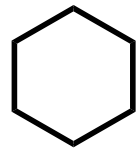
Chap. 3　Nature of Organic Reactions: Alkene

Alkane　飽和化合物　saturated compound

sp^3炭素のみ



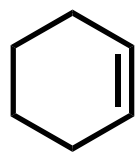
σ結合のみ

⇒ 反応性が乏しい

Alkene　C＝Cのみを含む

不飽和化合物　unsaturated compound

sp^2炭素を含む



π結合を含む

⇒ 反応性が高い

⇒ 有機化学的に重要

3-1. アルケンの命名法　①

hexane

3-hexene

2-ethyl-1-pentene

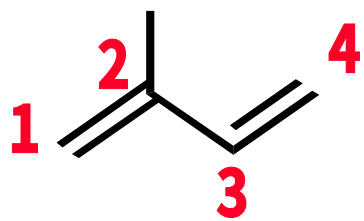
Step 1.　C=Cを含む最長な炭素鎖 (母体)

Step 2.　番号付け

Step 3.　命名　nomenclature

置換基はabc順　→　母体

2-methyl-3-hexene



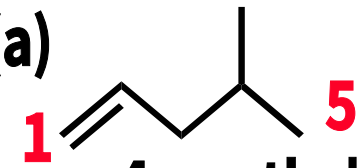
2-methyl-1,3-butadiene

3-1. アルケンの命名法　②

表3-1 アルケンの慣用名 common name

問題3-1 IUPAC名

(a)



4-methyl-1-pentene

(b)

3-heptene

(c)

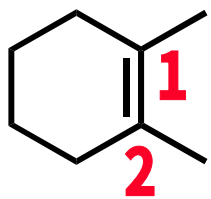
1,5-heptadiene

(d)

2-methyl-3-hexene

問題3-2

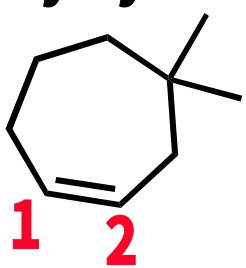
(a)



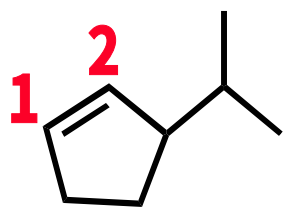
1,2-dimethylcyclohexene

4,4-dimethylcycloheptene

(b)



(c)

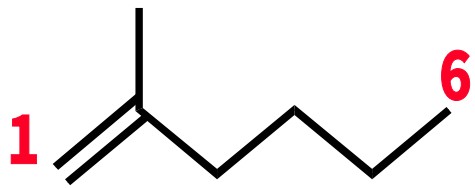


3-isopropylcyclopentene

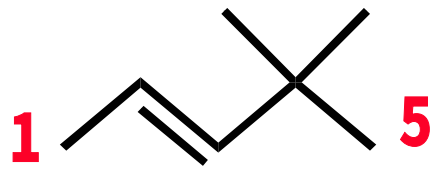
3-1. アルケンの命名法　③

問題3-3

(a)　2-methyl-1-hexene

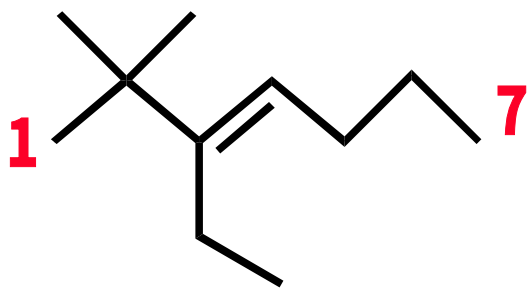


(b)　4,4-dimethyl-2-pentene

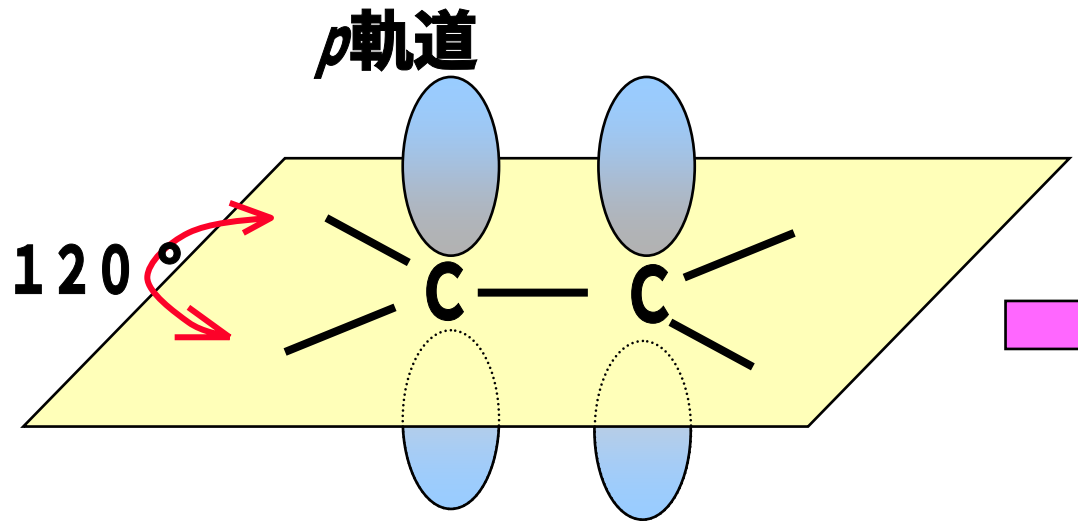


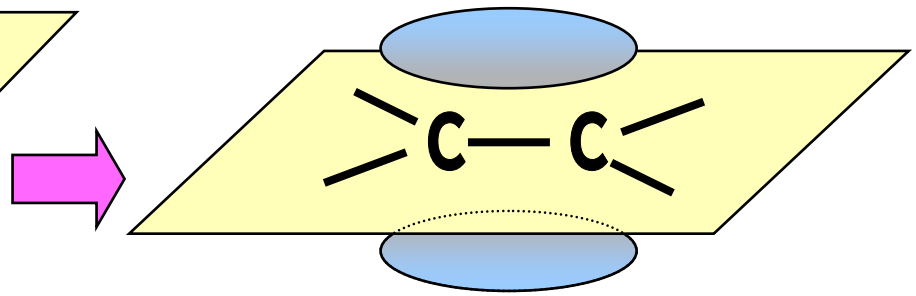
(c)　2-methyl-1,5-hexadiene

(d)　3-ethyl-2,2-dimethyl-3-hentene



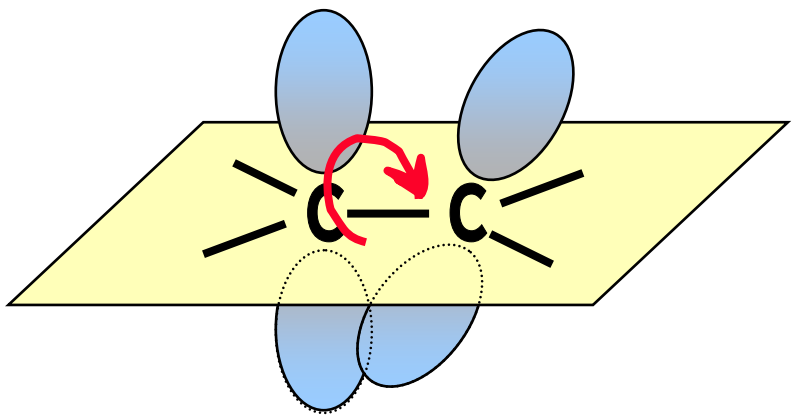
3-2. アルケンの電子構造





C=C結合を回転させる

→ π結合の切断



π結合　268 KJ/mol

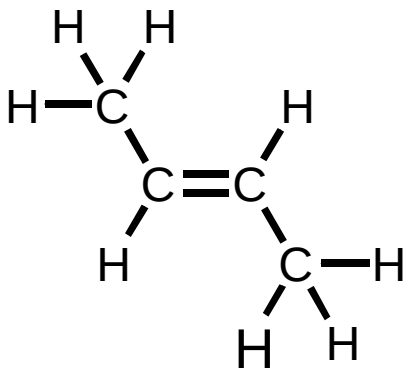
自由回転しない

C-C結合の回転障壁

12 KJ/mol

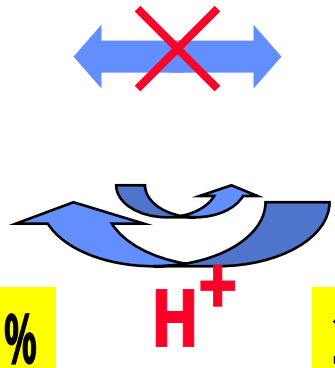
自由回転

3-3. シス-トランス異性

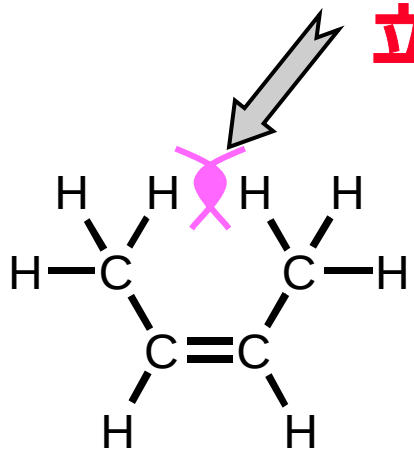


trans-2-butene

76 %



24 %



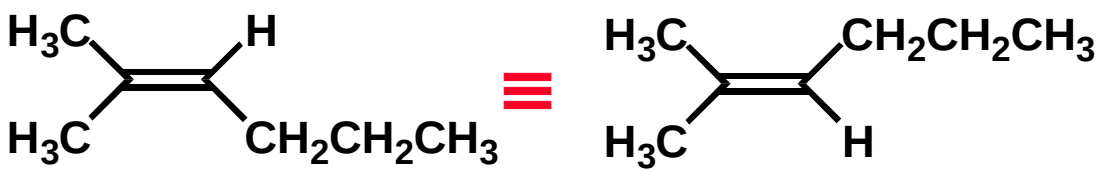
cis-2-butene

立体ひずみ

不安定

シス-トランス異性が無い場合

例) $(CH_3)_2C{=}CHCH_2CH_2CH_3$　　2-methyl-2-hexene



問題3-4

無い場合　(a) $CH_3CH{=}CH_2$　　(b) $(CH_3)_2CH{=}CHCH_3$

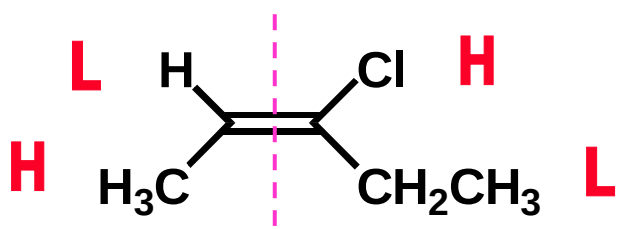
3-4. *E,Z* 命名法 ①

cis, trans 異性 ⟶ 3置換、4置換アルケンの場合 ？

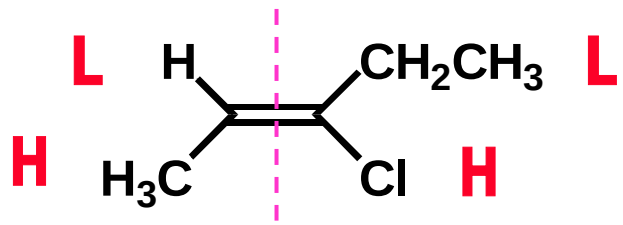
⇒ すべての置換基に優劣をつける

順位則

1. 原子番号順 Br > Cl > O > N > C > H



(E)-3-chloro-2-pentane



(Z)-3-chloro-2-pentane

2. 二重結合のα位、β位、γ位・・・と、違いが出るまで

$-CH_3$ < $-CH_2CH_3$

$-CH_2CH_3$ < $-CH(CH_3)_2$

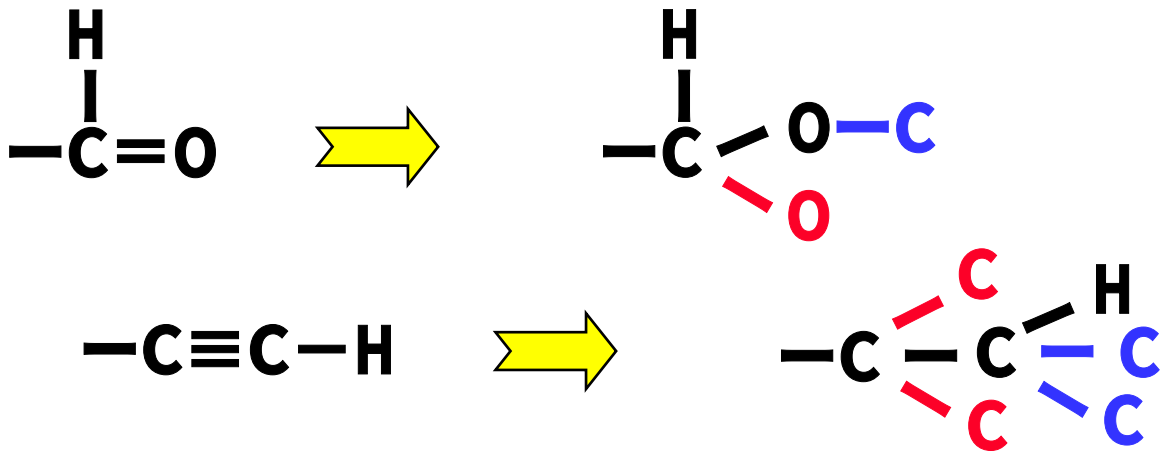
$-OH$ < $-OCH_3$

$-C(CH_3)_2NH_2$ < $-CH_2OH$

$-C(CH_3)_2NH_2$ > $-CHCH_3NH_2$

3-4. *E,Z* 命名法 ②

1. 原子番号順　　Br > Cl > O > N > C > H
2. 二重結合のα位、β位、γ位・・・と、違いが出るまで
3. 多重結合には**レプリカ原子**を充てる



問題3-6

(a) -H < -Br　　(b) -Cl < -Br　　(c) $-CH_3$ < $-CH_2CH_3$

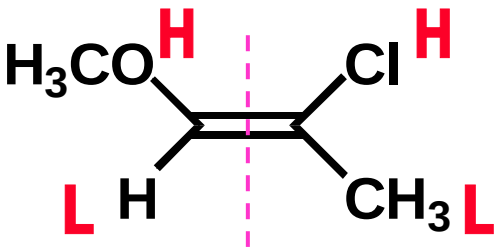
(d) $-NH_2$ < -OH　　(e) $-CH_2OH$ > $-CH_3$　　(f) $-CH_2OH$ < -CH=O

3-4. *E,Z* 命名法 ③

問題3-7 -CO-OH < -CO-OCH_3

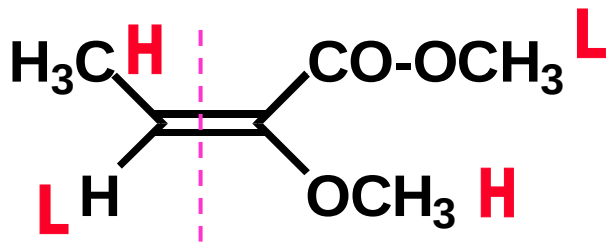
問題3-8

(a)



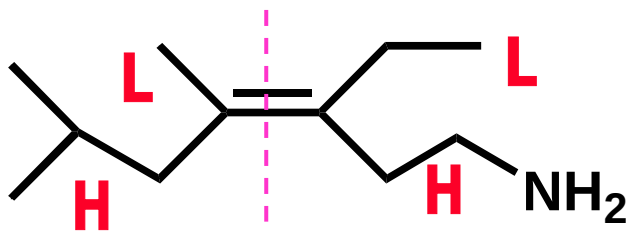
Z 配置

(b)



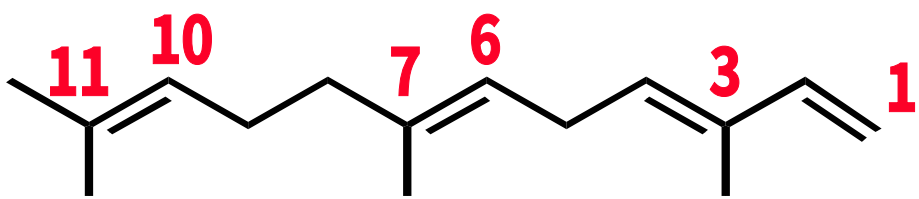
E 配置

問題3-9



Z 配置

補充問題3-48 α-farnesene



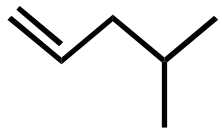
(3*E*,6*E*)-3,7,11-trimethyl-1,3,6,10-dococatetraene

3-4. *E,Z*命名法 ④

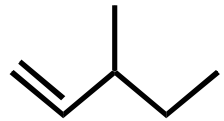
補充問題3-36

(a)

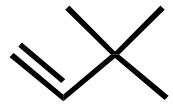
1-hexene



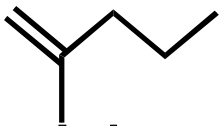
4-methyl-1-pentene



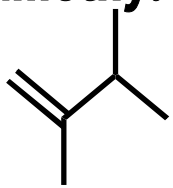
3-methyl-1-pentene



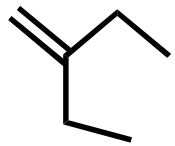
3,3-dimethyl-1-butene



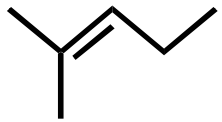
2-methyl-1-pentene



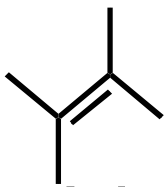
2,3-dimethyl-1-butene



2-ethyl-1-butene

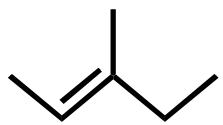


2-methyl-2-pentene



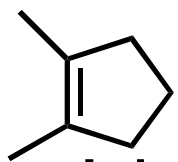
2,3-dimethyl-2-butene

(b)



(E)-3-methyl-2-pentene

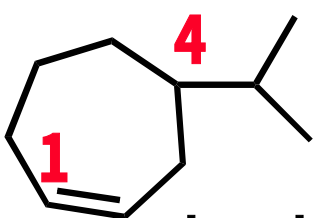
(c)



1,2-dimethylcyclopentene

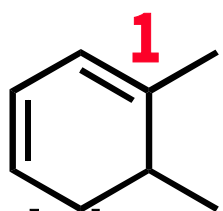
補充問題3-47

(a)



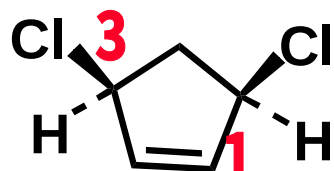
4-isopropylcycloheptene

(b)



1,6-dimethyl-1,3-cyclohexadine

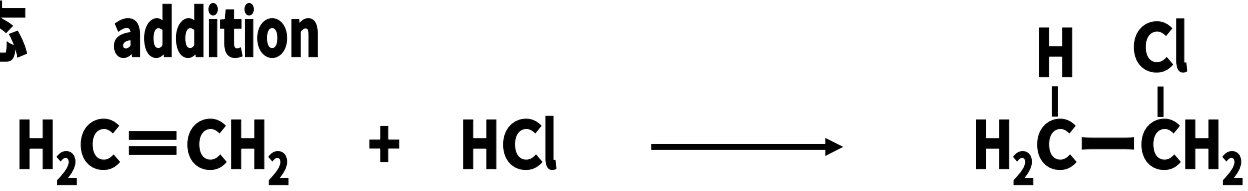
(c)



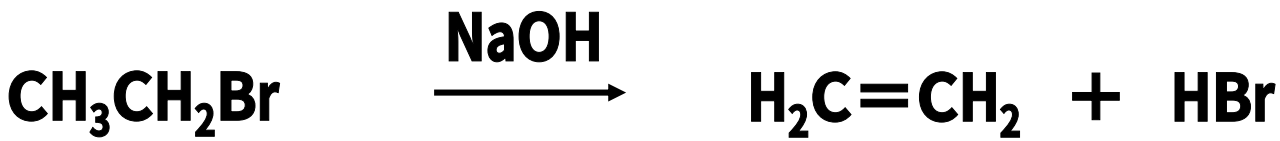
cis-3,5-dichlorocyclopentene

3-5. 有機反応の種類 ①

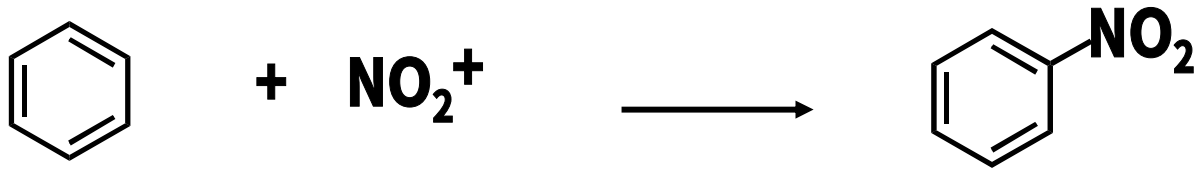
(A) 付加反応 addition



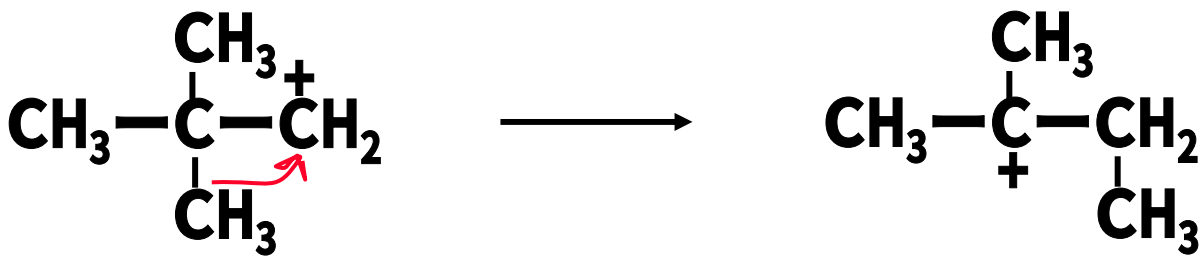
(B) 脱離反応 elimination



(C) 置換反応 substitution



(D) 転移反応 rearrangement



3-5. 有機反応の種類　②

問題3-10

(a)　$CH_3Br + KOH \longrightarrow CH_3OH + KBr$

置換反応　substitution

(b)　$CH_3CH_2OH \longrightarrow H_2C{=}CH_2 + H_2O$

脱離反応　elimination

(c)　$H_2C{=}CH_2 + H_2 \longrightarrow CH_3CH_3$

付加反応　addition

⇒ 有機反応とは？

共有結合の切断と新たな結合

3-6. 反応機構　①

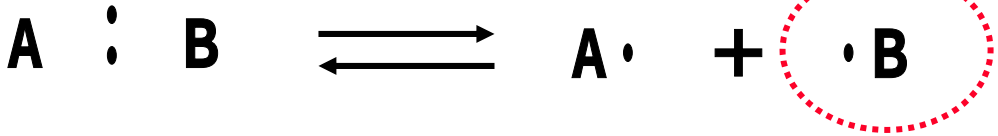
有機反応とは？　　共有結合の切断と新たな結合

⇒ 反応機構

1） どのようなステップを経て切断し、
どのようなステップで新たな結合するか？

2） 各ステップの起こりやすさと速度？

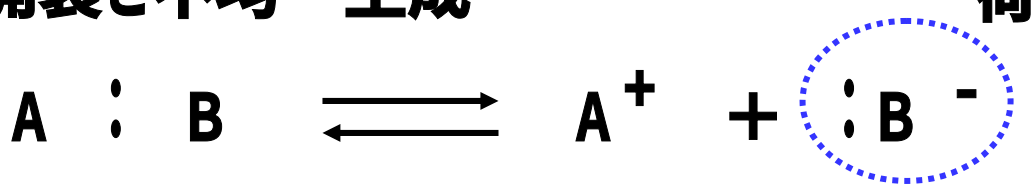
均一開裂と均一生成



ラジカル反応

ラジカル

不均一開裂と不均一生成



荷電のかたより

極性反応

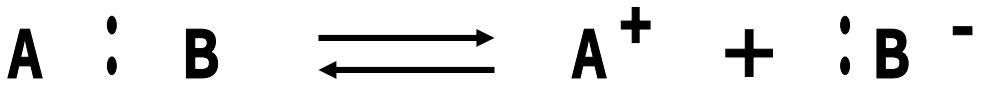
多くの有機反応

3-6. 反応機構 ②

不均一開裂と不均一生成

荷電のかたより

極性反応



多くの有機反応

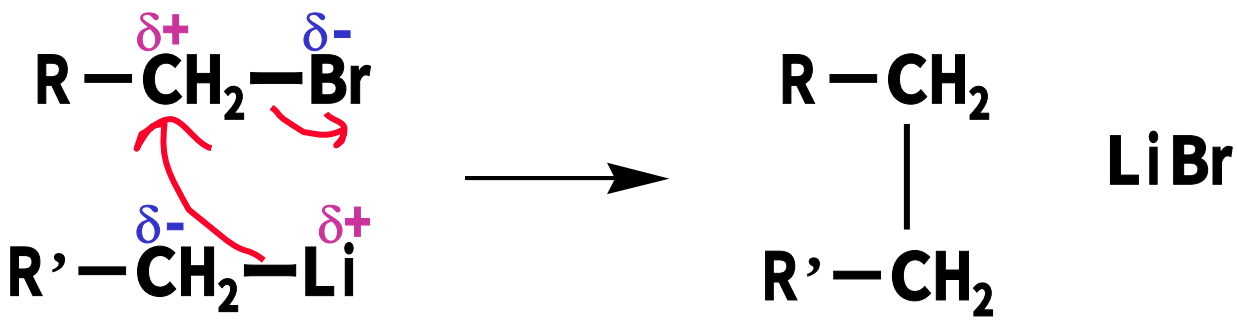
求電子試薬　求核試薬

求電子試薬　electrophile

電子不足の状態。電子対を受け取り、新たな結合を形成。

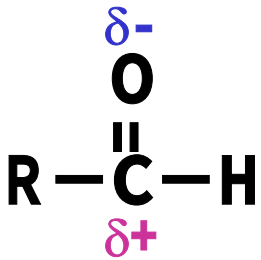
求核試薬　nucleophile

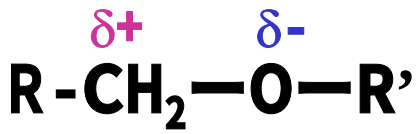
電子過多の状態。電子対を供与し、新たな結合を形成。

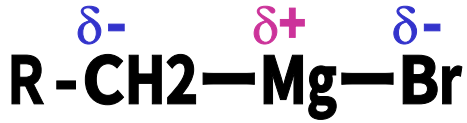


3-6. 反応機構 ③

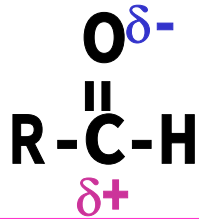
問題3-11

(a) 

(b) 

(d) 

求電子試薬 electrophile

H_3O^+　NO_2^+　NH_4^+　Br^+　  　BF_3

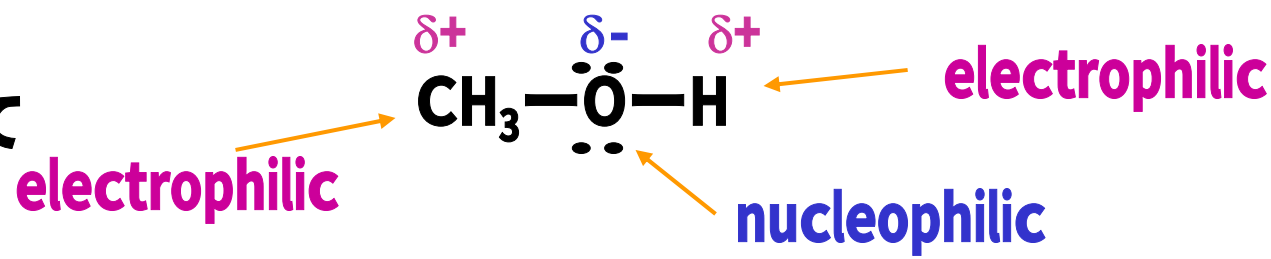
Lewis酸

求核試薬 nucleophile

OH^-　CN^-　$:NH_3$　$CH_3\ddot{N}H_2$

Lewis塩基

炭素に対する
結合反応において



3-7～ 3-9. アルケンへのHClの付加 ①

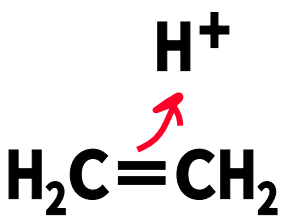
$H_2C{=}CH_2 + HCl \longrightarrow CH_3{-}CH_2Cl$

反応機構 ？

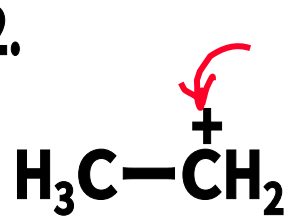
アルケン： 2重結合 (σとπ結合) 電子が一杯ある ⇨ nucleophile

⇨ H^+ (electrophile) の攻撃

Step 1.

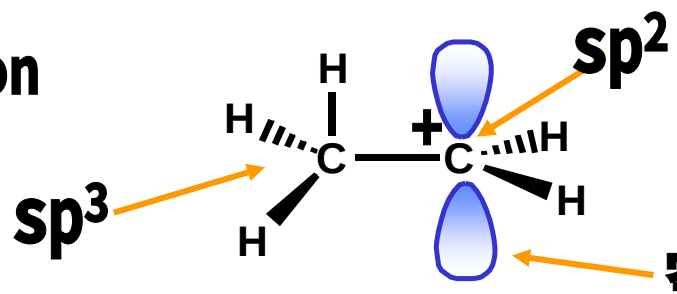


Step 2.



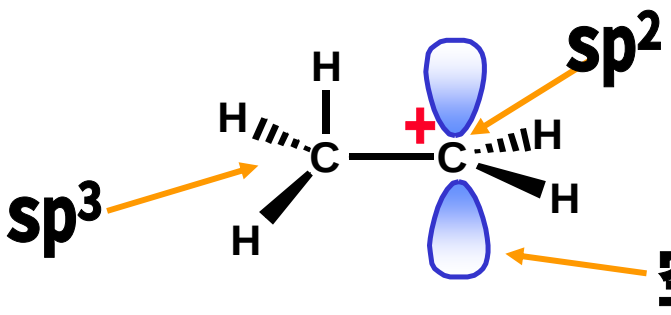
求電子付加反応
electrophilic addition

中間体
(intermediate)



3-7～ 3-9． アルケンへのHClの付加　②

$H_3C-\overset{+}{C}H_2$　　カルボカチオン　carbocation

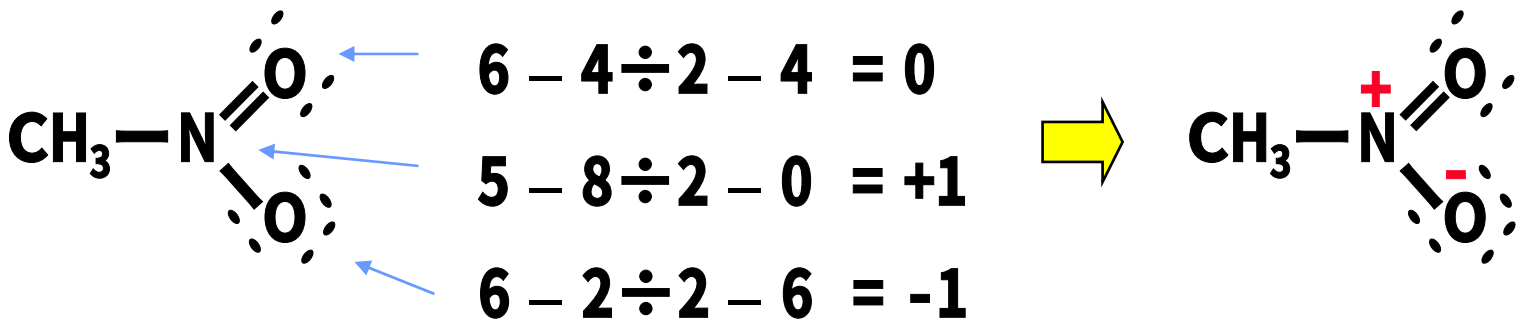


反応中間体
反応性に富み、単離できない

形式荷電

＝（荷電子の数）－（結合電子の半数）－（非結合電子の数）

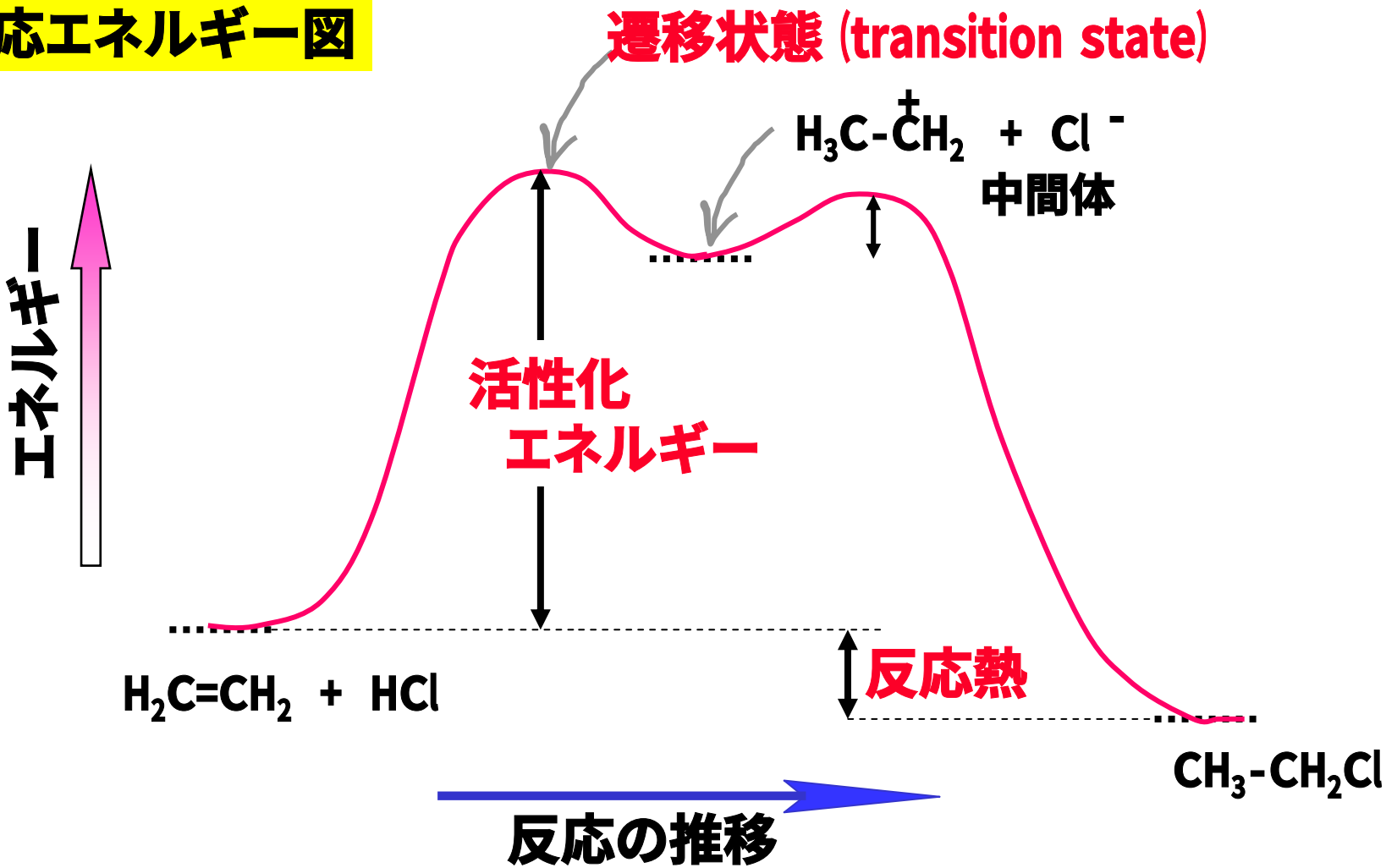
例）



3-7～ 3-9． アルケンへのHClの付加 ③

$H_2C{=}CH_2 + HCl \xrightarrow[\text{slow}]{} \left(H_3C{-}\overset{+}{C}H_2 + Cl^- \right) \xrightarrow[\text{fast}]{} CH_3{-}CH_2Cl$

反応エネルギー図



3-7～ 3-9. アルケンへのHClの付加 ④

平衡　すべての化学反応は平衡過程である

$$H_2C{=}CH_2 + HCl \rightleftharpoons CH_3CH_2Cl$$

$$\text{平衡定数}\ (K_{eq}) = \frac{[\text{生成物}]}{[\text{反応物}]} = \frac{[\,CH_3CH_2Cl\,]}{[\,H_2C{=}CH_2\,]\ [HCl]} = 7.5 \times 10^7$$

⇒ 99.9999997 %のエチレンが反応

反応が起こる
生成物のエネルギー準位が低い
⇓
発熱反応