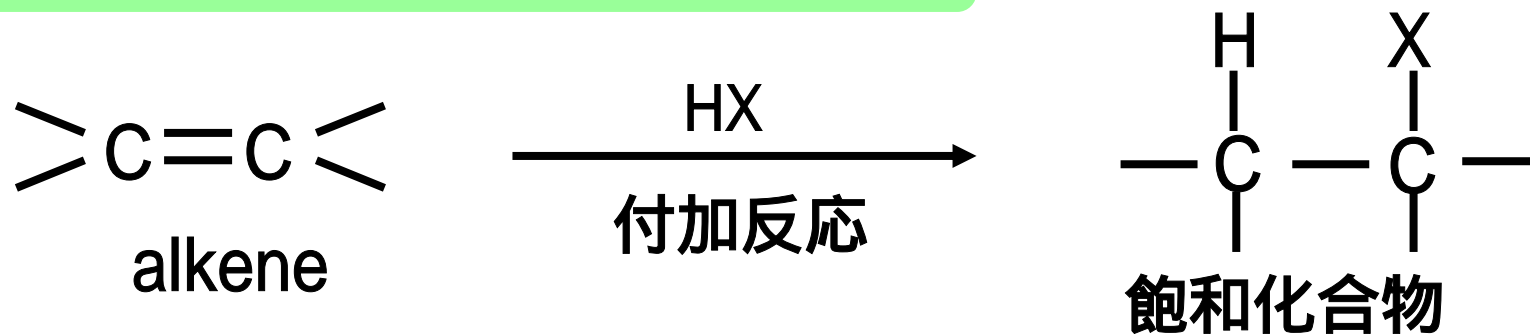


Chap. 4 Alkenes and Alkynes

4-1. アルケンへのHXの付加



反応性に富む

ハロゲン化物：新たな反応特性
第7章 置換反応

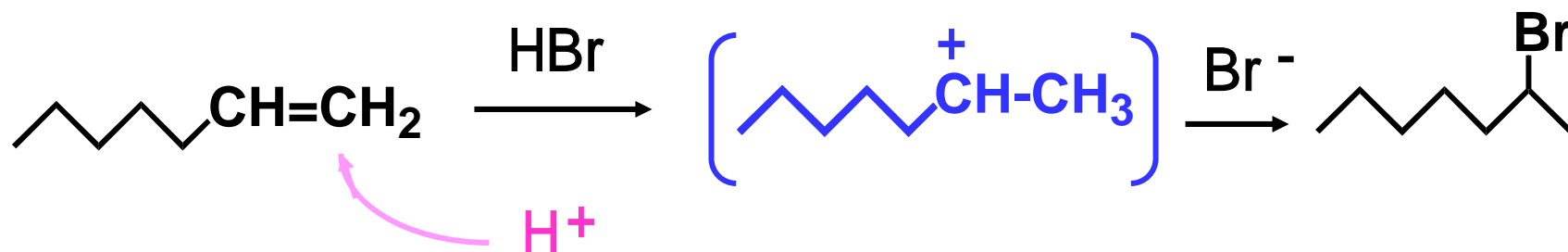
反応機構？

求電子付加反応 (step 1)

カルボカチオン中間体

規則性？

Markovnikov則



4-2 ~ 4-3. 付加の配向性



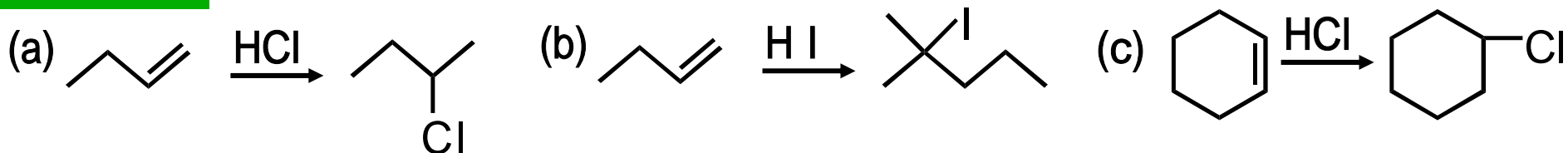
位置特異的 (regiospecific)

Markovnikov則

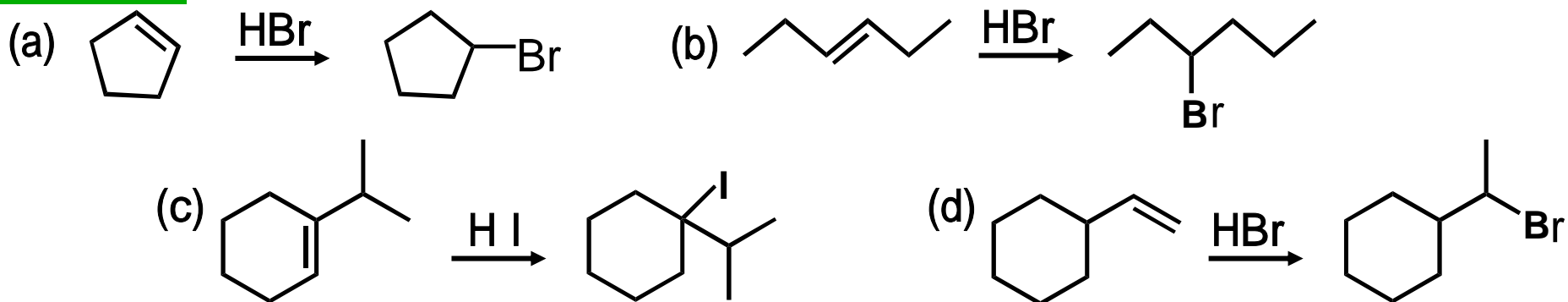
アルケンへのHXの付加において、Hはアルキル置換基の少ない炭素に、Xは多い炭素に結合する。

Why ?

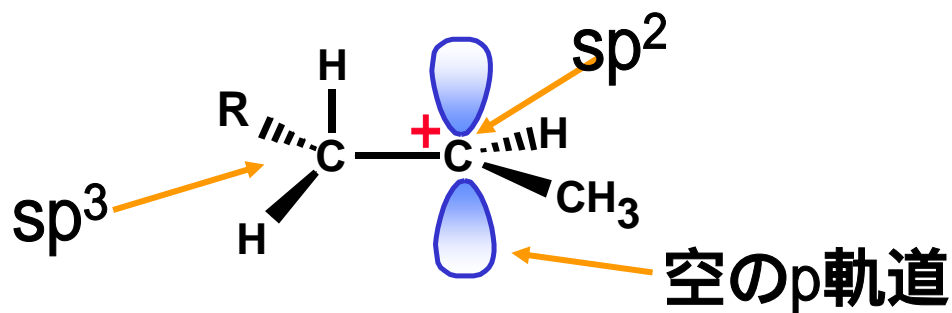
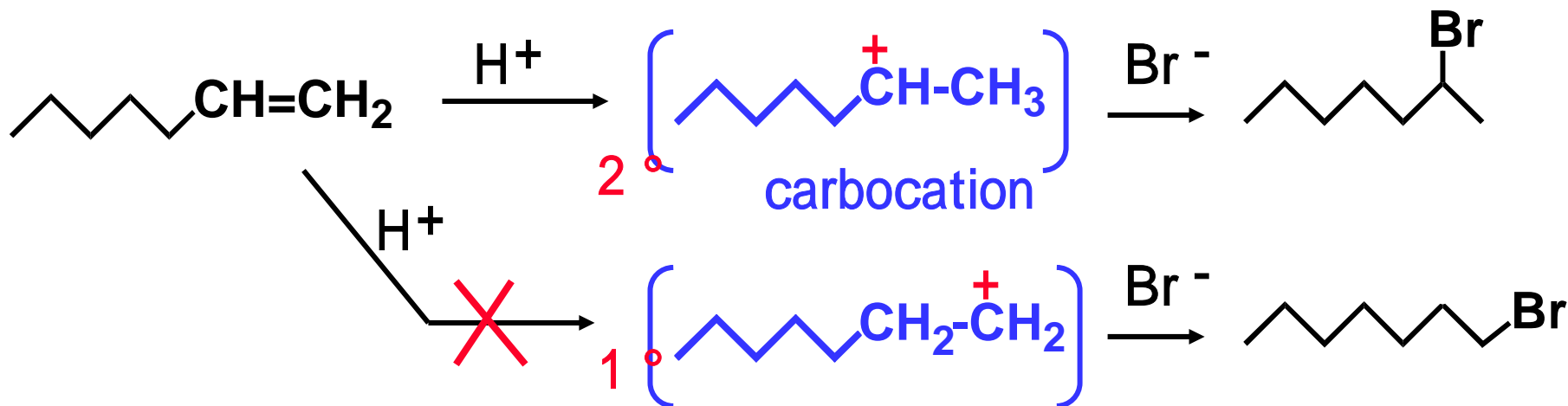
問題4-1



問題4-2



4-2 ~ 4-3. 付加の配向性

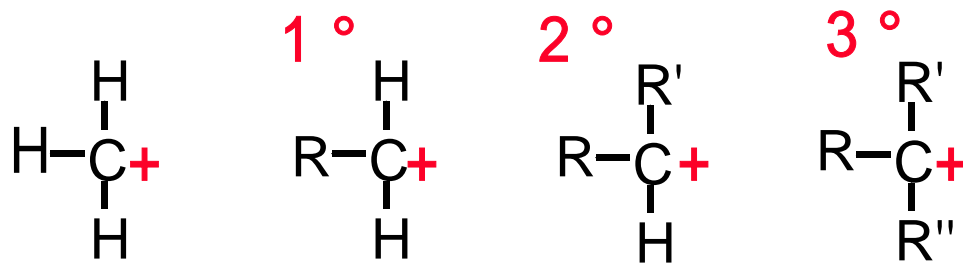


反応中間体
 反応性に富み、単離できない

カルボカチオンの安定性

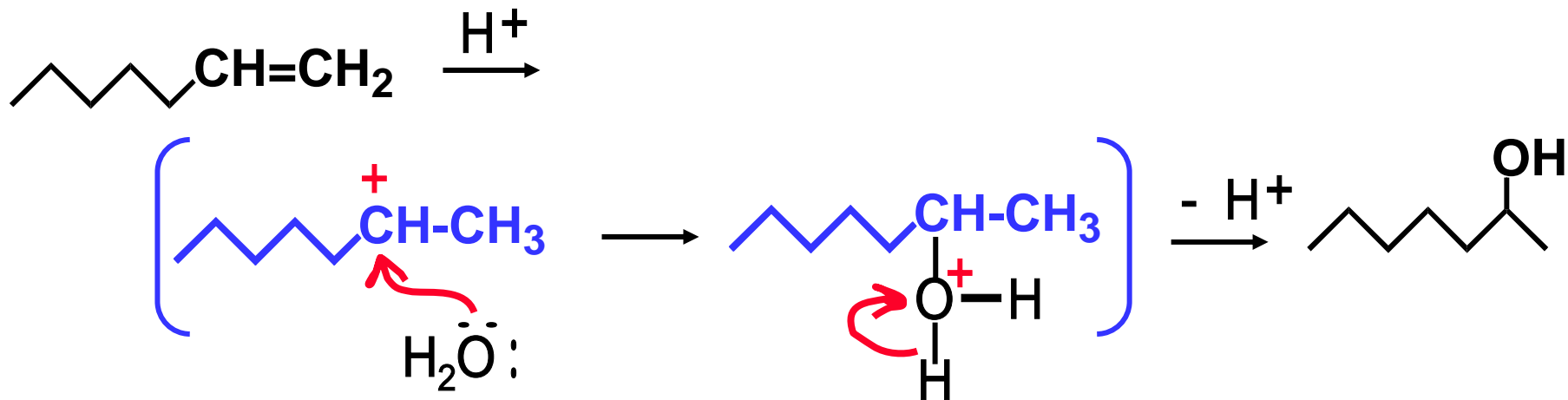
アルキル基 電子供与基

→ 荷電の非局在化



安定

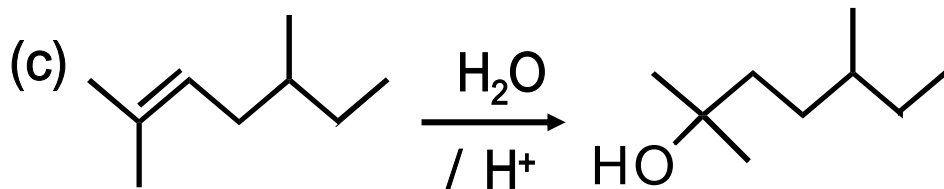
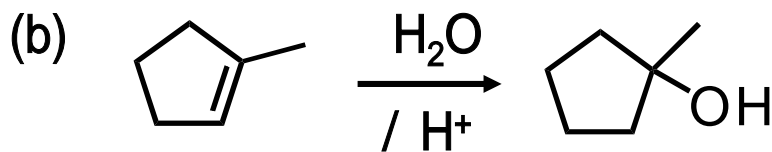
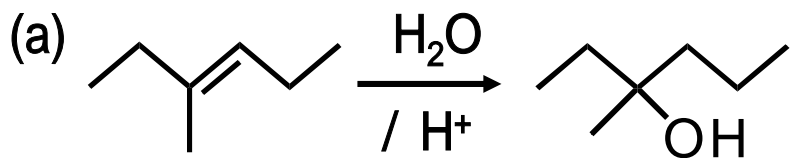
4-4. H₂Oの付加：水和



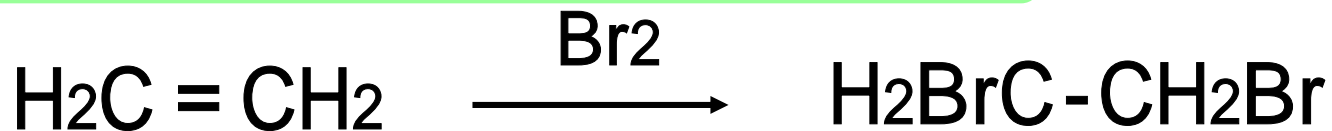
高温 (200)、強酸性条件が必要

Markovnikov則に従う

問題4-4



4-5. X₂の付加: ハロゲン化



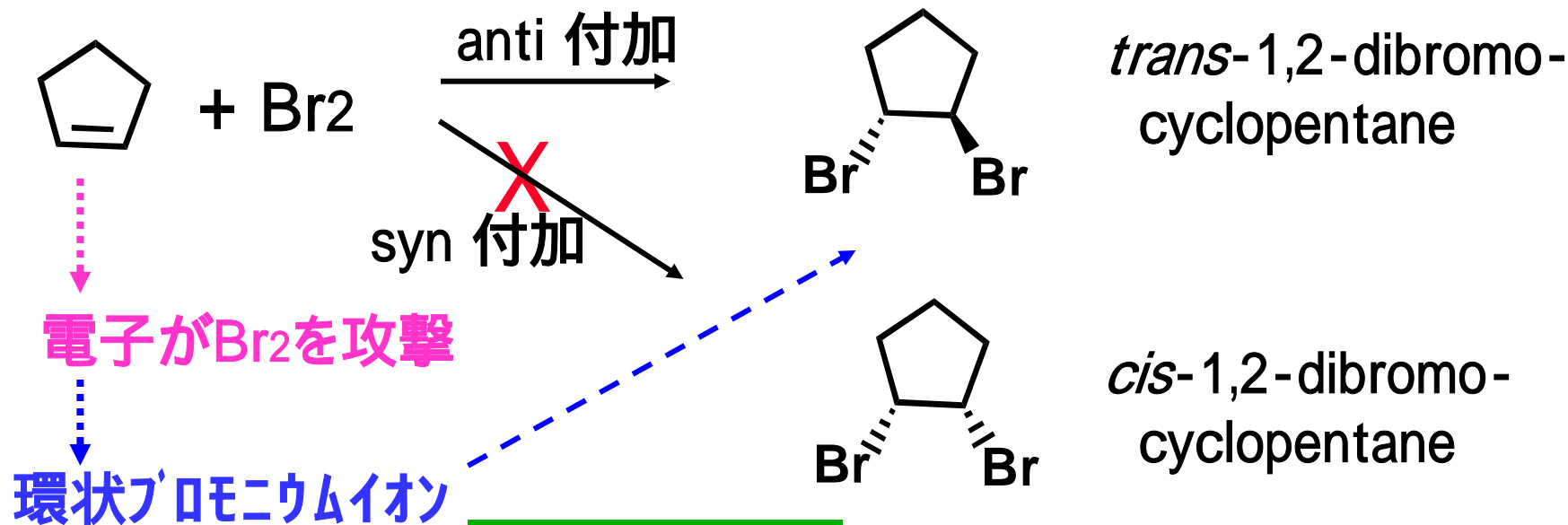
反応機構?

求電子付加反応 (step 1)
カルボカチオン中間体

HBrの付加
と同様 ?

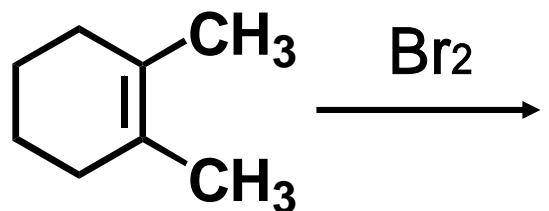
step 1: B.⁺の攻撃

step 2: B.⁻の攻撃

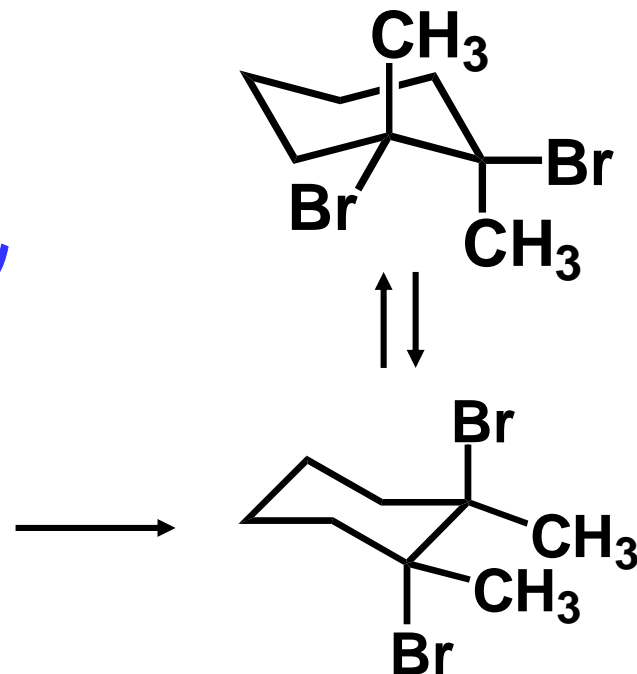
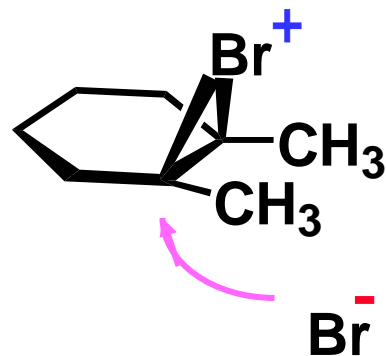


4-5. X₂の付加: ハロゲン化

テキスト 問題4.6
4.7,



環状ブromoniumイオン



trans-1,2-dibromo-
1,2-dimethylcyclohexane

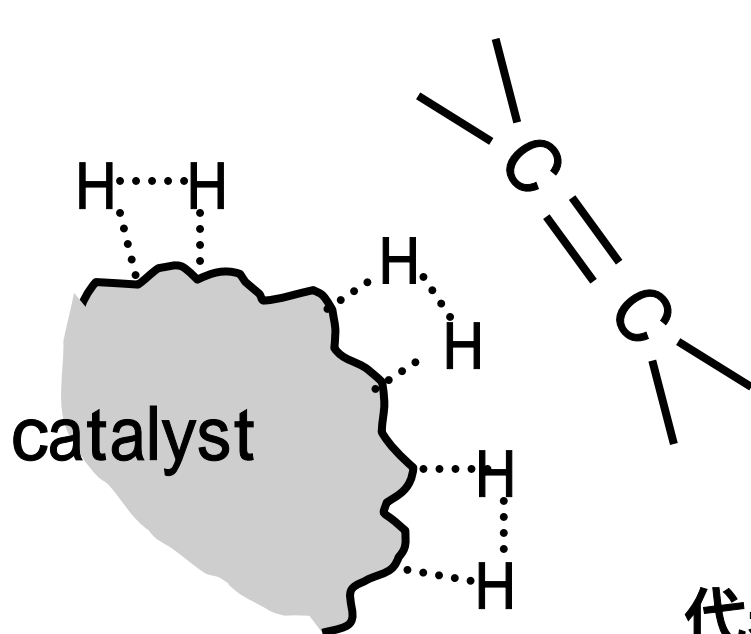
1,2-dimethylcyclohexene

4-6. H₂の付加: Hydrogenation

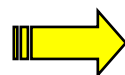
水素化、水素添加(水添)、水素付加

金属触媒を用いる
アルケンが還元される

接触還元 catalytic reduction
接触水素化 catalytic hydrogenation

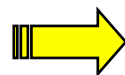


触媒表面上での反応



不均一系

heterogeneous



syn 付加

水素は 2コとも
同じ側から

代表的な触媒

PtO₂, Pd-C, Pd-BaSO₄, Raney Ni

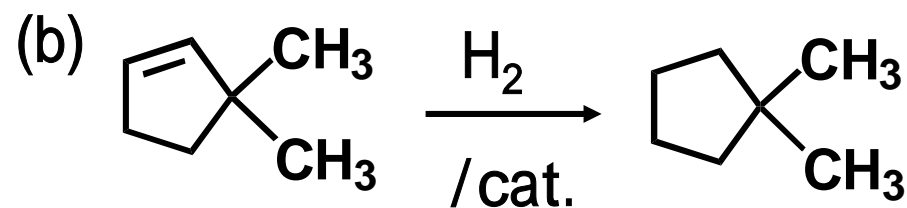
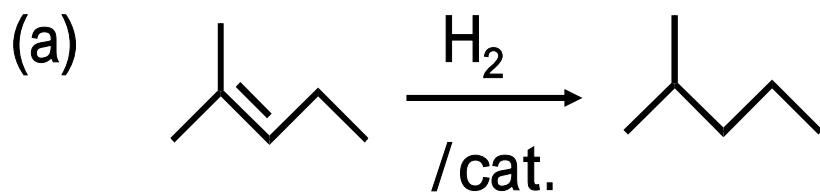
触媒毒

含N化合物(アミン類)

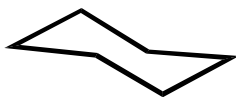
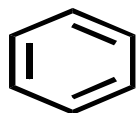
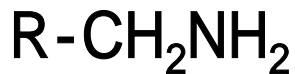
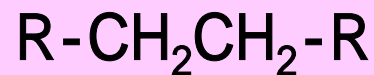
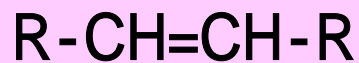
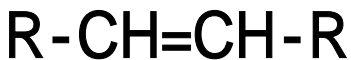
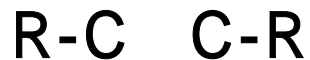
SH化合物

4-6. H₂の付加: Hydrogenation

テキスト 問題4.8



接触水素化における反応性



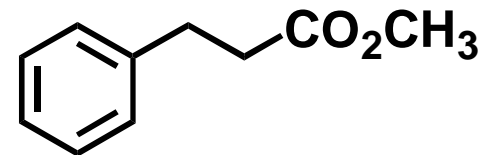
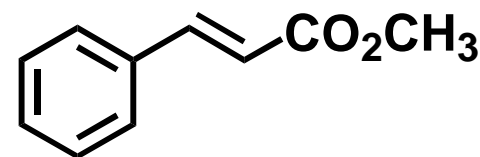
高

低

反応性 ↑

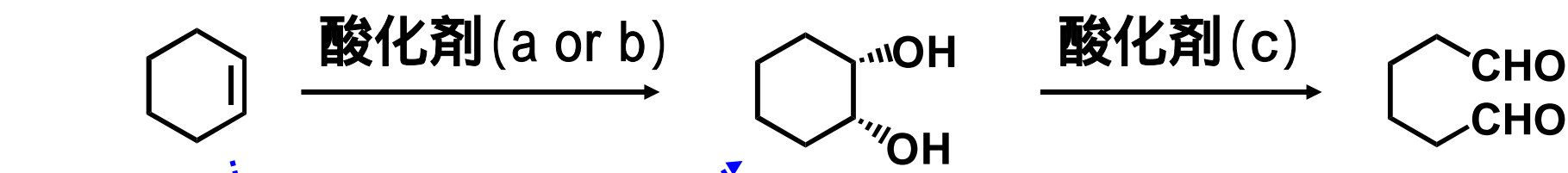


選択性 あり

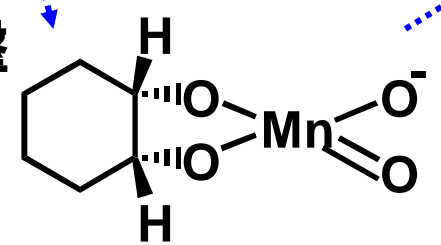


4-7. 酸化: Oxydation

[A] *cis*-diol への変換と開裂



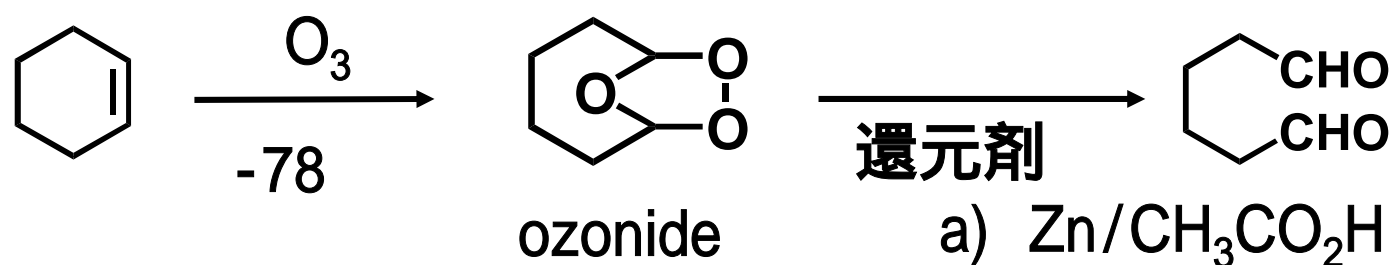
syn 攻撃



- 酸化剤
- a) $\text{KMnO}_4 / \text{aq. NaOH}$
 - b) OsO_4
 - c) HIO_4
 - d) $\text{OsO}_4\text{-HIO}_4$
 - e) $\text{KMnO}_4 / \text{H}_3\text{O}^+$

直接的なアルケンの開裂

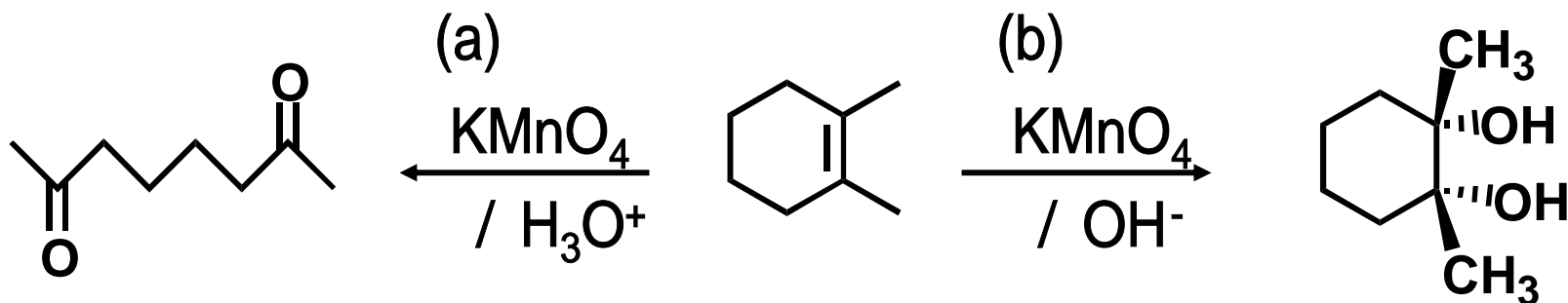
[B] オゾン分解



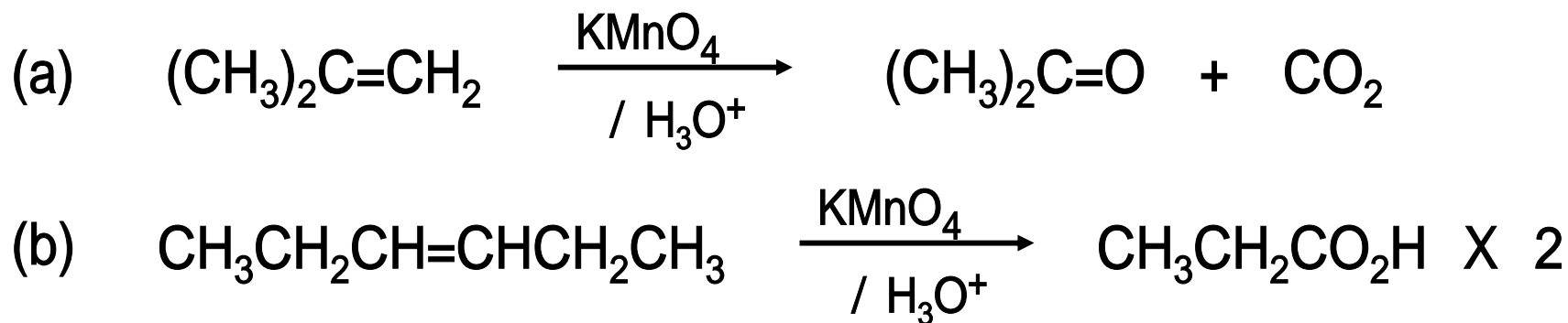
- 還元剤
- a) $\text{Zn}/\text{CH}_3\text{CO}_2\text{H}$
 - b) $\text{CH}_3\text{S-SCH}_3$

4-7. 酸化: Oxydation

テキスト 問題 4.9



テキスト 問題 4.10

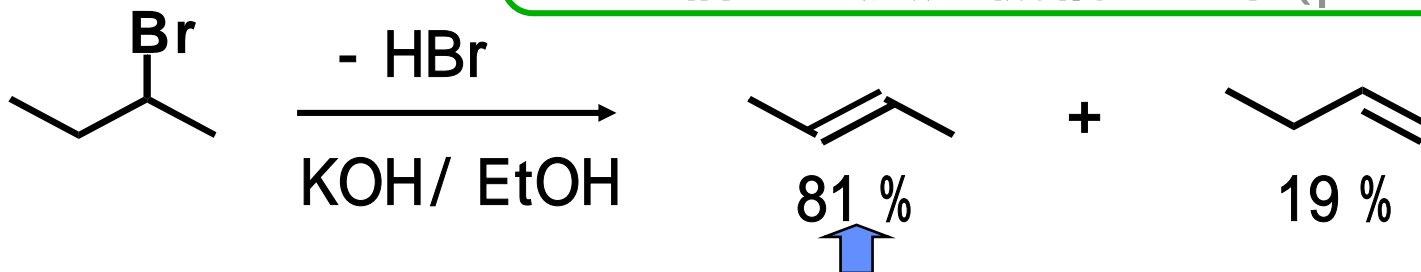


4-8. アルケンの製法

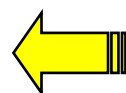
[A] HXの脱離

脱離反応 elimination

詳しい反応機構は7章 (p. 222 ~ 224)



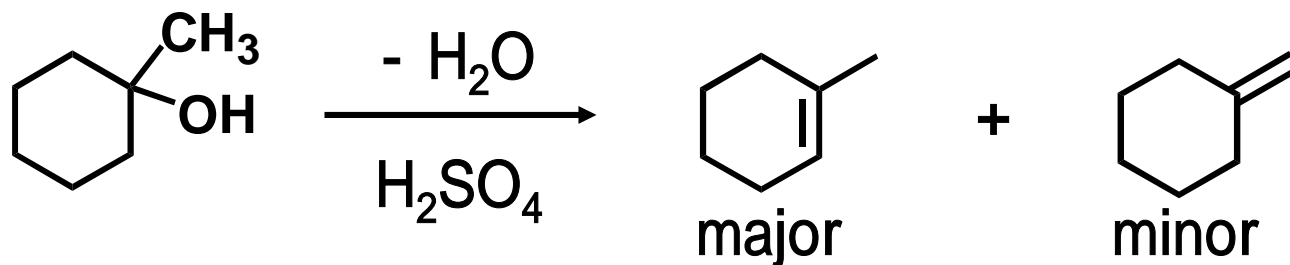
Zaitsev則



主成分: より多く置換されたもの

[B] 脱水反応

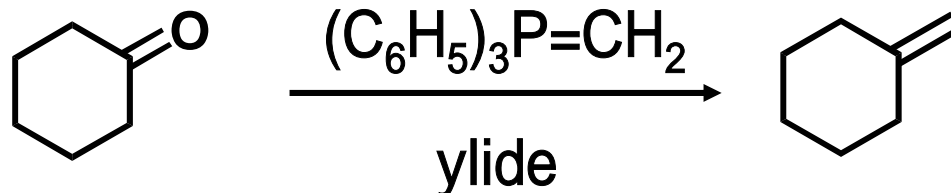
H₂Oの脱離



[C] Wittig反応 (1979年のノーベル賞)

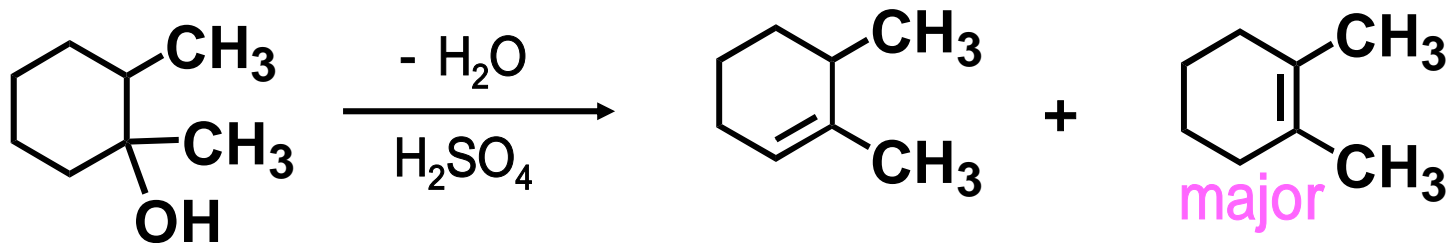
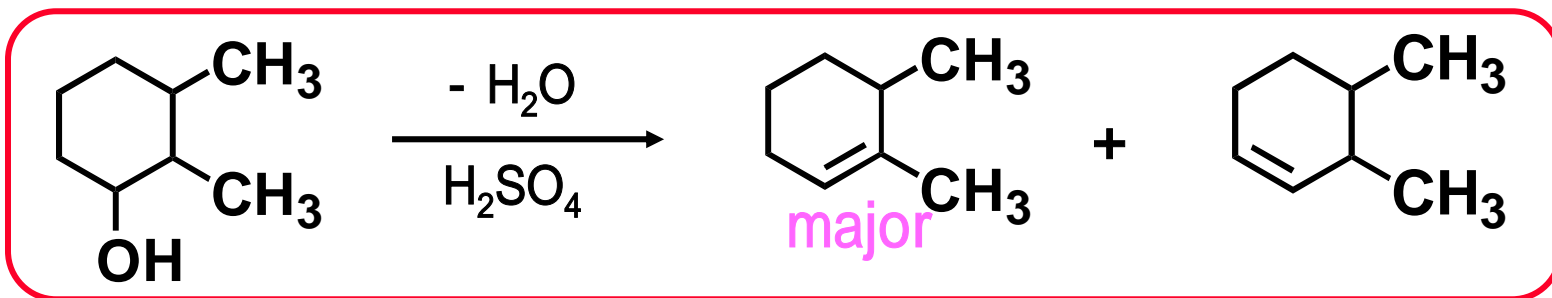
アルデヒド、ケトンの
求核付加反応

(p. 286)

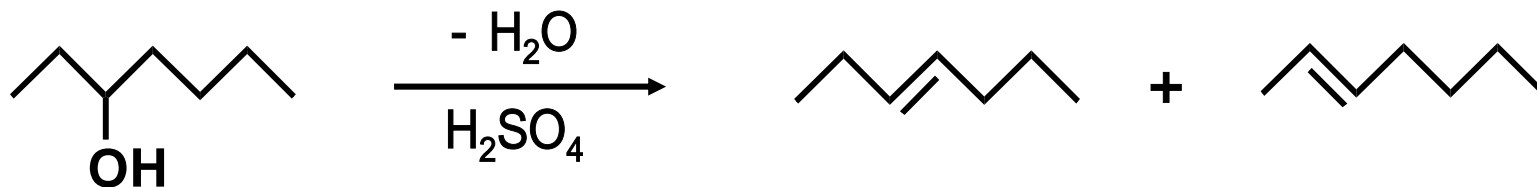
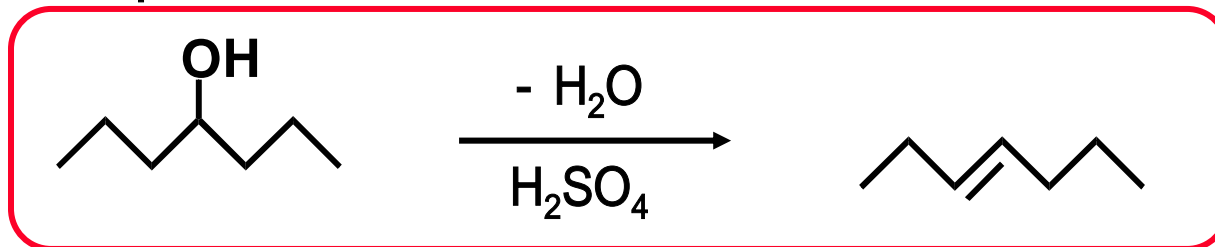


4-8. アルケンの製法

(a) 1,6-dimethylcyclohexene

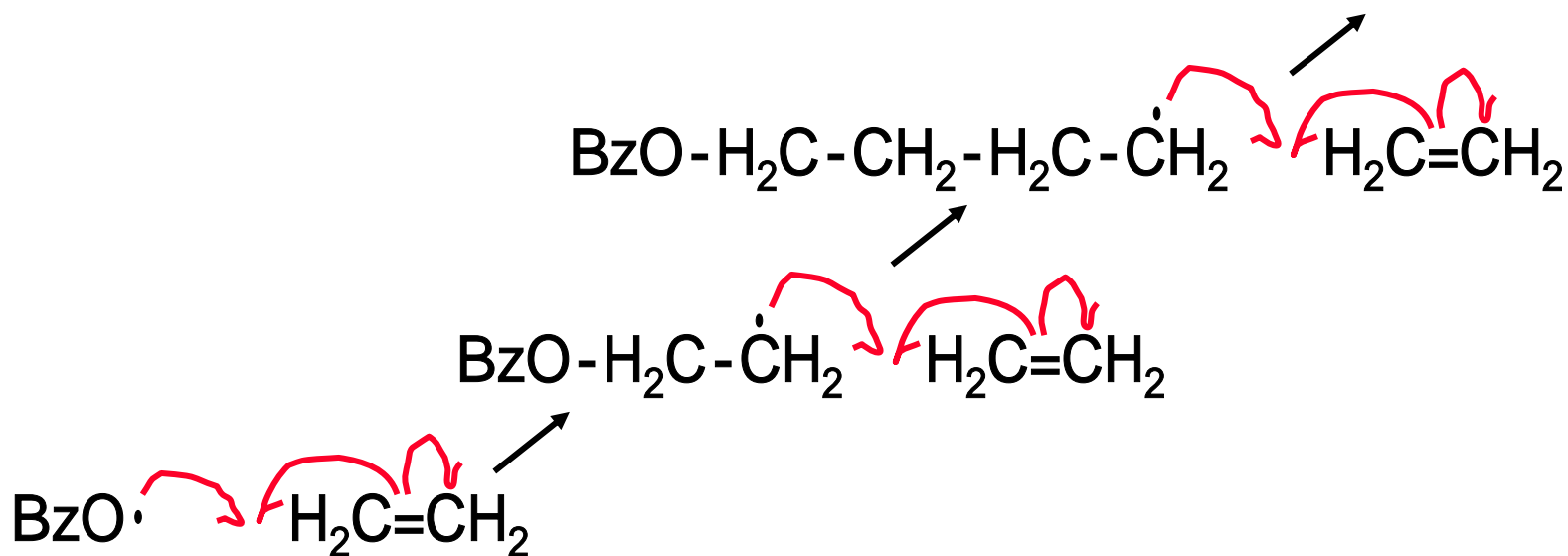
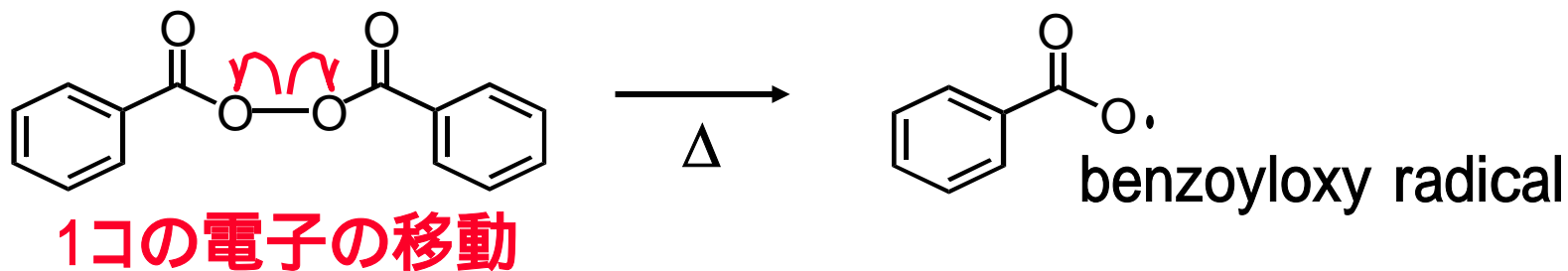
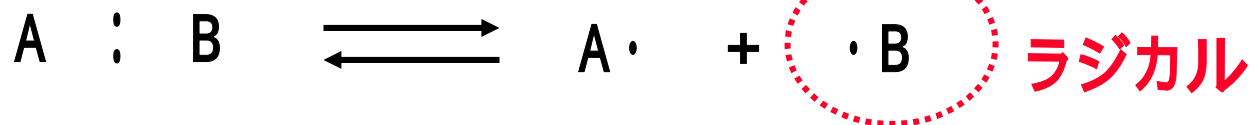


(b) 3-heptene



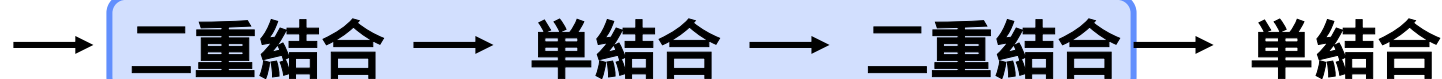
4-9. アルケンへのラジカル付加

均一開裂と均一生成

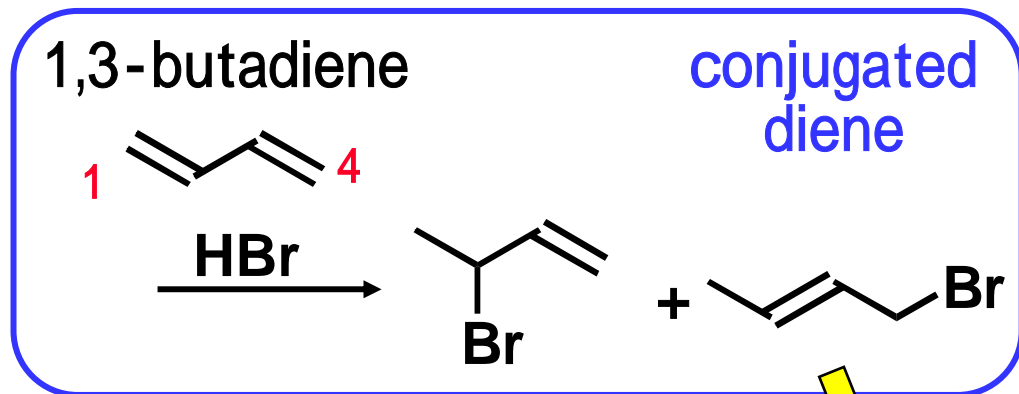
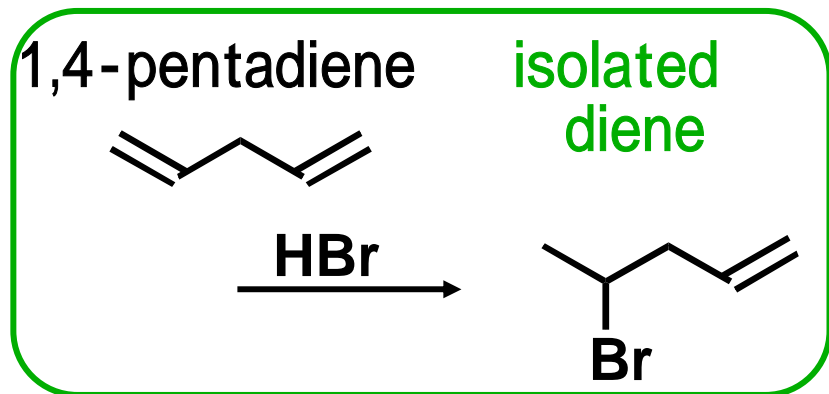
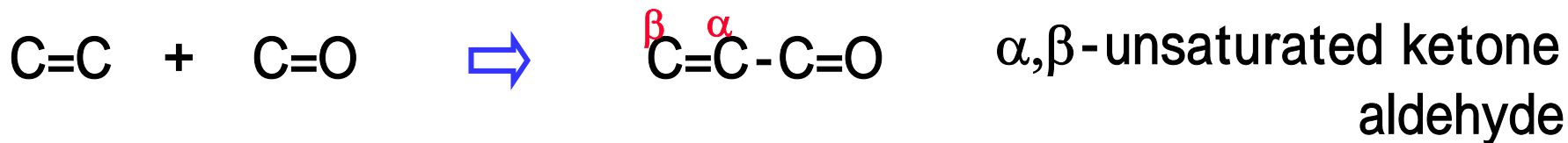
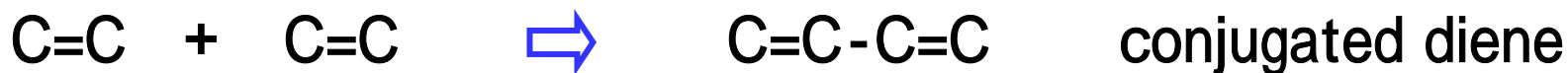


4-10. 共役ジエン

共役 conjugation



↳ conjugated system 共役系



単結合を乗り越えた

p-軌道の相互作用

1,4-付加
共役ジエンの特異な反応

紫外線(UV)吸収 (p.411)

4-10. 共役ジエン

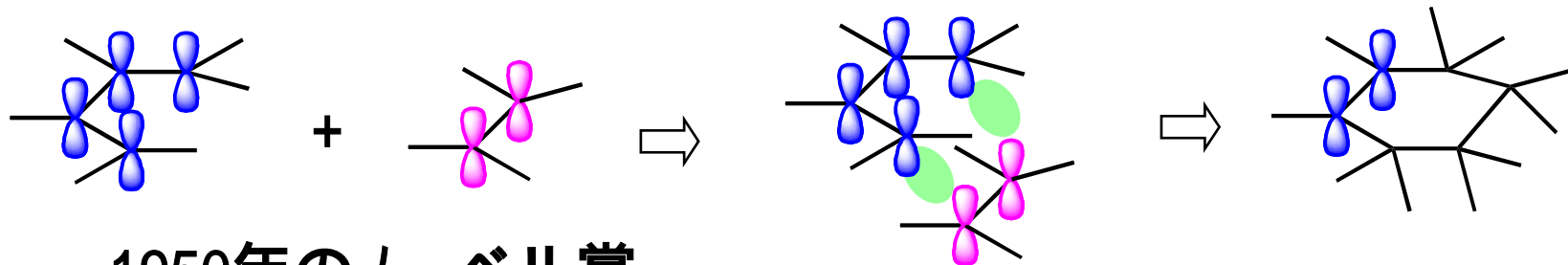
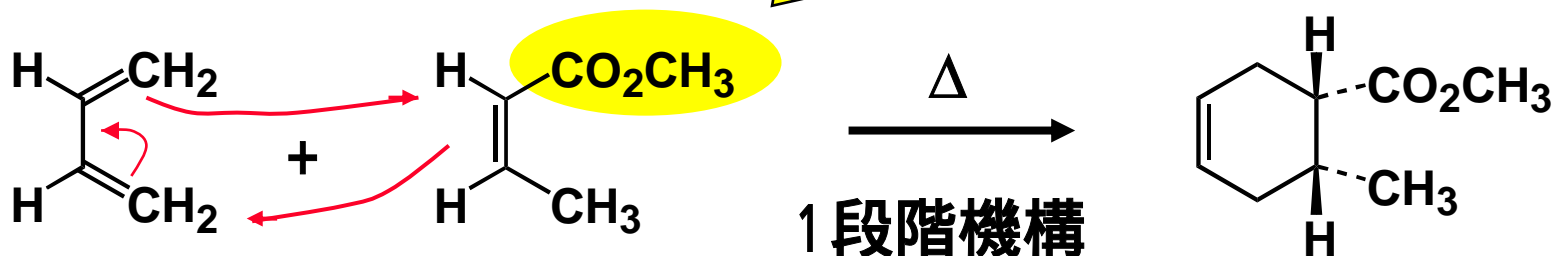
Diels-Alder 反応

diene

dienophile

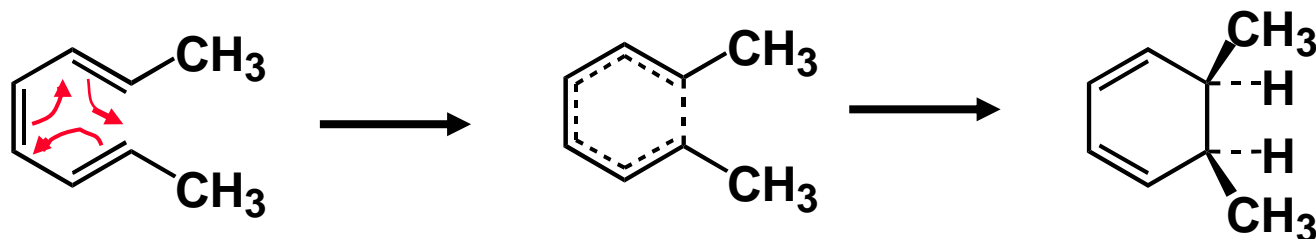
電子吸引基

cis 付加環化物

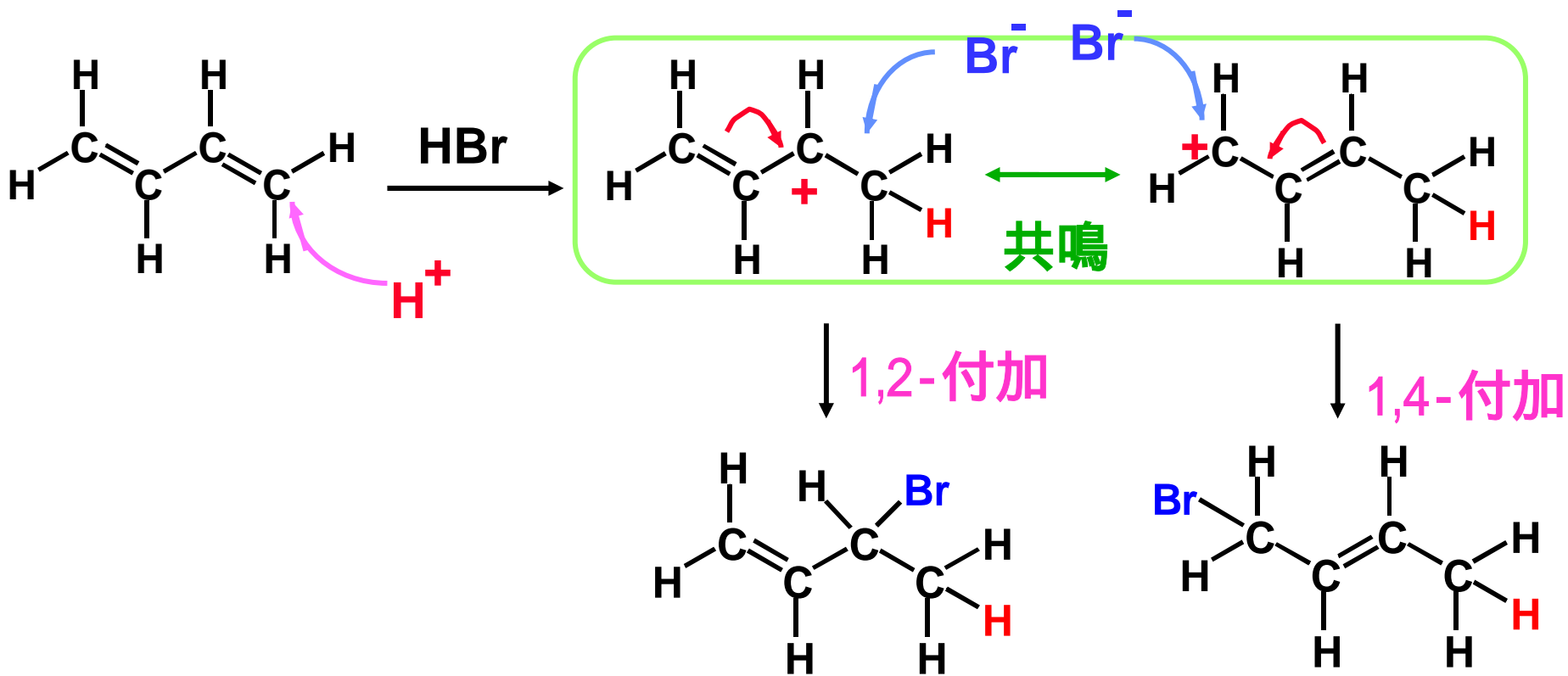


1950年のノーベル賞

ペリ環状反応 pericyclic reaction



4-11, 4-12. 共鳴

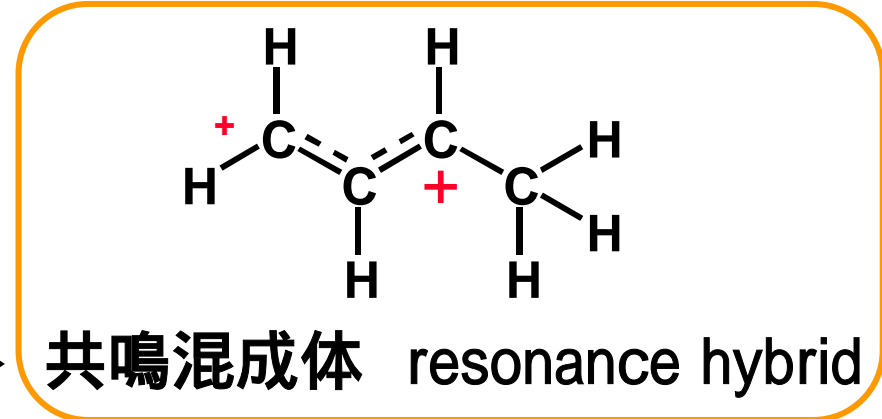


共鳴形 resonance form

結合電子の位置のみ異なる

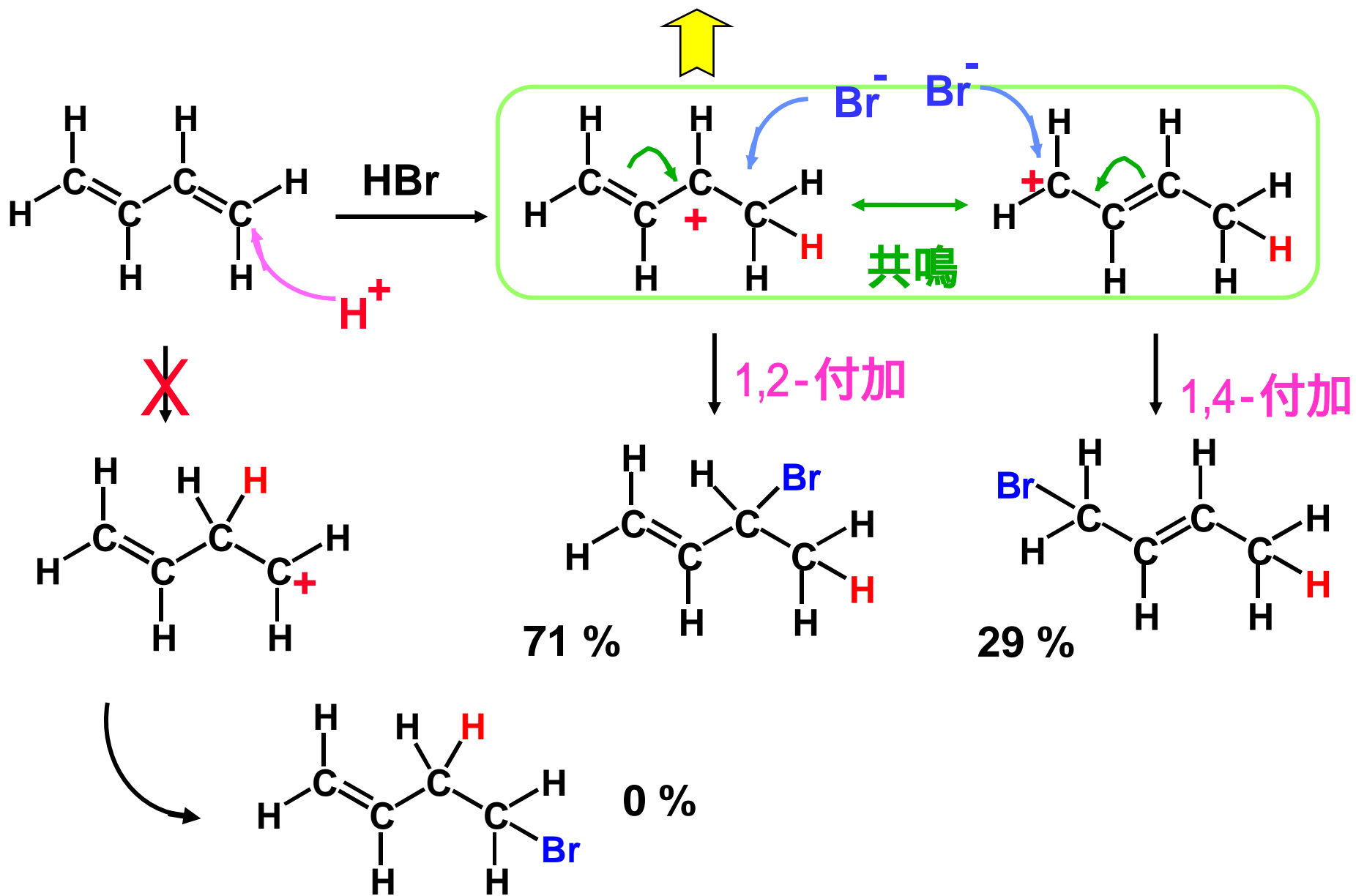
極限構造式 limited structure

真の構造は、両者の中間

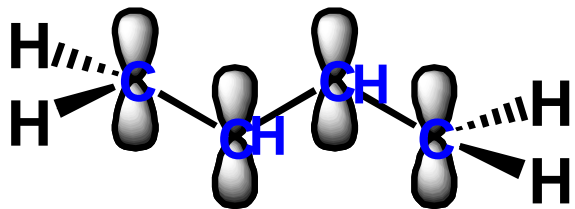
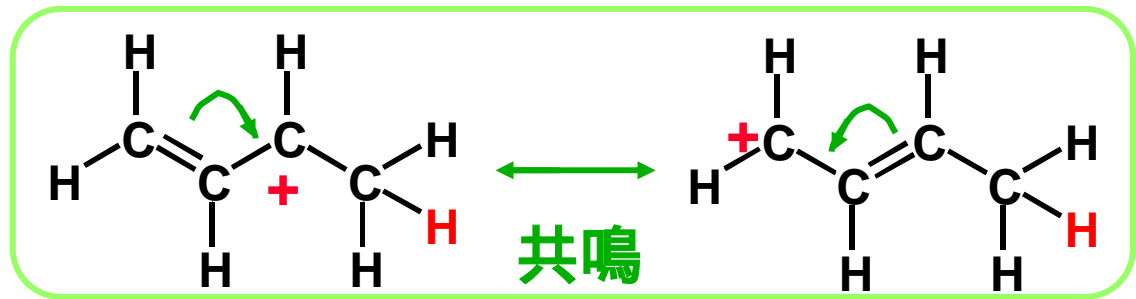
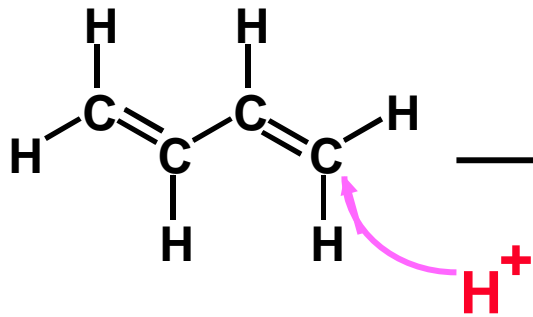


4-11, 4-12. 共鳴

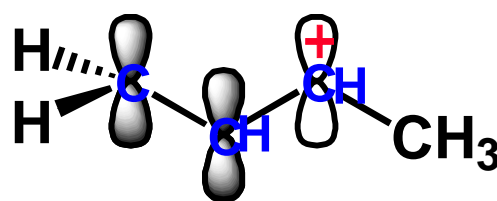
安定 (2級) allylic carbocation



4-11, 4-12. 共鳴

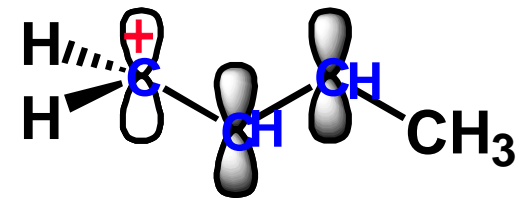


4つの電子は、4つの軌道上を自由に移動

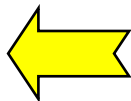


カルボカチオン:

sp^2 混成、空のp軌道を持つ



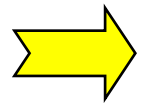
安定性



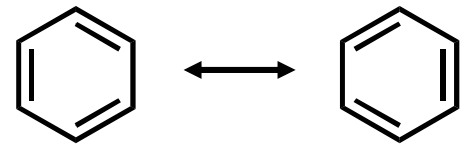
2つの電子は、3つの軌道上を自由に移動

4-11, 4-12. 共鳴

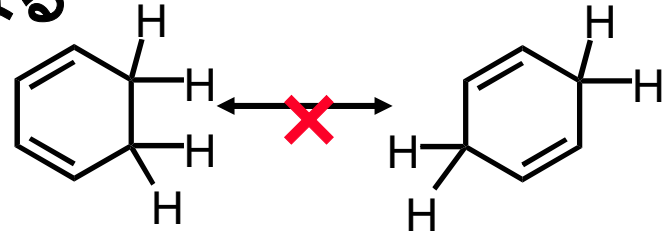
共鳴系の書き方 (5つの規則)



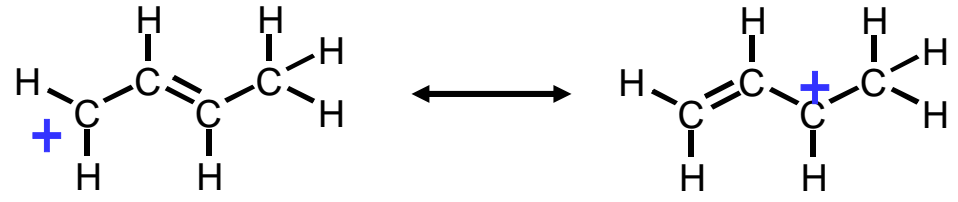
1. 架空のもので、実在しない



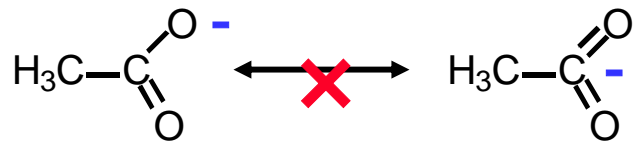
2. π 電子やn電子の位置のみが異なる



3. 等価である必要はない



4. 正常な原子価の規則(オクテット則)に従う

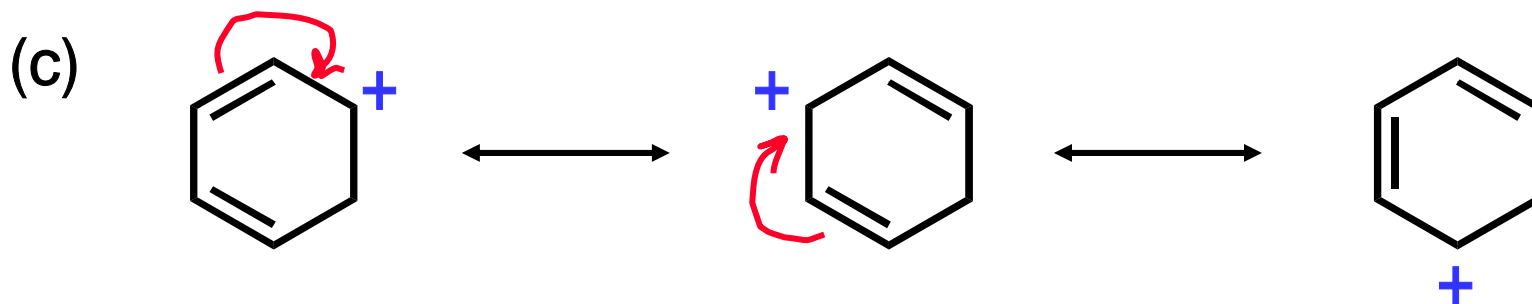
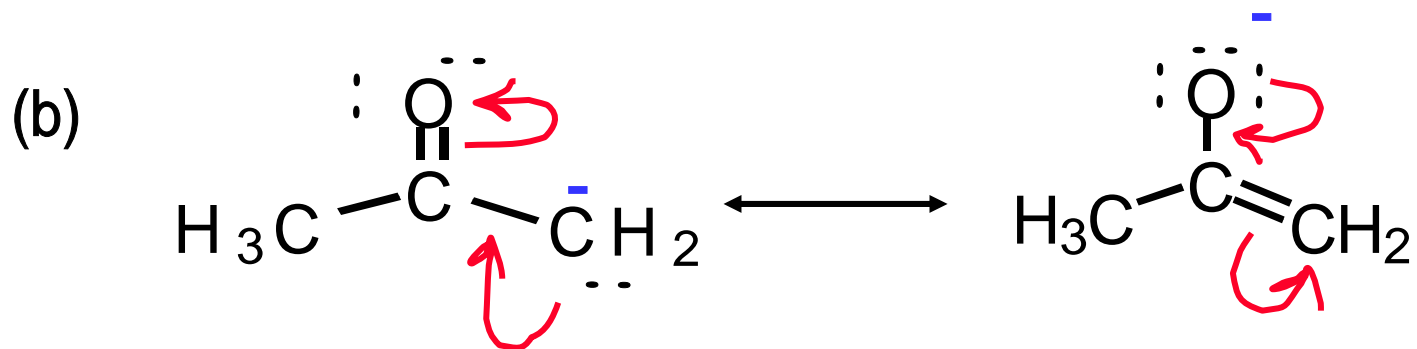
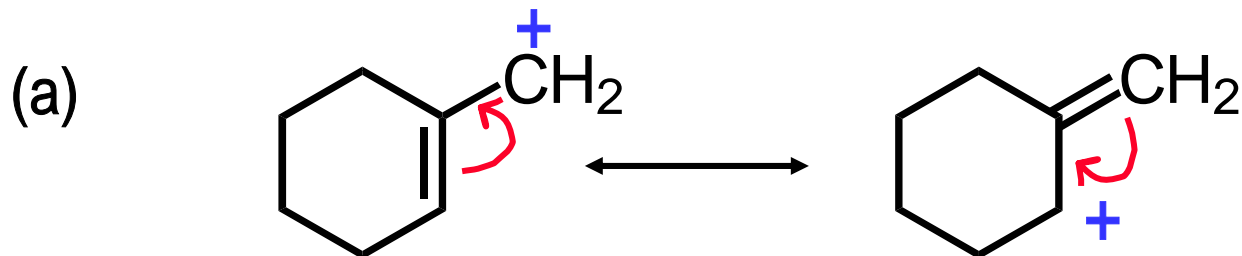


5. 非局在化(delocalized)は安定化をもたらす



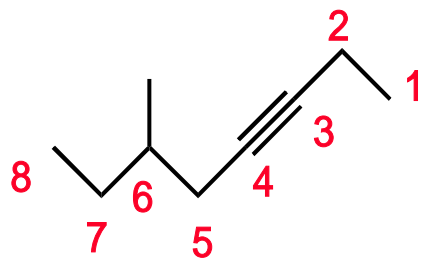
4-11, 4-12. 共鳴

テキスト 問題4.15

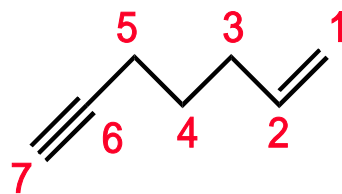


4-13. Alkyne

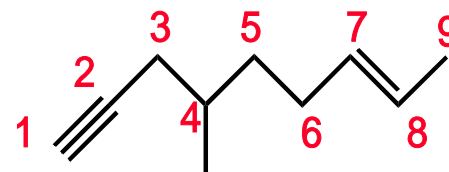
命名法 nomenclature



6-methyl-3-octyne

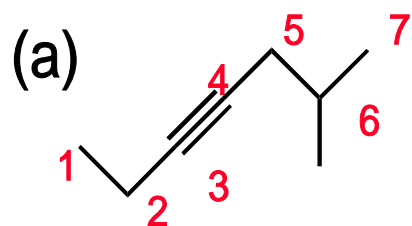


1-hepten-6-yne

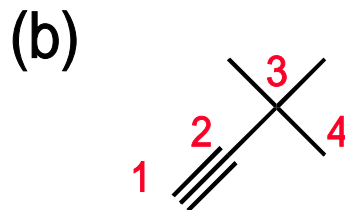


4-methyl-7-nonen-1-yne

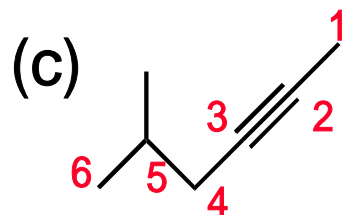
テキスト問題 4-16



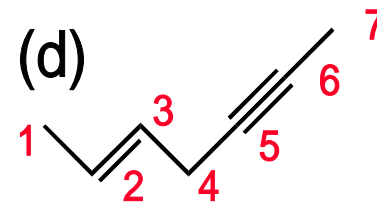
6-methyl-3-heptyne



3,3-dimethyl-1-butyne



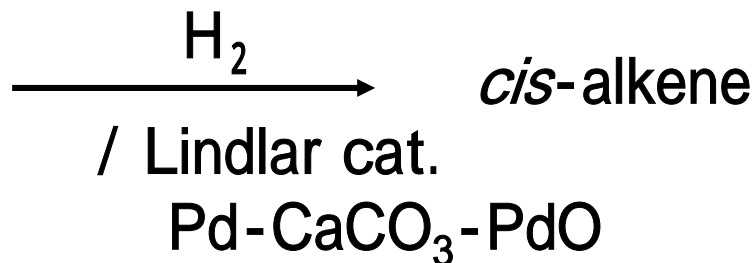
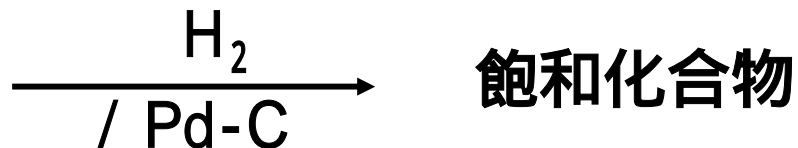
5-methyl-2-hexyne



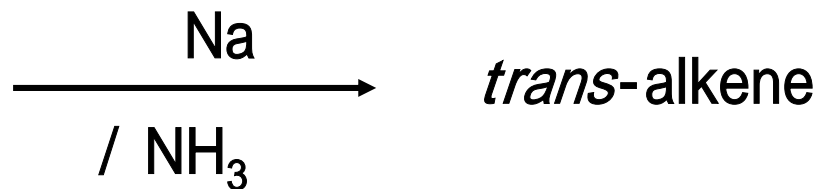
2-hepten-5-yne

還元反応

1) 水素添加 hydrogenation



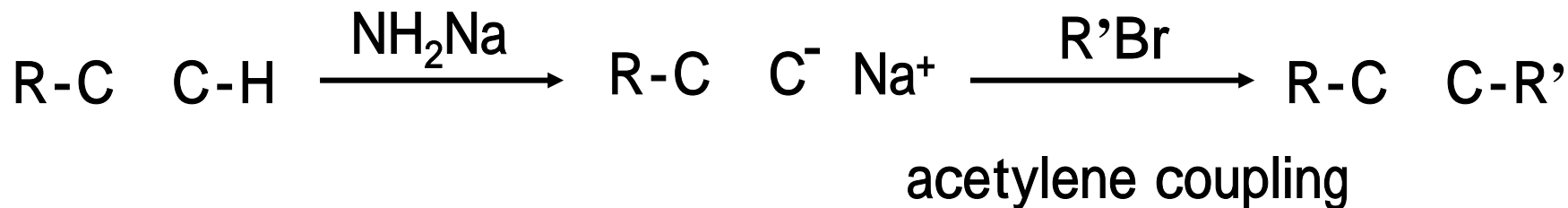
2) Birch還元



求電子付加

Markovnikov則に従う

4-13. Alkyne acetylide anion



末端アルキン：弱い酸
p. 24 表 1.3

