

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

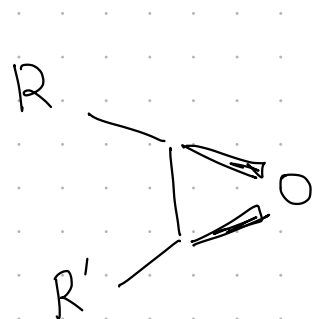
S. Gerber

Spring 2025



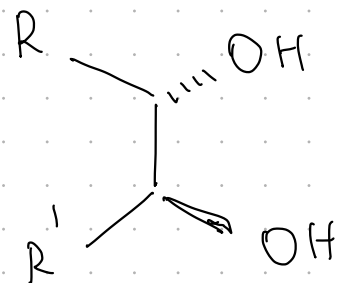
I - Composés bifonctionnels - 1,2

1) fonctionnalisation des alcènes



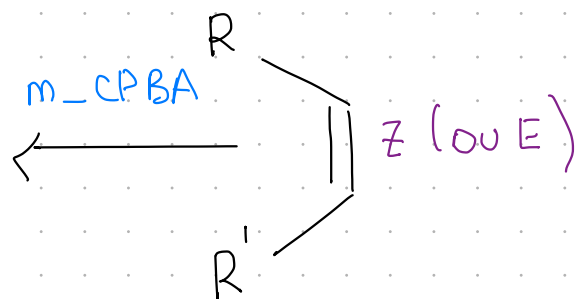
+ enant.

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

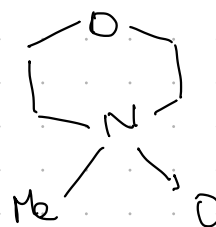


+ enant.

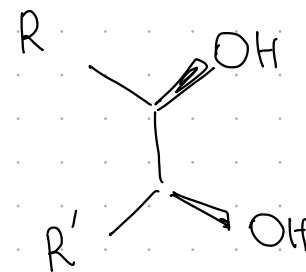
diol-1,2-anti



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



diol-1,2-syn



+ enant.

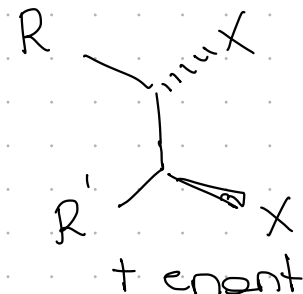
version asymétrique

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

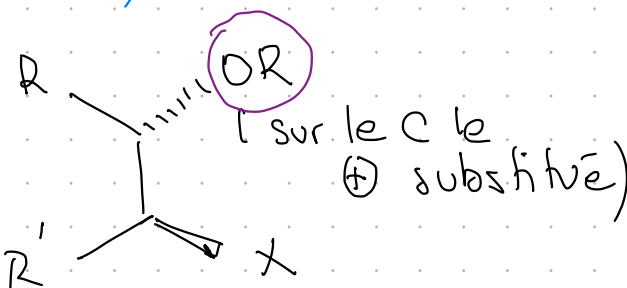
(AD-mix α et β)

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

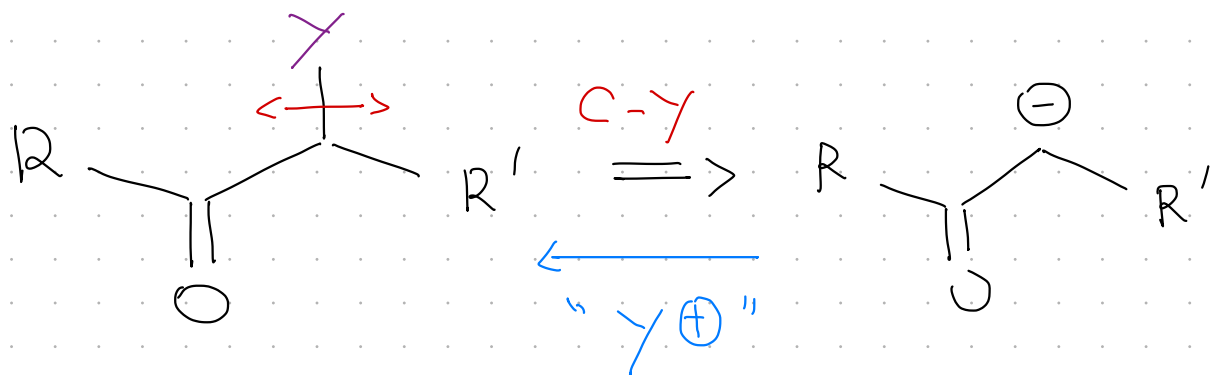
X_2
 ROH
($\text{R} = \text{H}$
alkyl)



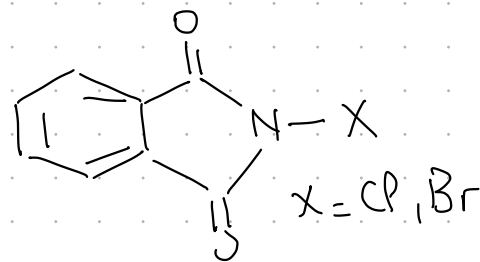
+ enant.



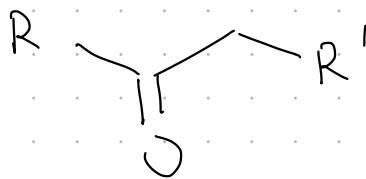
2) Fonctionnalisation en X d'un carbonyle



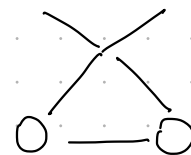
"Y[⊕]" : "Br[⊕]", "Cl[⊕]"



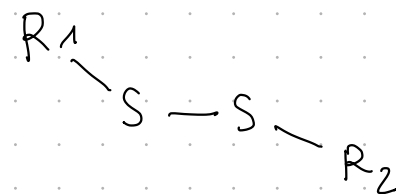
|| IGF



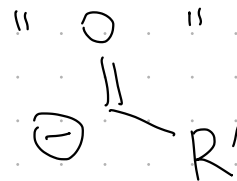
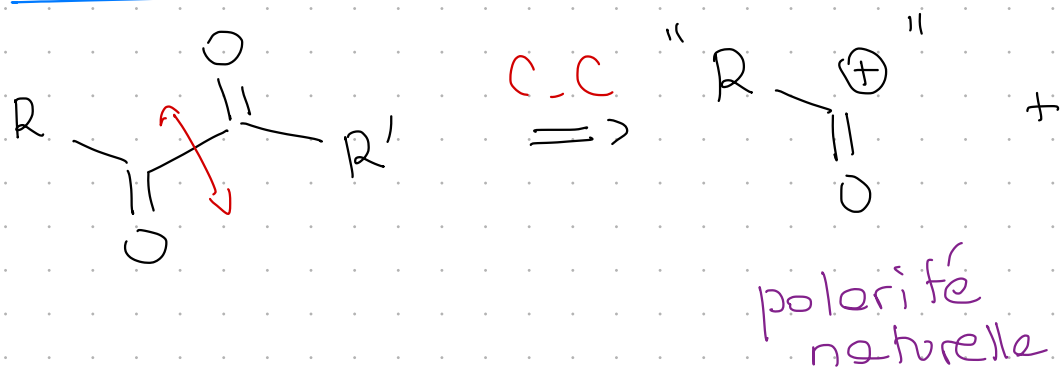
"OH[⊕]"



"SH[⊕]"



3) Equivalents d'anions acyles



inversion de polarité

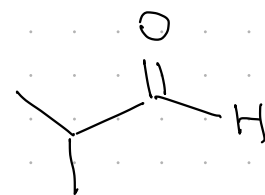
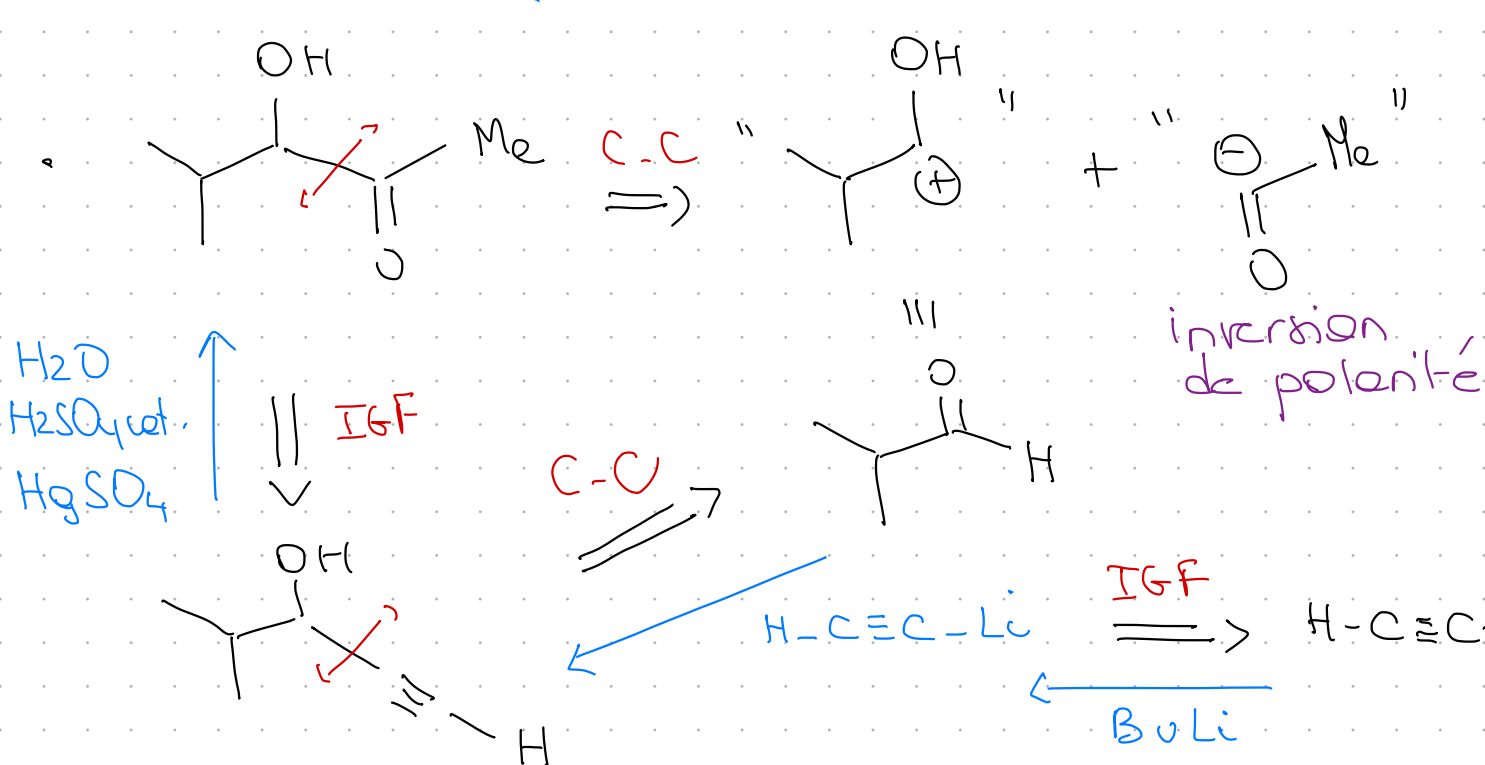
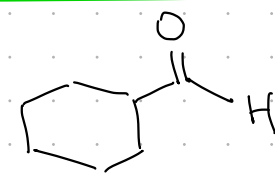
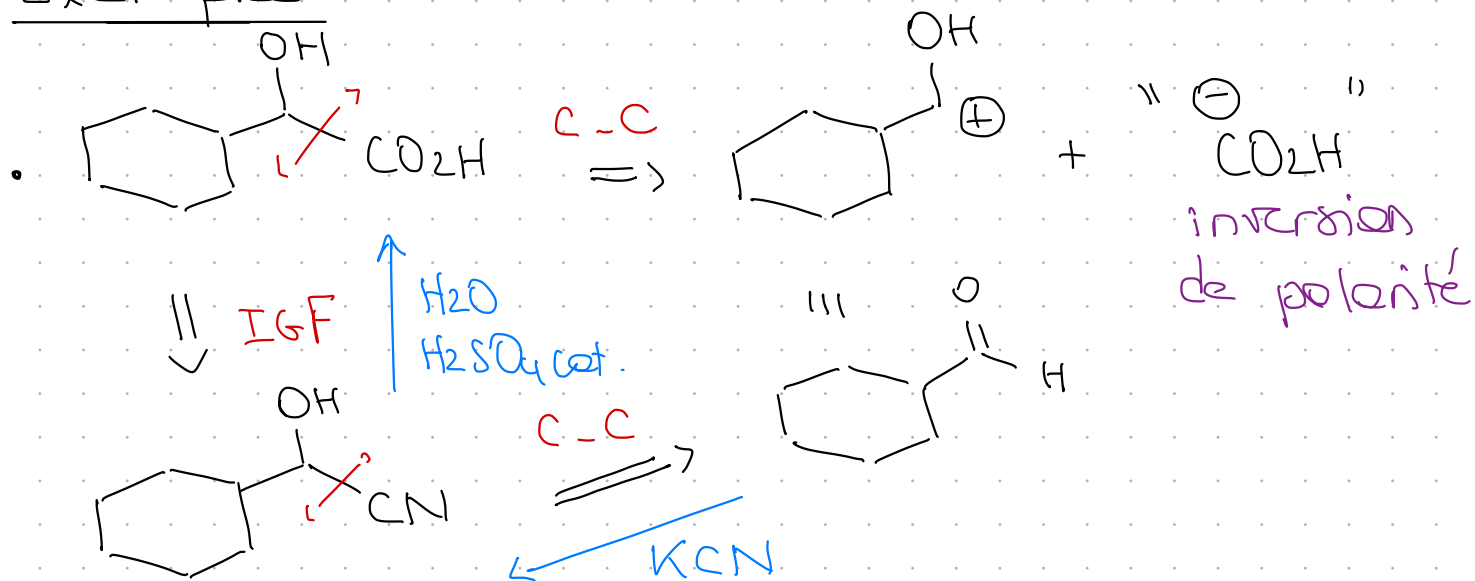
équivalents

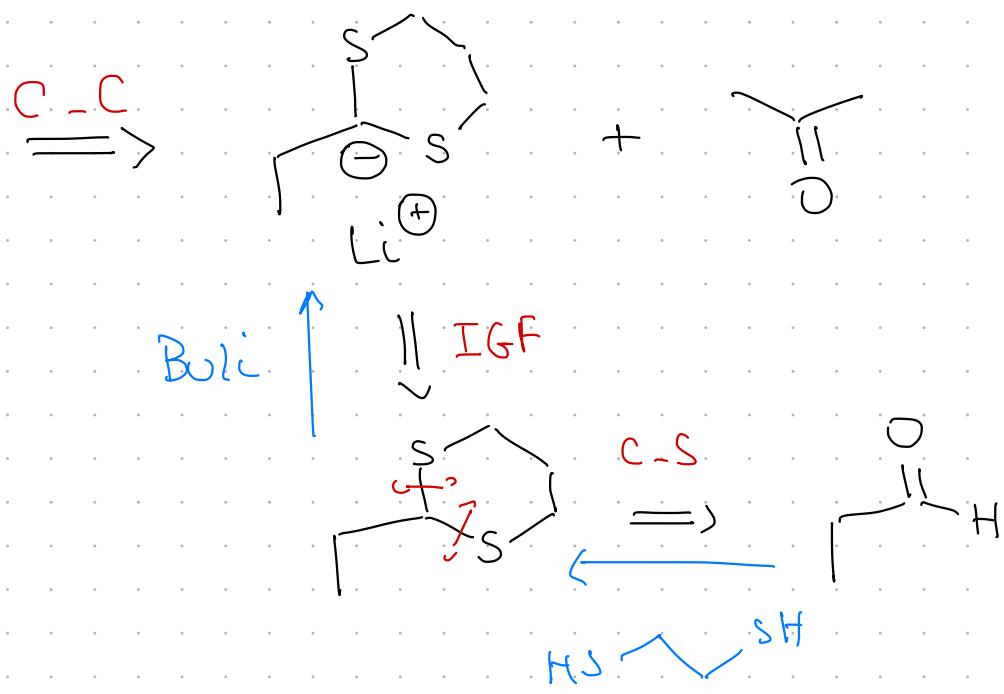
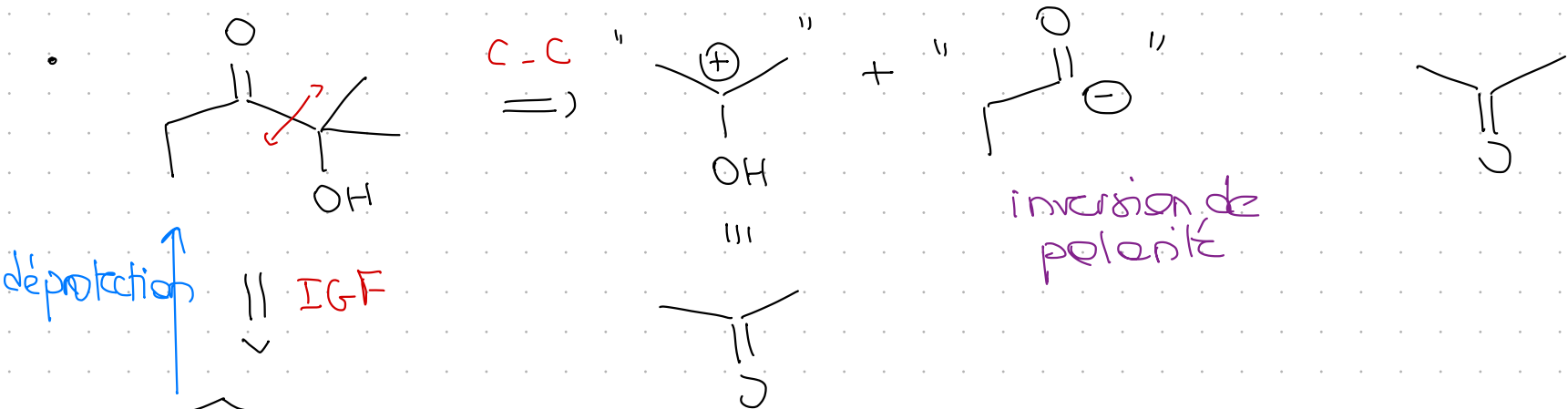
- anions dithiones
- cyanures
- anions acétylénures

Exemples

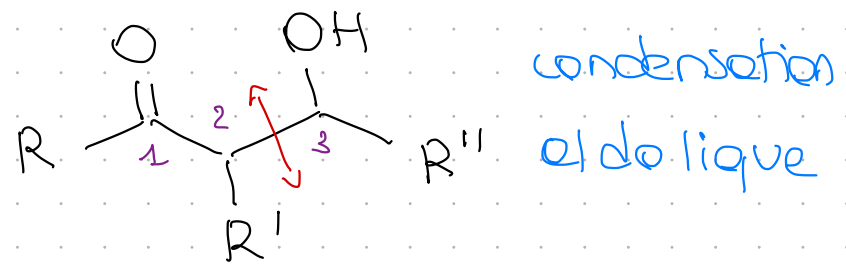
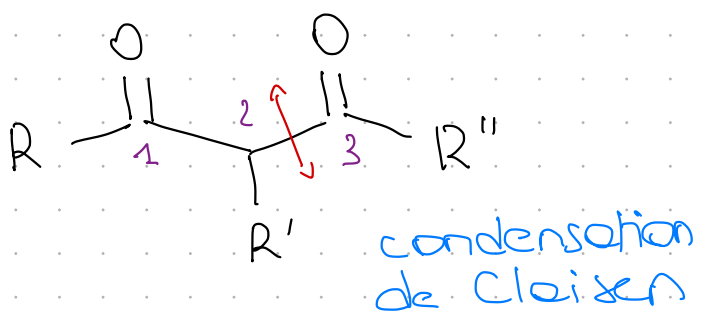
produit de départ

3



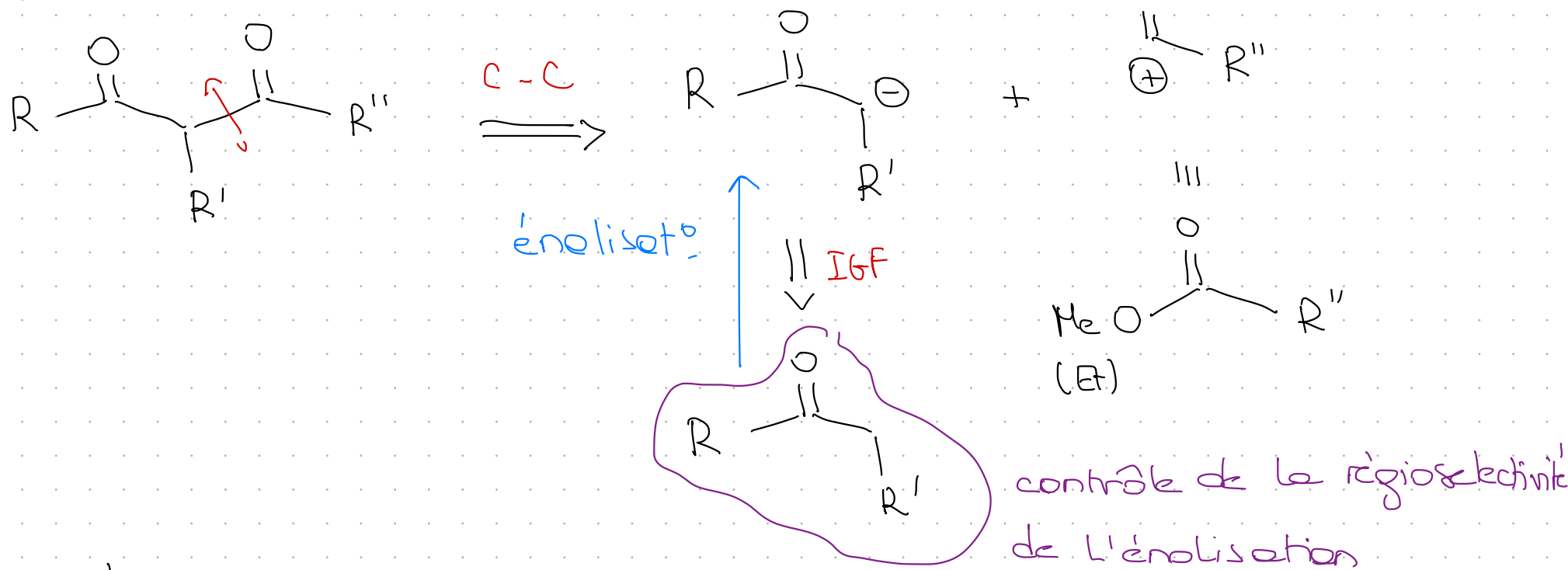


II - Composés bifonctionnels - 1,3

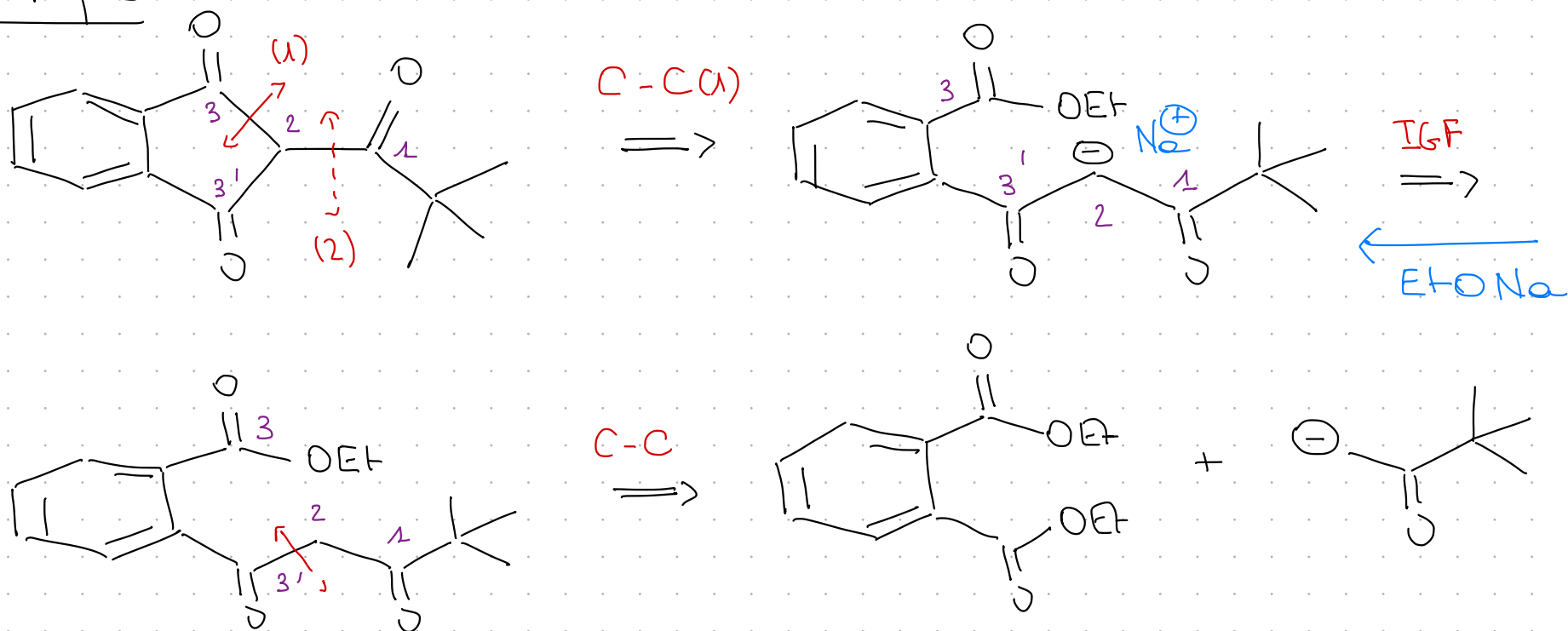


1) Condensation de Claisen

5

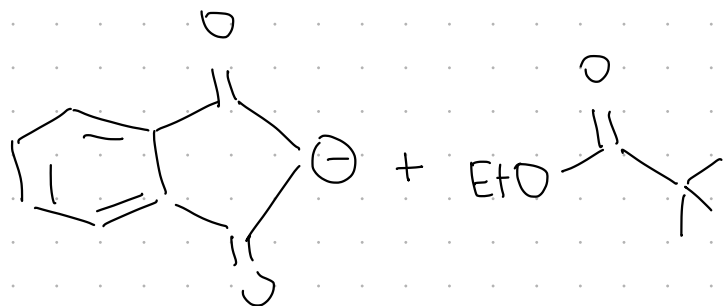


Exemple



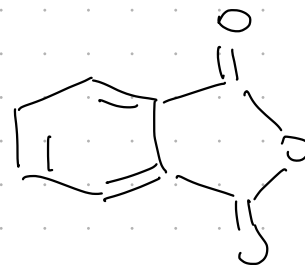
C-C (2)

=>

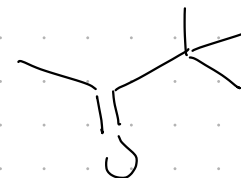


reconnection

LDA

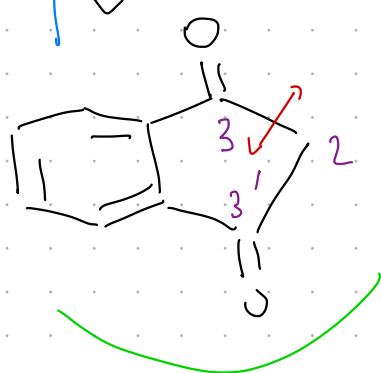


IGF



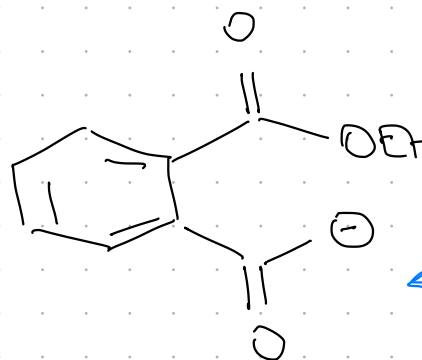
enolisation

IGF



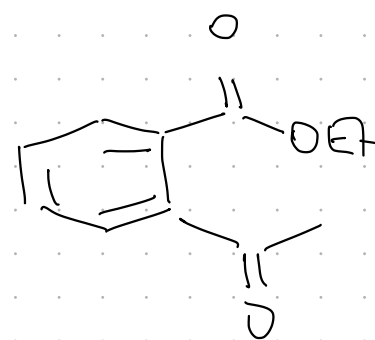
C-C

=>



IGF

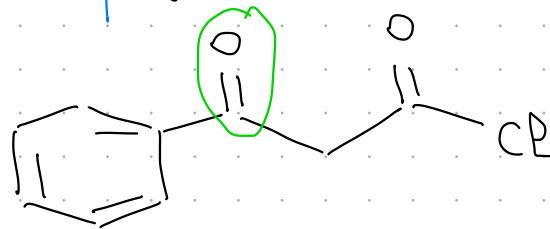
=>



LDA

AlCl₃

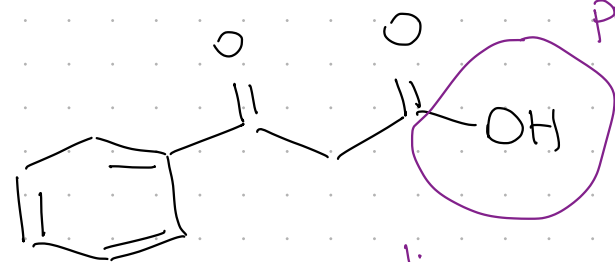
C-C



IGF

=>

SOCl₂

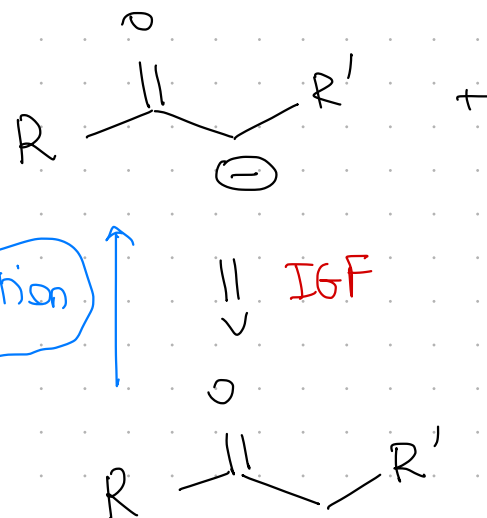
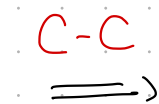
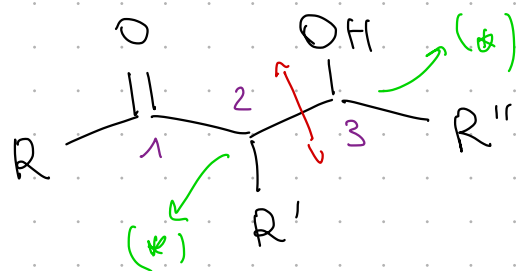


protection

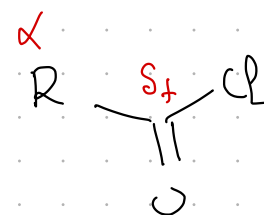
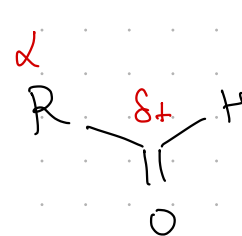
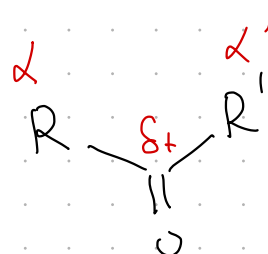
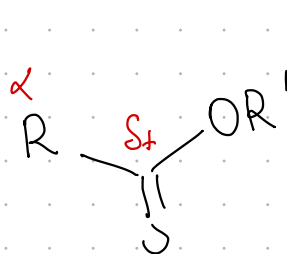
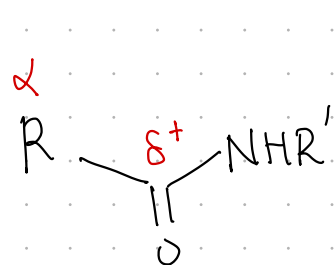
disconnection

Friedel-Crafts

2) Condensation aldolique



Réactivité



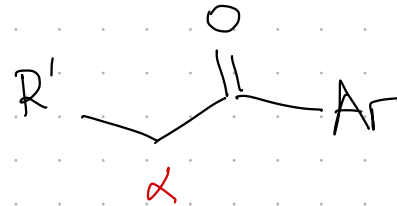
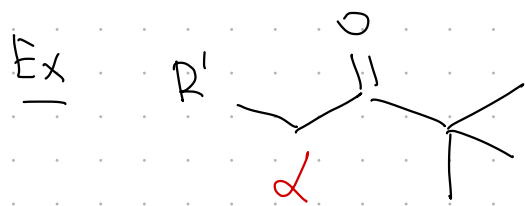
électrophilie $\nearrow$

capacité à être
énolisé $\nearrow$

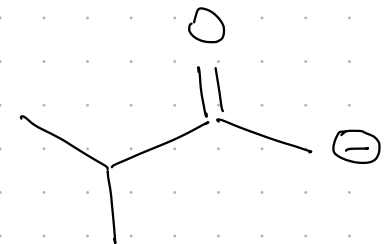
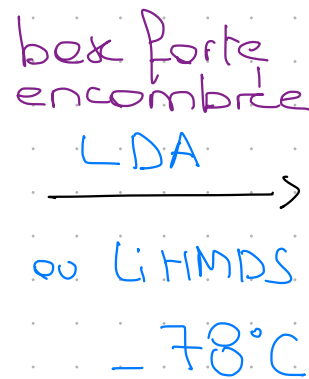
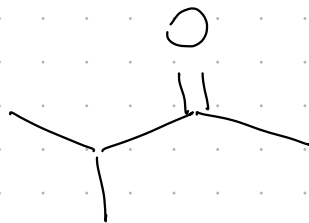
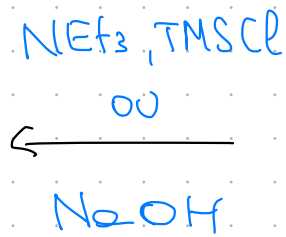
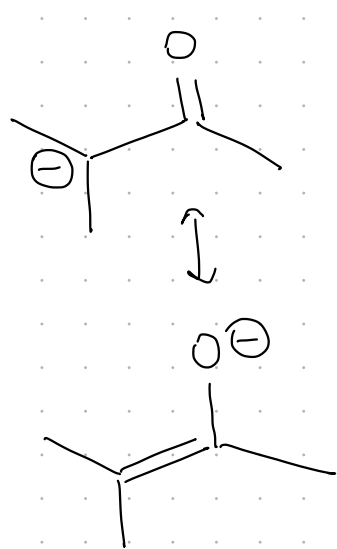
Contrôle de l'énolisation

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

18



• Facteurs stériques



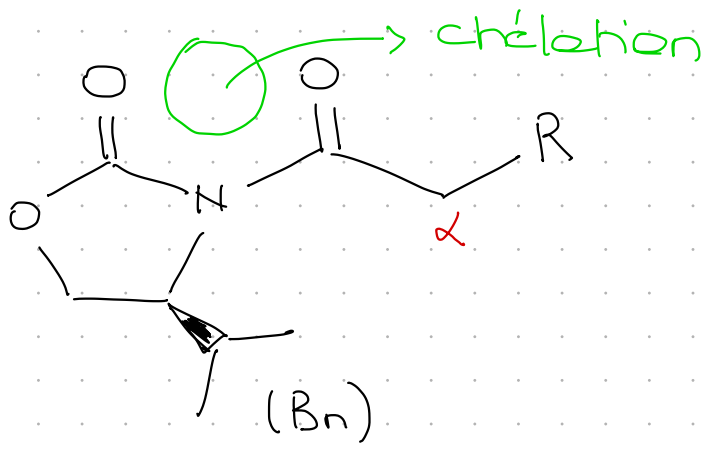
énolate cinétique

énolate thermodynamique

3) Aldolisation stéréosélective

• Enolate chiral

Enolates de bore



B : 3 liaisons covalentes
+ 1 Liaison de coordination

