

## CH-335 / VII - C-C - Disconnections - Two functional groups

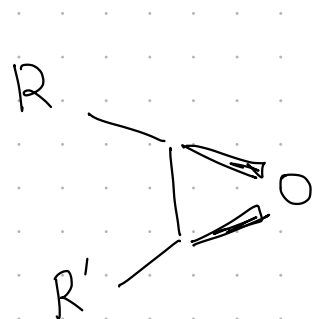
S. Gerber

Spring 2025



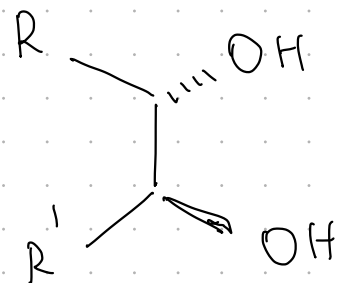
# I - Composés bifonctionnels - 1,2

## 1) fonctionnalisation des alcènes



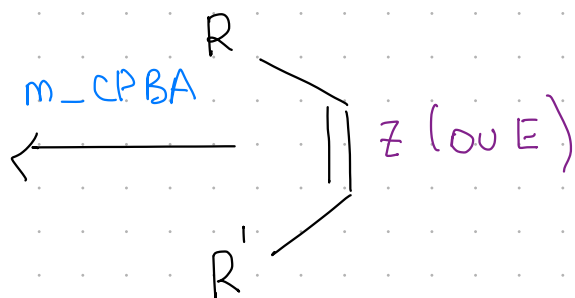
+ enant.

$\text{H}_2\text{O}, \text{H}^+ \text{cat.}$   
ou  $\text{NaOH}$

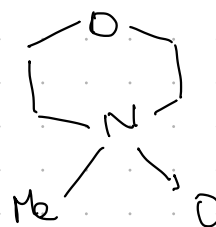


+ enant.

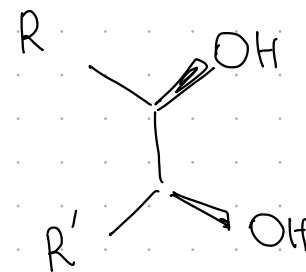
diol-1,2-anti



$\text{OsO}_4 \text{ cat.}$   
 $\text{NMO}$



diol-1,2-syn



+ enant.

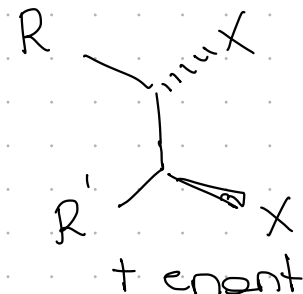
version asymétrique

$\text{OsO}_4 \text{ cat. } L^*$

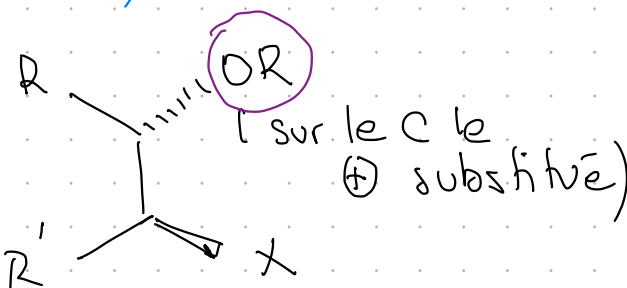
(AD-mix  $\alpha$  et  $\beta$ )

$\text{X}_2 (\text{Cl}_2, \text{Br}_2)$

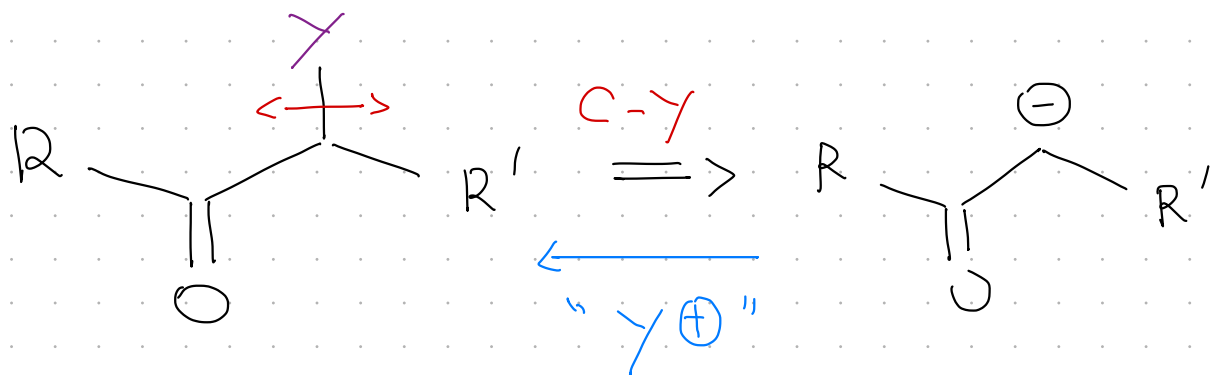
$\text{X}_2$   
 $\text{ROH}$   
( $\text{R} = \text{H}$   
alkyl)



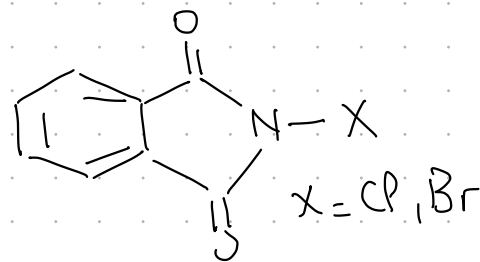
+ enant.



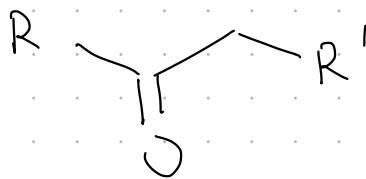
## 2) Fonctionnalisation en X d'un carbonyle



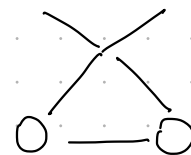
"Y<sup>⊕</sup>" : "Br<sup>⊕</sup>", "Cl<sup>⊕</sup>"



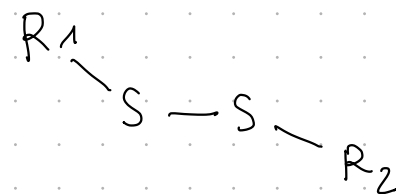
|| IGF  
v



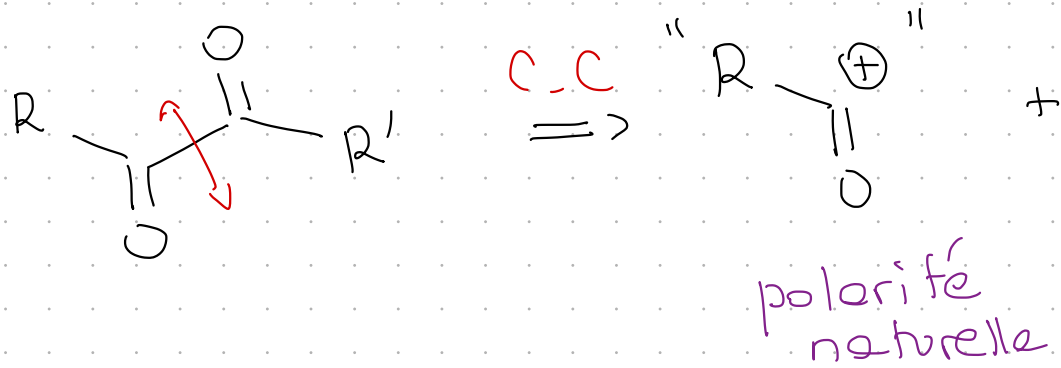
"OH<sup>⊕</sup>"



"SH<sup>⊕</sup>"



## 3) Equivalents d'anions acyles



inversion de polarité

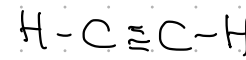
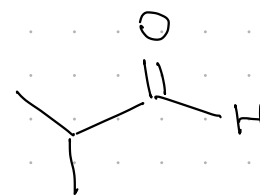
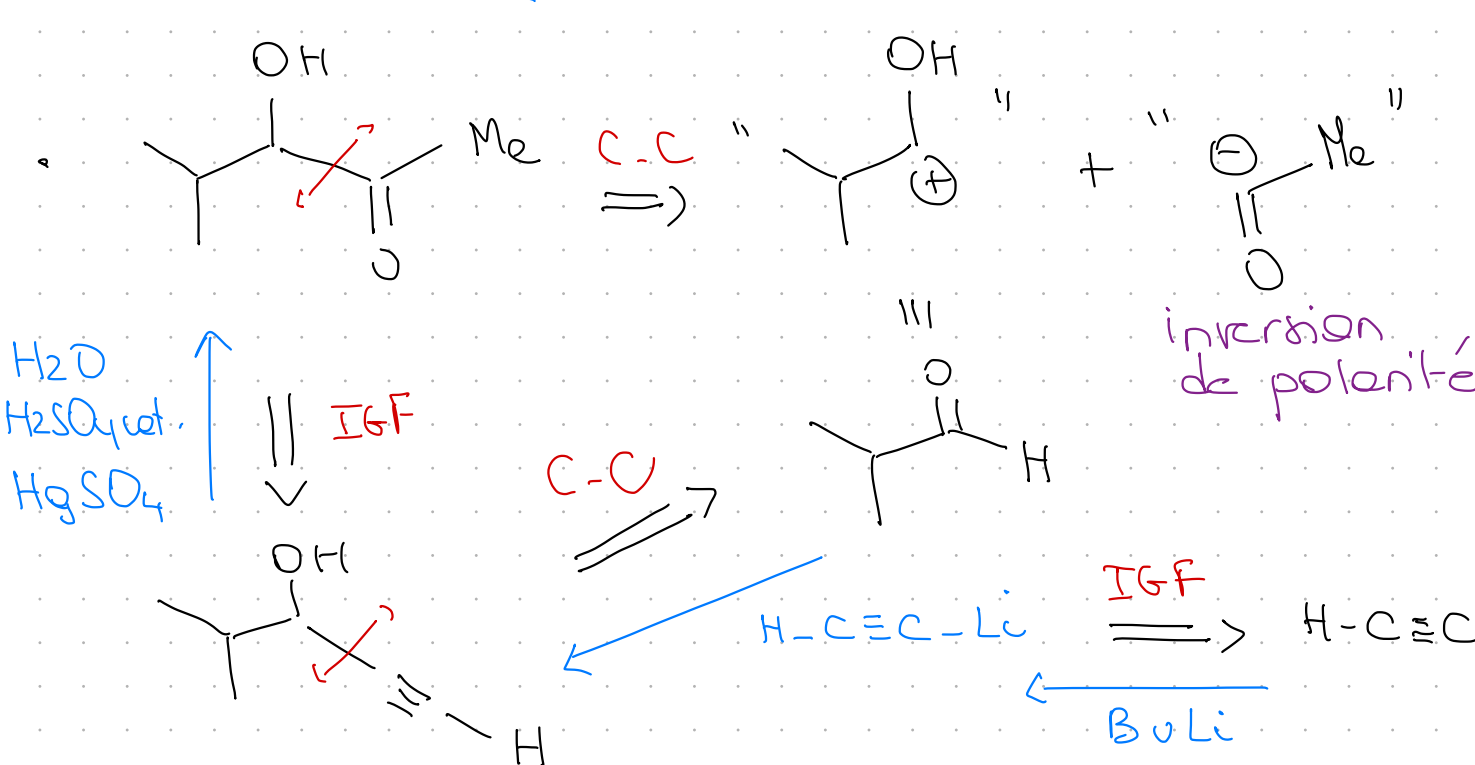
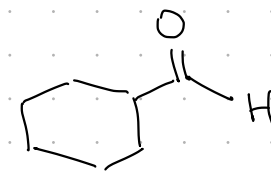
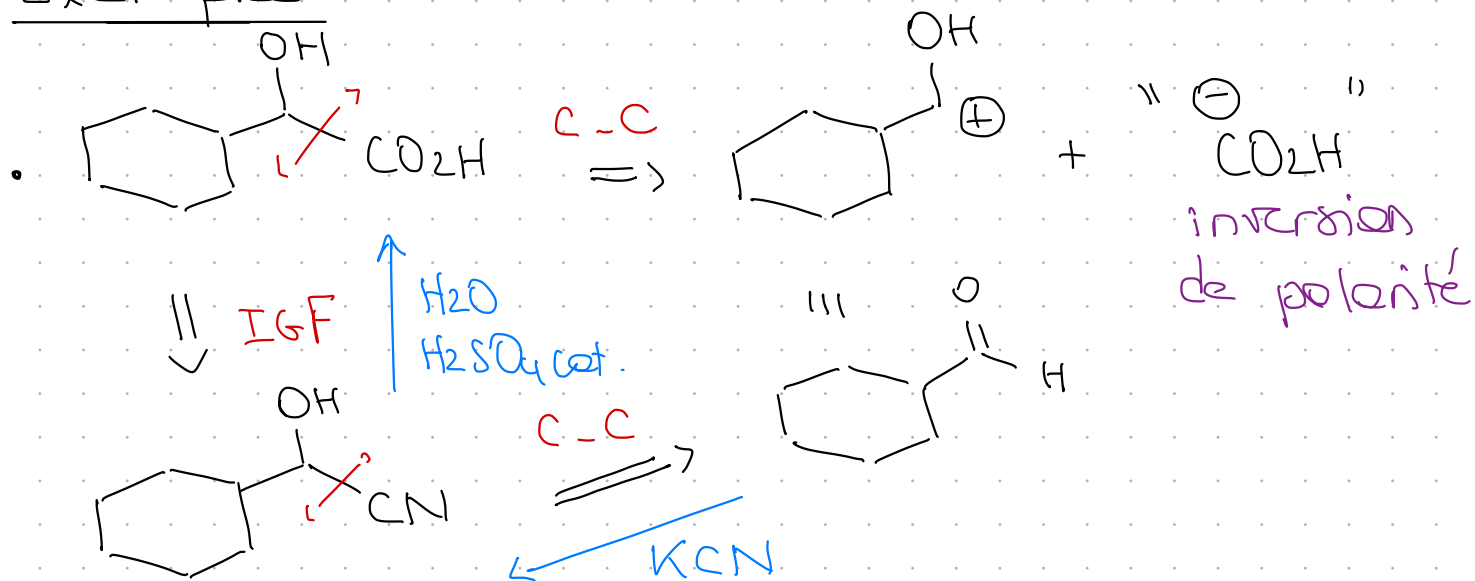
### équivalents

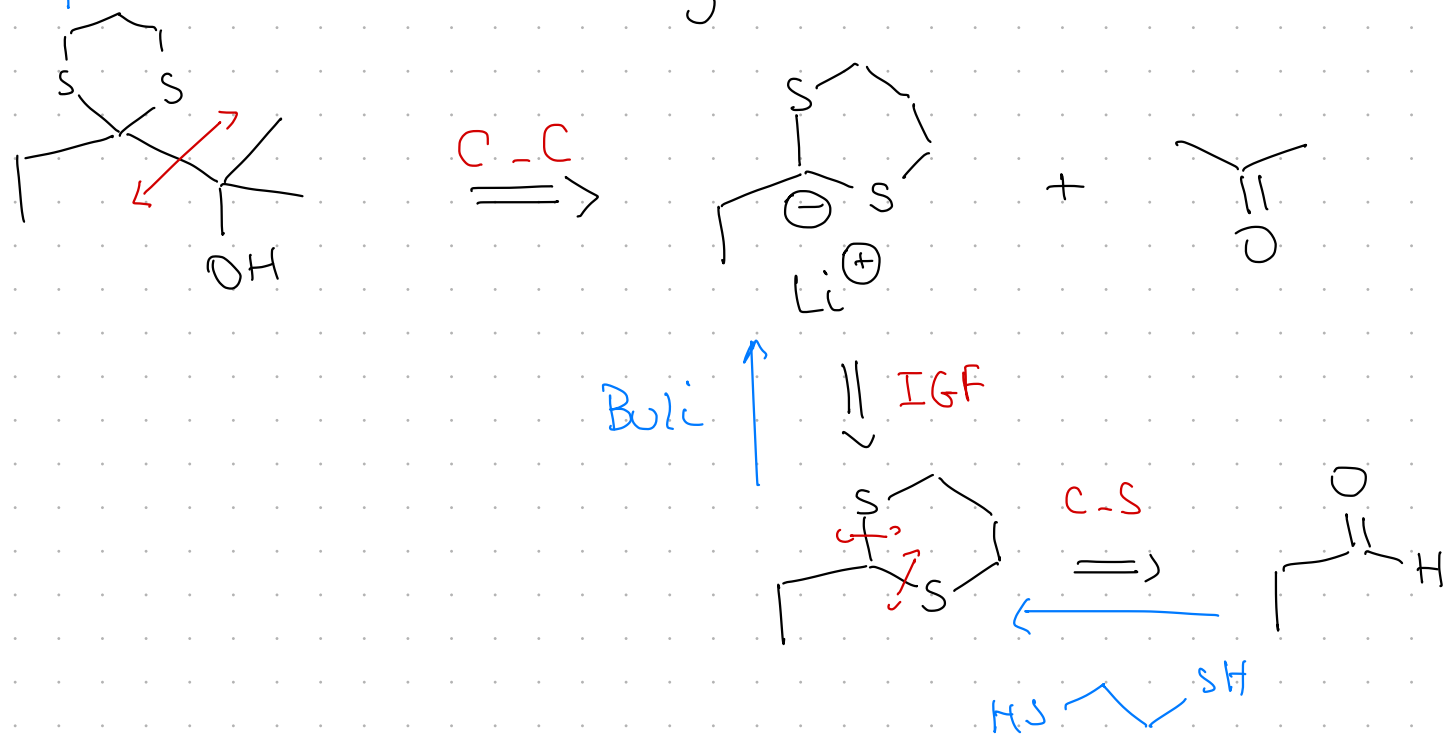
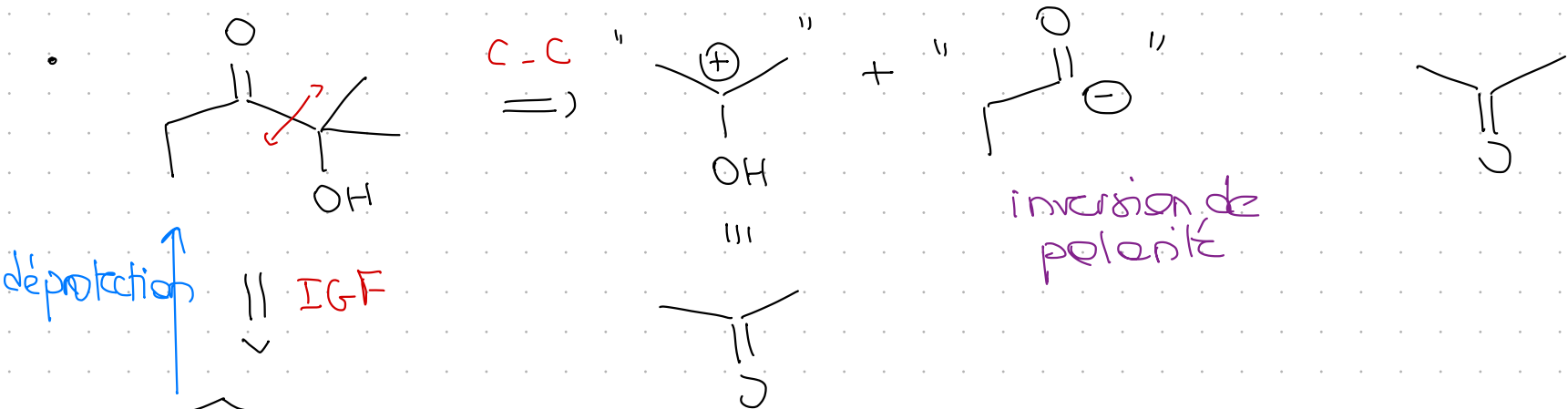
- anions dithiones
- cyanures
- anions acétylénures

# Exemples

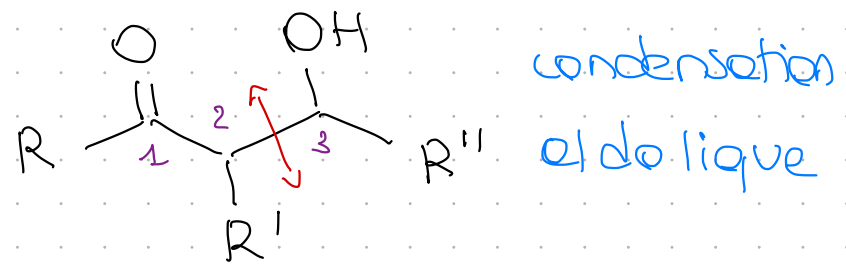
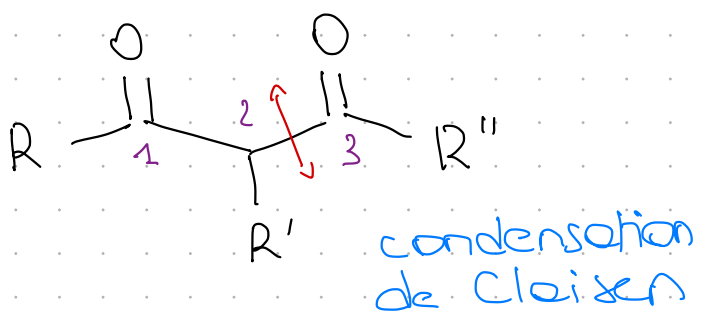
produit de départ

3



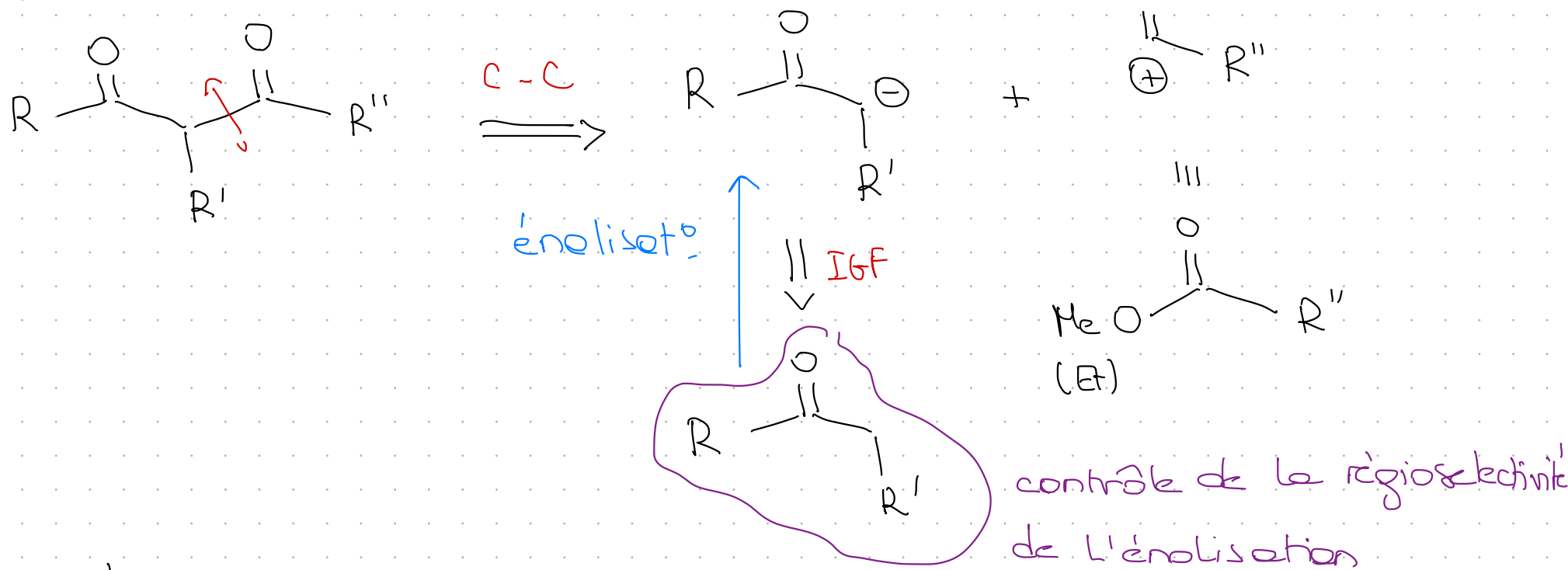


## II - Composés bifonctionnels - 1,3

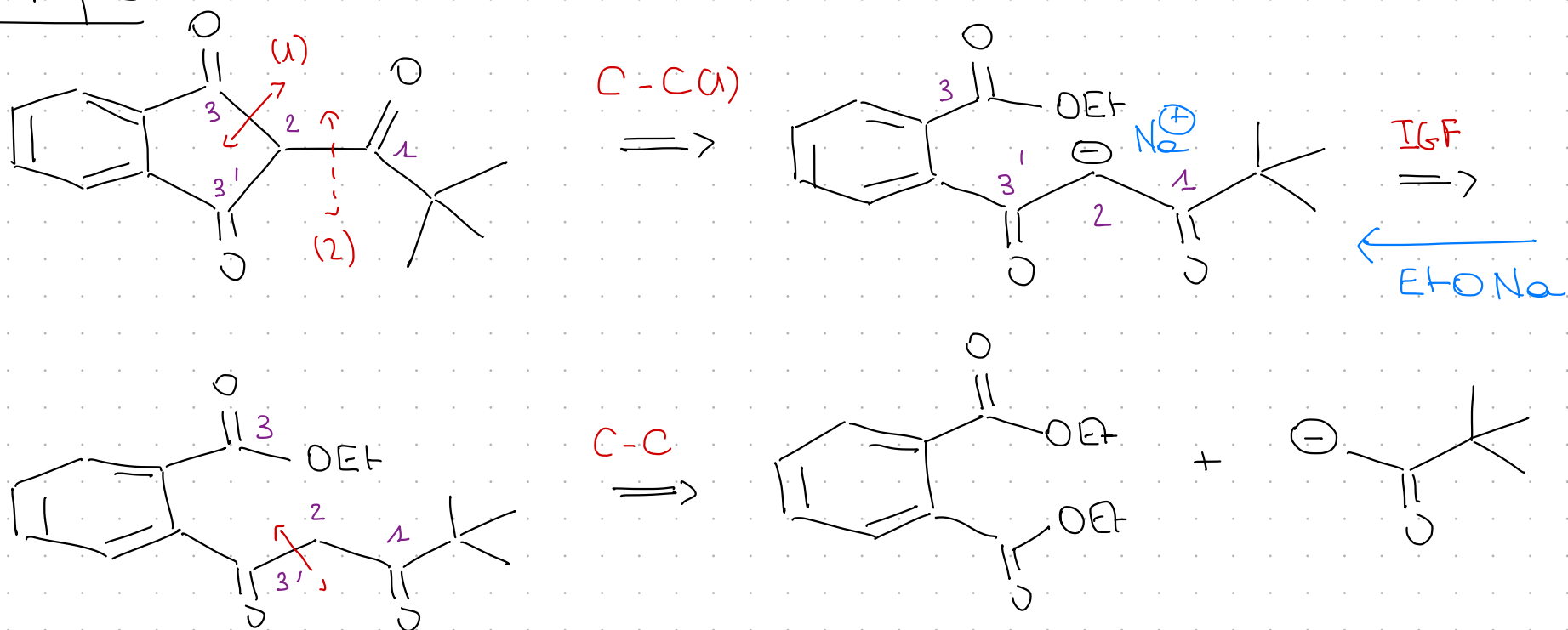


# 1) Condensation de Claisen

5

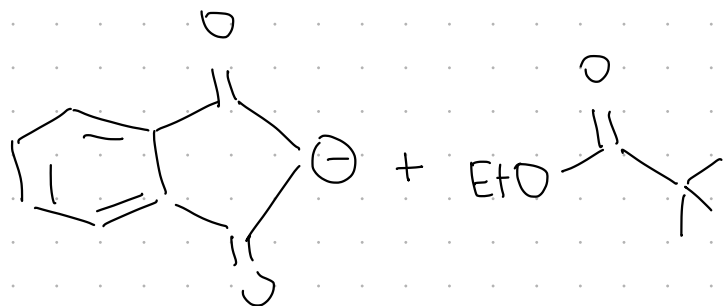


## Exemple



C-C (2)

=>

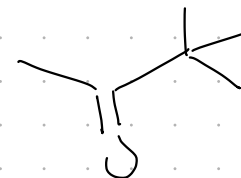
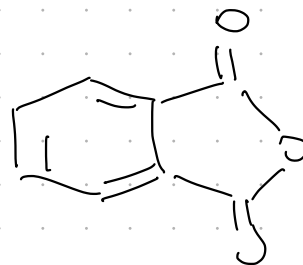


reconnection

LDA

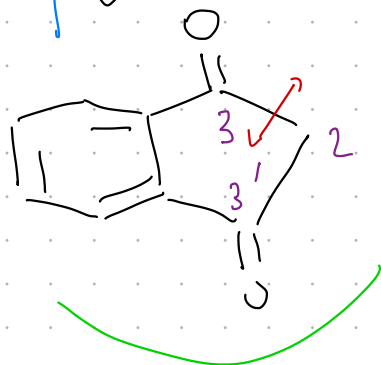
IGF

6



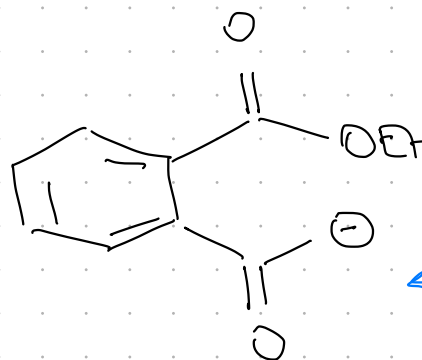
enolisation

IGF



C-C

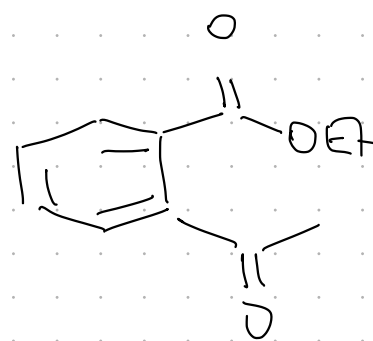
=>



IGF

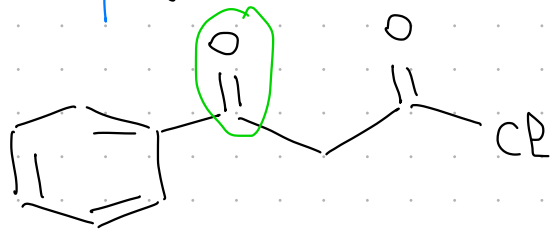
=>

LDA



$AlCl_3$

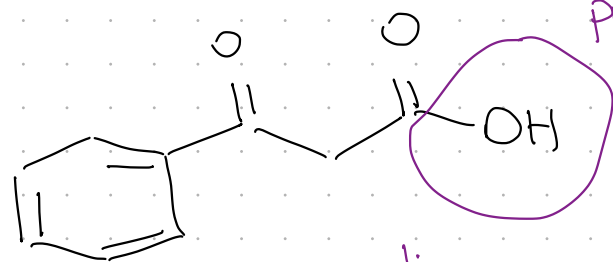
C-C



IGF

=>

$SOCl_2$

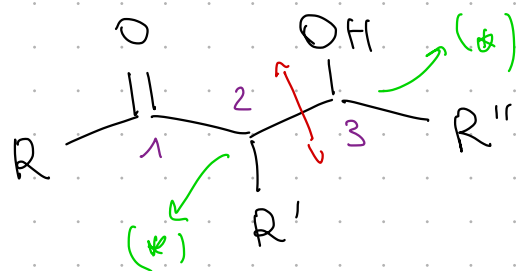


protection

disconnection

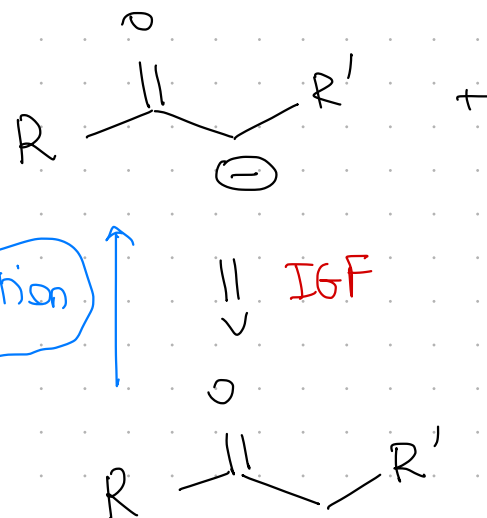
Friedel-Crafts

## 2) Condensation aldolique

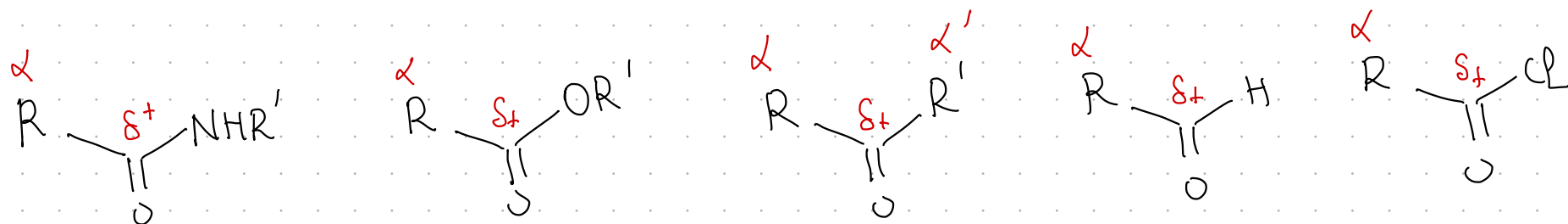


$C-C \Rightarrow$

enolisation



## Réactivité



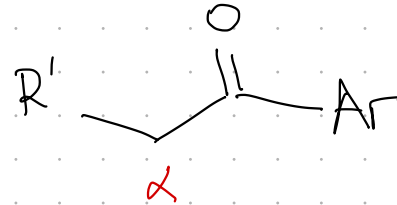
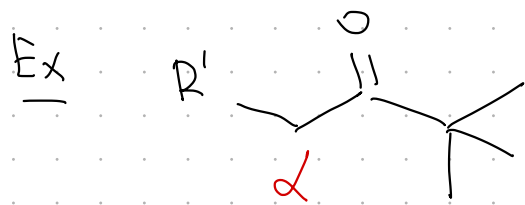
électrophilie  $\nearrow$

capacité à être  
énolisé  $\nearrow$

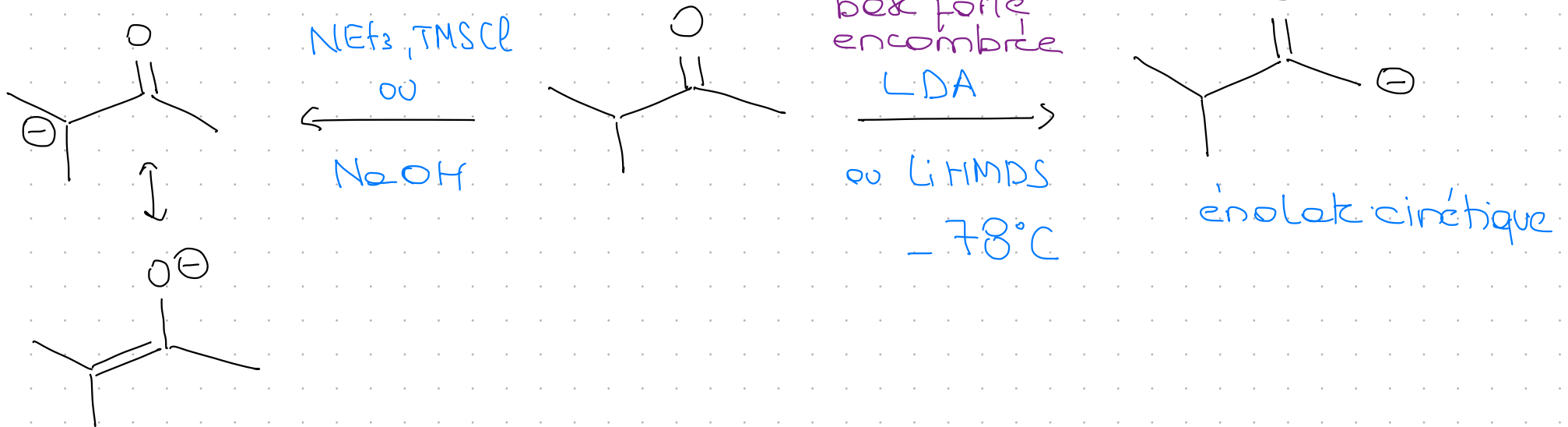
## Contrôle de l'énolisation

- Faire une disconnection qui conduit à un partenaire ayant une seule position énolisable

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• Facteurs stériques



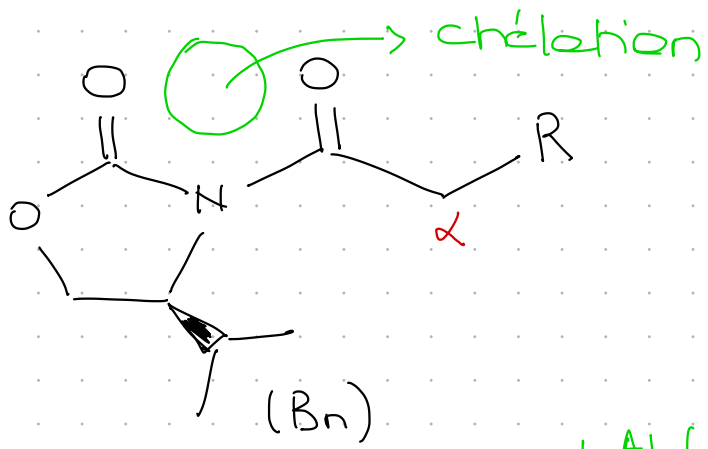
enolate thermodynamique

### 3) Aldolisation stéréosélective

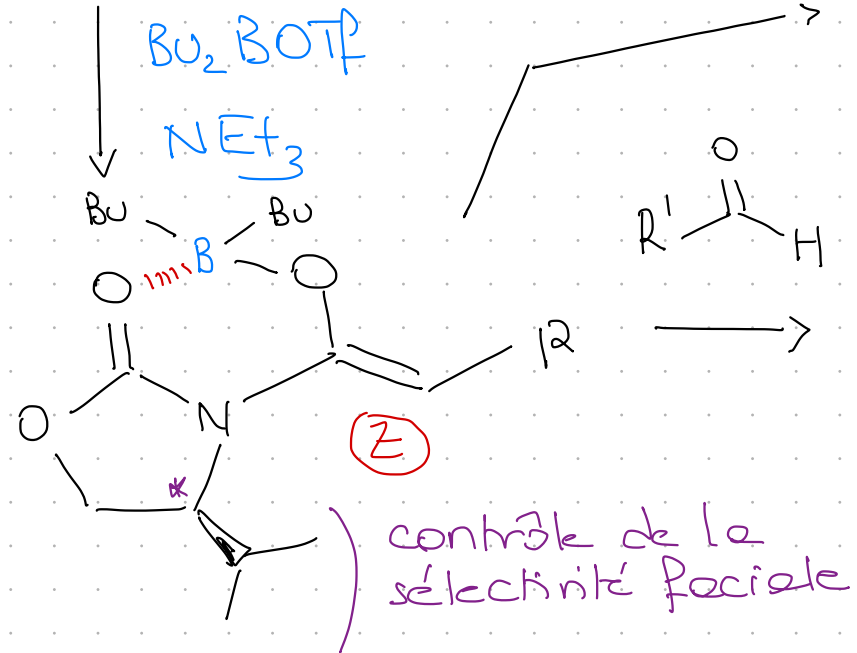
• Enolate chiral

# Enolates de bore

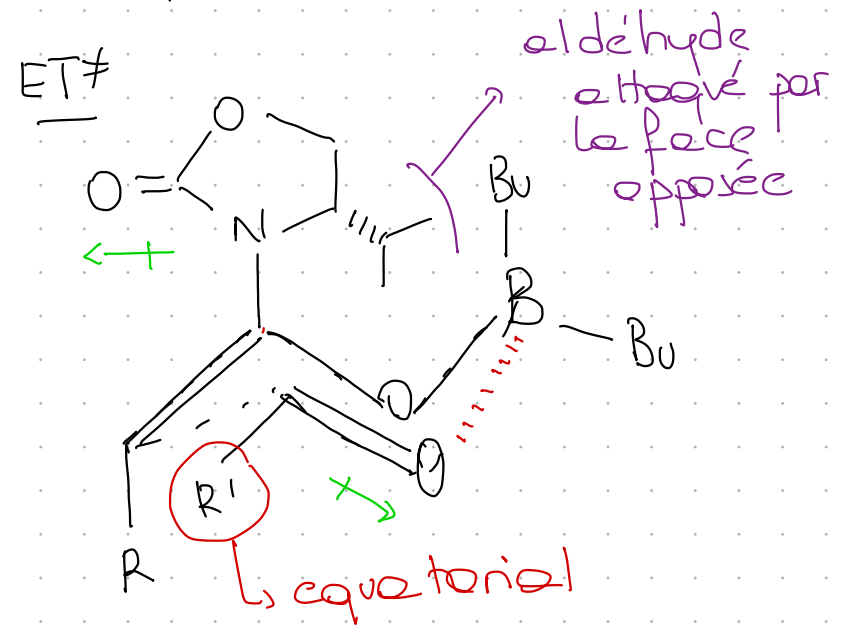
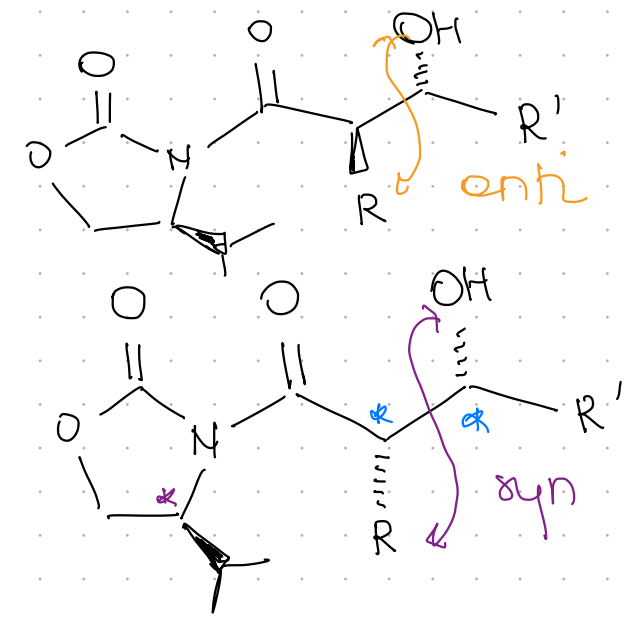
B : 3 liaisons covalentes  
+ 1 Liaison de coordination



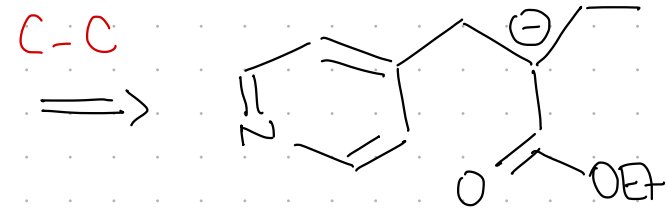
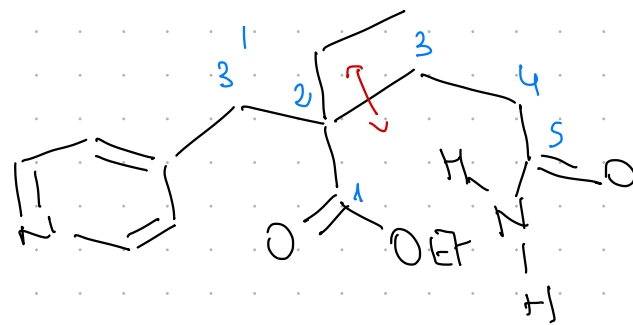
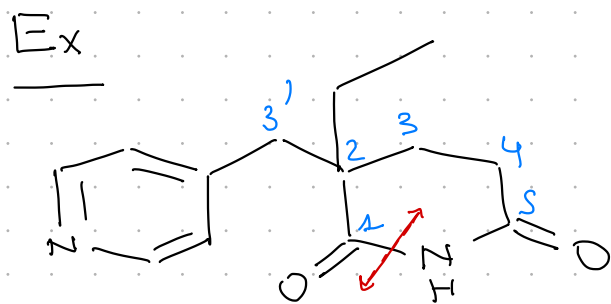
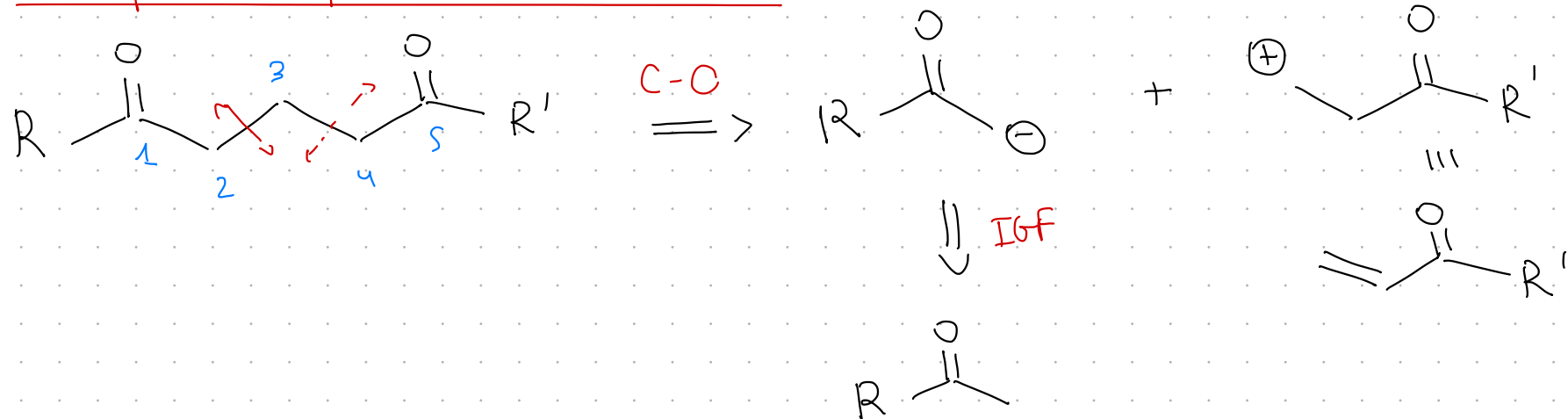
+ AL (Et<sub>2</sub> AlCl)



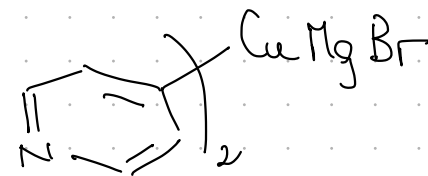
• minimisation des interactions entre dipôle



### III - Composés bi fonctionnels - 1,5

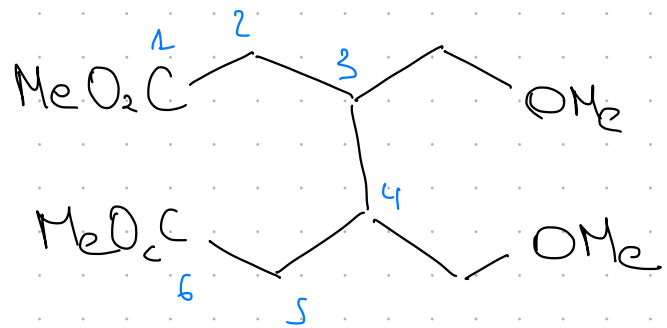


produit de départ

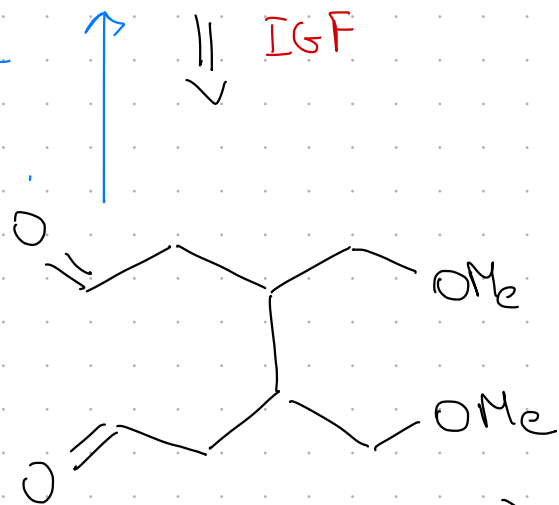




## Exemple

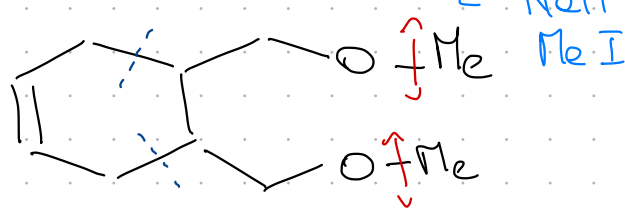


1.  $\text{NaCPO}_2$   
2.  $\text{MeOH}$   
 $\text{p-TSOH cat.}$

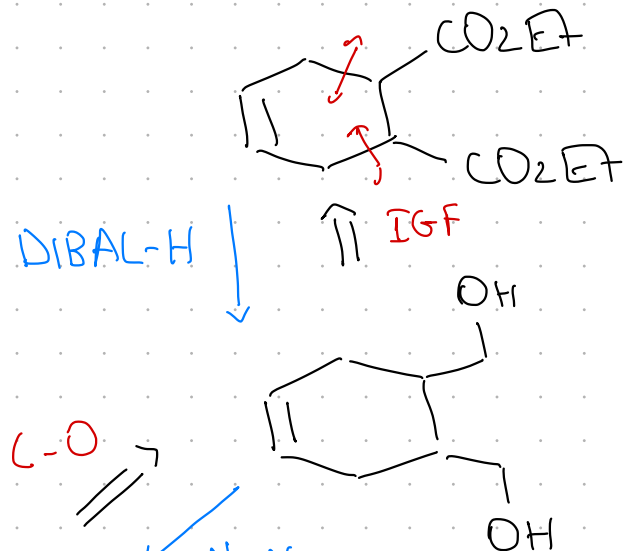
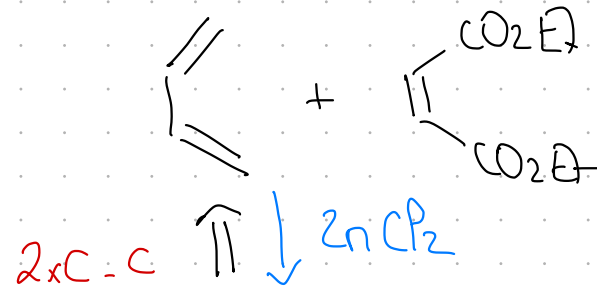


1.  $\text{O}_3, -78^\circ\text{C}$   
2.  $\text{Me}_2\text{S}$

reconnection



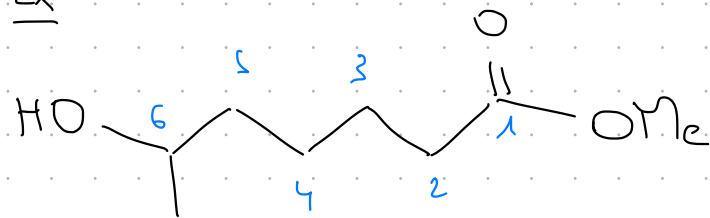
produit de  
de part



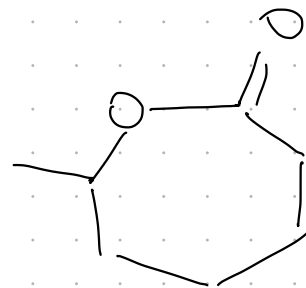
## 2) Compose's 6-hydroxycarbonyl

- reconnection : lactone à 7 chaînons
- obtenue par oxydation de Baeyer-Villiger

Ex

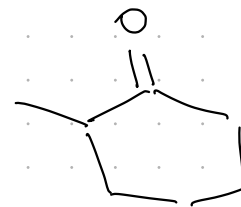
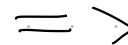


reconnection



MeOH  
p-TsOH cat.

IGF



m-CPBA

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