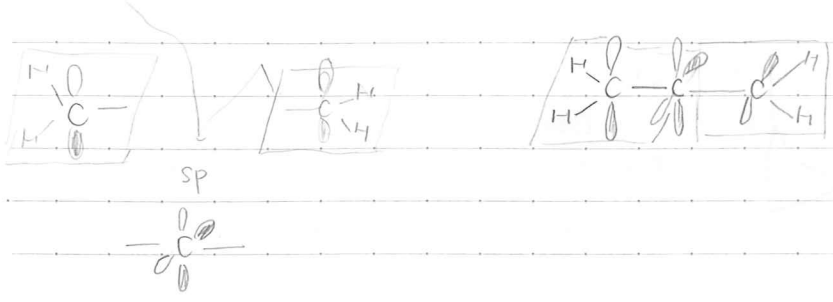
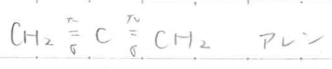


# 反応化学



## 3 酸と塩基

3.1 定義 Arrhenius

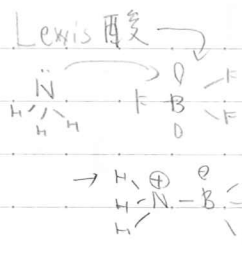
酸  $\text{H}^+$  塩基  $\text{OH}^-$

Brønsted-Lowry

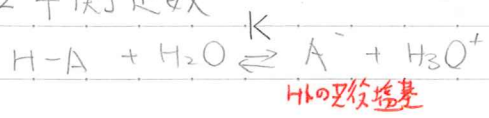
$\text{H}^+$  供与体  $\text{H}^+$  受容体

Lewis

電子授受体 電子対授与体



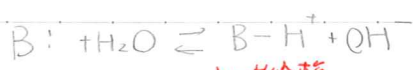
## 3.2 平衡定数



$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

常用対数  
 $\text{p}K_a = -\log K_a$

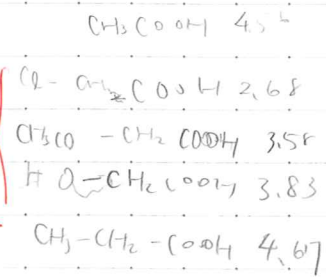
$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} = K[\text{H}_2\text{O}]$$



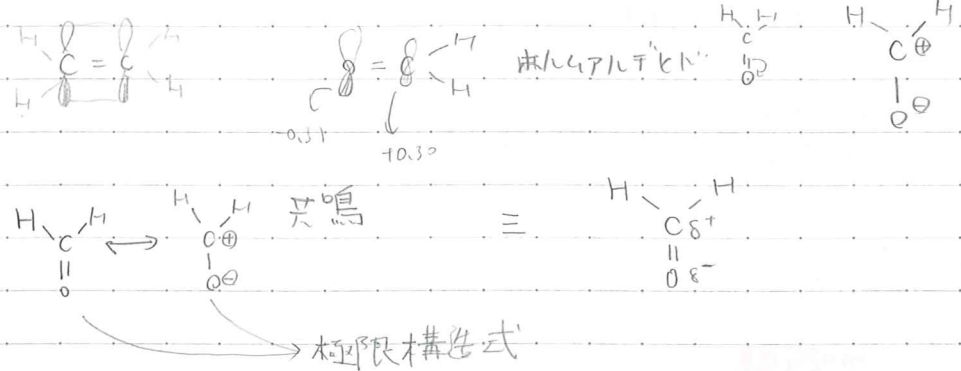
B の共役酸  
 $\downarrow$   
 $\text{p}K_a$

### 3.3 誘起効果

$X \leftarrow C \quad C \leftarrow M$   
電子求引性 電子供与性

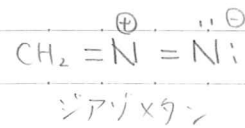


### 3.4 共鳴効果



#### 共鳴のルール

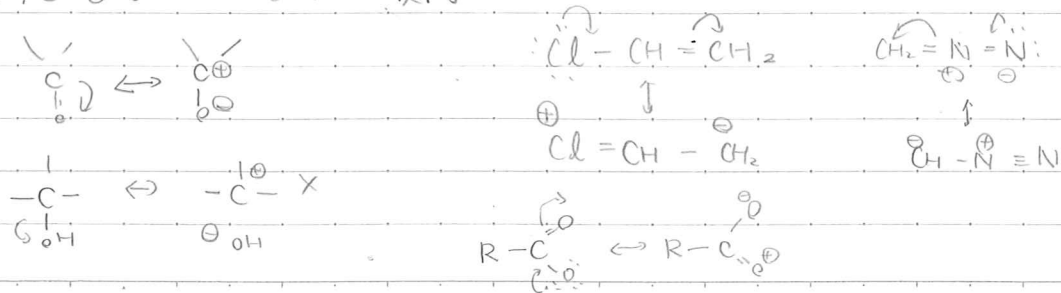
① 原子はうごかない



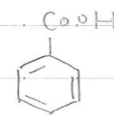
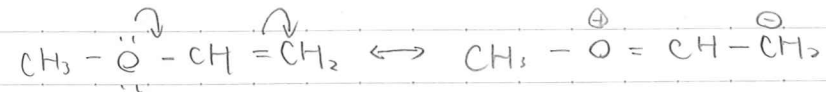
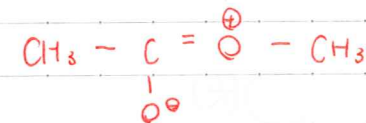
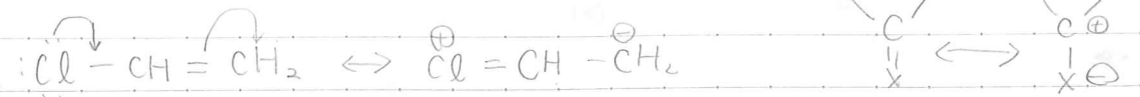
② C, N, O のまわりには最大8電子 (Octet)

O, N はなるべく8電子

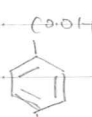
③ 単電子・非共有電子対が関与



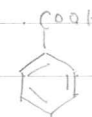
### 反応化学



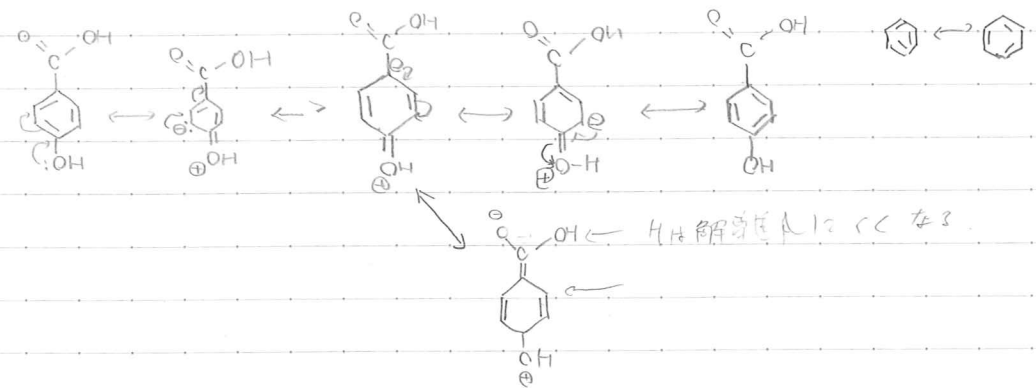
$pK_a: 4.2$

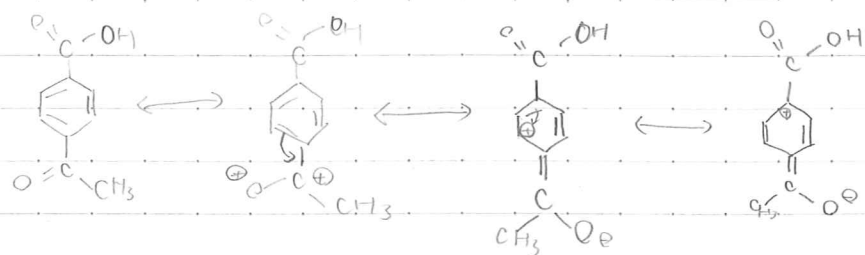


4.61



3.68





置換基 共鳴効果 誘起効果

-OH } 供与性 (大)

-OCH<sub>3</sub> } 供与性

求

F, Br, Cl } 供与性

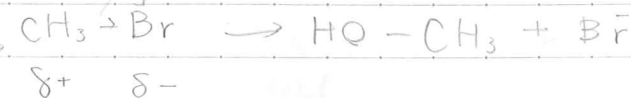
求 (大)

CDCH<sub>3</sub> } 求引性

求

## 反応化学

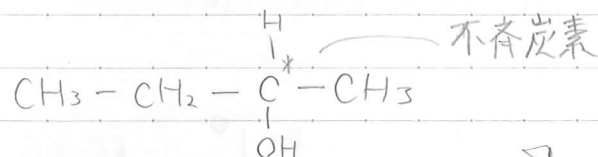
### 4. 求核置換反応 Nucleophilic Substitution



$\text{O}^--\text{H}$  求核剤 Nucleophile

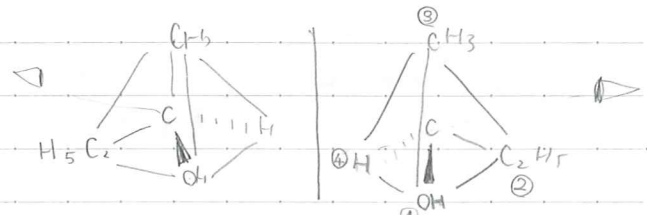
## 立体化学

エナンチオマー (鏡像異性体、光学異性体)



不斉炭素のまわりの置換型の  
順位規則 → ナット

Butan-2-ol



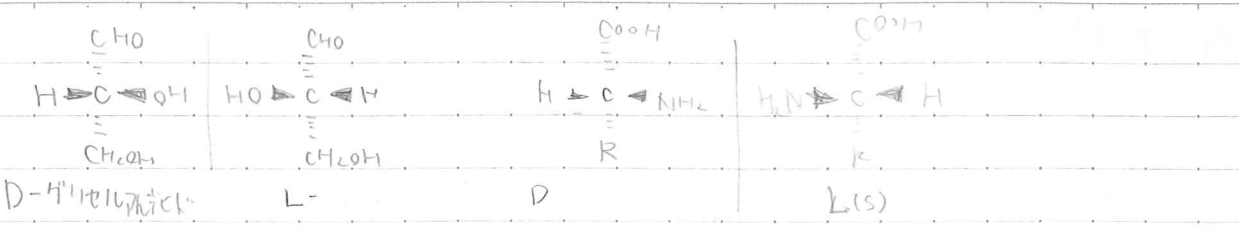
### エナンチオマーの性質

- ほとんどの化学的・物理的性質は同じ
- 旋光度の絶対値が同じ符号が逆  
→ 偏光面を回転させる

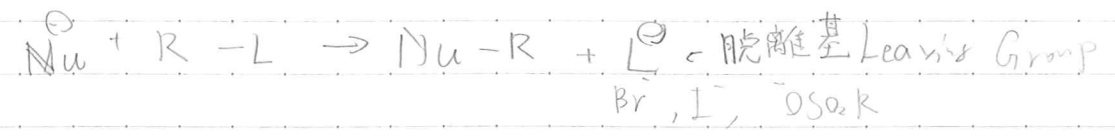
(R)-Butan-2-ol | (S)-Butan-2-ol

対称面の存在する場合

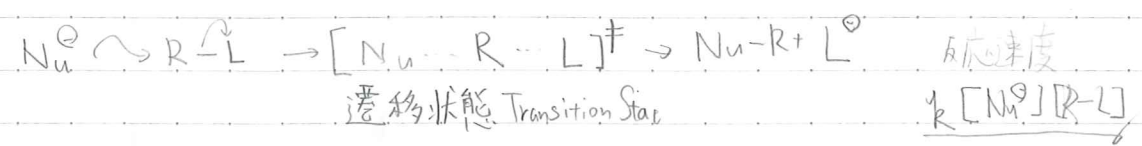
エナンチオマーは存在しない  
エナンチオマーは存在しないが不斉炭素原子  
がある場合、Xソ体と呼ぶ



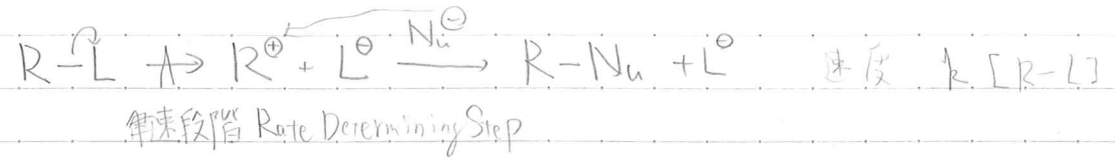
4. 求核置換反応 Nucleophilic Substitution



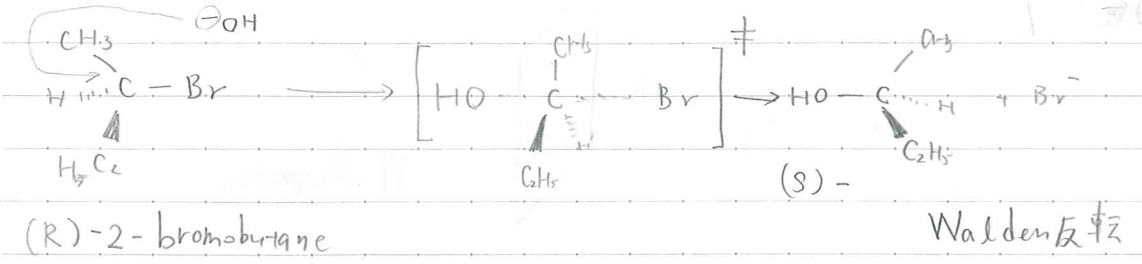
・二分子的求核置換反応 (Bimolecular Nucleophilic Substitution)  
S<sub>N</sub>2 反応



・一分子的求核置換反応 (Unimolecular Nucleophilic Substitution)  
S<sub>N</sub>1 反応

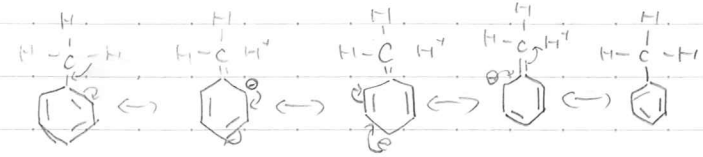
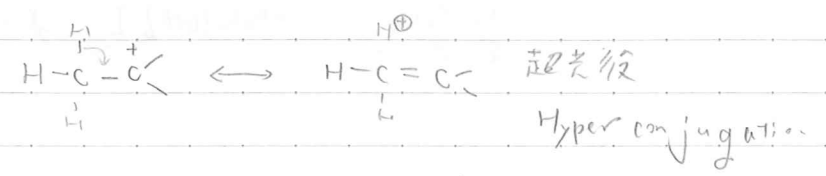
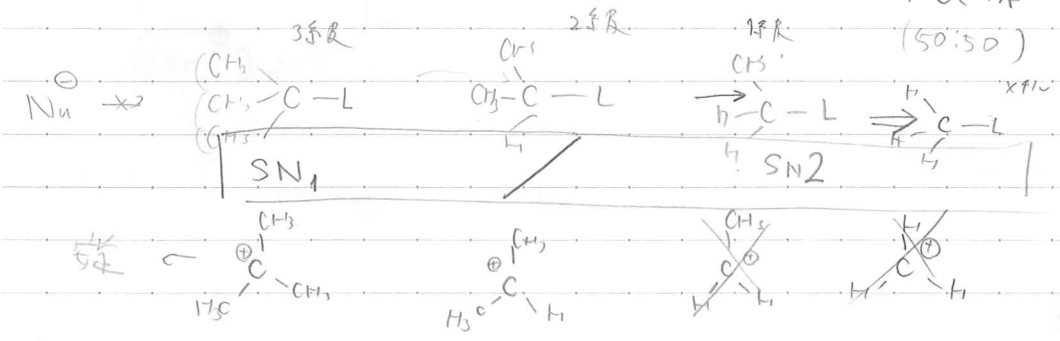
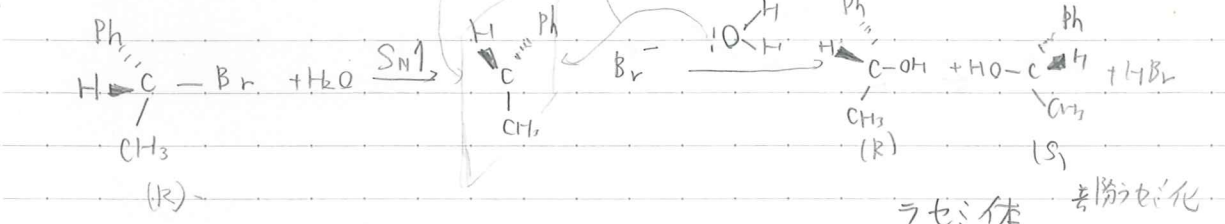


S<sub>N</sub>2 反応の立体化学



(R) → (S) 1対1対応 → 立体特異的反応  
(S) → (R)

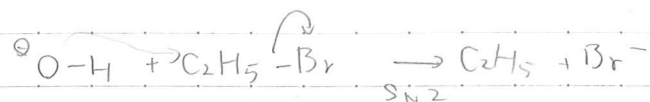
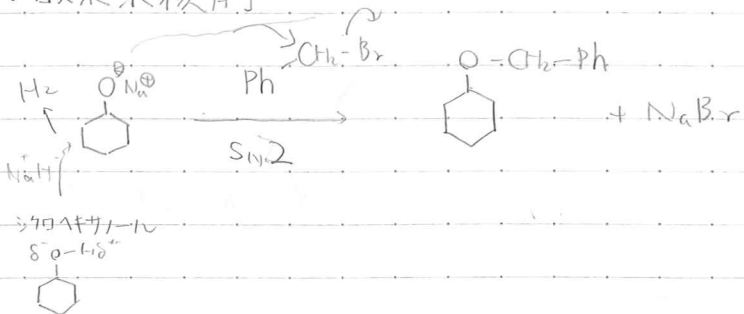
S<sub>N</sub>1 反応



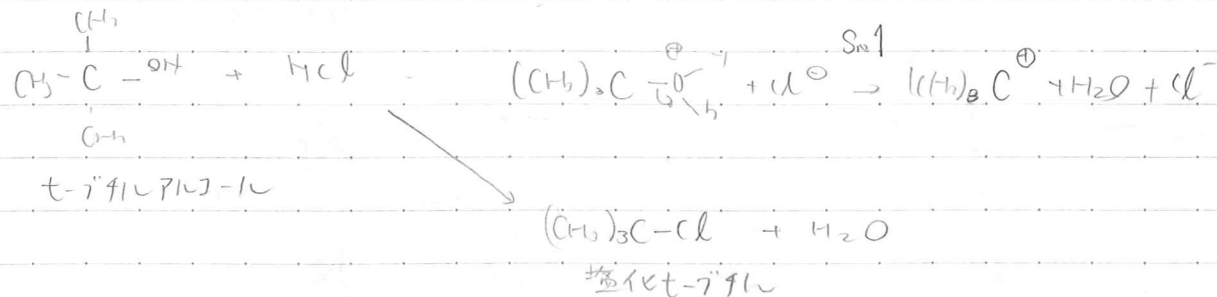
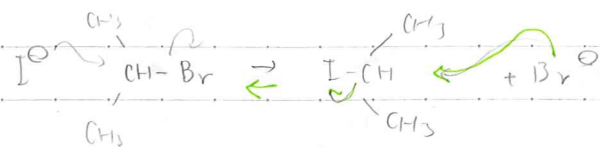


## 反応例

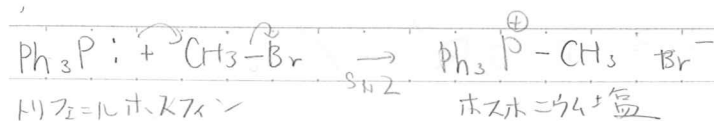
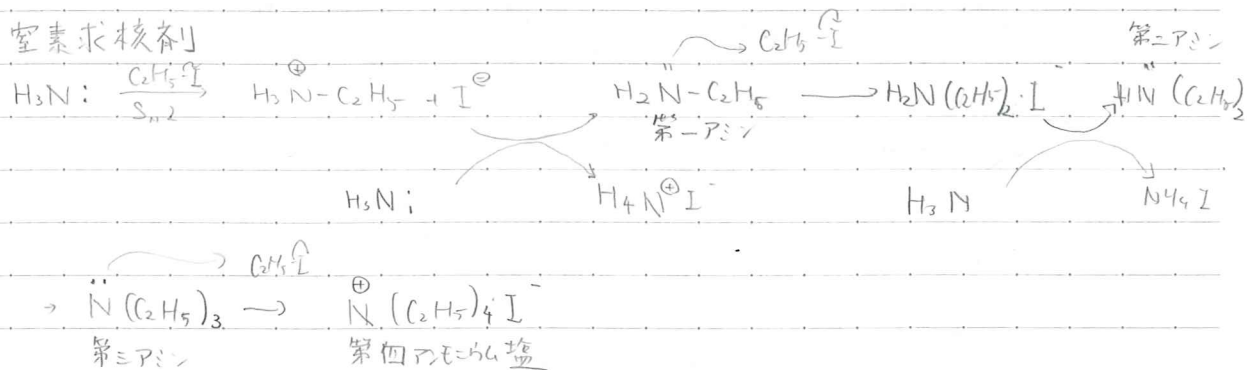
### 1) 酸素求核剤



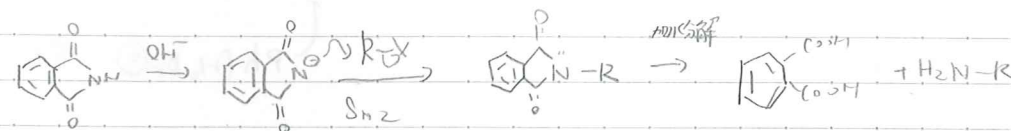
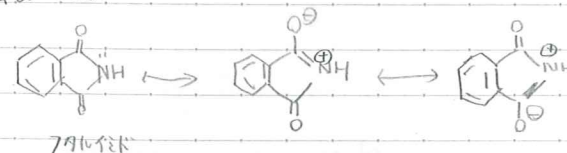
### 2) ハロゲン求核剤



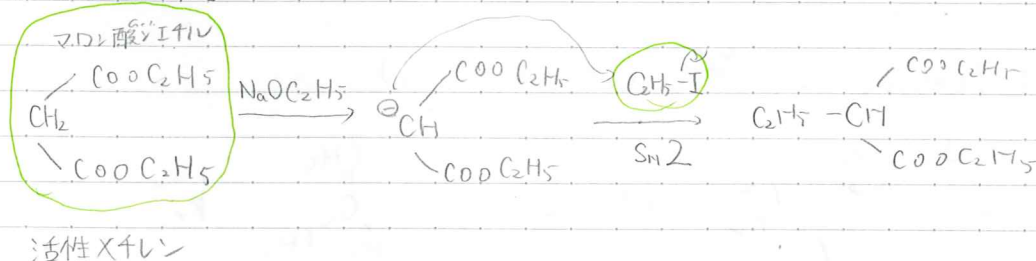
### 3) 窒素求核剤



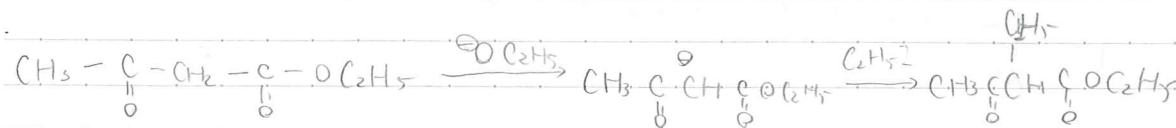
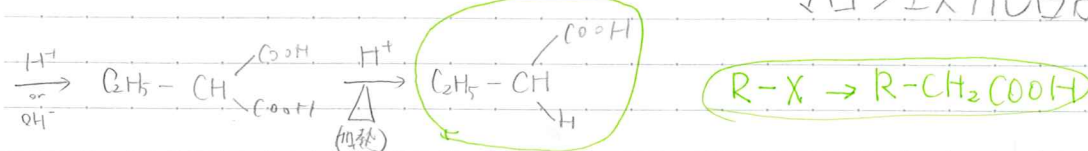
### Gabriel 合成法



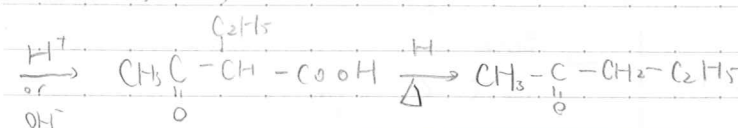
### 4) 炭素求核剤



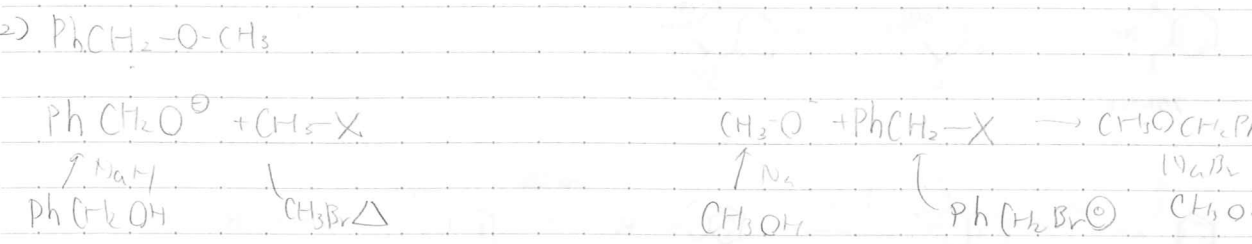
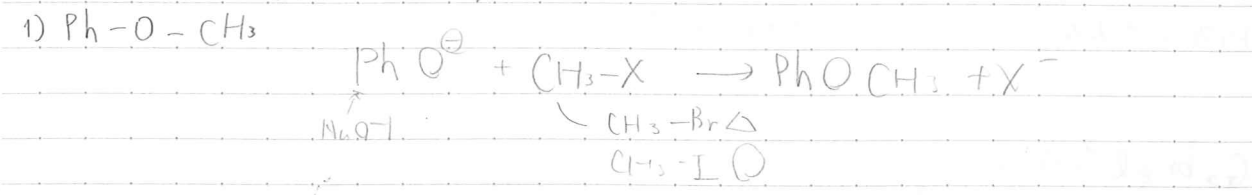
### マロンエステル合成



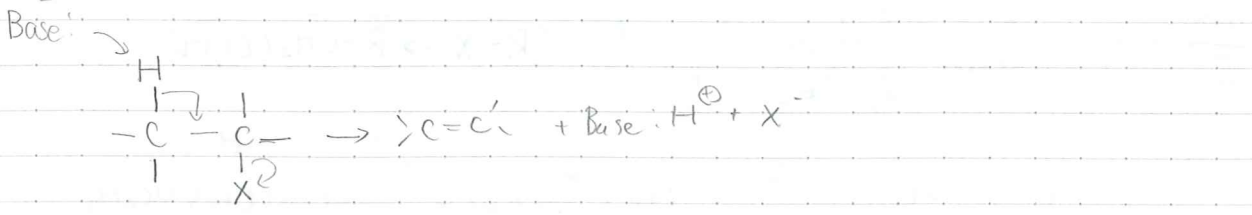
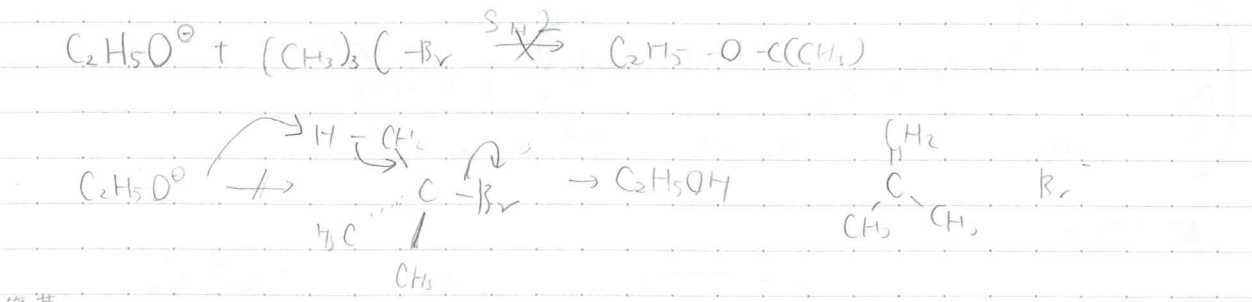
アセト酢酸エチル  
(活性Xチン)



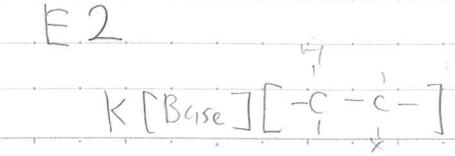
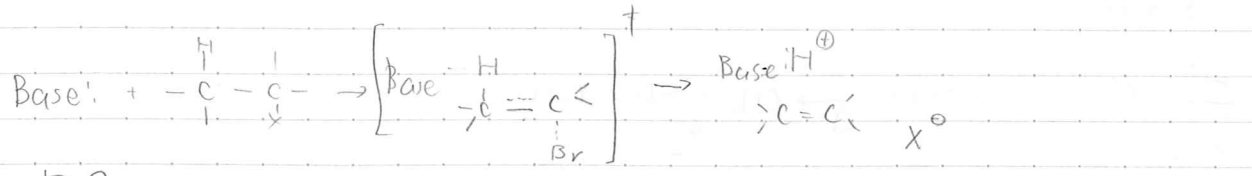
Williamson  $R-O^- + R'-X \xrightarrow{S_N2} R-OR' + X^-$



### 5. 脱離反応 (Elimination)

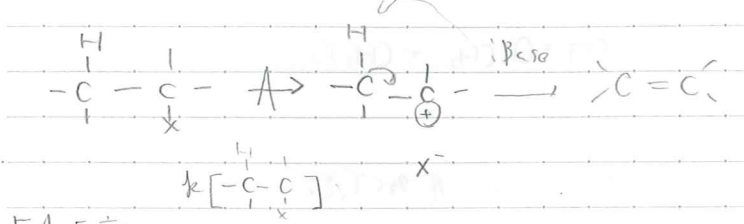


### ・二分子的脱離 (Bimolecular Elimination)



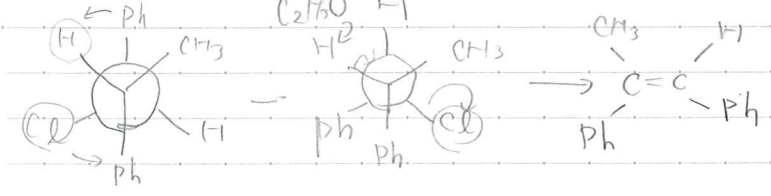
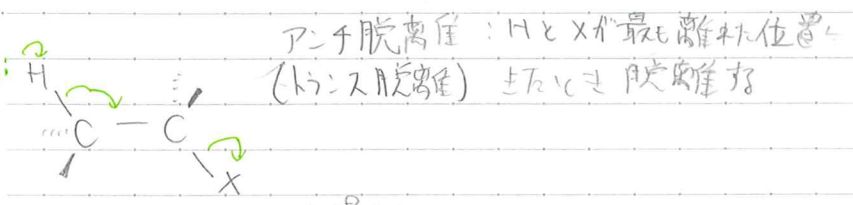
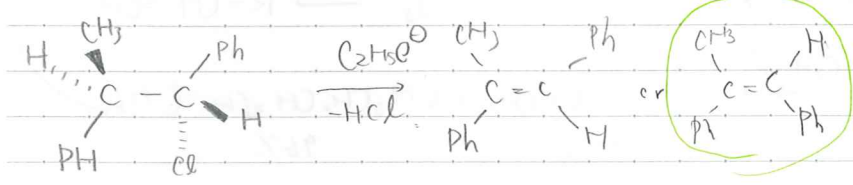
### 反応化学

### 一分子的脱離反応 (unimolecular Elimination)



### E1 反応

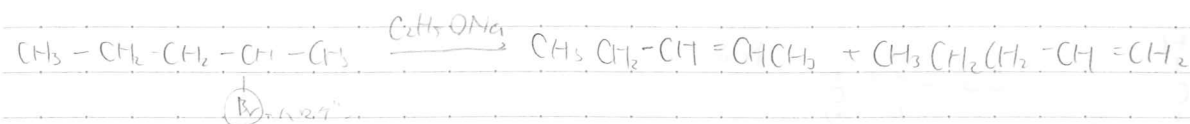
### E2 反応の立体化学



### ジアステルオマー

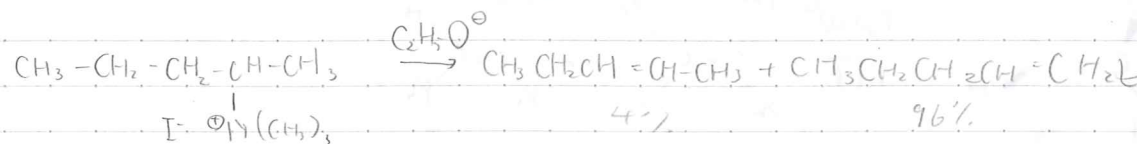
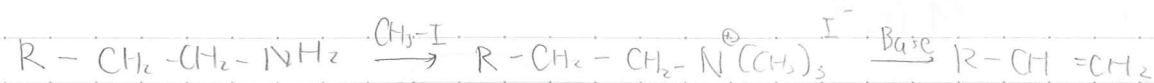
立体特異的 反応: 原料・生成物が一対一対応  
 $(R,R)(S,S) \rightarrow シス$   
 $R,S (S,R) \rightarrow トランス$

## E2 反応の配向性



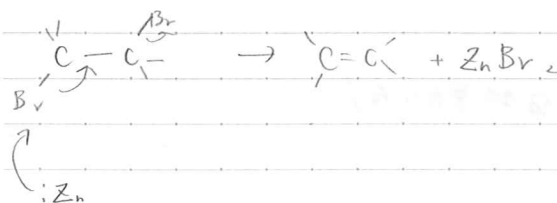
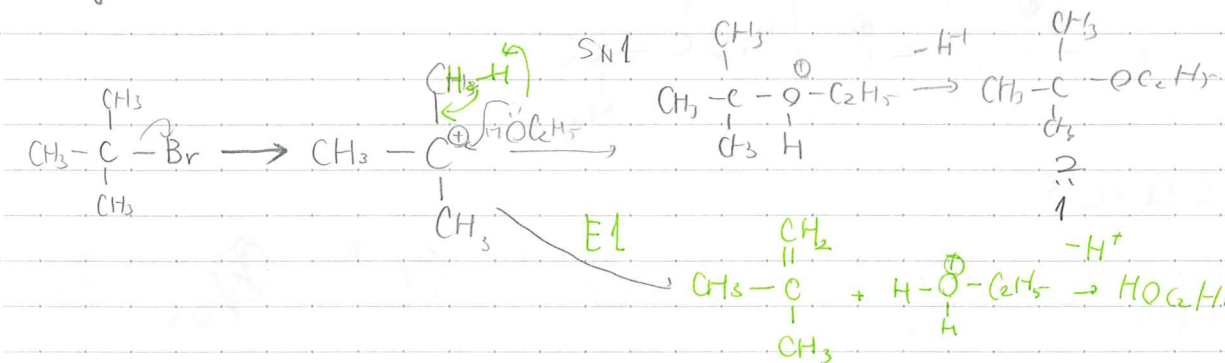
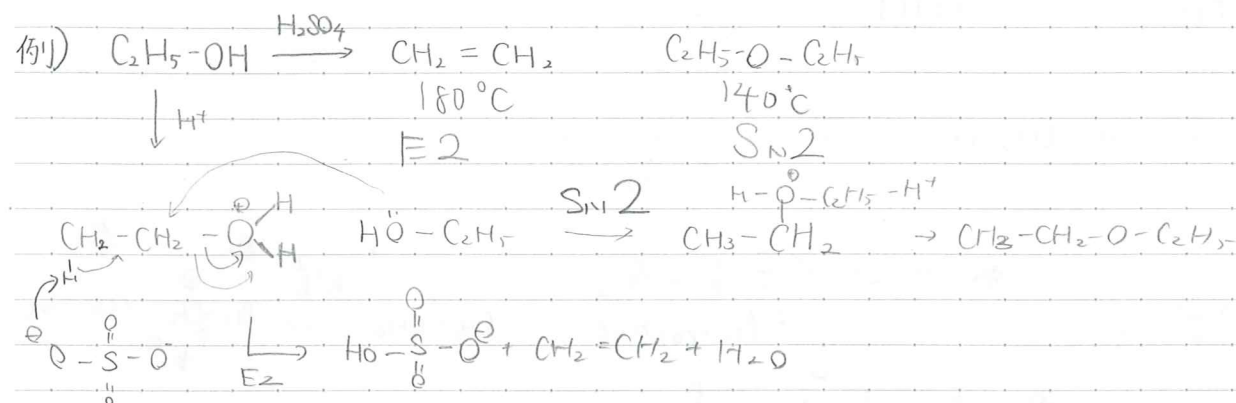
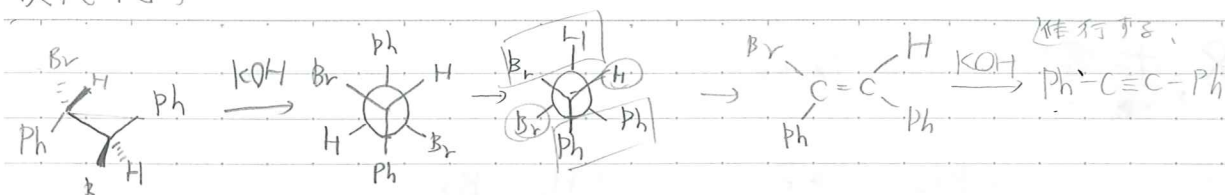
Saytzeff 則: 置換基が多いアルケンが主生成物。

## Hofmann 脱離



Hofmann 則: 置換基が少ない。

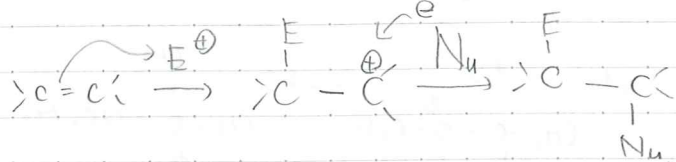
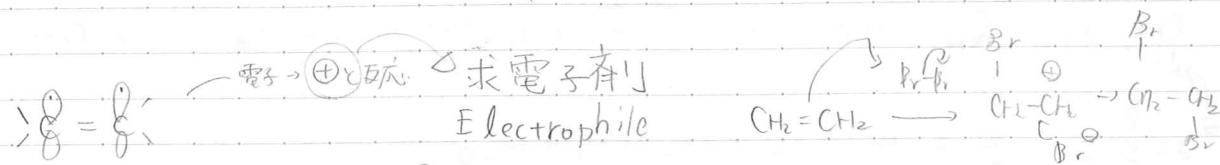
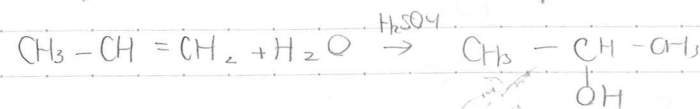
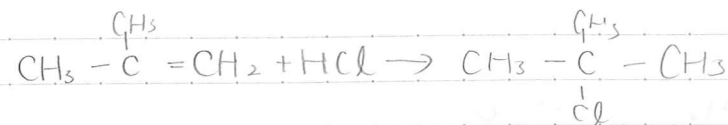
## 反応化学



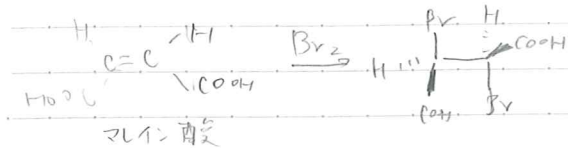
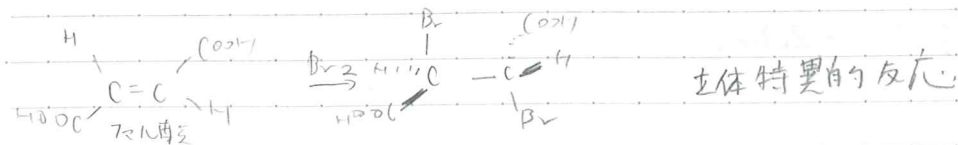
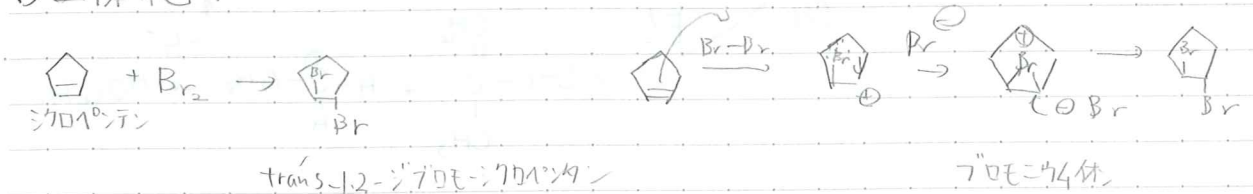


8-11

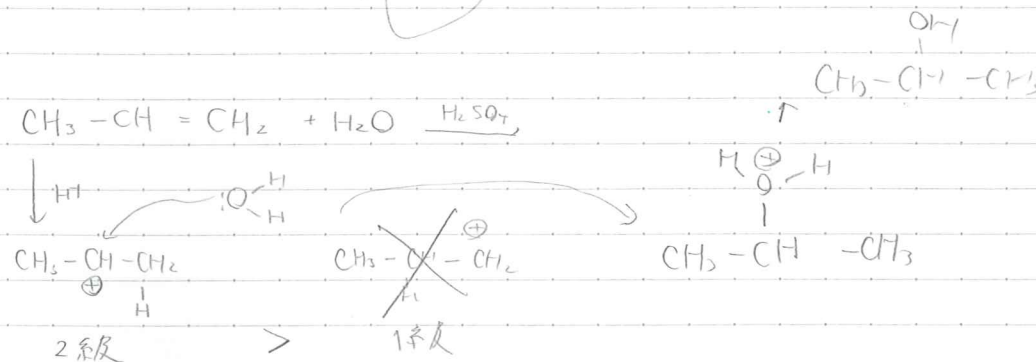
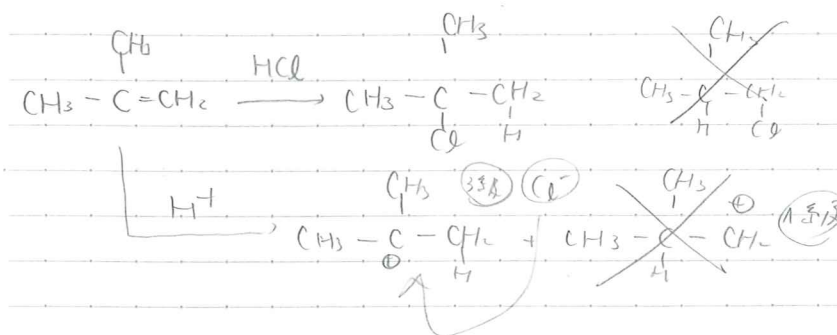
## 8. 求電子付加反応



## 1) 立体化学



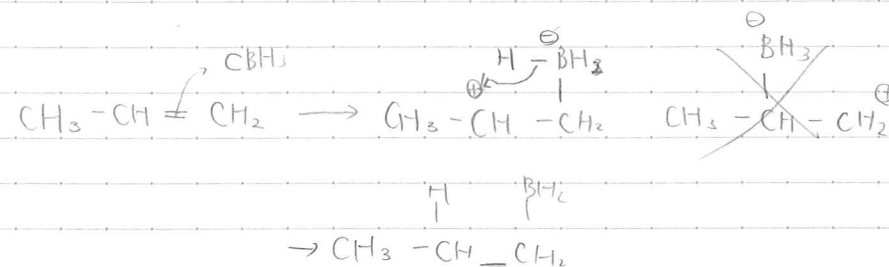
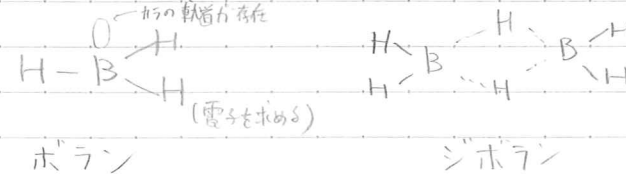
## 2) 配向性



## Markovnikov 則

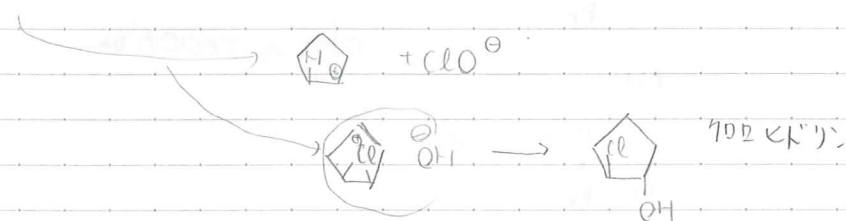
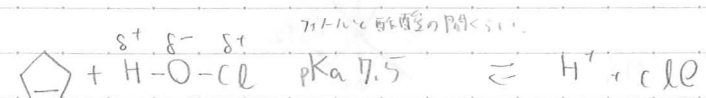
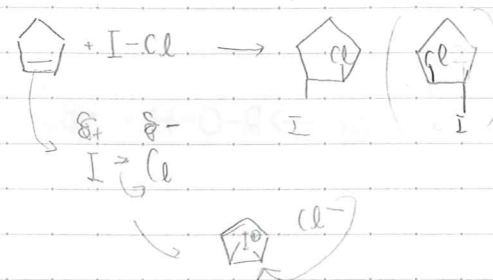
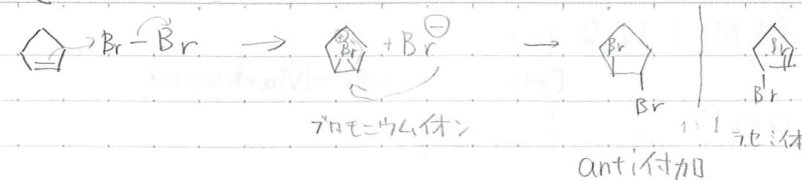
X は -H の少ない方に付加する

## 3) ヒドロボウ素化反応

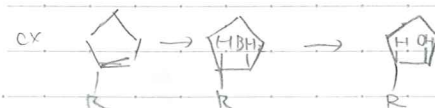
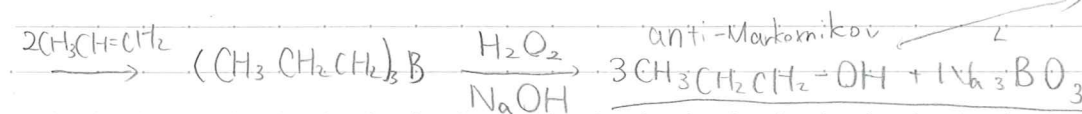
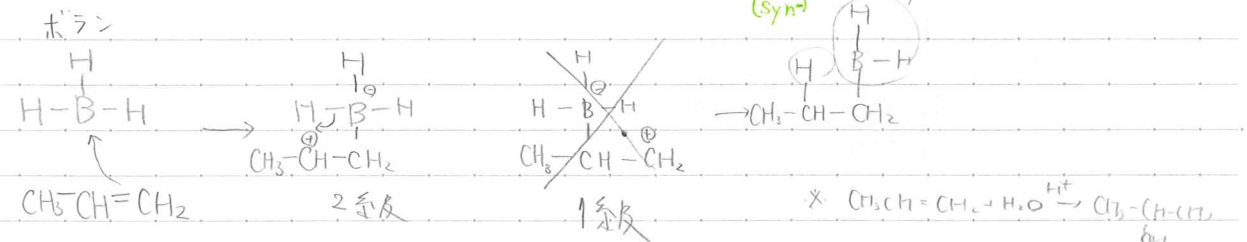




## 反応化学

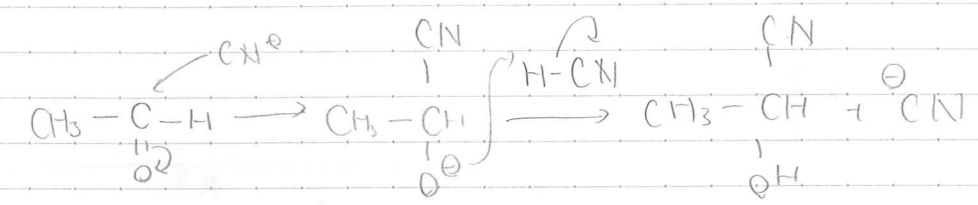
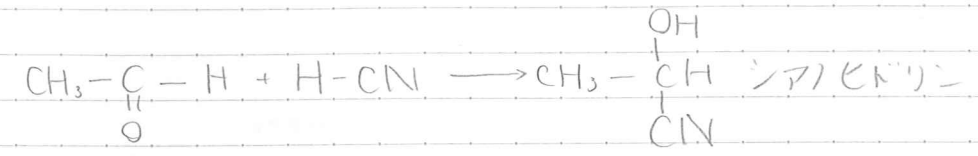
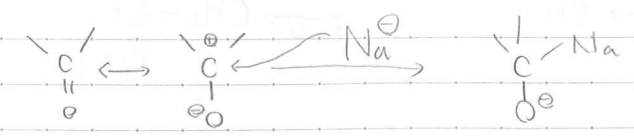


## 3) ヒドロホウ素 (hydroboration)

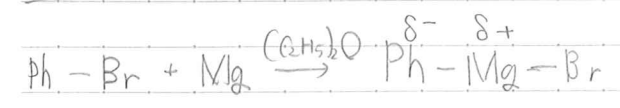


反応化学

6. 求核付加 (Nucleophilic Addition)

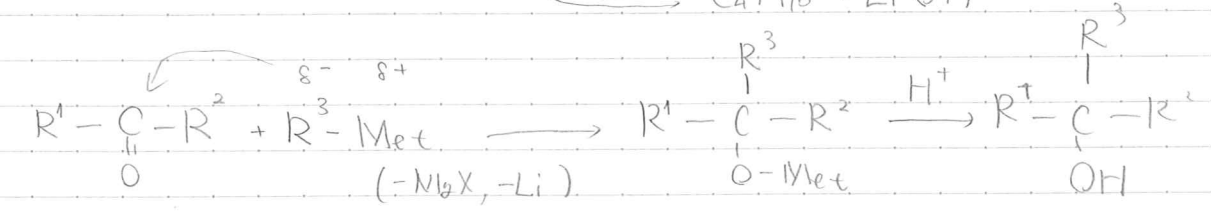
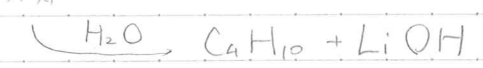
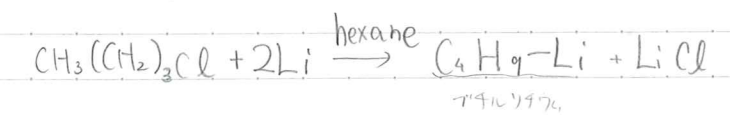
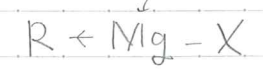


§1 有機金属の付加

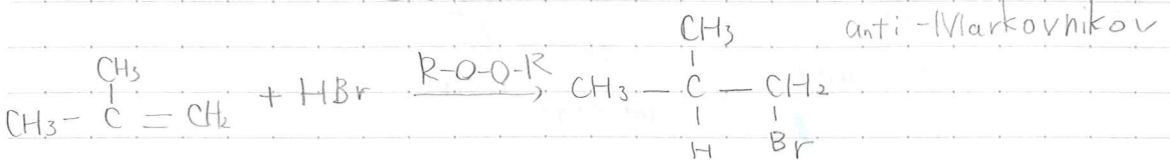


Grignard 試薬

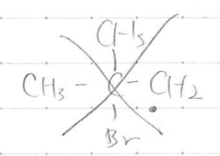
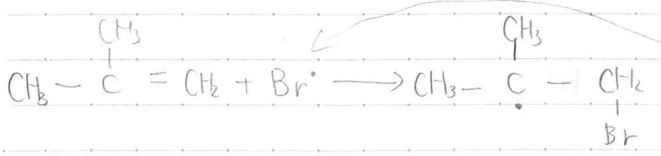
電子供与性



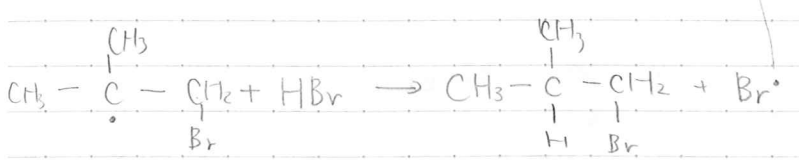
4) ラジカル付加 (求電子付加ではない)



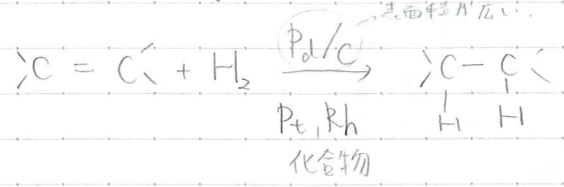
ラジカル  
不対電子  
(不安定)



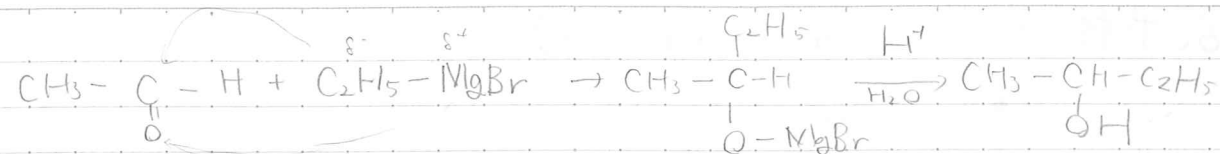
chain reaction



5) 水素添加 (求電子付加ではない)

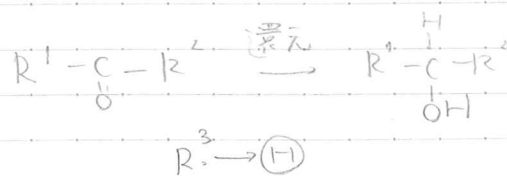
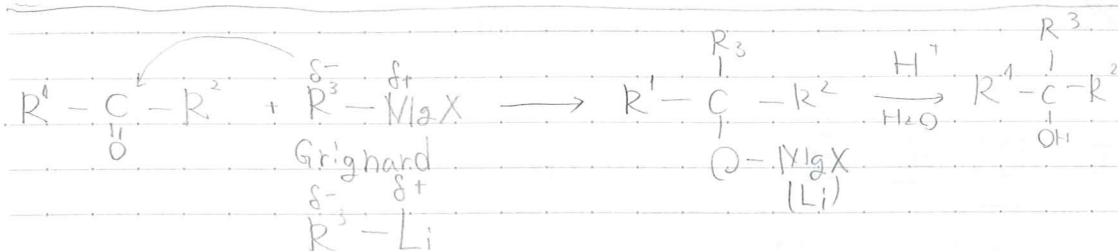
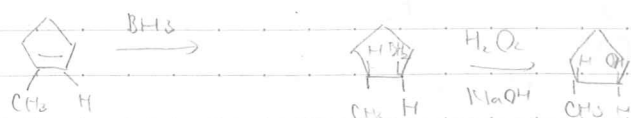
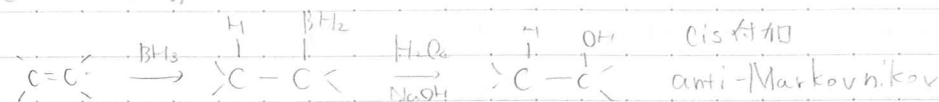


両面付加

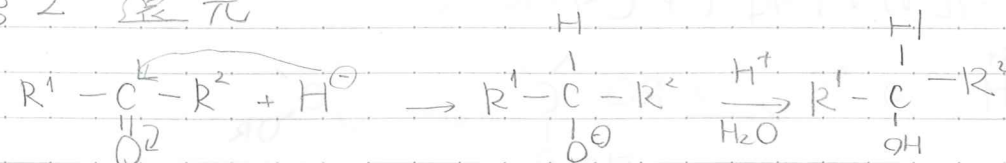


(1)

by hydroboration



## §2 還元



還元剤

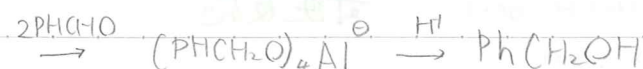
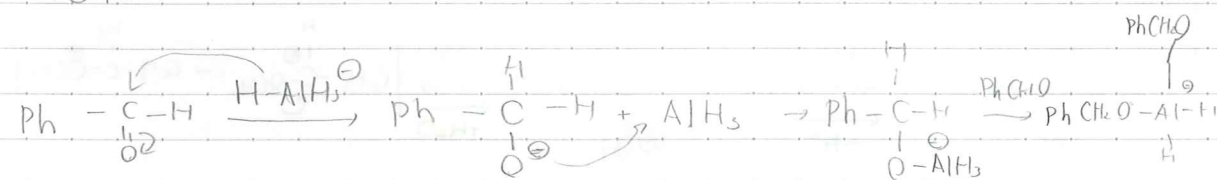
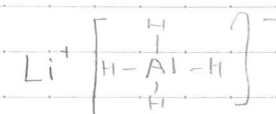
NaBH<sub>4</sub>

水素化ホウ素ナトリウム

LiAlH<sub>4</sub>

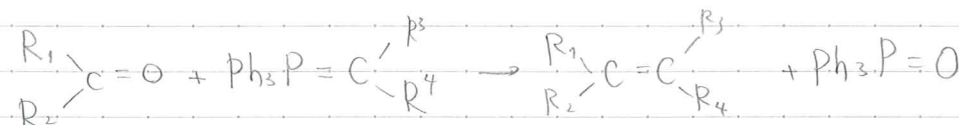
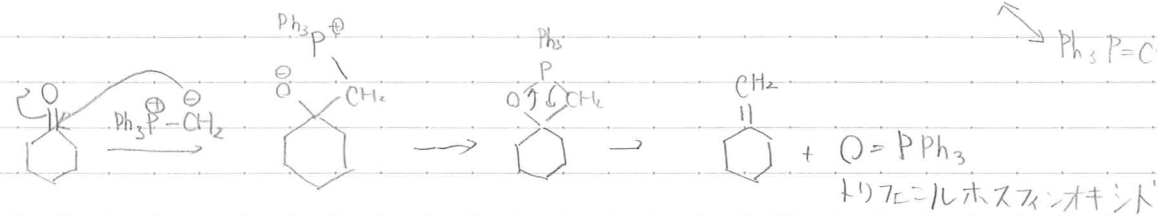
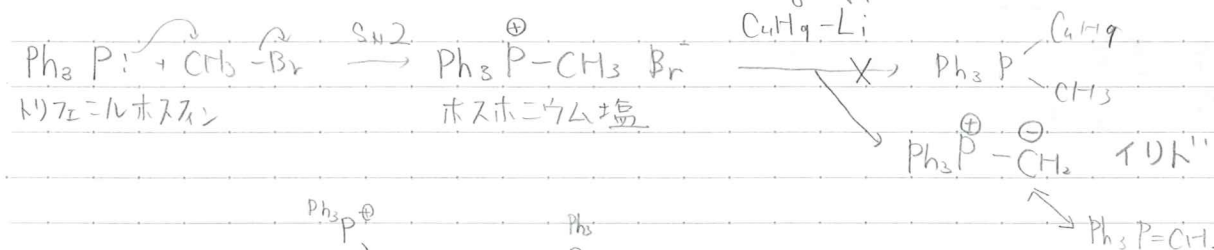
水素化リチウムアルミニウム

ether (エーテル)



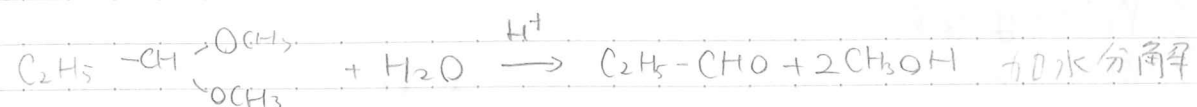
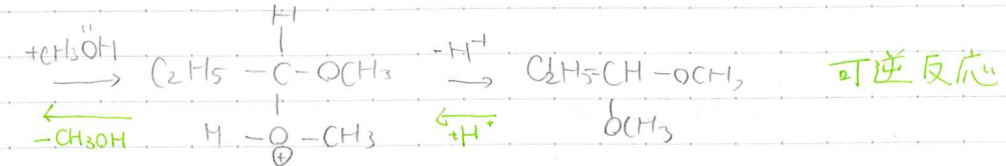
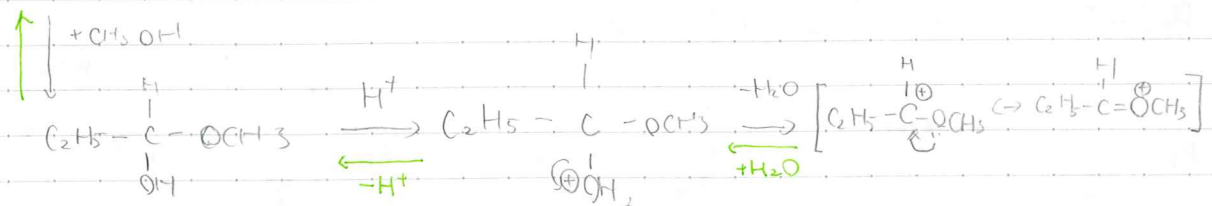
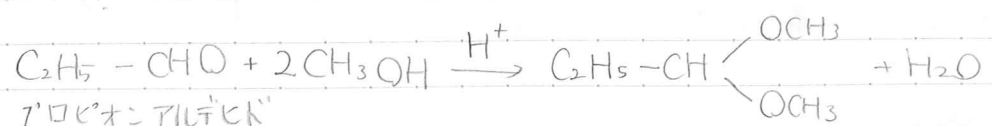
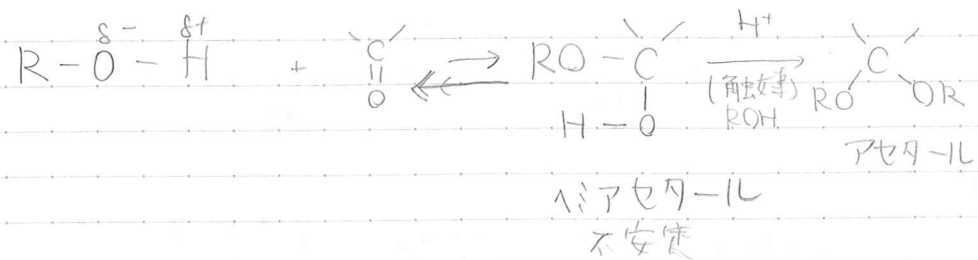
## §3 Wittig 反応

5ヶ所のリン



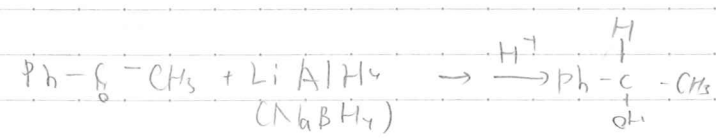
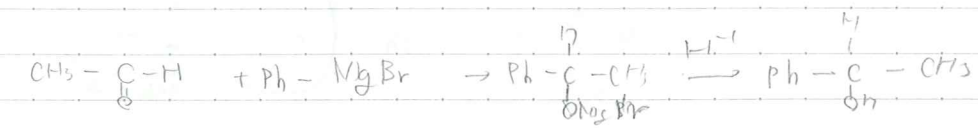
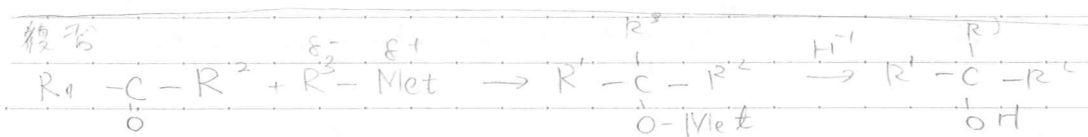
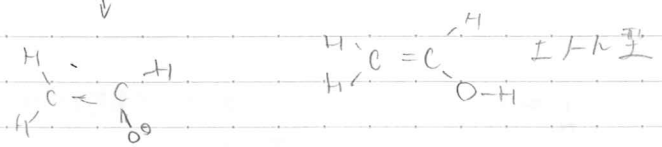
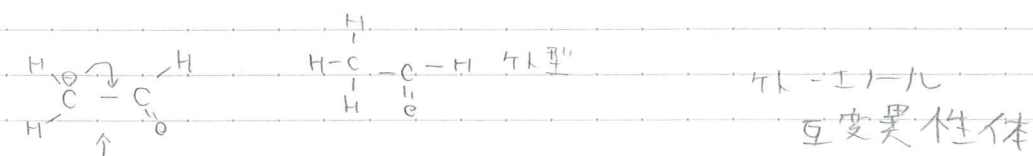
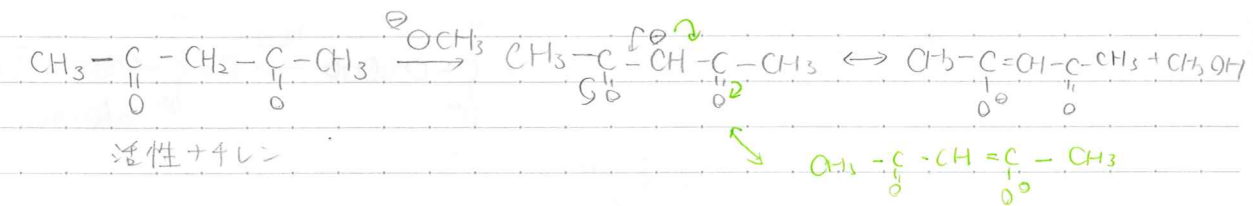
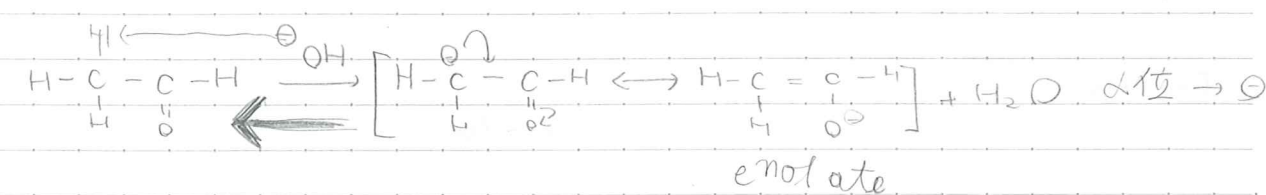
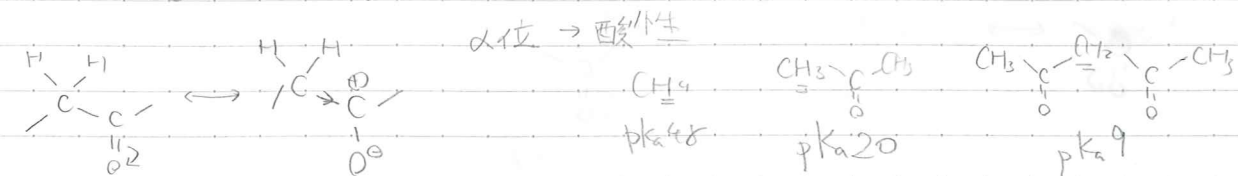


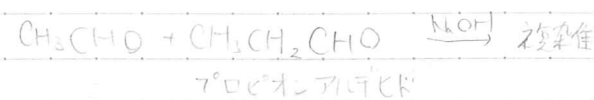
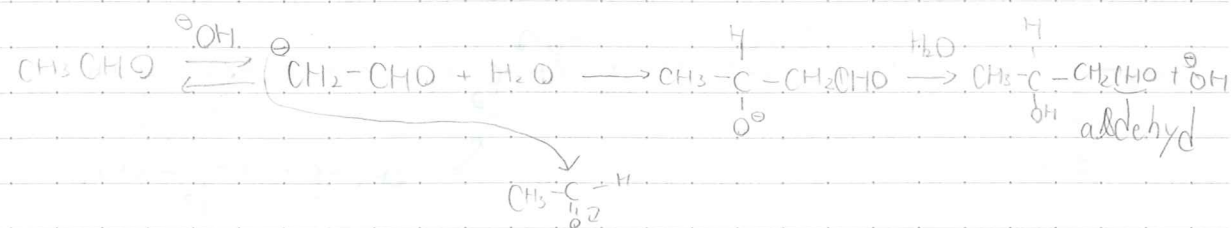
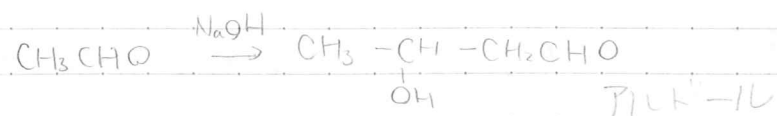
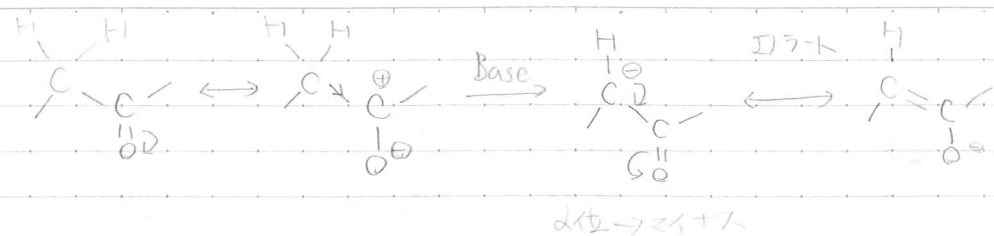
### §4 アルコールの付加 (アセタール化)



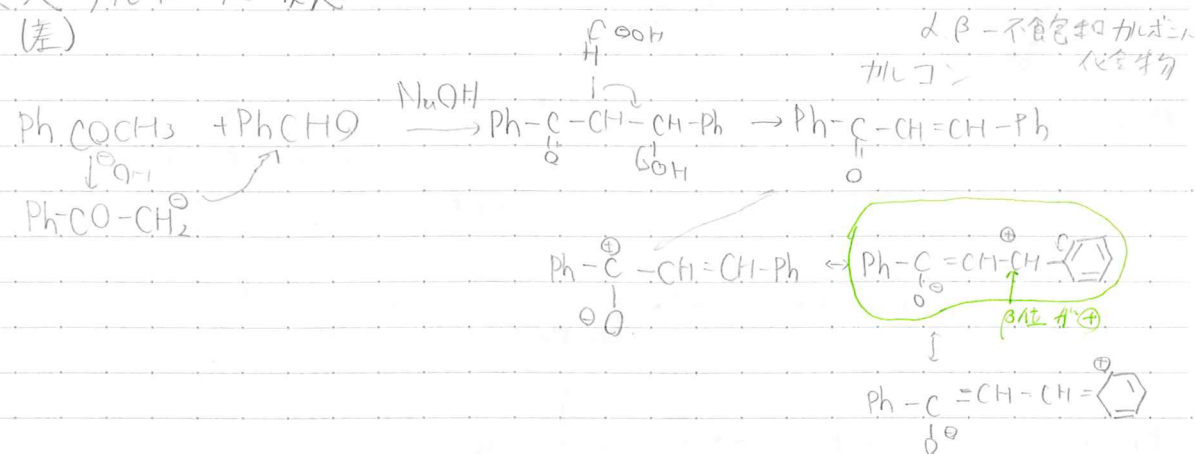
保護基  
Protecting Group

### §5 アルドール反応



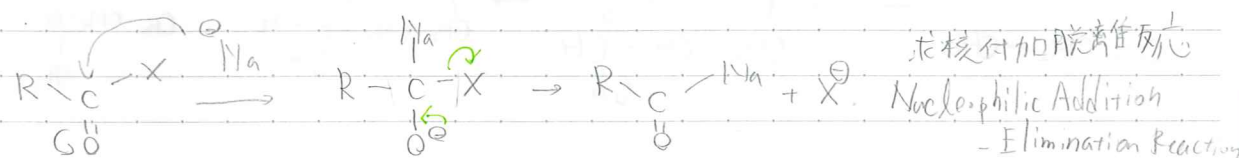
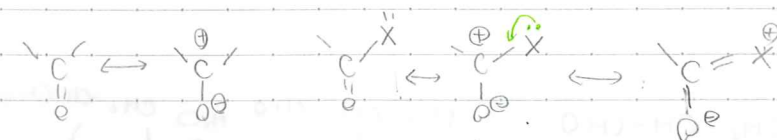
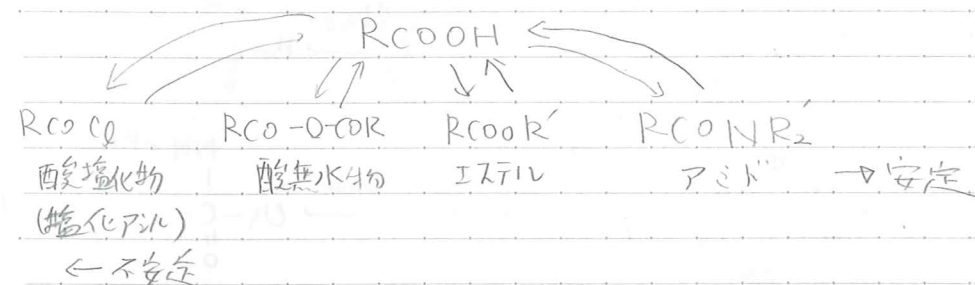


交叉アルドール反応  
(差)

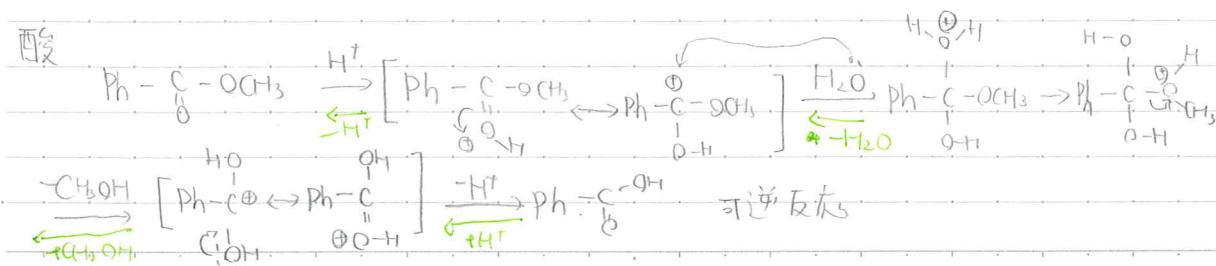
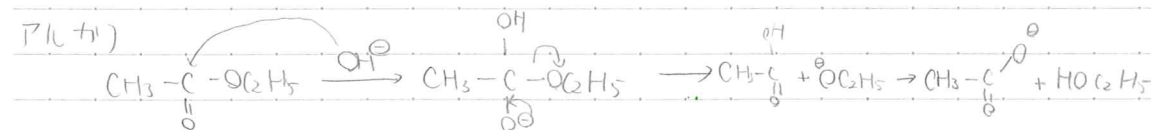
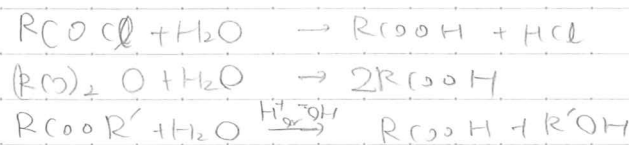


## 7. 求核付加-脱離反応

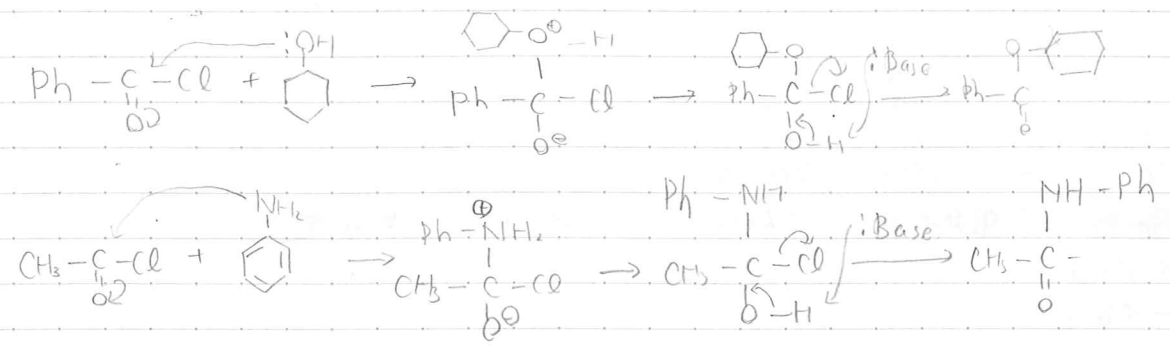
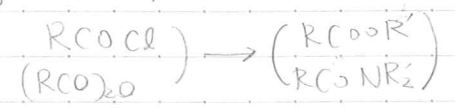
### §1 カルボン配誘導体



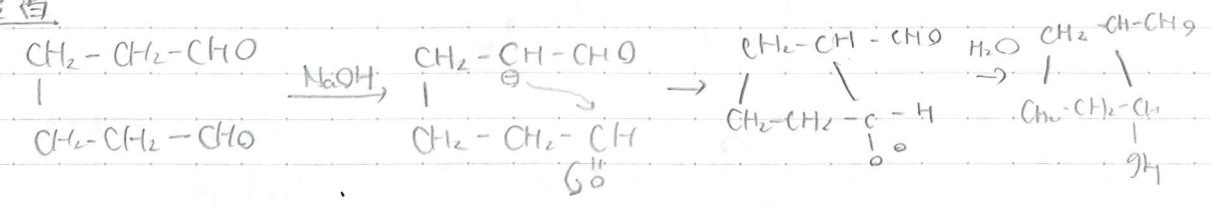
### §2 加水分解



### §3-5 アルコール・アミンとの反応

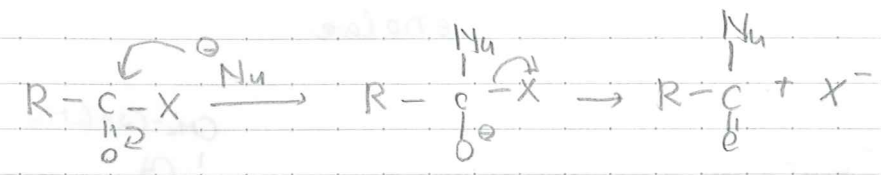
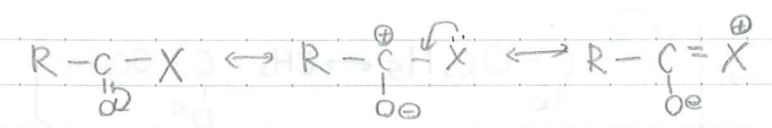


### 復習

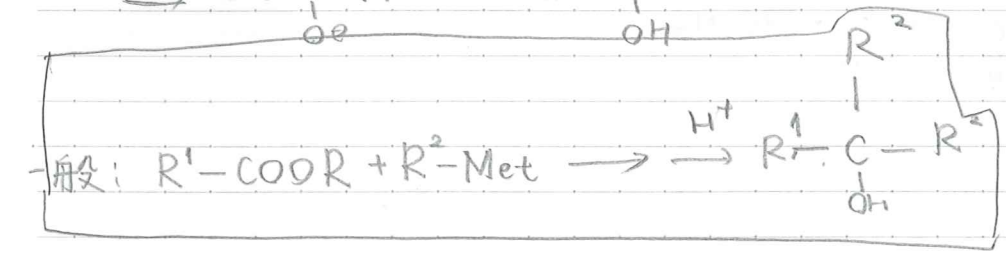
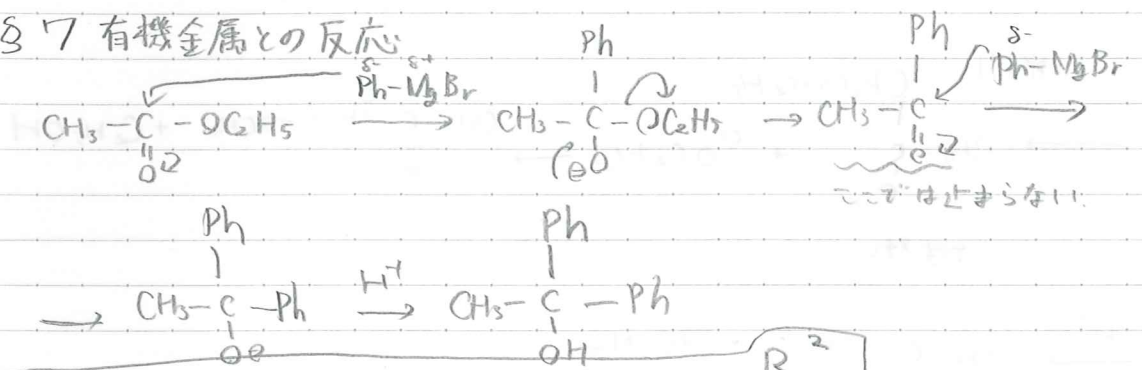


### 反応化学

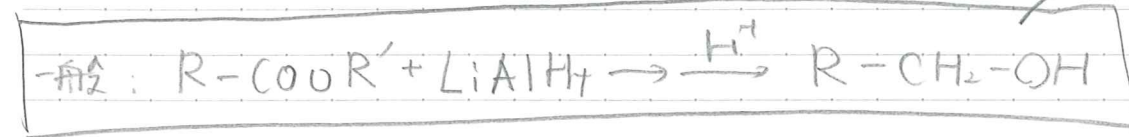
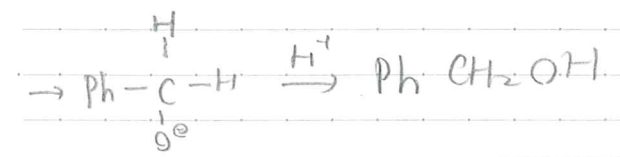
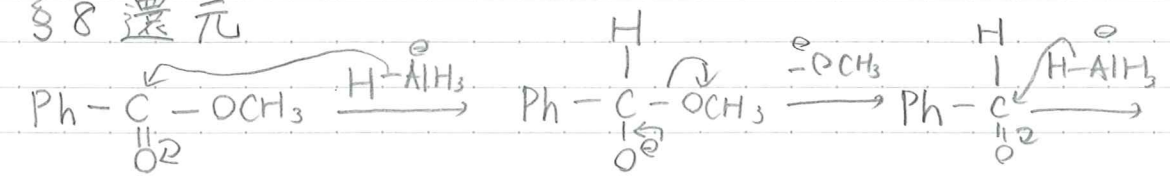
#### 7. 求核付加-脱離



#### §7 有機金属との反応



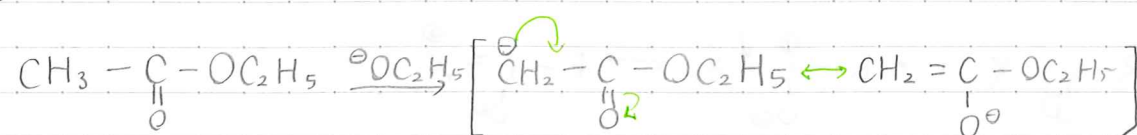
#### §8 還元



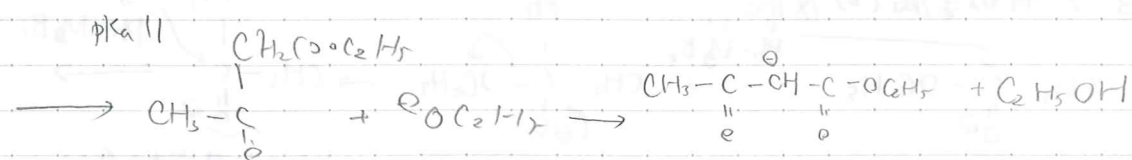
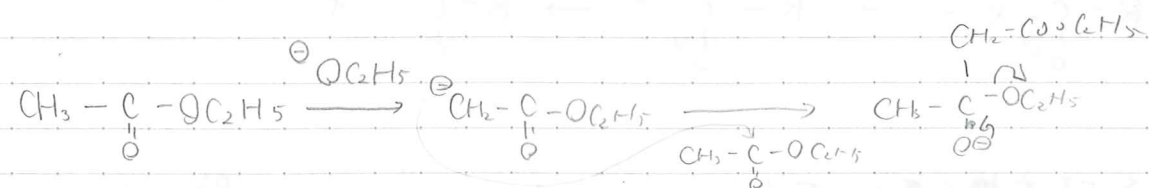
~~NaBH<sub>4</sub> / Zr / U~~



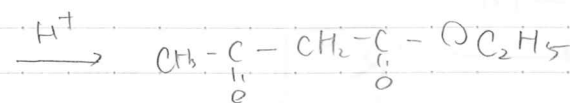
# §6 Claisen 縮合



enolate



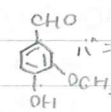
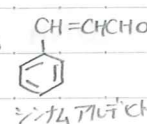
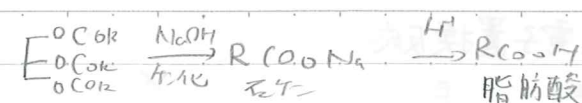
活性X+レ-



## 反応化学

### 10 芳香族性

(脂肪族  
芳香族)

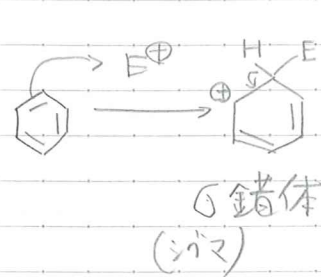


芳香環をもつ

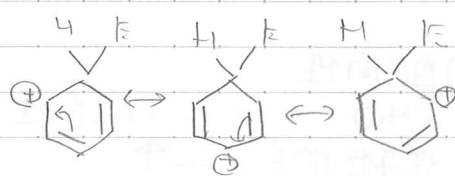


ピリジン

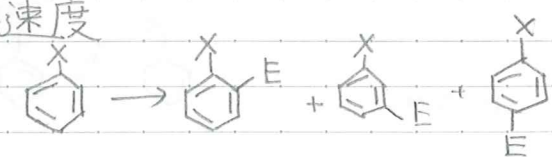
### 11. 芳香族求電子置換反応



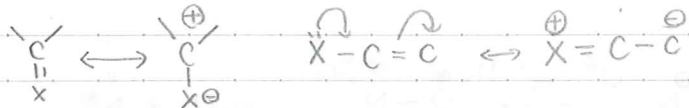
σ錯体 (シマ)



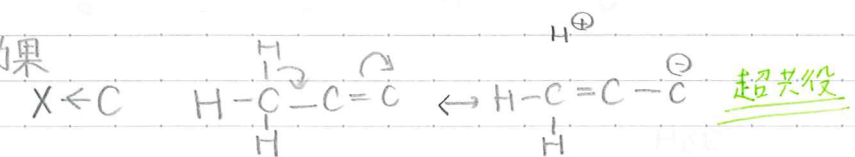
### 1) 反応速度



共鳴効果

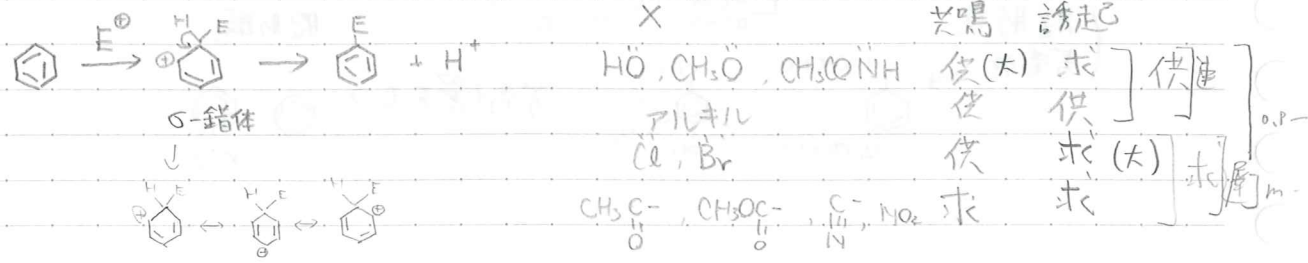


誘起効果



HO-	CH <sub>3</sub> O-	CH <sub>3</sub> CONH-	共鳴 供与(大)	誘起 求引	供与(大)
CH <sub>3</sub> (π+π)	Cl-	Br-	供与	求引(大)	求引(大)
CH <sub>3</sub> -C(=O)-	CH <sub>3</sub> O-C(=O)-	C≡N-	求引	求引	求引(大)

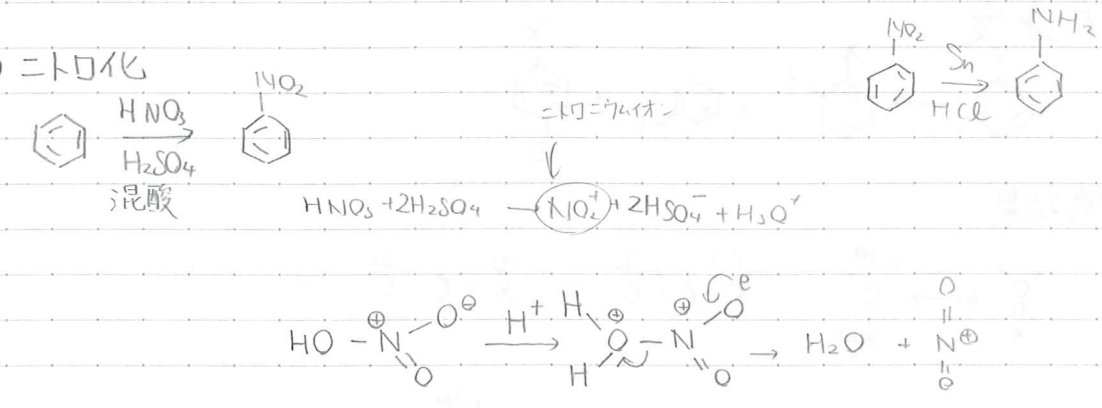
# 11. 芳香族求電子置換反応



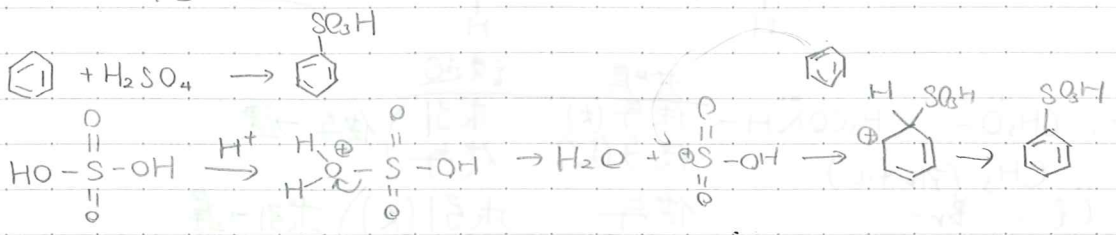
## 2) 配向性

$CH_3O$  オルト・パラ配向性  
 供与性(共鳴)  $\rightarrow$   
  
 $CH_3-C(=O)-$  対位配向性  
 求引性(共鳴)  $\leftarrow$

## 3) ニトロ化

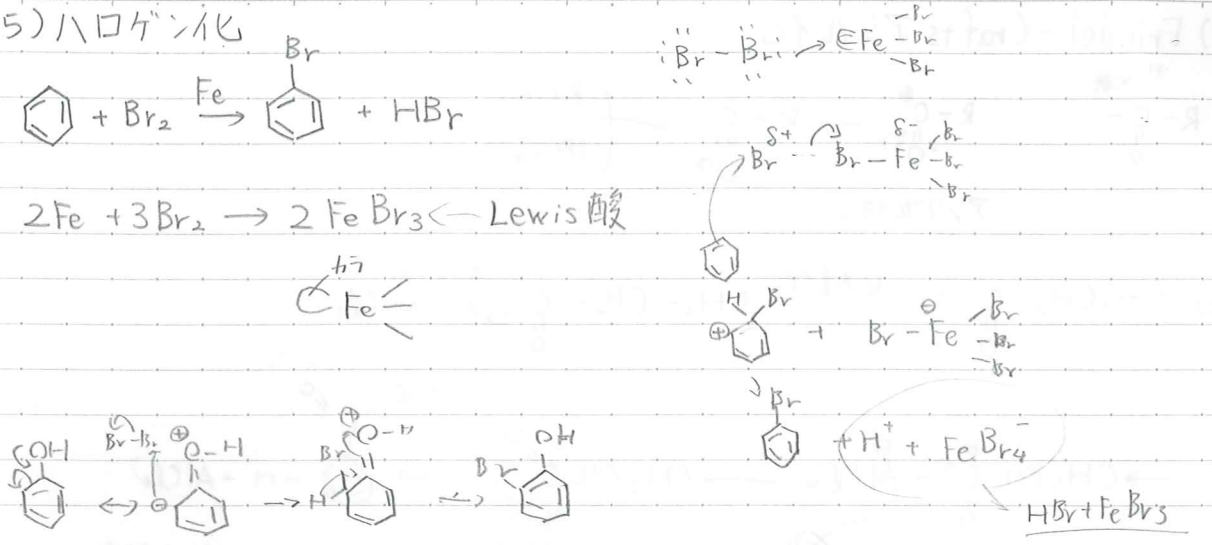


## 4) スルホン化

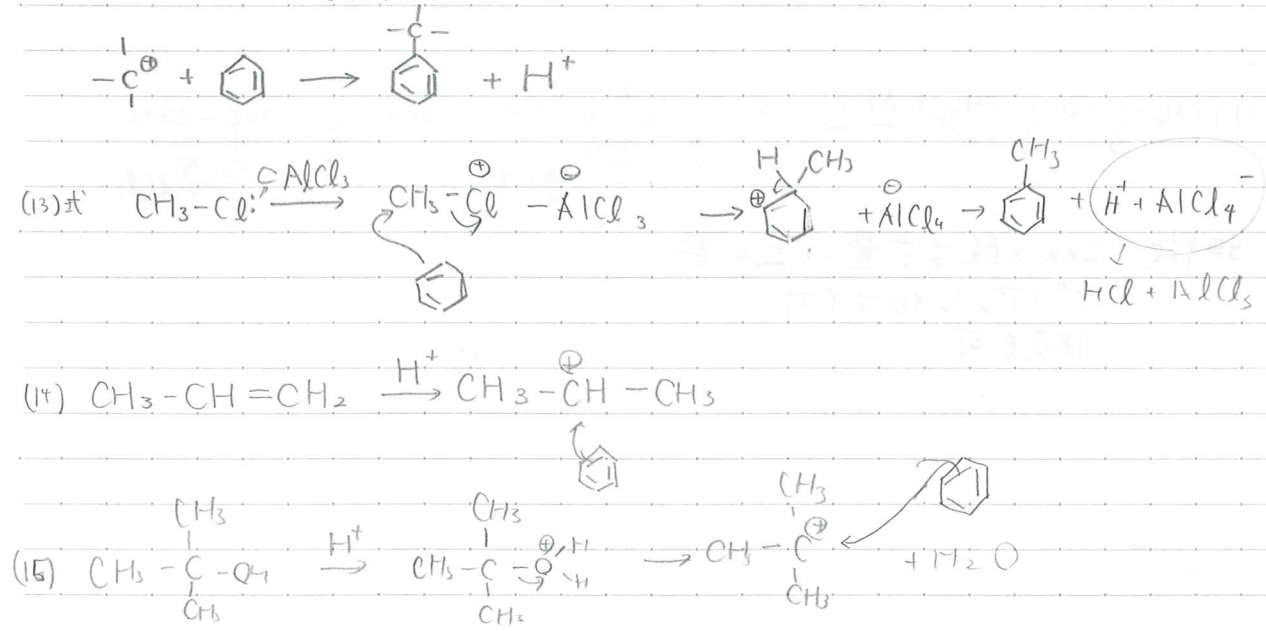


# 反応化学

## 5) ハロゲン化

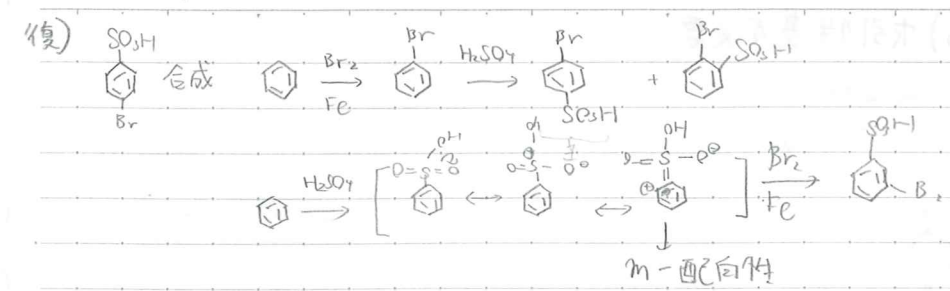


## 6) Friedel-Crafts アルキル化

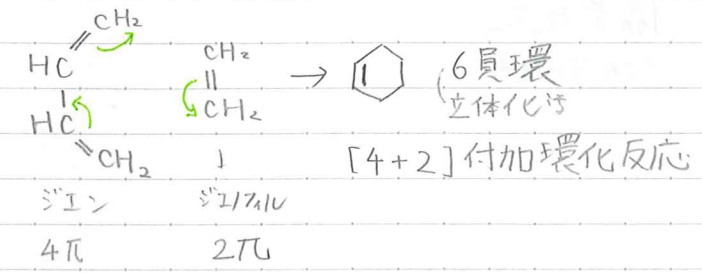


特徴・Lewis 酸は少量で O.K  
 ・ポリアルキル化(欠点)  
 ・級困難

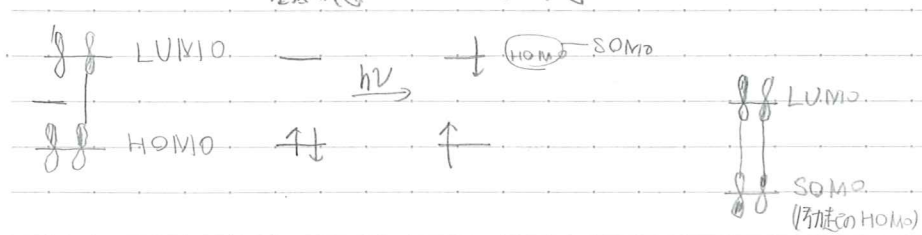
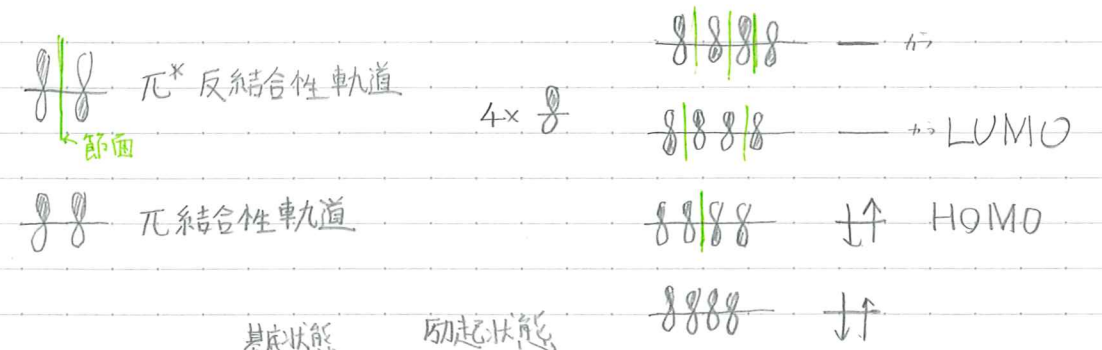
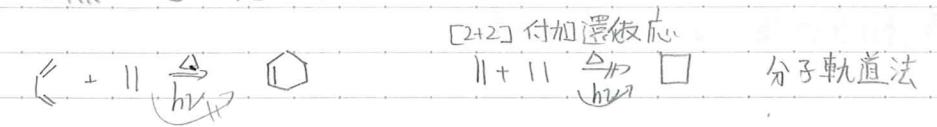
# 反応化学



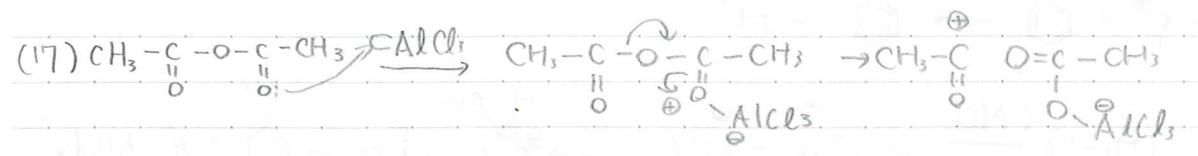
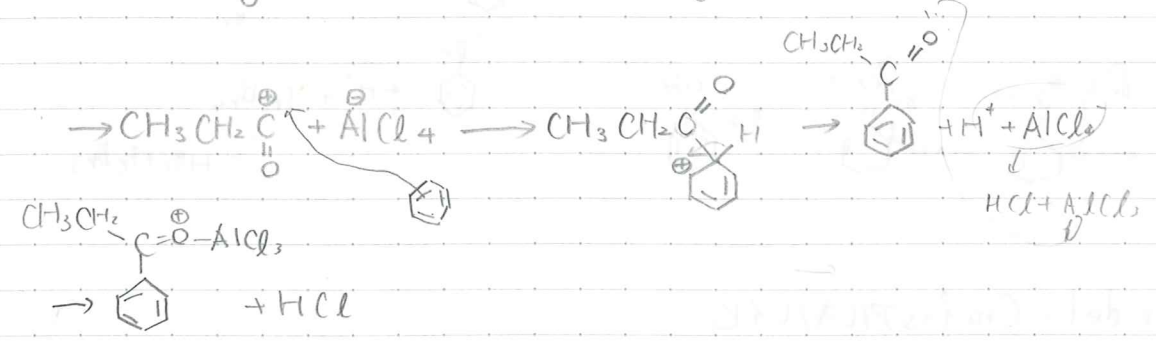
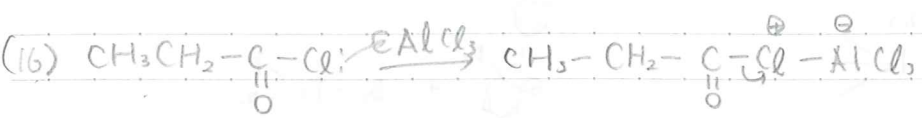
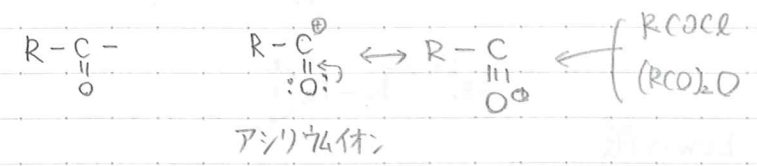
## Diels-Alder 反応 (9. 共役化合物の化学) 分子軌道法



Diels-Alder 反応の特徴  
 1) 熱... O    光... X



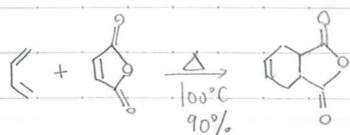
## 7) Friedel-Crafts アシル化



特徴: Lewis 酸は当量以上必要  
 ・ホロアシル化は不可  
 ・1級も可



2) シエノフィル (共鳴) 求引性基が必要



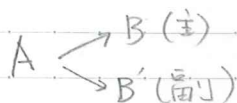
3) 立体特異的

(trans  $\rightarrow$  trans  
cis  $\rightarrow$  cis)



協奏反応  
concerted

4) 立体選択的 (endo 則)



Print No.15 (4)

2 次的軌道相互作用により endo の方が速