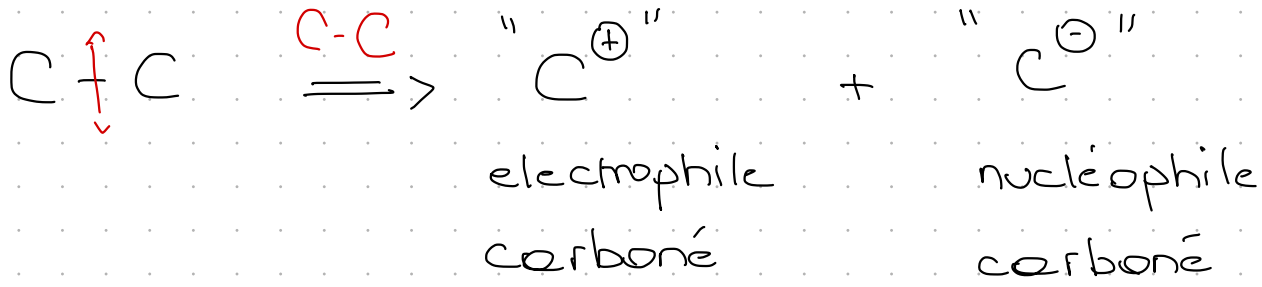
CH-335 / VI - Disconnections C-C / Monofonctionnel

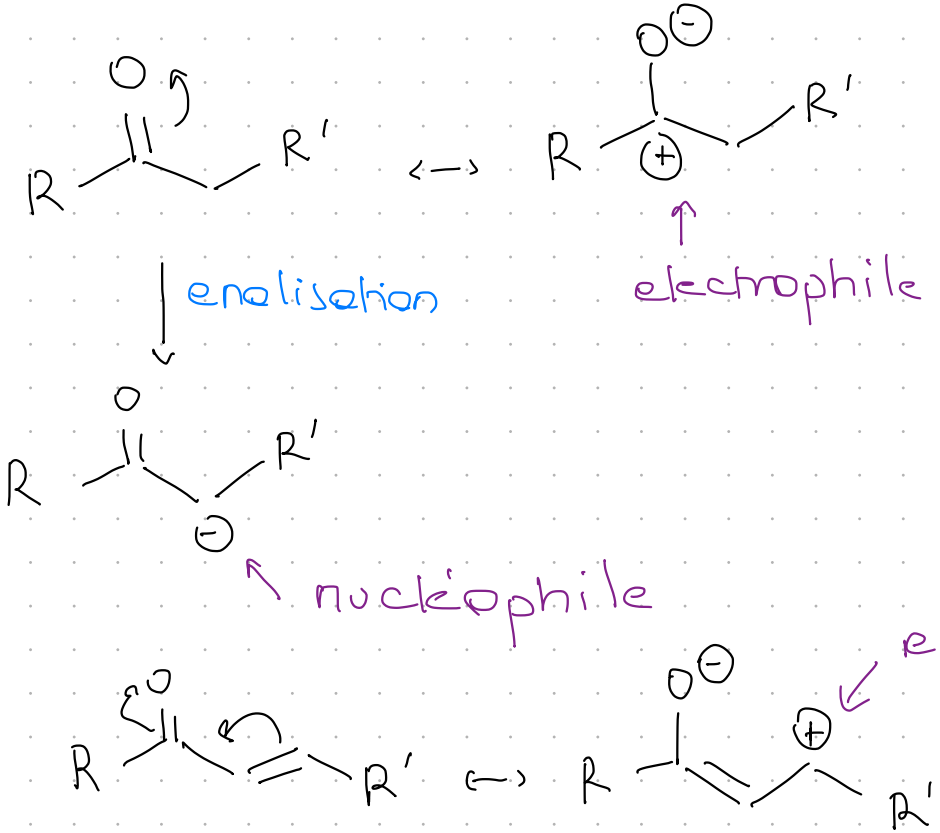
S. Gerber

2025

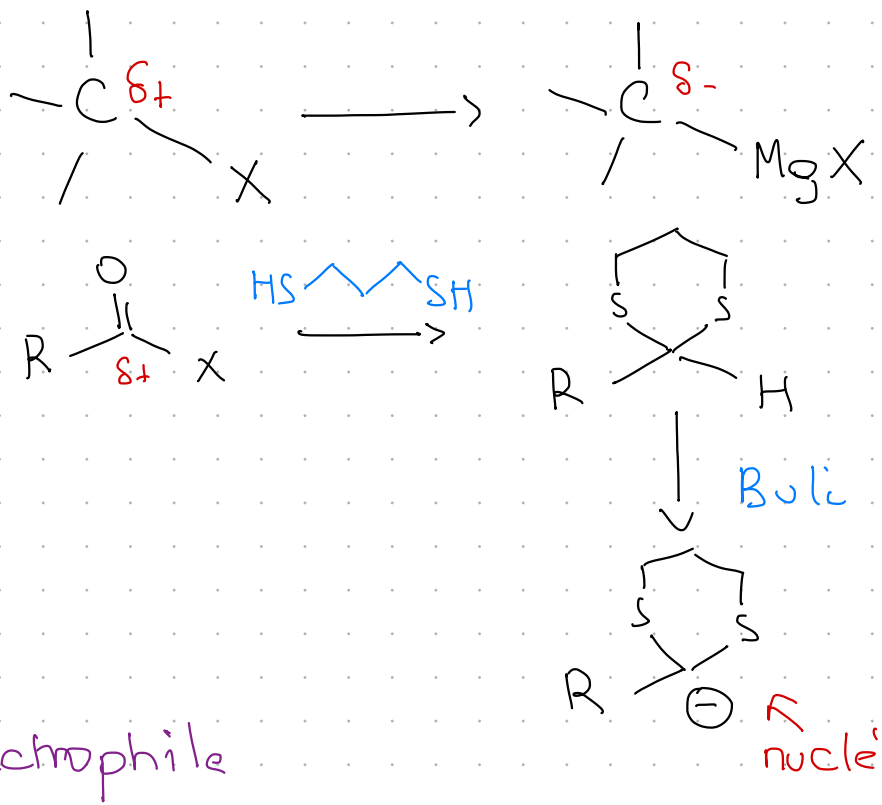
Généralités



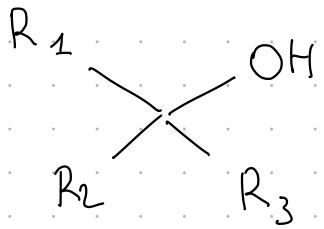
Utiliser la polarité naturelle des fonctions organiques

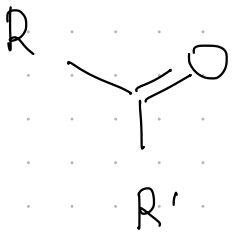


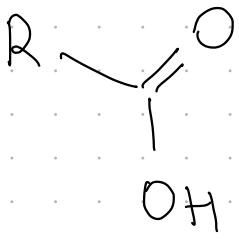
Inversion de polarisation



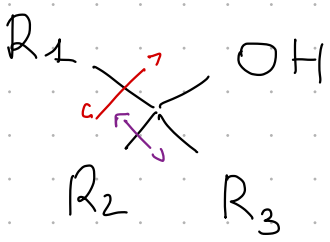
I - Disconnections 1,1 - C-C



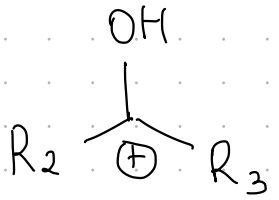




1) Le cas des alcools



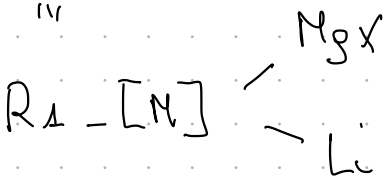
C-C
⇒



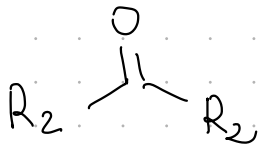
III

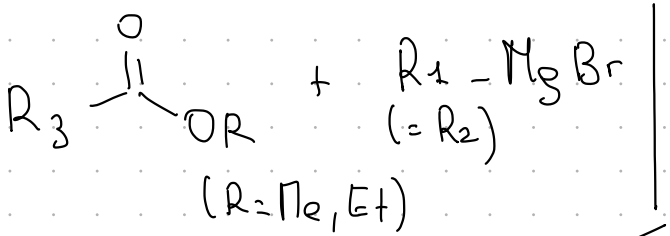
\+

IV

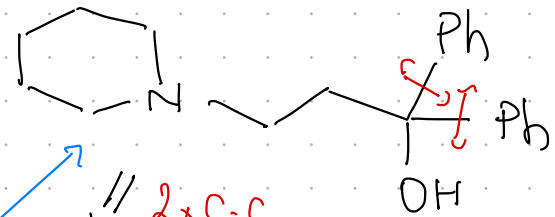


Si $R_1 = R_2$ ⟹ 2x C-C





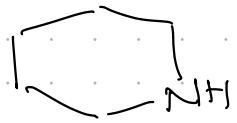
Ex



PhMgBr

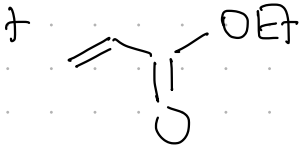
// 2x C-C

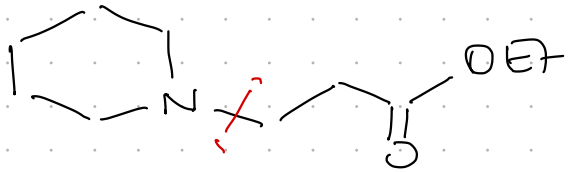
produit de départ



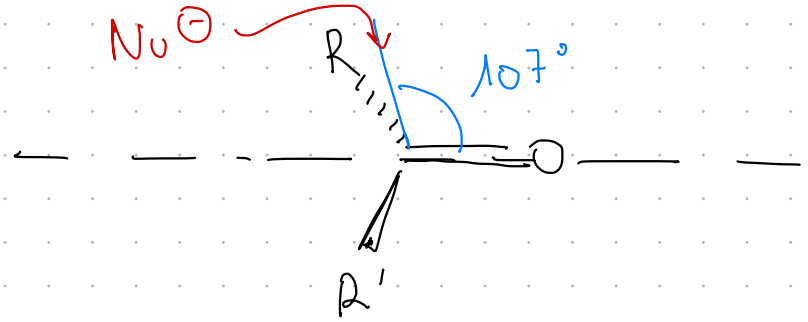
C-N

addition 1,4

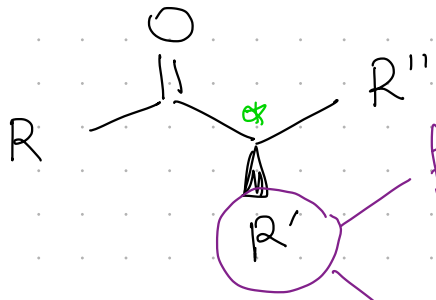




Version asymétrique



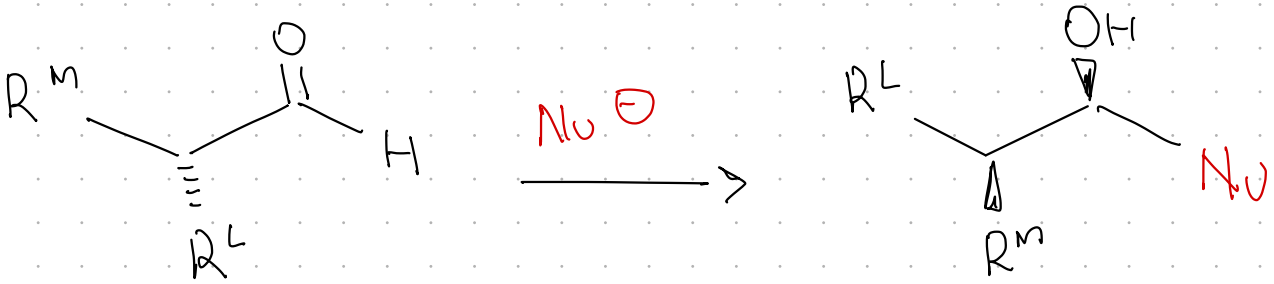
Substrats



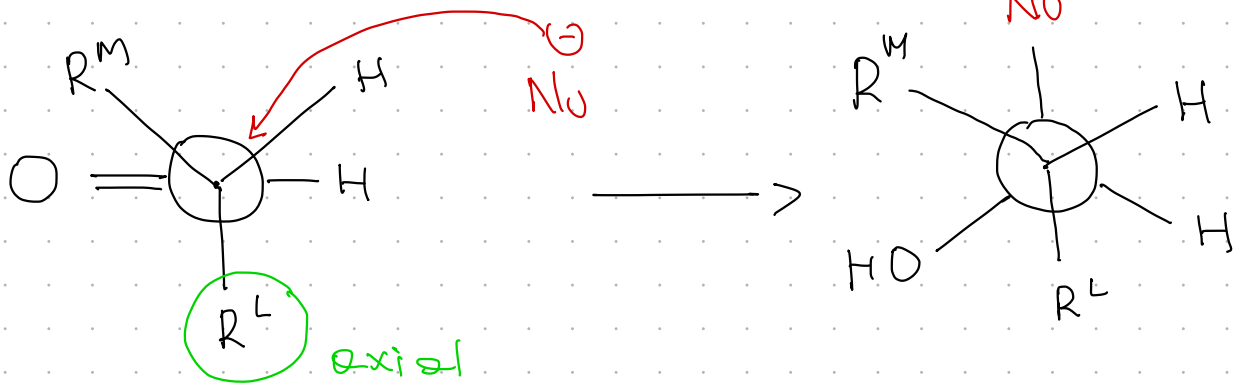
Facteurs stériques

Facteurs électroniques

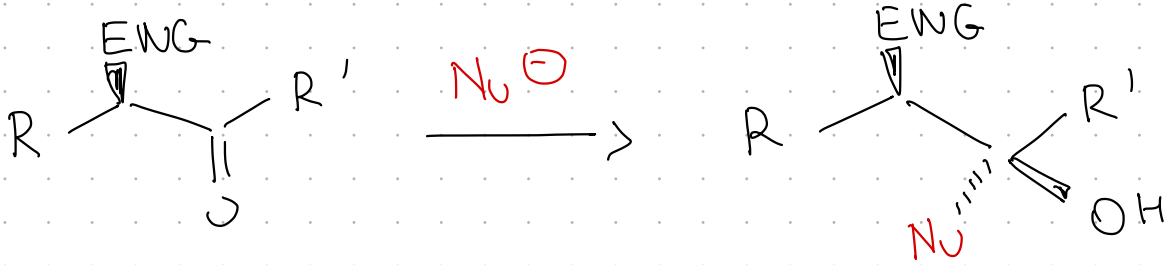
- R' ≠ EWG : Facteurs stériques



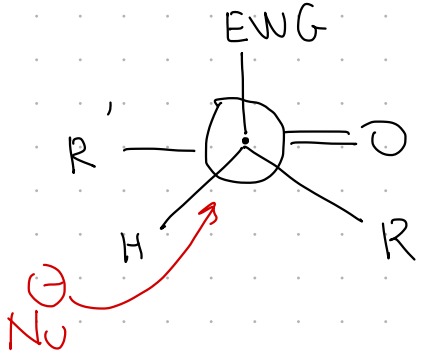
Modèle de Cram



- R' = OH, OR_1, NH_2, X ; Facteurs électroniques

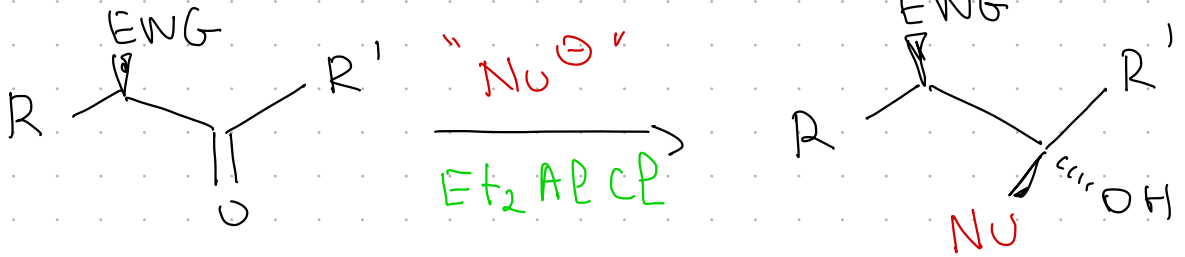


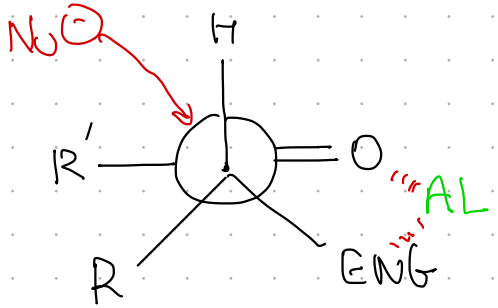
Modèle de Felkin-Anh



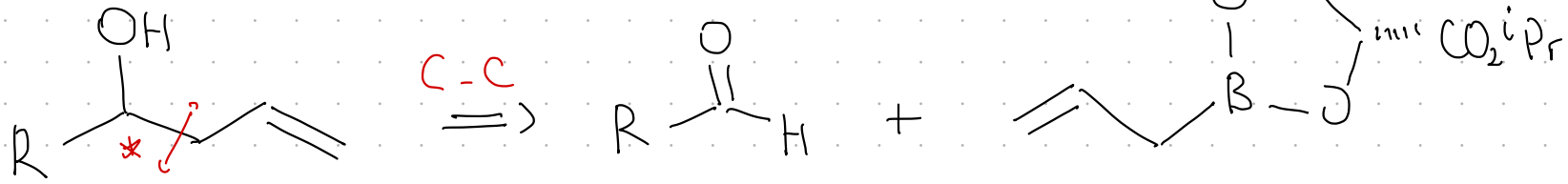
formation de la liaison en anti de l'orbitale σ^*_{C-EWG}

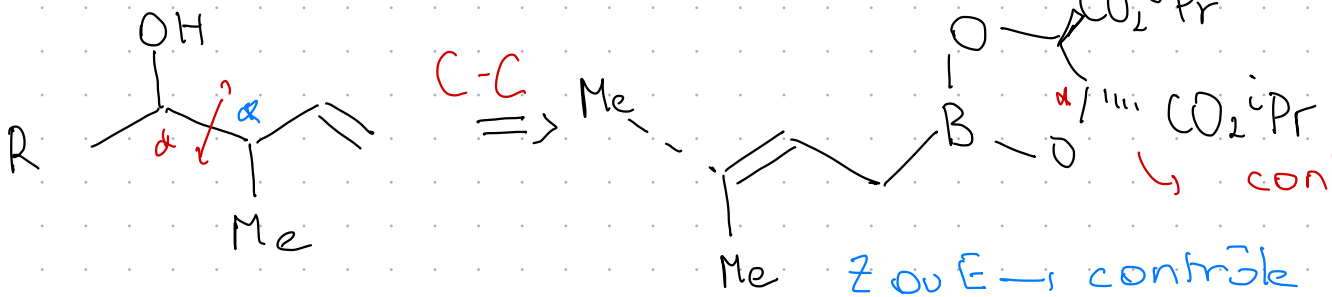
Effet chelate





Allylation, crotylation

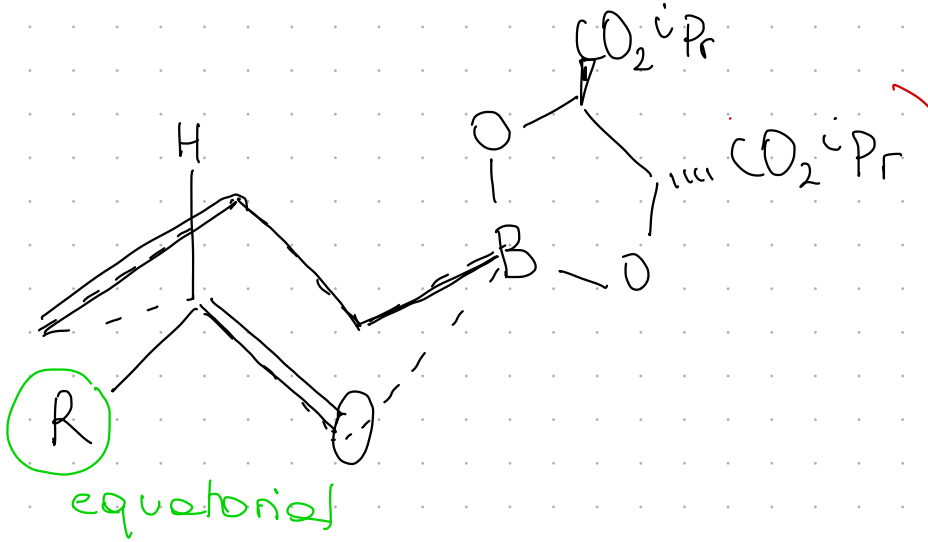




↳ contrôle * sur le produit final

Z ou E → contrôle *

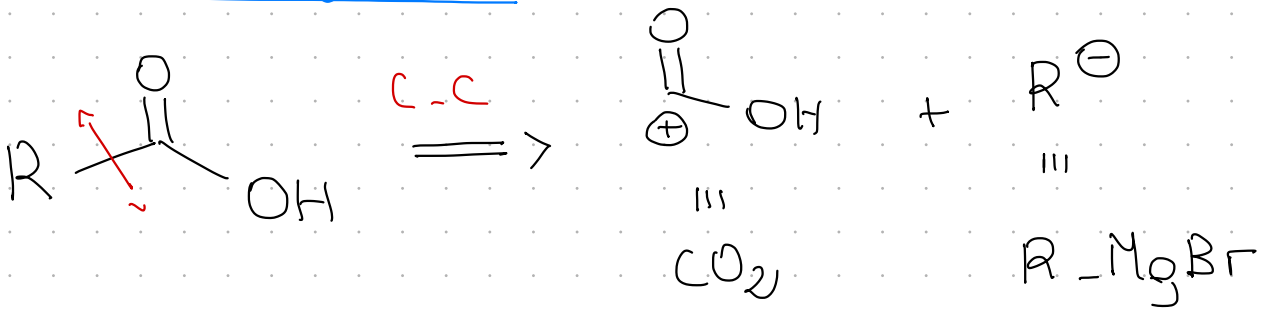
ET ≠ chaise



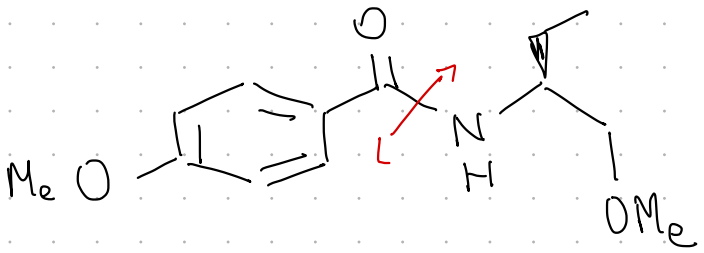
equatorial

dirige l'attaque de l'aldéhyde sur la face opposée

2) Acides carboxyliques

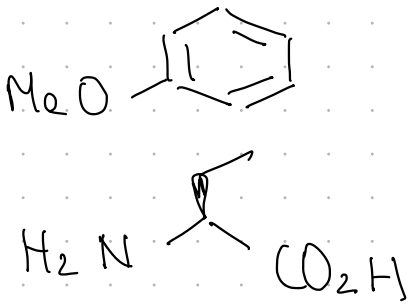


Ex

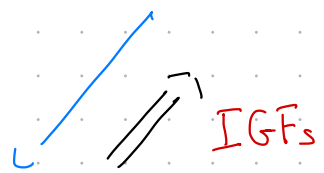


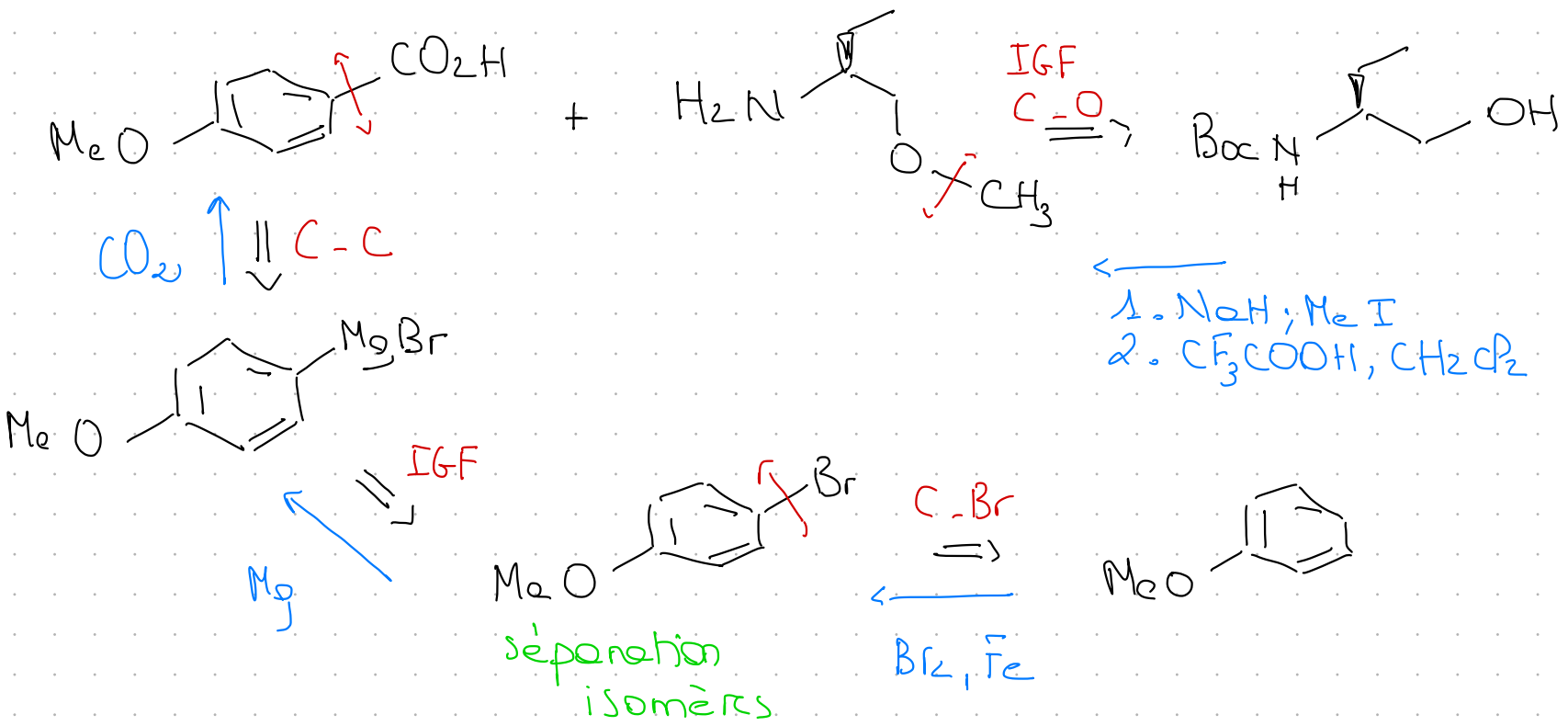
HOBt ↑ C-N

produits de départ

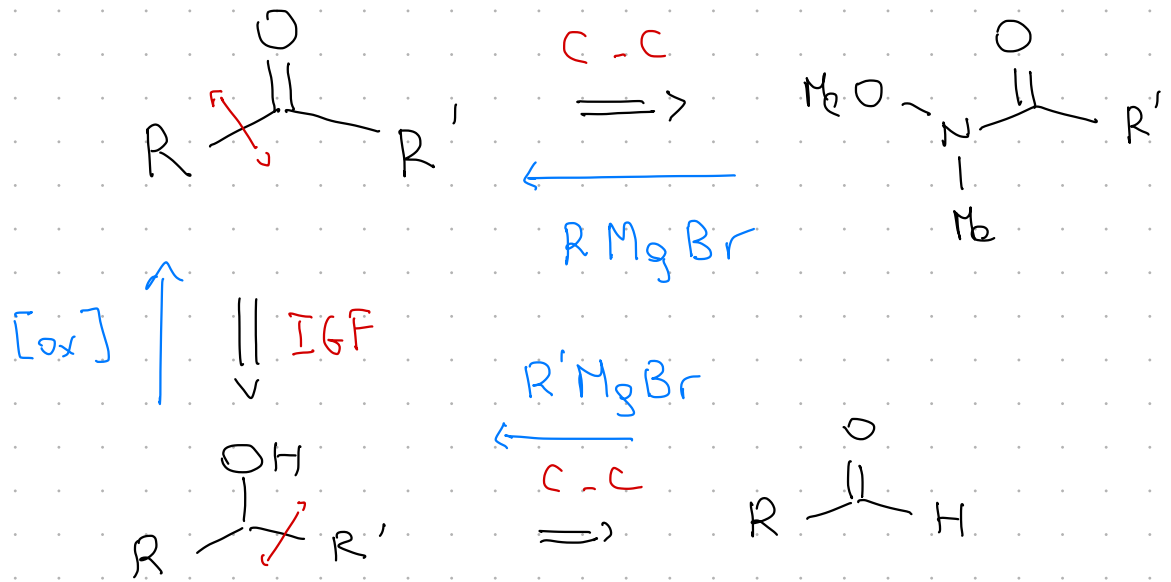


1. Boc_2O
2. $LiAlH_4$



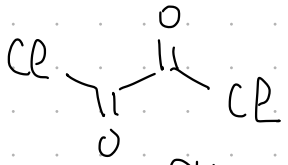
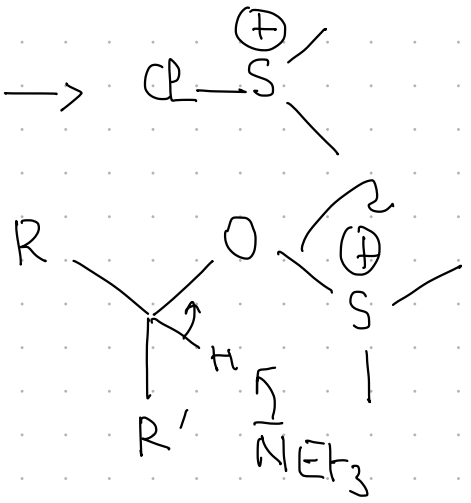


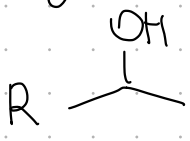
3) Le cas des carbonyles



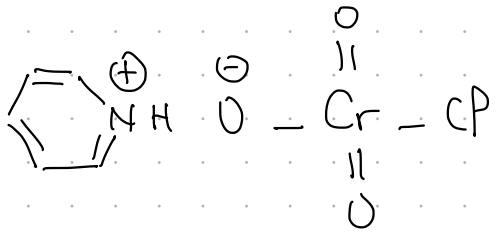
Oxydation des alcools

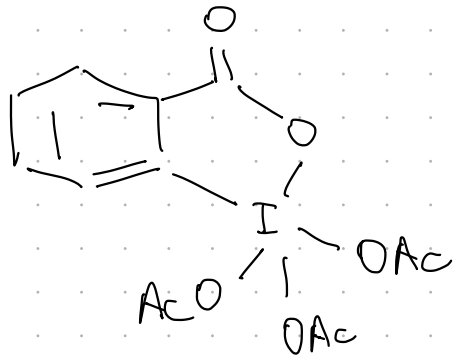
- Swern

1. 
; DMSO ; -78°C → 

2. 
; -78°C

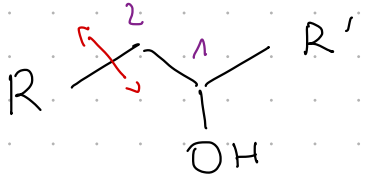
3. NEt_3 -78°C → RT

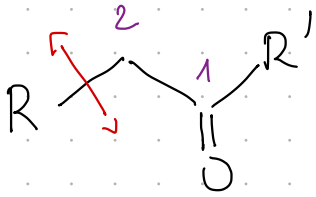
- PCC 

- Periodinane 

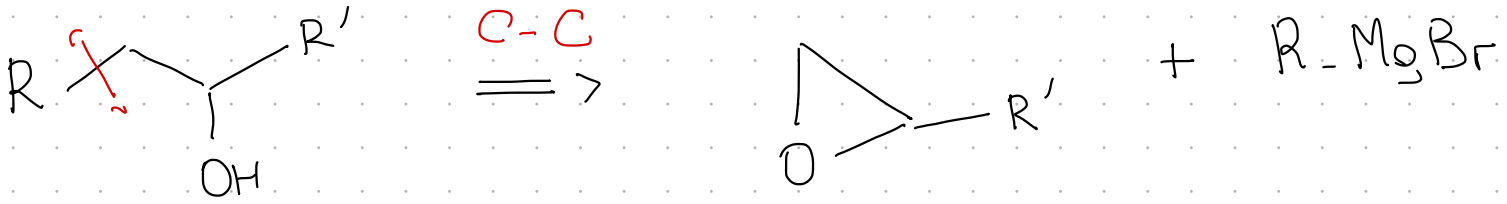
- TEMPO

II - Disconnections 1,2-C-C

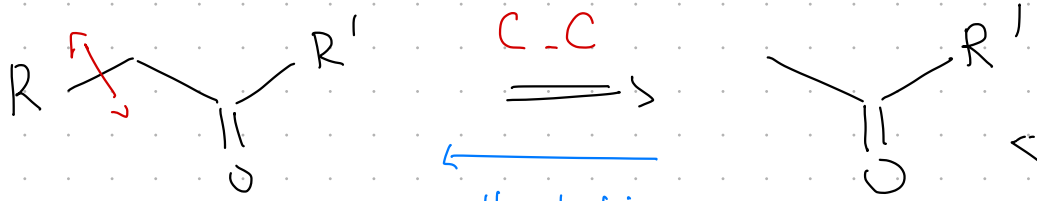




1) Le cas des alcools



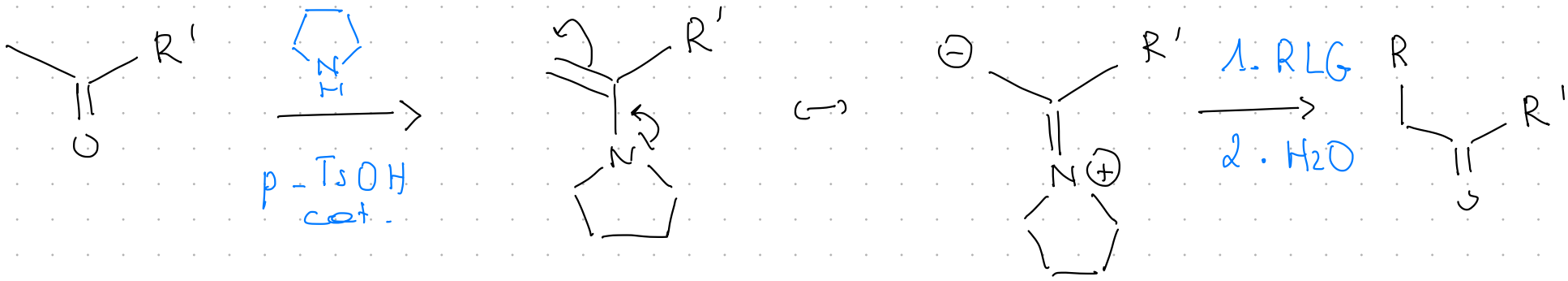
2) Le cas des carbonyles



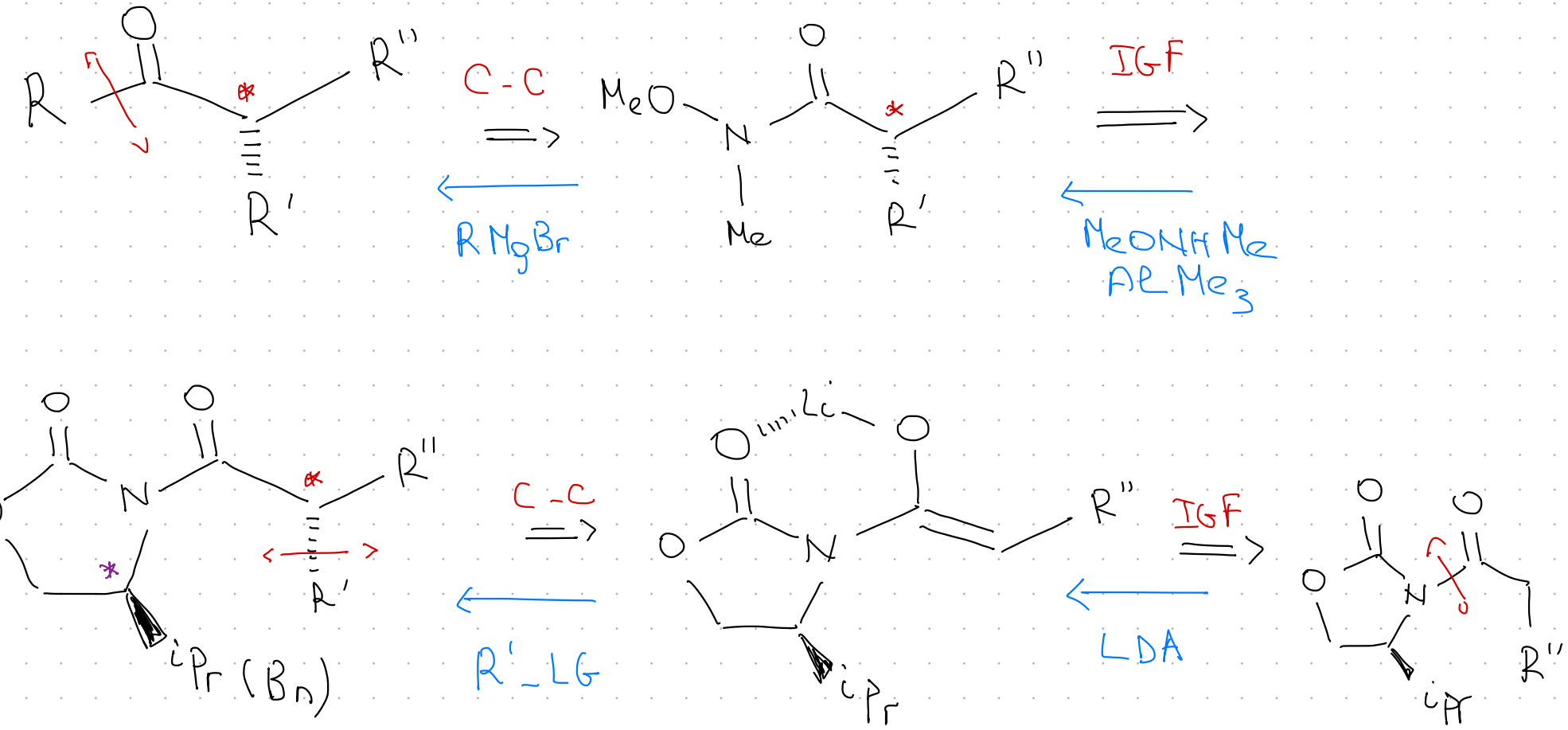
↳ suralkylation

↳ compétition avec la condensation aldolique

- utilisation des énamines



Alkylations stéréosélectives



III - Disconnections 1,3-C-C