

CH-33S / IV - Disconnections C-X

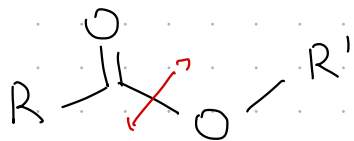
S. Gerber

2025

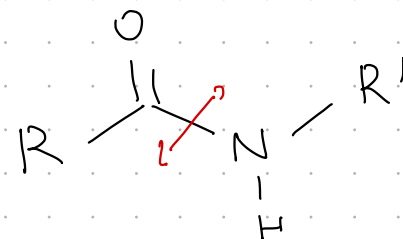


1. Disconnections C-X / un groupe Fonctionnel

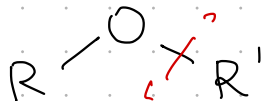
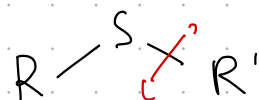
esters



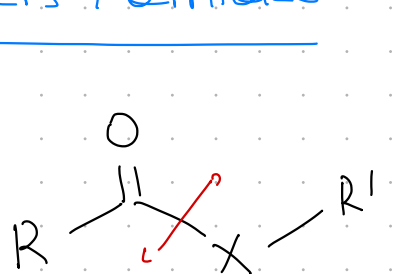
amides



ethers / sulfures

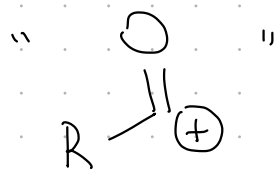


1) Esters / amides

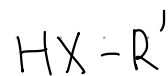
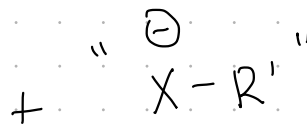


$X = O, NH$

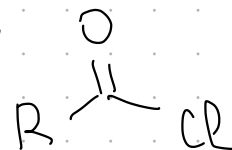
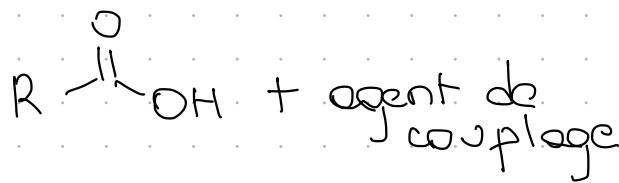
$C-X \Rightarrow$



électrophile
actif

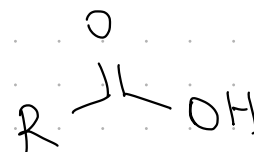


nucleophile non
actif



IGF

$\Rightarrow$



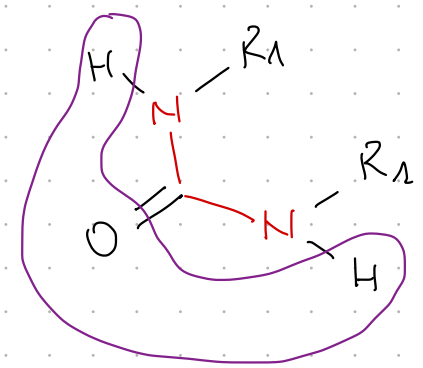
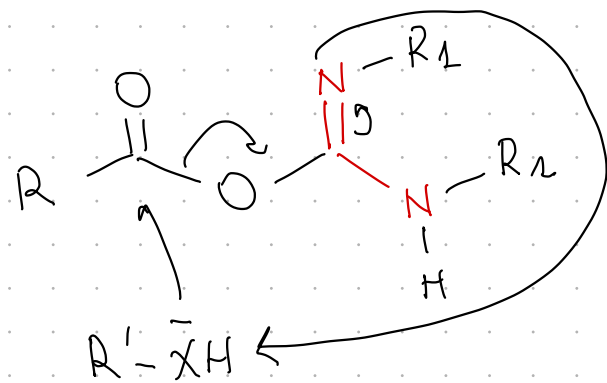
Agents de couplage

• carbodiimides



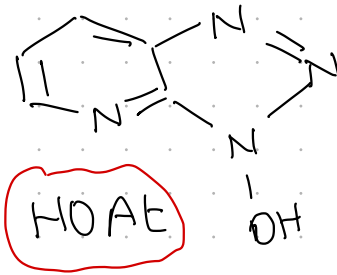
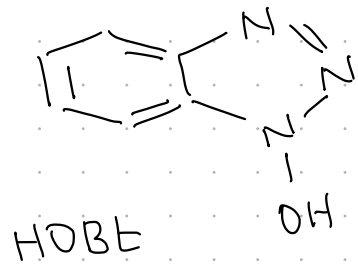
$R_1: Cy \quad DCC$

intermédiaire activé

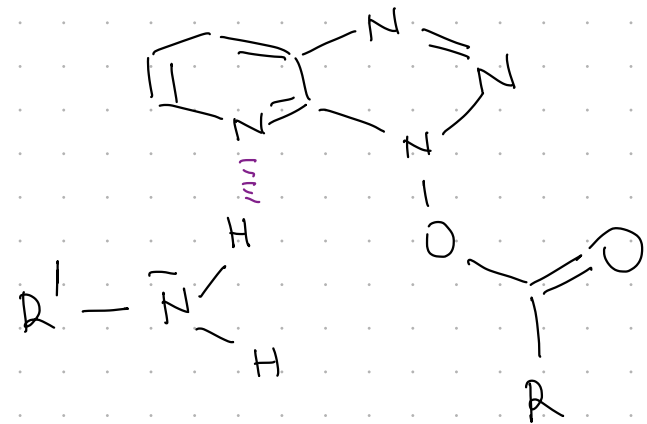


12

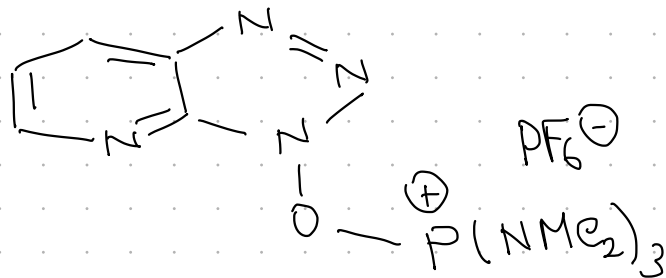
- HOBT, HOAT (synthèse peptidique, molécules complexes)



double
activation

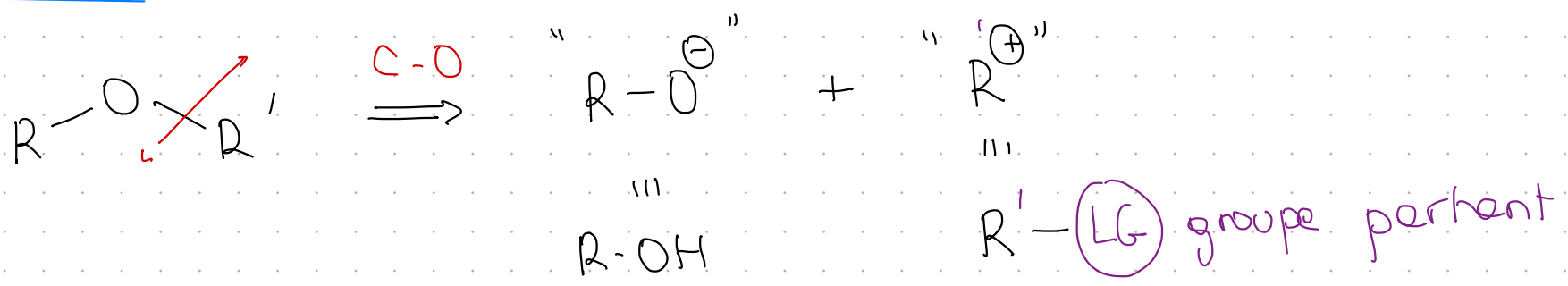


- HATU



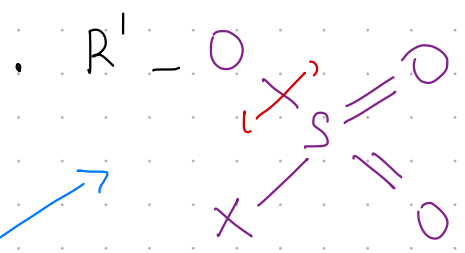
sous-produits solubles en milieu aqueux

2) Ethers



R'-LG

• $R'-X$ $X = I, Br, Cl$



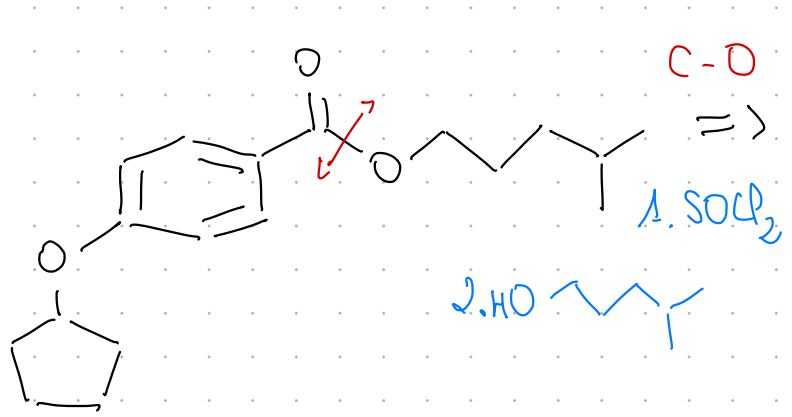
$R'-OH$

réactivité ↑

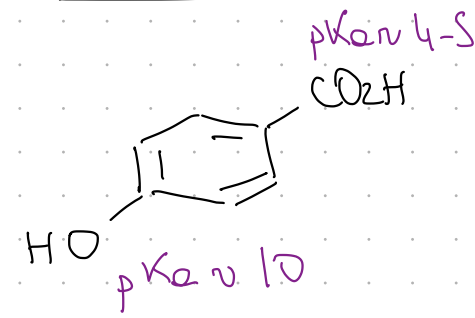
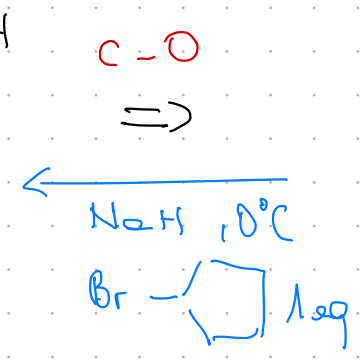
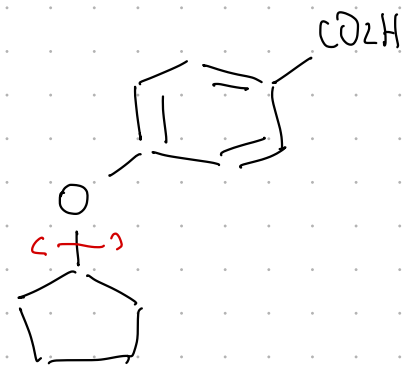
$X = Me, \text{mesyle (OMs)}$
 tosyle (OTs)
 $CF_3, \text{triflate (OTf)}$

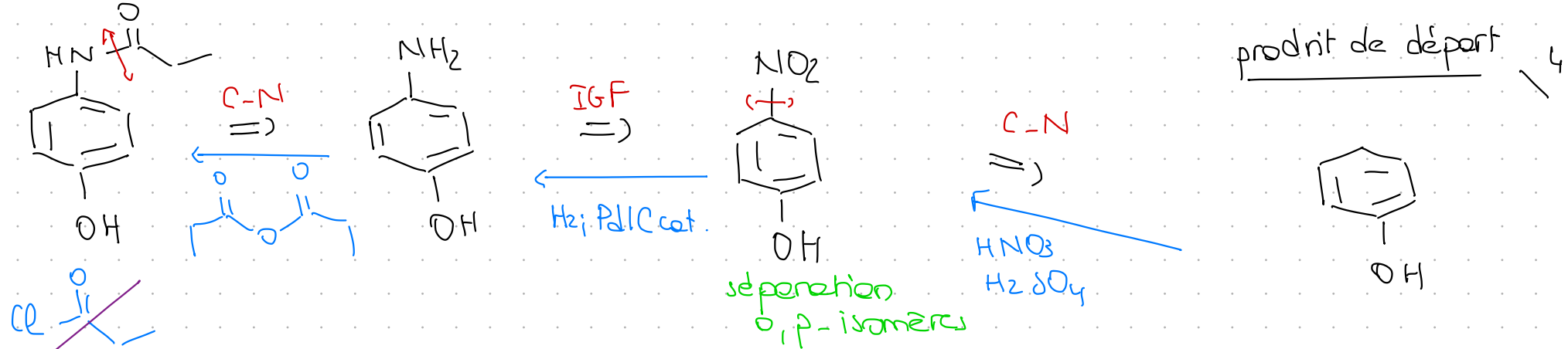
Sélectivité

produit de départ

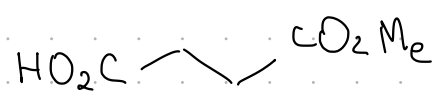


2. HO-CH₂-CH₂-CH₂-CH₃

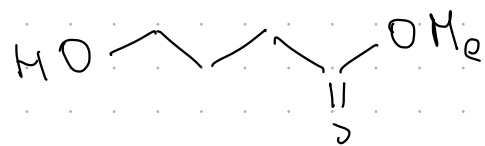
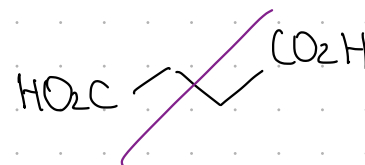
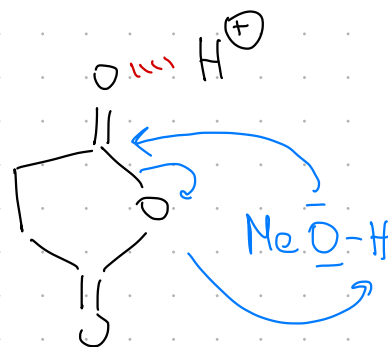
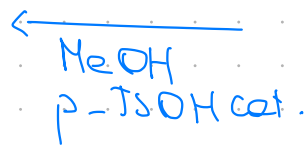




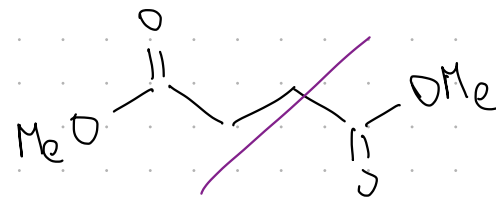
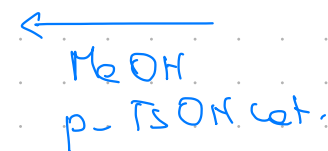
Monofonctionnalisation



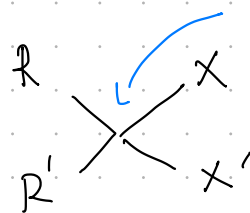
reconnection $\Rightarrow$



reconnection $\Rightarrow$



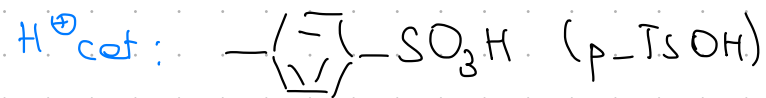
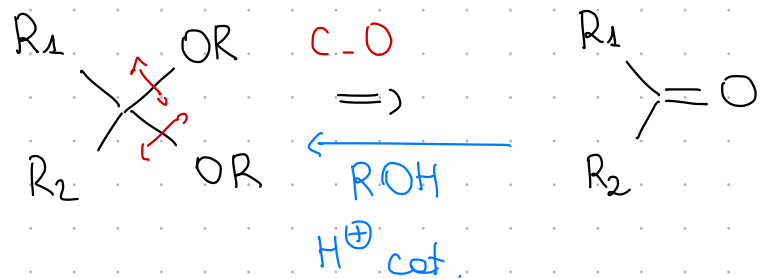
II - Disconnections C-X ; deux groupes fonctionnels



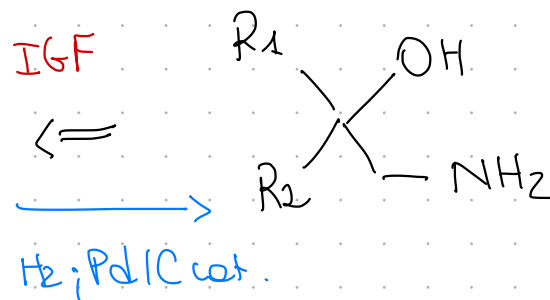
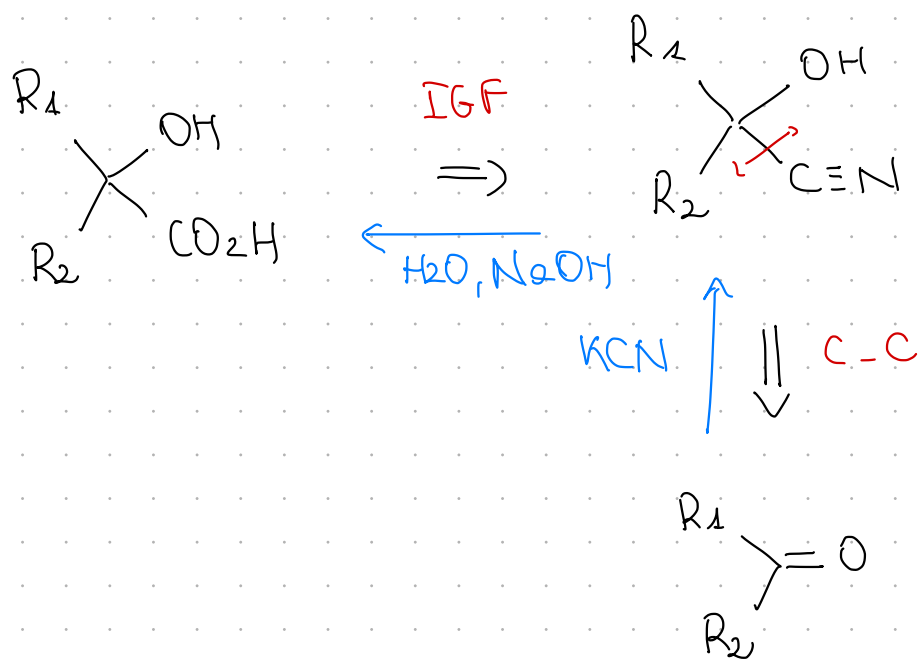
degré d'oxydation d'un carbonyle

$\text{X}, \text{X}' = \text{OR}'' , \text{OH} , \text{CN} , \text{H}_2\text{N}$

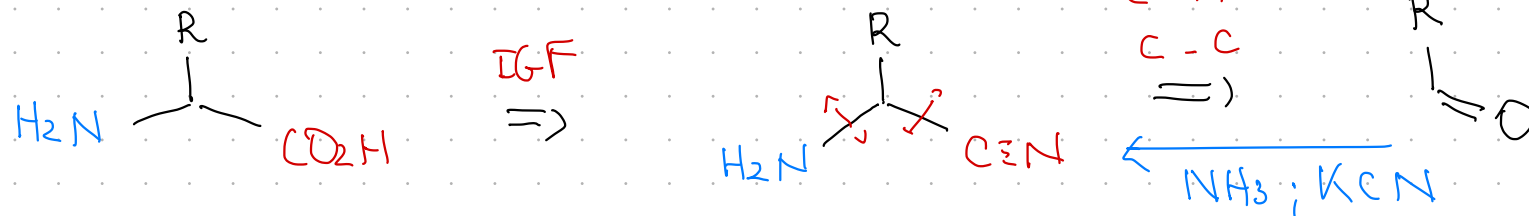
1) Acétals



2) Cyanohydrines

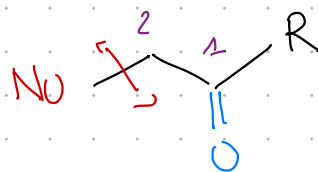
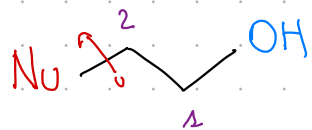


Acides α-aminés non naturels

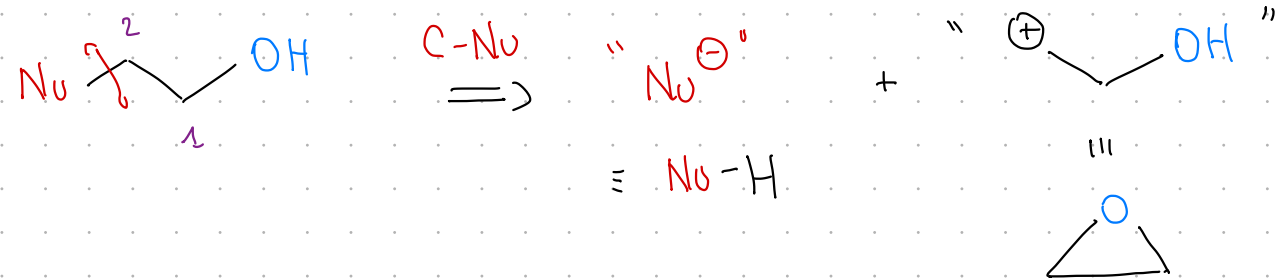


III - Disconnections 1,2 - C-X

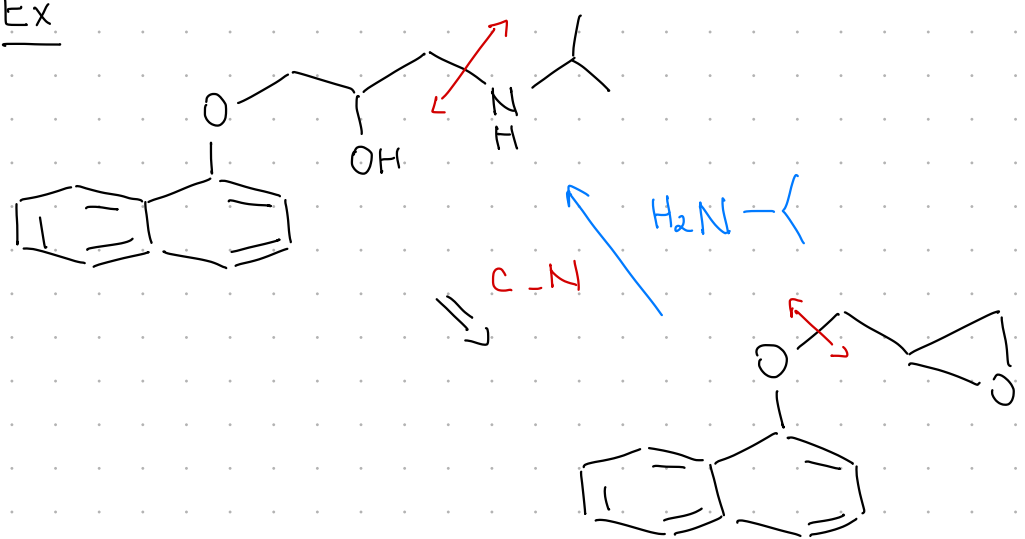
6



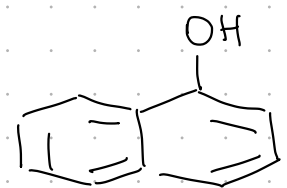
1) En 1,2 d'un alcool



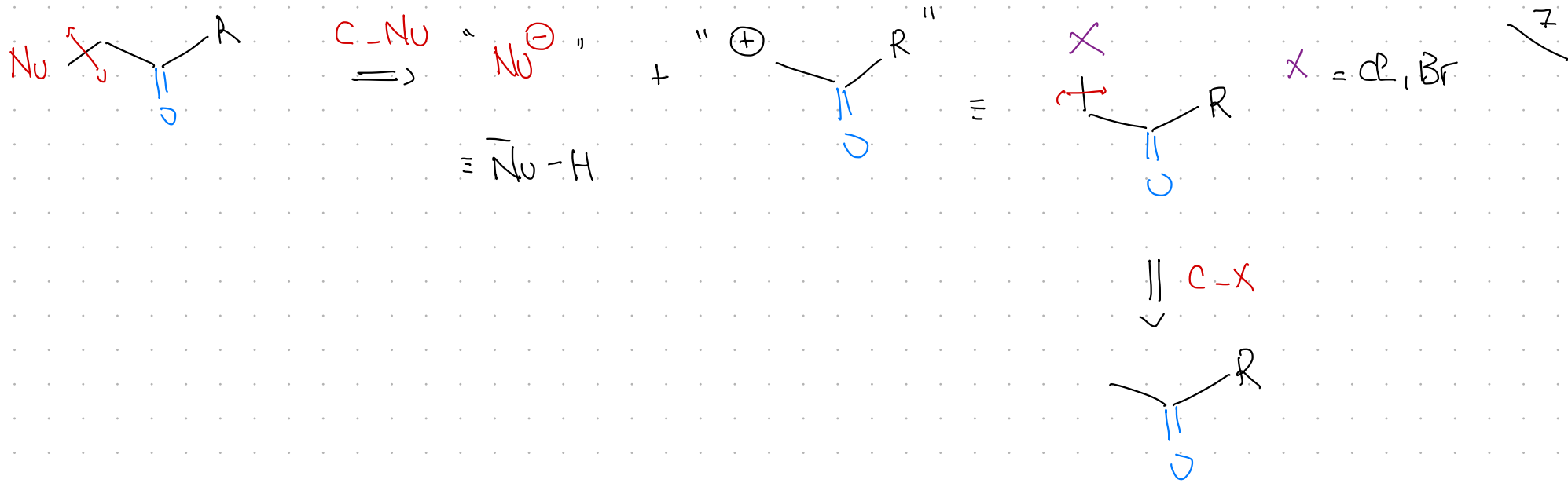
Ex



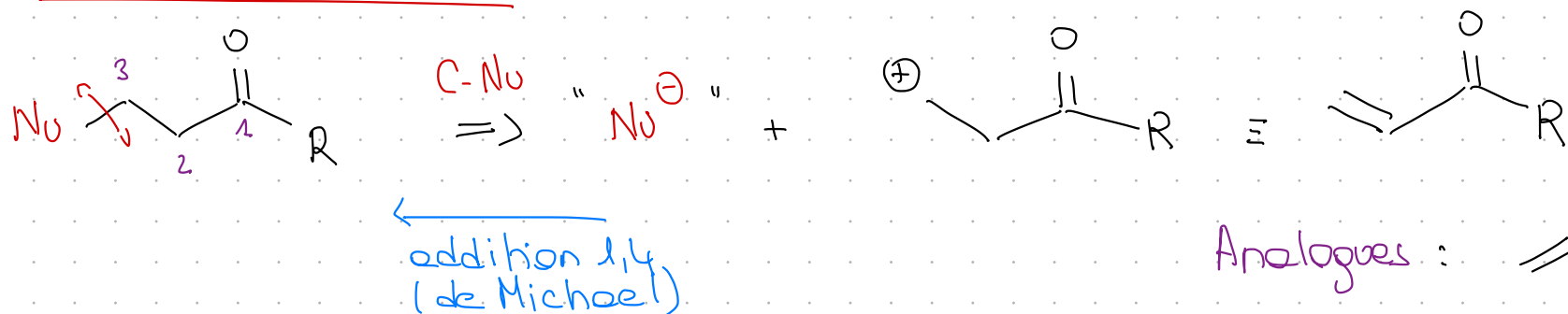
produit de départ



2) En 1,2 d'un carbonyle



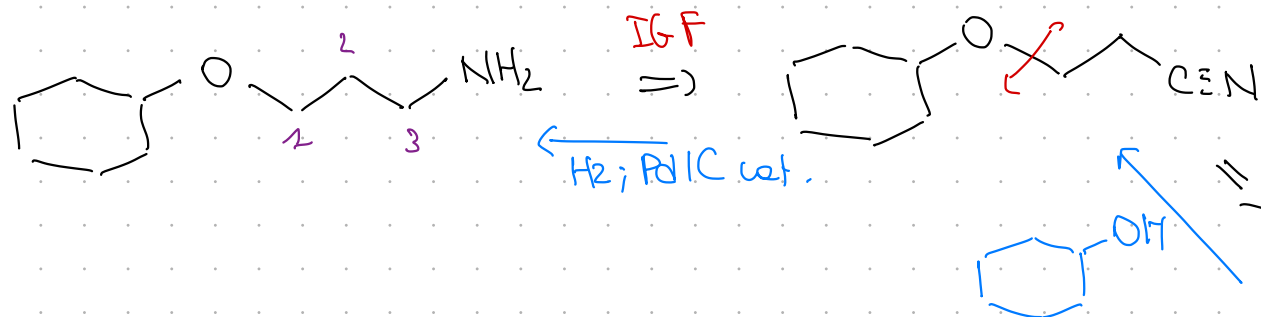
IV - Disconnections - 1,3



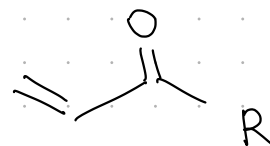
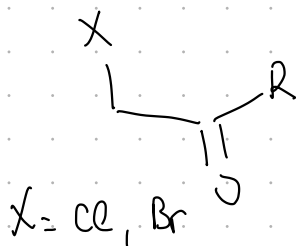
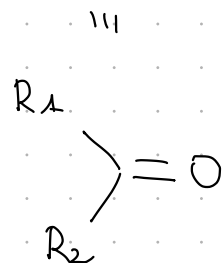
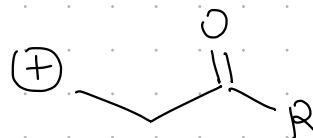
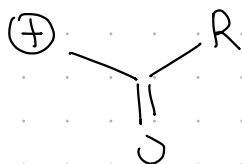
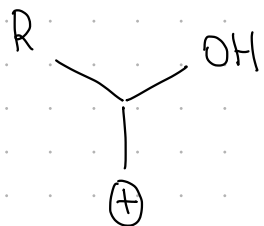
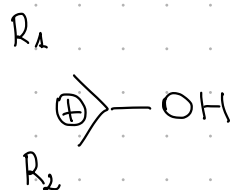
Analogues: $\text{CH}_2\text{=CH-CN}$

$\text{CH}_2\text{=CH-NO}_2$

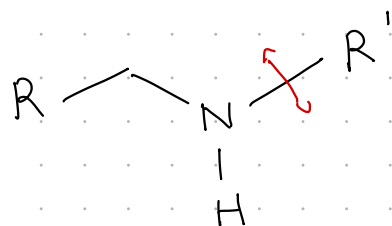
Ex



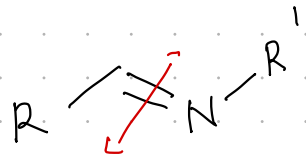
$\text{CH}_2\text{=CH-C}\equiv\text{N}$



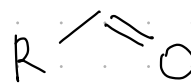
V - Le cas des amines



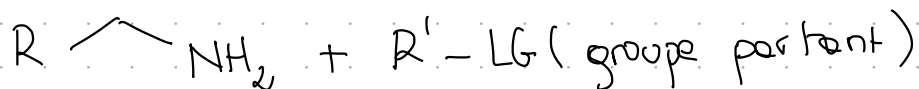
IGF
 $\Rightarrow$



C-N
 $\Rightarrow$

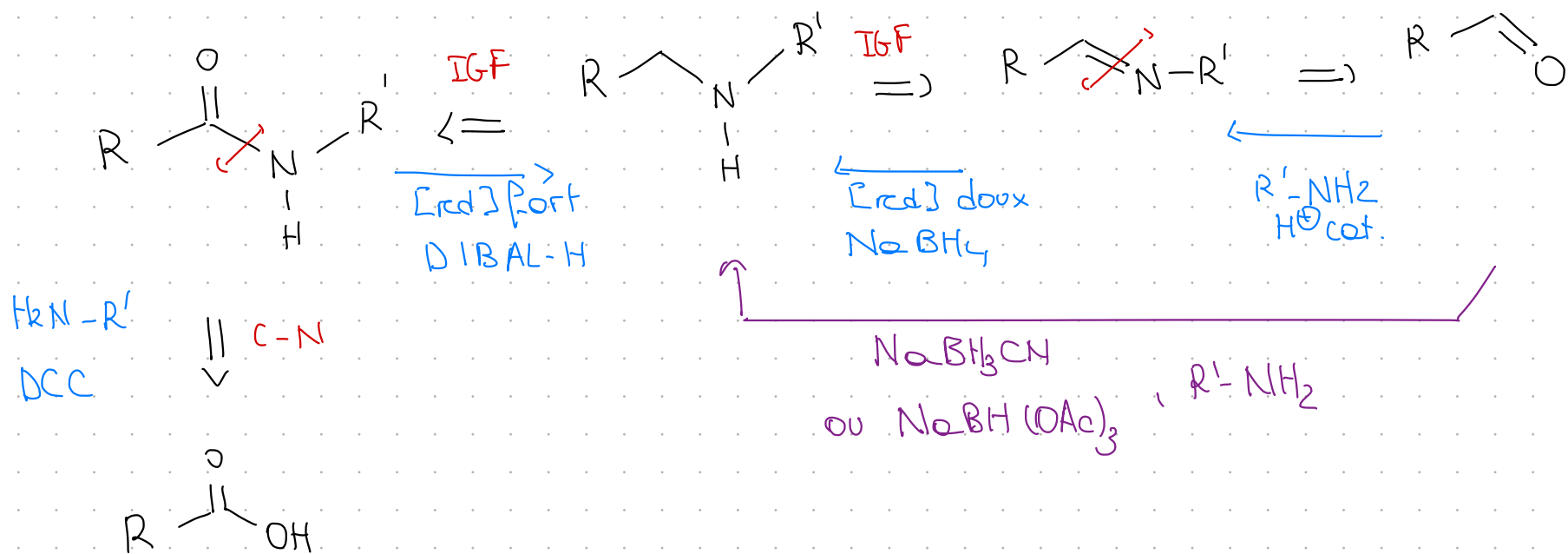


~~C-N~~ Δ suralkylation

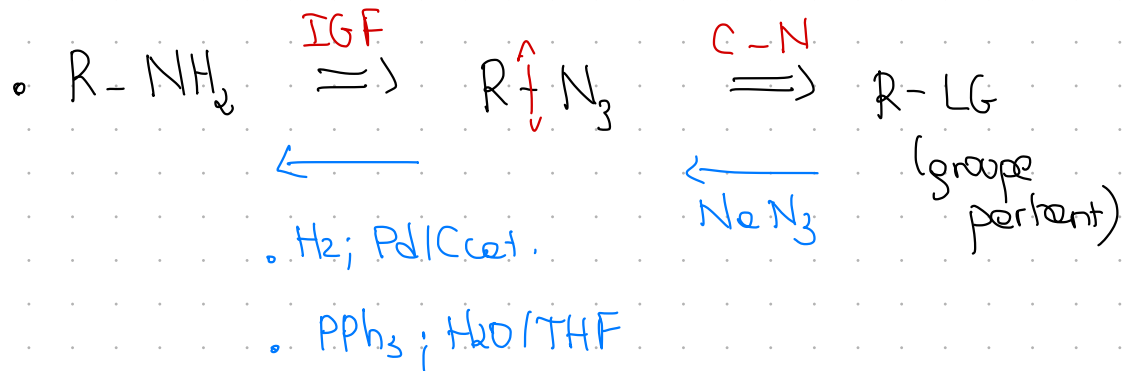


Préparation des amines substituées

9



Préparation des amines primaires



⚠ caractère explosif des azotures ($R = \text{alkyl petit}$)

Synthèse de Gabriel

