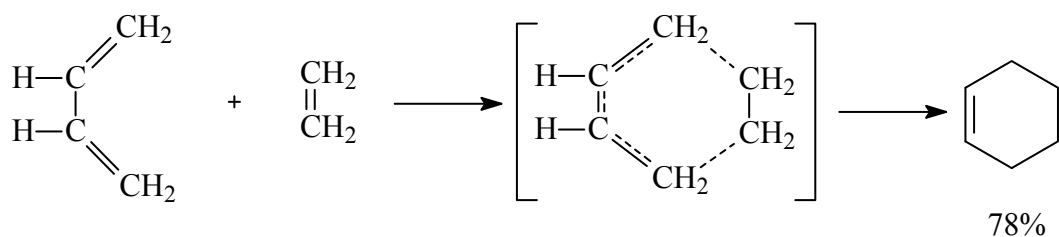


速度控制
(动力学)

平衡控制
(热力学)

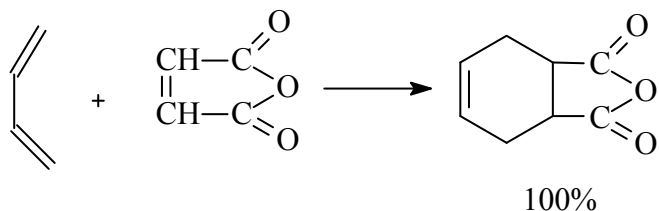
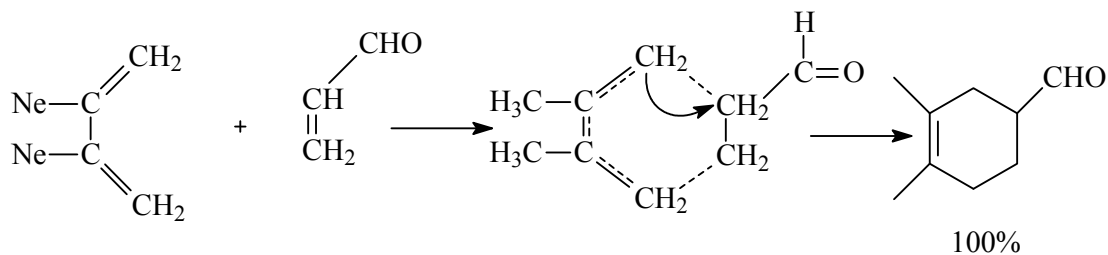
二、Diels-Aldes反应: 一步完成的协同反应 (同环反应)

用于鉴别或者提纯共轭二烯烃

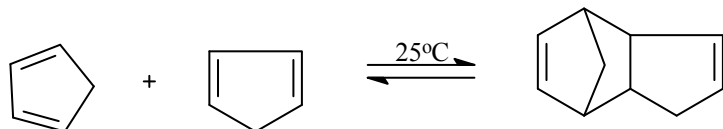


双烯烃 亲双烯
 (有供电子基, 有吸电子基时, 反应较易进行)

例如:



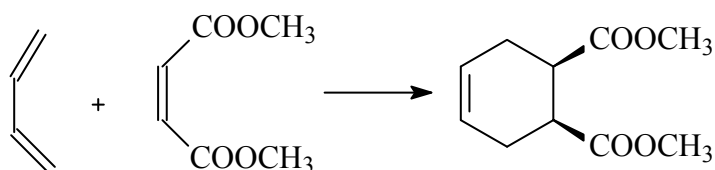
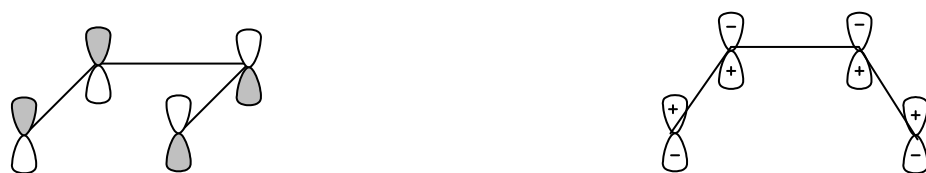
顺 4—四氢化邻苯二甲酸酐 (用于检验共轭烯烃, 产物为固体)

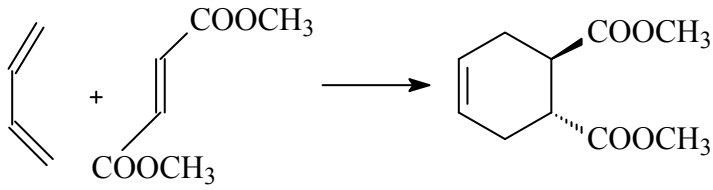


双环戊二烯

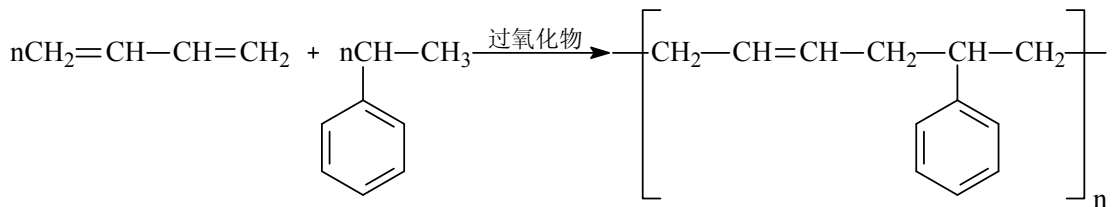
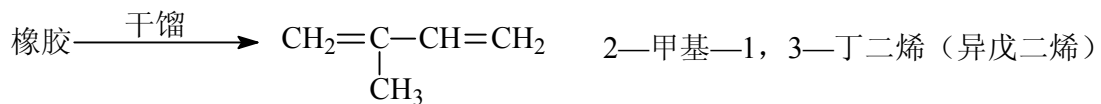
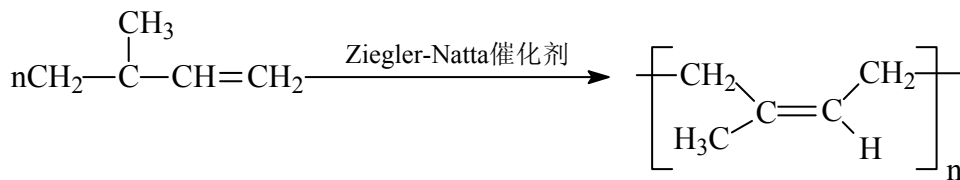
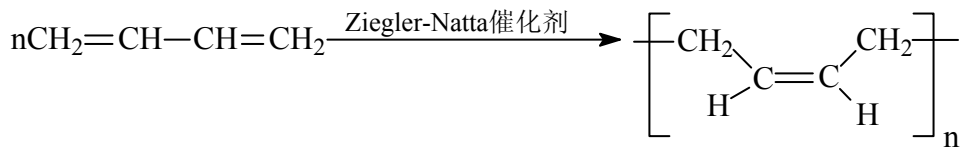
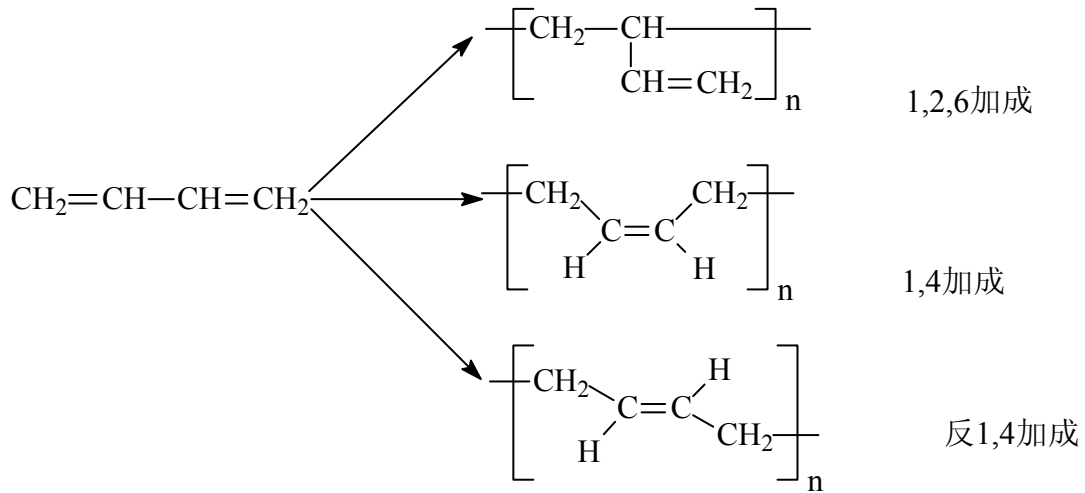
上述反应称为[4+2]环加成——周环反应。

R.B. Woodward 和 R. Hofmann 分子对称原理。可推测反应进行的可能性及其立体化学。(产物构型保持)

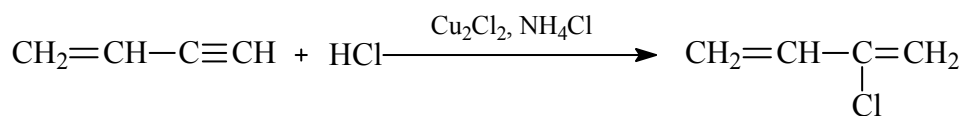
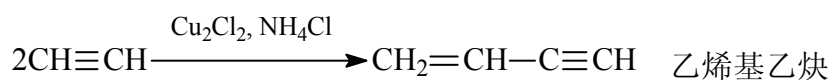




3、聚合反应和合成橡胶



(耐老化、耐磨、耐油，丁苯橡胶)



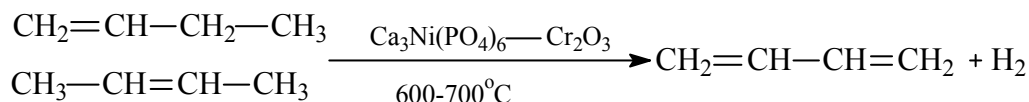
思考题:

- 1、试选择适当的反应把顺-2-丁烯变为反-2-丁烯，再把反-2-丁烯转变为顺-2-丁烯。
- 2、1, 3-环戊二烯与一分子 HCl 在低温时进行加成反应主要生成 3-氯环戊烯，而很少有 4-氯环戊烯生成，如何解释这样的实验事实？
- 3、1, 3, 5-己三烯与 1mol Br₂ 反应，可能生成那集中加成产物？实际并没有 3, 4-二溴产物生成，为什么？如果反应是热力学稳定性（即化学平衡）控制的，试预期主要产物是哪一种？为什么？

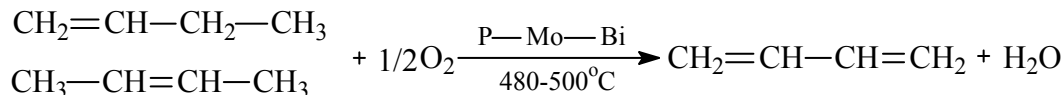
1. 1,3-丁二烯的制备

(1) 丁烯脱氢

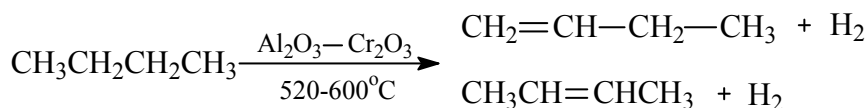
a) 催化脱氢:



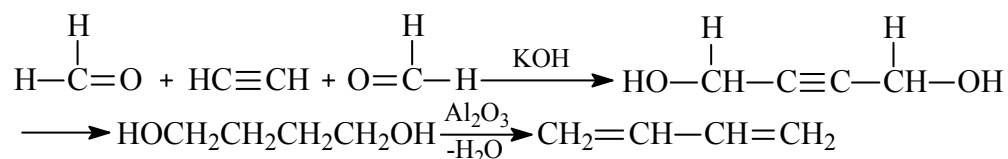
b) 氧化脱氢:



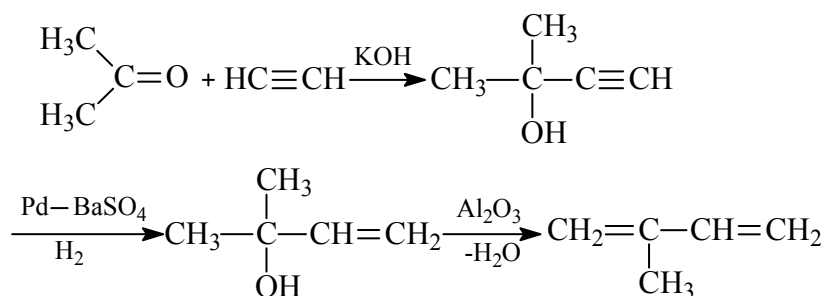
(2) 丁烷脱氢:



(3) 由乙炔+甲醛



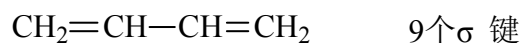
2. 2-甲基-1, 3-丁二烯的制备



5-2. 电子离域与共轭效应

一、1, 3-丁二烯的结构与 π , π 共轭

1. 1, 3-丁二烯的结构特征:



单双键平均在, 一般 C—C 键长为 0.154nm, 而丁二烯中 C2—C3, 0.147nm

C 原子均为 SP^2 杂化, 共平面。

每个 C 原子下一个 P 轨道 (单电子) 相互交盖 $\pi-\pi$ 共轭, P96, 特别是 C2—C3 间的交盖。

分子轨道理论: P96

成键 π 电子在整个四个 C 原子之间

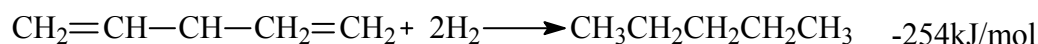
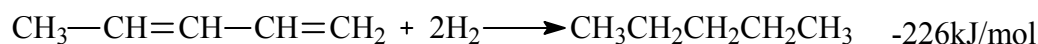
与的叠加, 不仅使 C1 与 C2、C3 与 C4 之间的电子云密度增加, 而且也部分增加了 C2 与 C3 之间的电子云密度, 使之与一般统统键不同, 具有部分双键的性质。

2. 介电子离域与 π , π 共轭效应 (+C, -C)

(1) 离域: 电子不是局限在原两个原子之间, 而是扩展到整个分子中。

(2) 共轭效应的体现: 1 键长趋于平均化

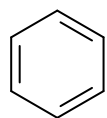
2 体系能量降低



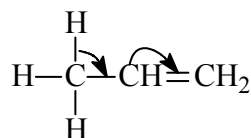
离域能 (共轭能) = 254 - 226 = 28 kJ/mol

(3) 共轭的前提: 组成共轭体系的原子共平面

例如:



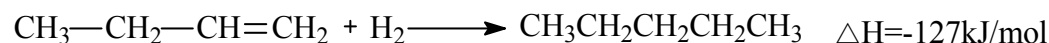
二、超共轭效应



1、超共轭效应:

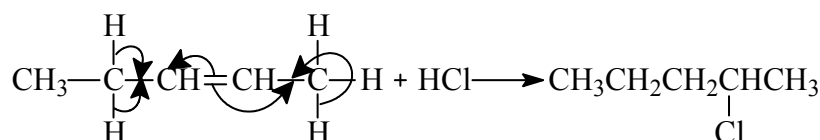
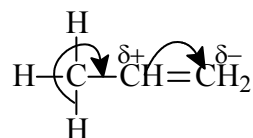
$\sigma - \pi$ 超共轭效应, C-H σ 键与 π 键的共轭体系

例如:



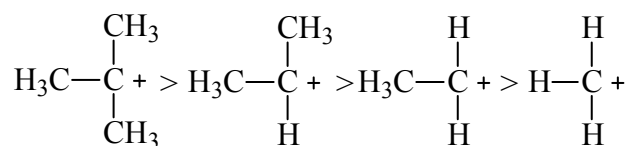
2、超共轭效应的影响

(1) 马氏规则:

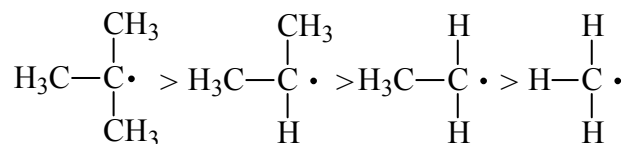


因为+I 效应, $\text{CH}_3\text{CH}_2\text{—} > \text{CH}_3$, 但是+C, $\text{CH}_3\text{—} > \text{CH}_3\text{CH}_2\text{—}$

(2) C^+ 的稳定性



(3) C^\cdot 的稳定性:



共轭效应是分子中原子之间相互影响的电子效应。只有共轭体系, 电子就会发生离域而显示 (+C, -C)

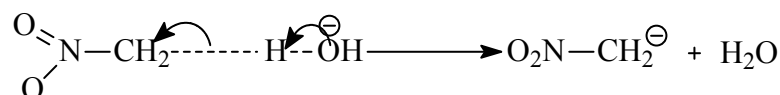
(+I, -I) 是由于原子间的电负性不同造成。

(+C, -C) 是通过电子的离域而产生。

静态诱导效应: 取代基的影响沿着单键(或重键)传到时分子的其他部分电子云依取代基对氢的电负性所决定的方向而转移的效应叫诱导效应, 表现在未起反应的分子中的效应叫静态诱导效应。

动态诱导效应: 由外来因素引起的暂时电子云分布状态的改变也叫可极化性。

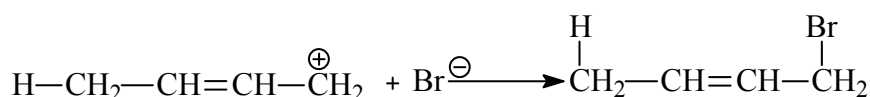
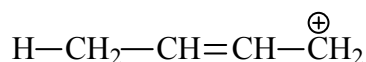
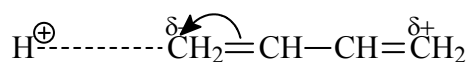
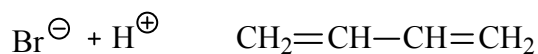
例如:



共轭效应:

静态: 电子离域、电子云平均化, 体系能量降低

动态: 共轭体系在发生化学反应时, 由于进攻试剂的影响或者其他外界条件的影响, 而使 P 中电子云密度在反映瞬间发生变形并重新分配。

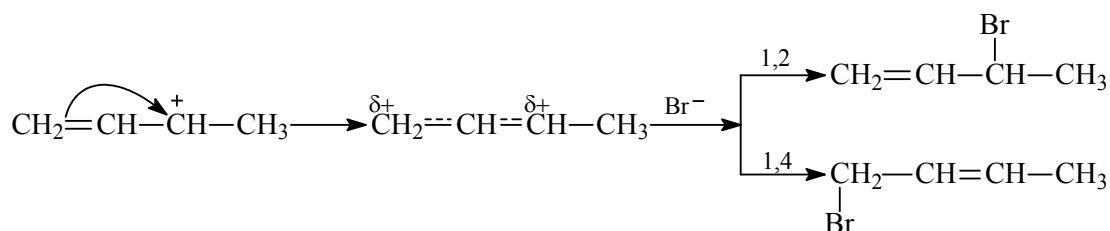
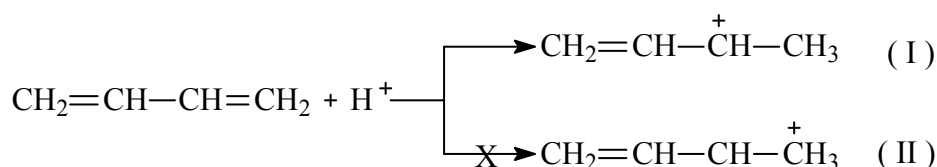
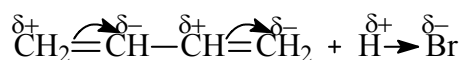


三、共轭二烯烃 1, 4-加成的理论解释

1. 动态共轭效应:

共轭体系在反应过程在外界影响下, 电子发生离域。

极化



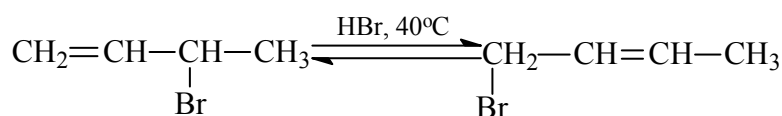
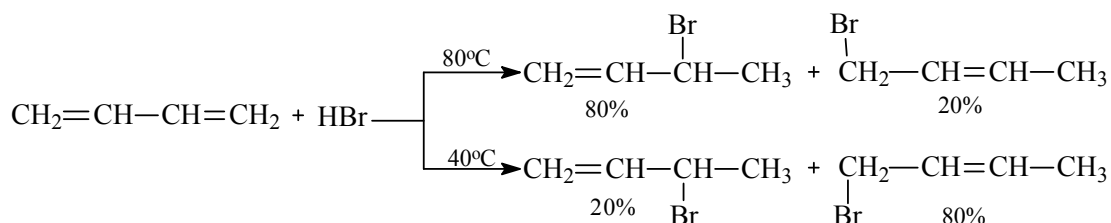
2. 影响因素

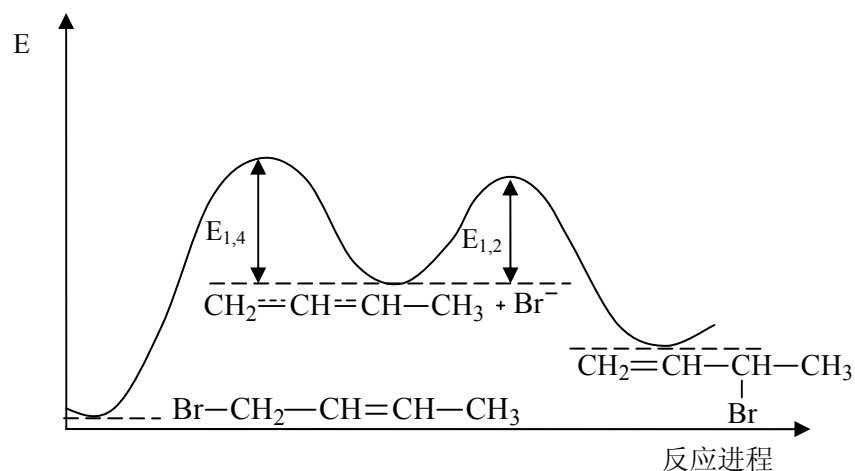
(1) 溶剂: 极性溶剂有利于 1, 4 加成

正己烷: 38% (1, 4)

氯仿 63% (1, 4)

(2) 温度: 低温 1, 2, 高温 1, 4

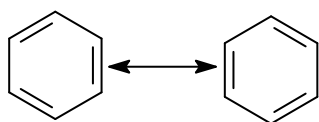




低温时，速度控制 1, 2 动力学控制
 高温时，平衡控制 1, 4 热力学控制

四、离域体系共极化表示法

共振：是为解决经典结构时表示复杂的离域体系而提出的。是一种表达方式的设想，分子的真实结构是极限结构的叠加。

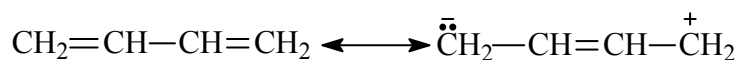
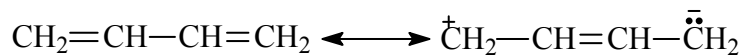


共振能：实际化合物与极限之间的能量差。

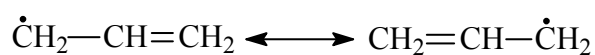
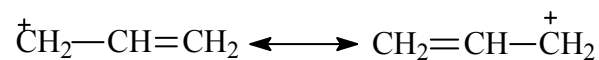
例如：1, 3-丁二烯为：28kJ/mol，环己三烯与苯的能差为 15kJ/mol

书写极限结构的原则：P104~105

应用及其局限性：解释一些反应，比如：丁二烯 1, 4 加成。



烯丙基的稳定性：



局限性：

