CH-335 / II - Groupes protecteurs

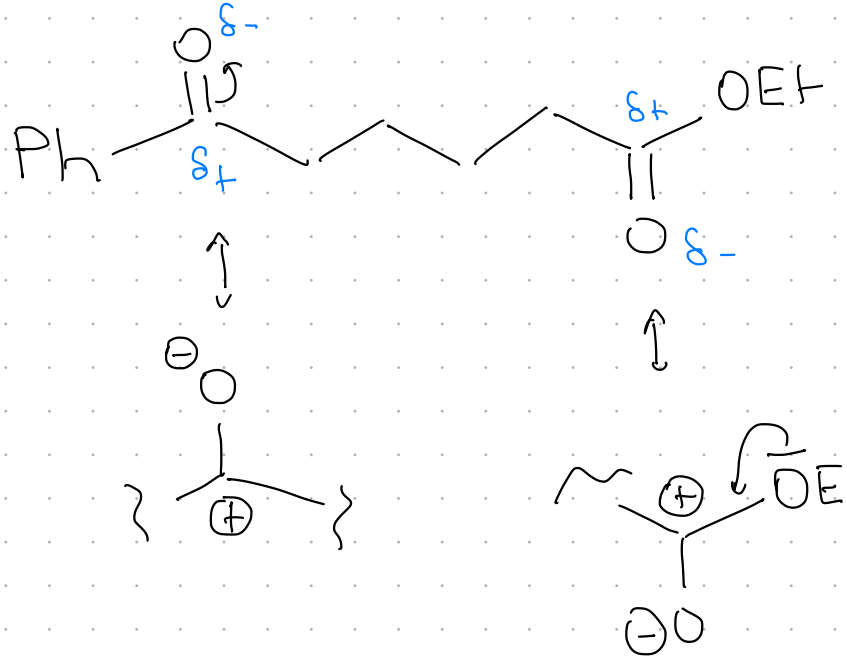
S. Gerber

2025

I - Introduction

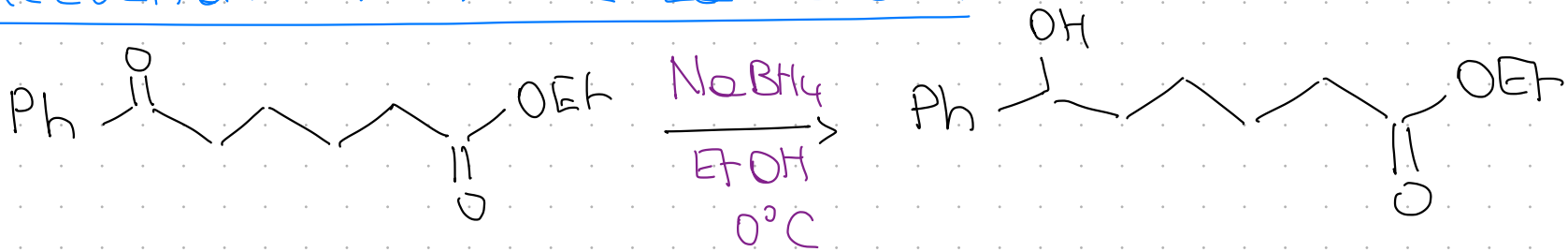
Ly résoudre Les problèmes de chimioselectivité

Ex



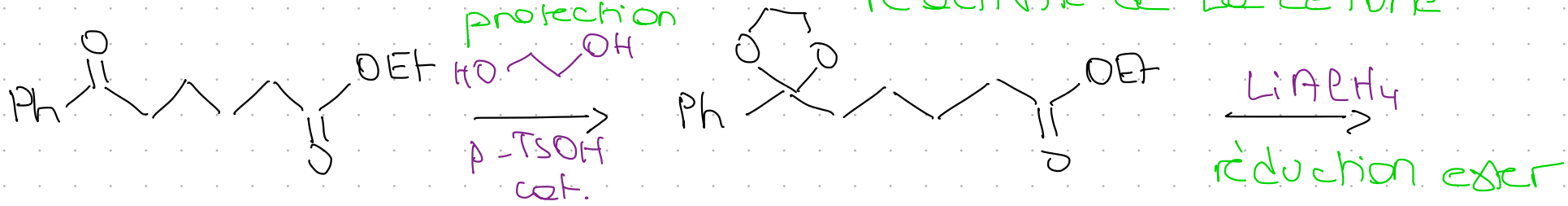
cétone >> ester

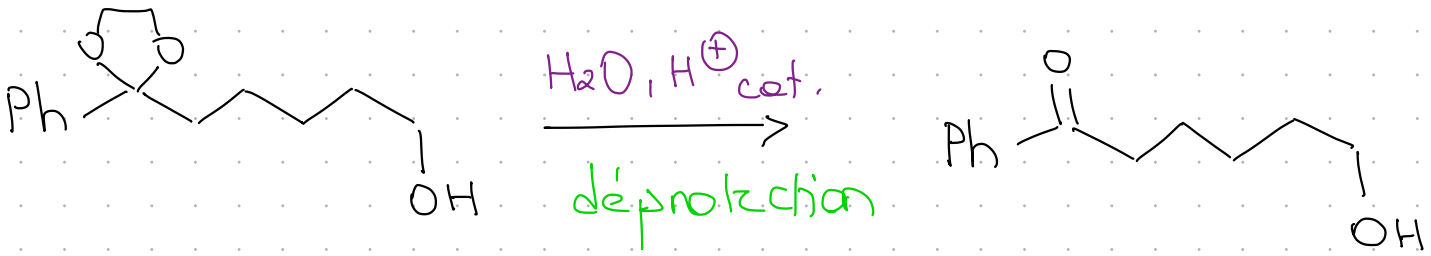
Réduction sélective de La cétone



Réduction sélective de L'ester

masquer temporairement La réactivité de La cétone



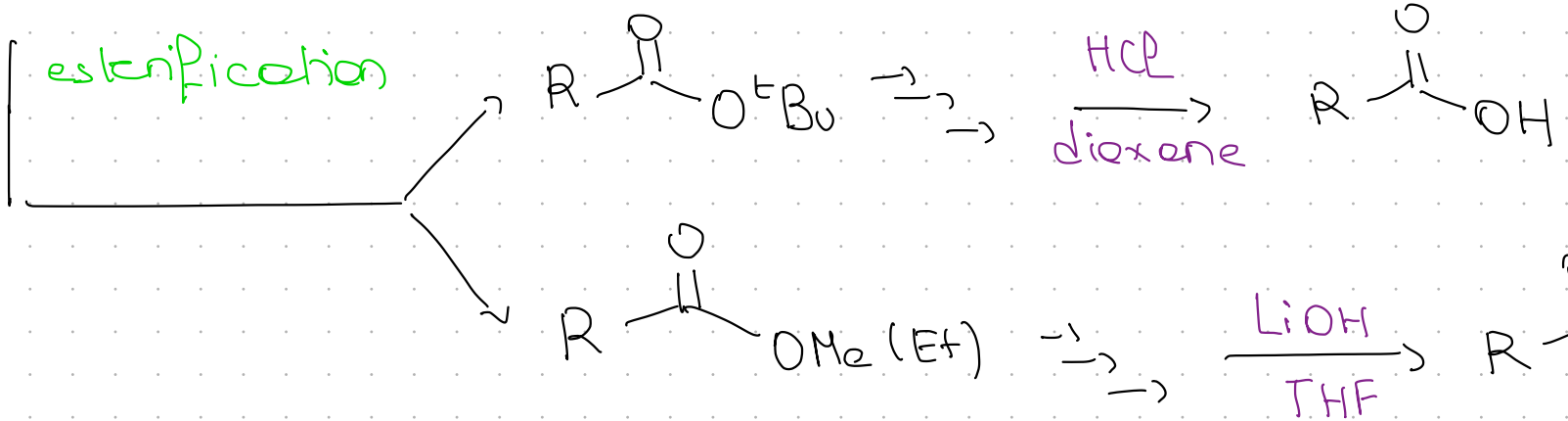


Propriétés d'un groupe protecteur

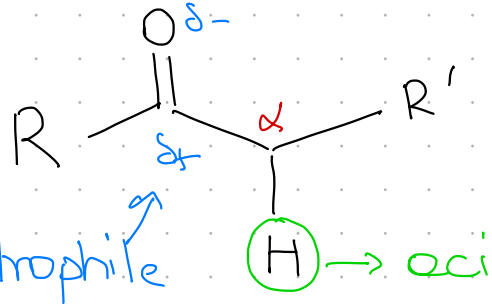
- protection / déprotection : réactions simples et efficaces
- doit résister aux conditions réactionnelles qui auraient affecter la fonction non protégée
- doit résister à de nombreux conditions réactionnelles

II - Acides carboxyliques

- polarité

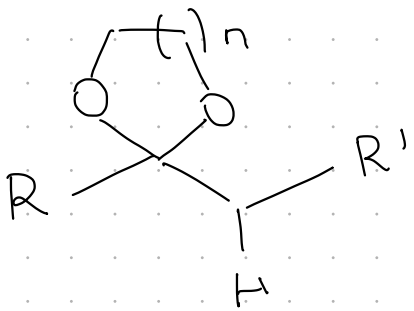


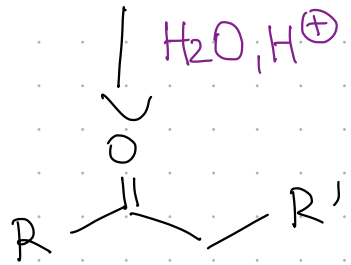
III - Composés carbonylés



acétalisation

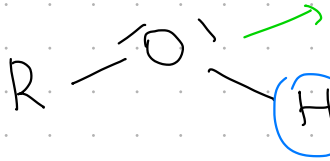
p-TsOH





Alternative : thioacétals

IV - Alcools



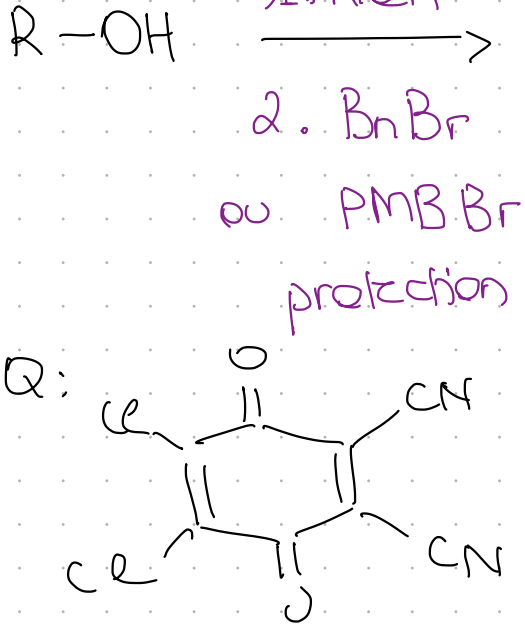
nucléophile, basique

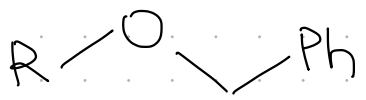
acide faible

protection

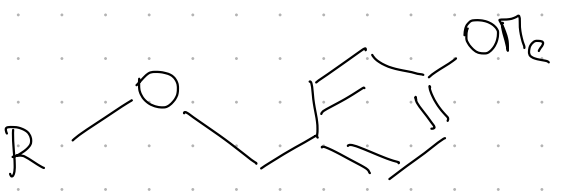
- éthers
  - benzyliques
  - sylilés
- acétals

Ethers benzyliques





ou



R–OBn

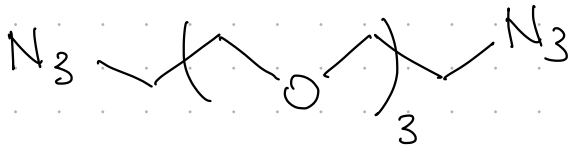
R–OPMB

déprotection
H_2 ; Pd/C cat.

déprotection
[ox] doux
DDQ

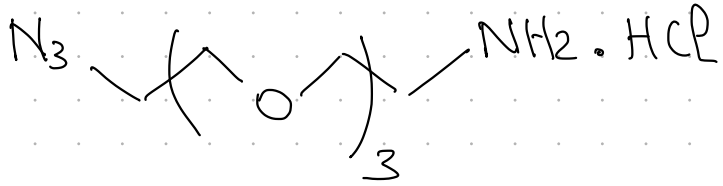
R–OH

R–OH

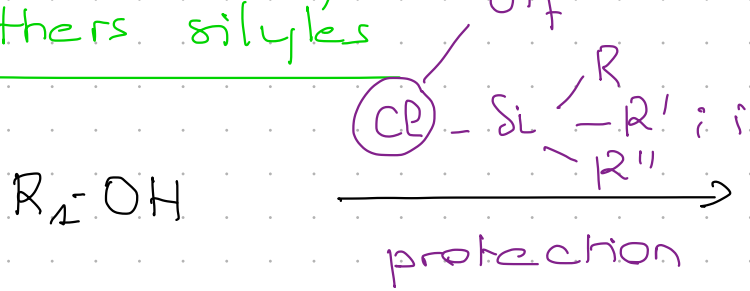


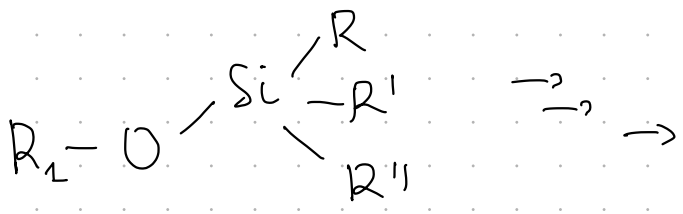
PPh_3

H_2O / toluène
HCl cat.



Ethers silylés





déprotection "F⊖"

- Bu_4NF
- HF aq
- HF. pyridine

$R-OH$

Structure / stabilité

$R-O-SiMe_3$ (R-OTMS)

$R-O-SiEt_3$ (R-OTES)

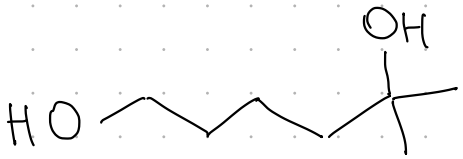
$R-O-Si(t)(t)(t)$ (R-OTBS)

$R-O-Si(iPr)_3$ (R-OTIPS)

$R-O-Si(Ph)(Ph)(t)$ (R-OTBDPS)

stabilité croissante

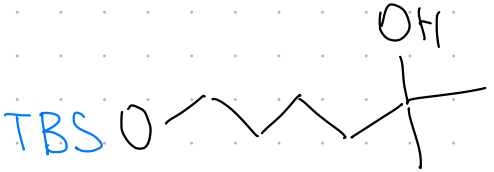
Protection sélective



$Cl-Si(t)(t)(t)$ 1 eq

imidazole

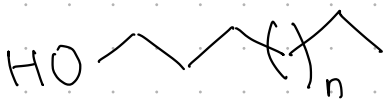
0°C



$Cl-Si(iPr)_3$ 1 eq

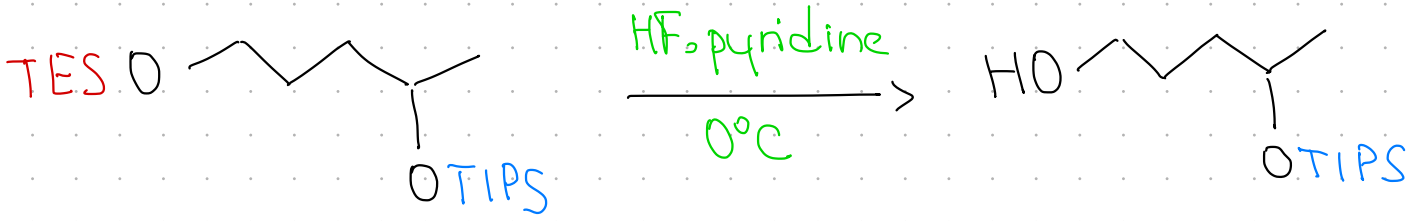
imidazole

0°C

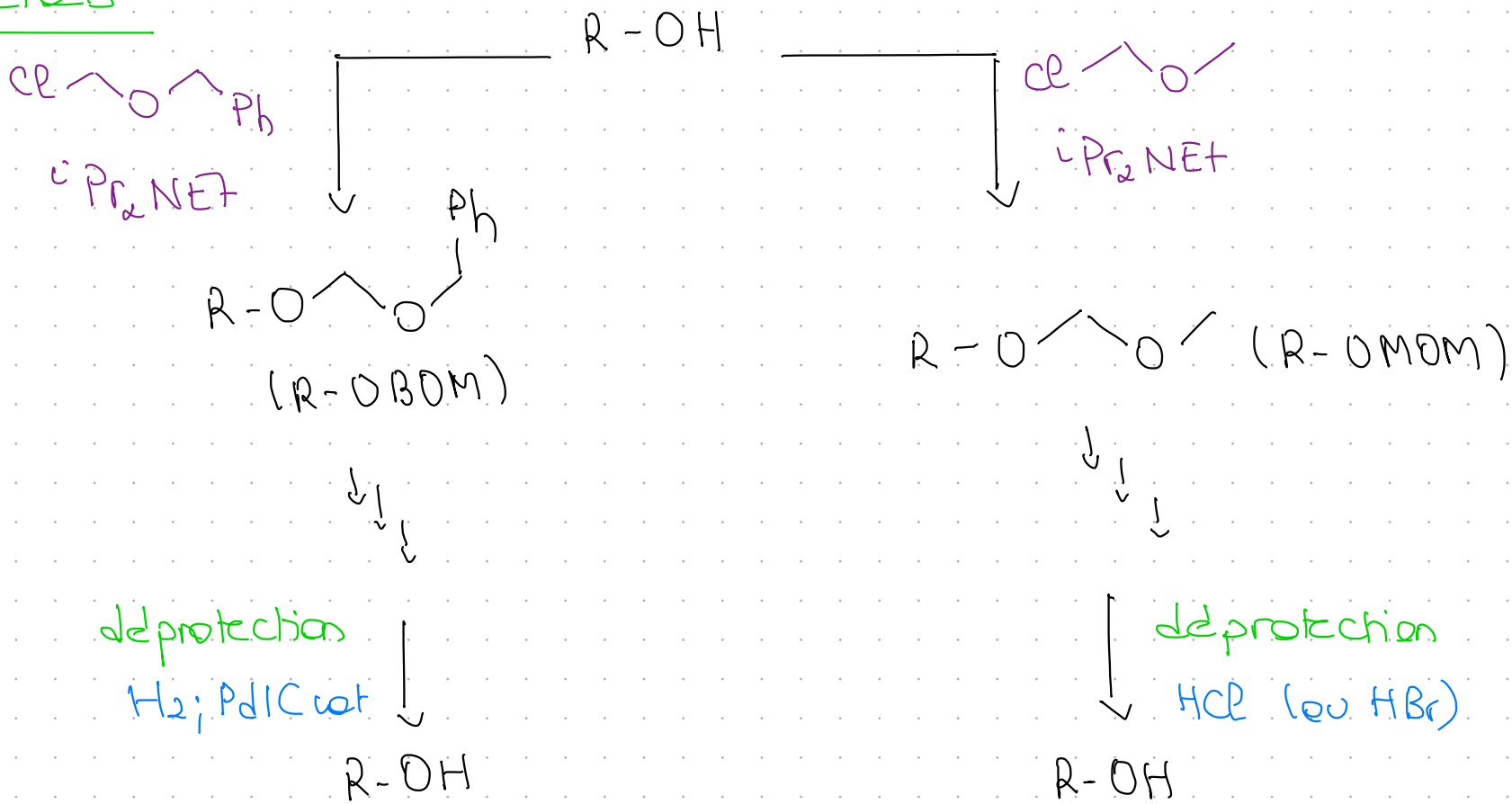


(OPMB)

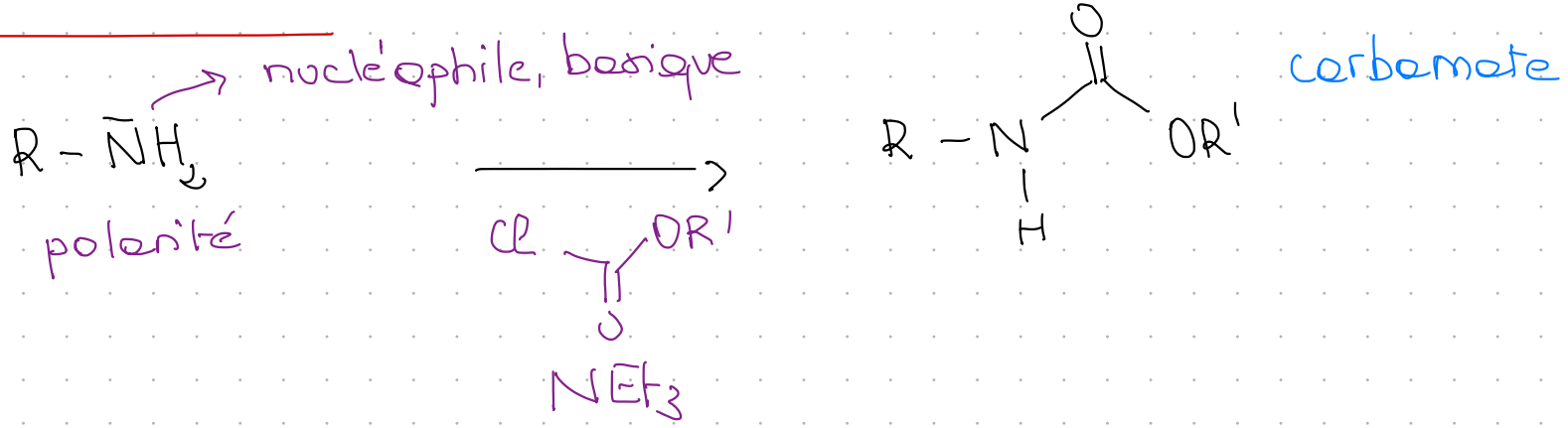
Déprotection sélective



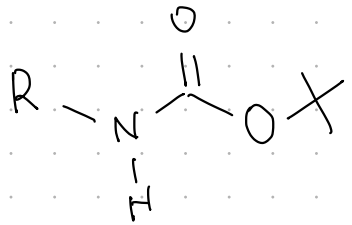
• Acétals



V - Amines



- $R' = {}^{t}Bu$



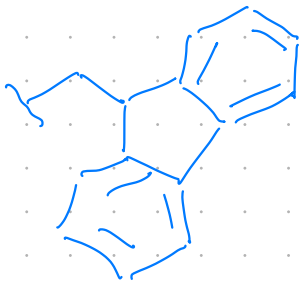
(R-NH Boc)

déprotection

- CF_3CO_2H, CH_2Cl_2
- HCl, dioxane

$R-NH_2$

- $R' =$



$R-NHFmoc$

déprotection

$R-NH_2$