

CH-335 - VII - Composés carbocycliques

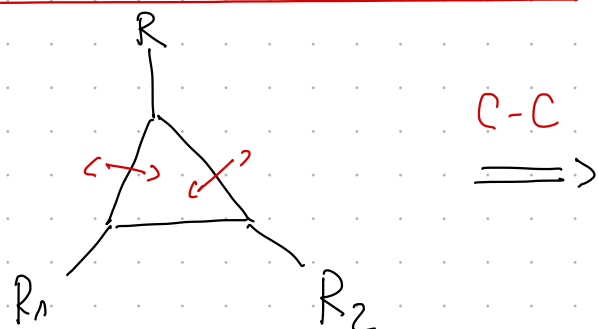
S. Gerber

Spring 2025

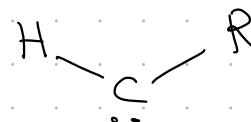


I - Cycle à 3 chaînons

/1



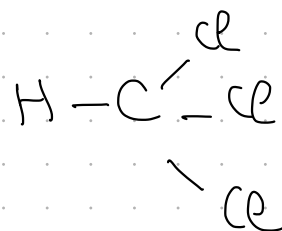
+



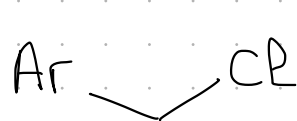
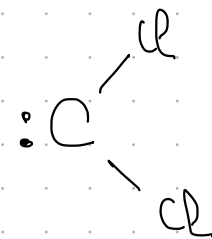
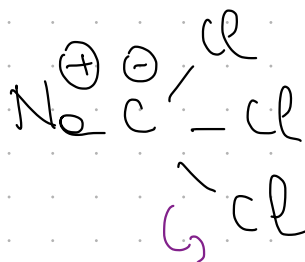
• carbènes
 • carbénoïdes

Préparation des carbènes

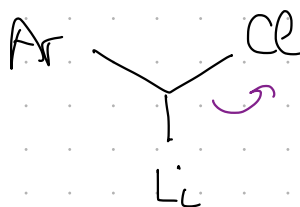
• Elimination - α



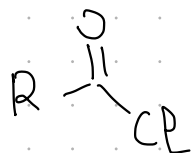
NaOH



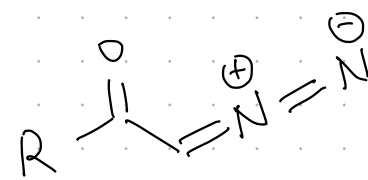
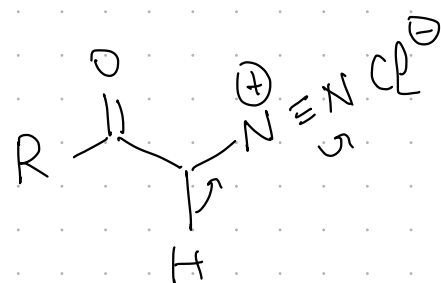
LDA



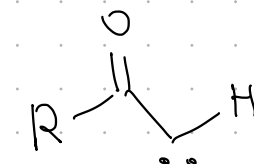
• Acylcarbène



CH2N2

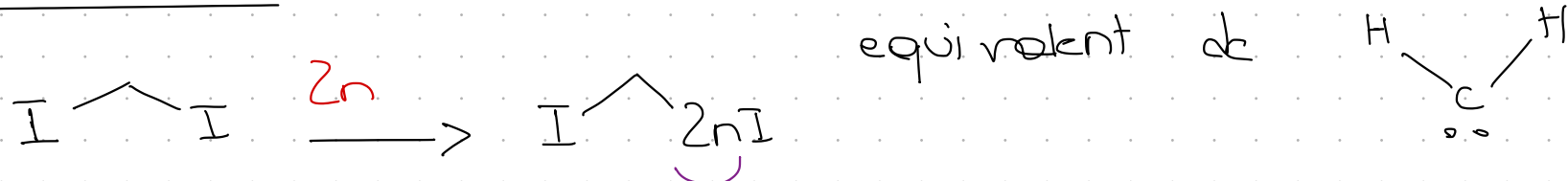


Δ

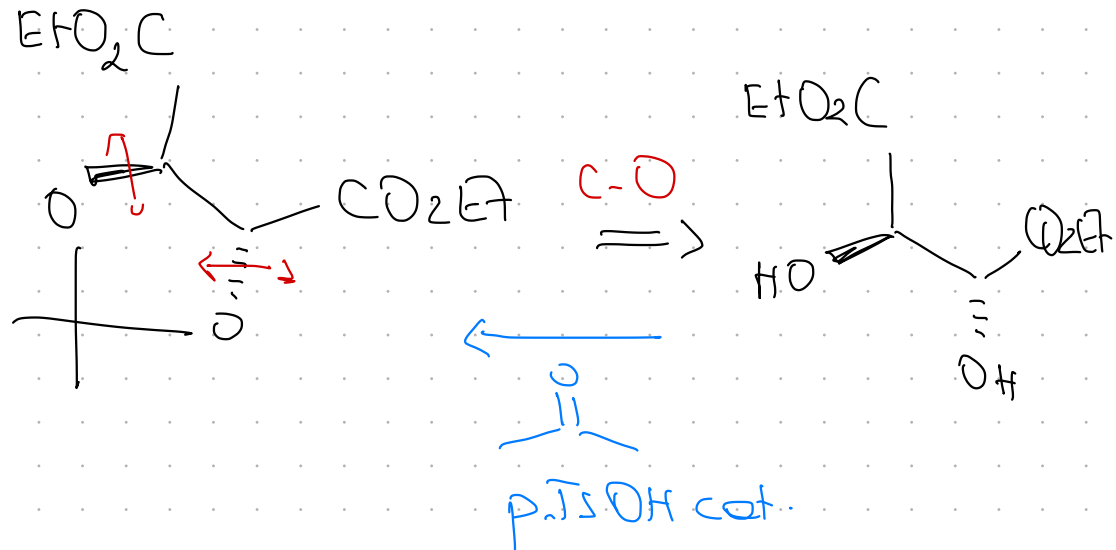
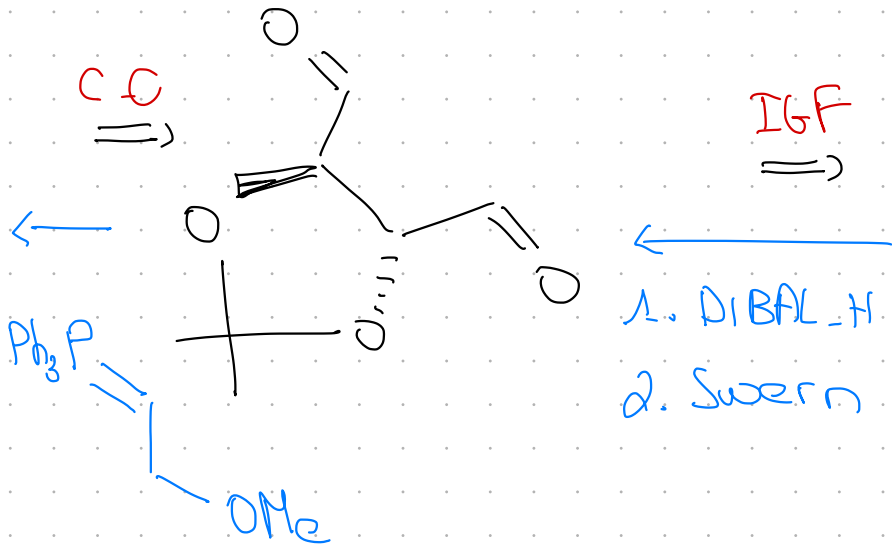
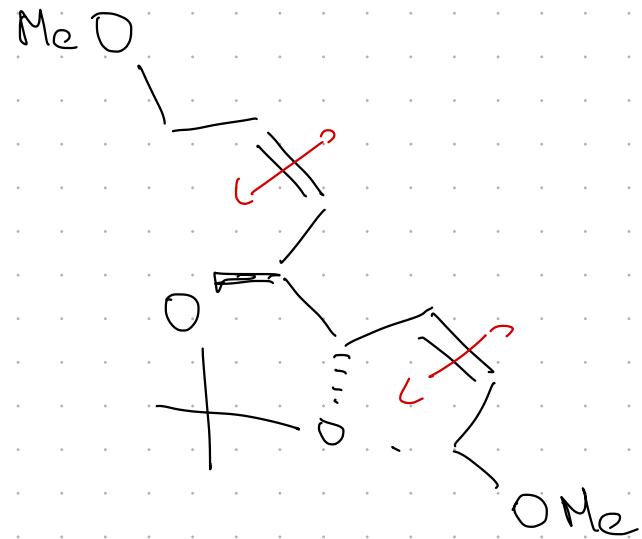
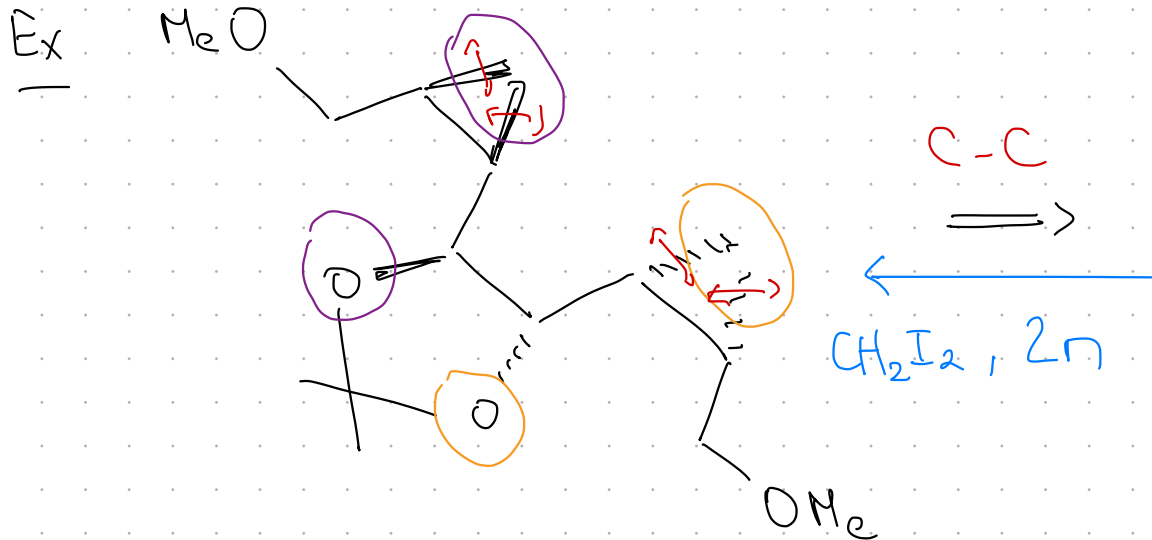


Carbénoides

12

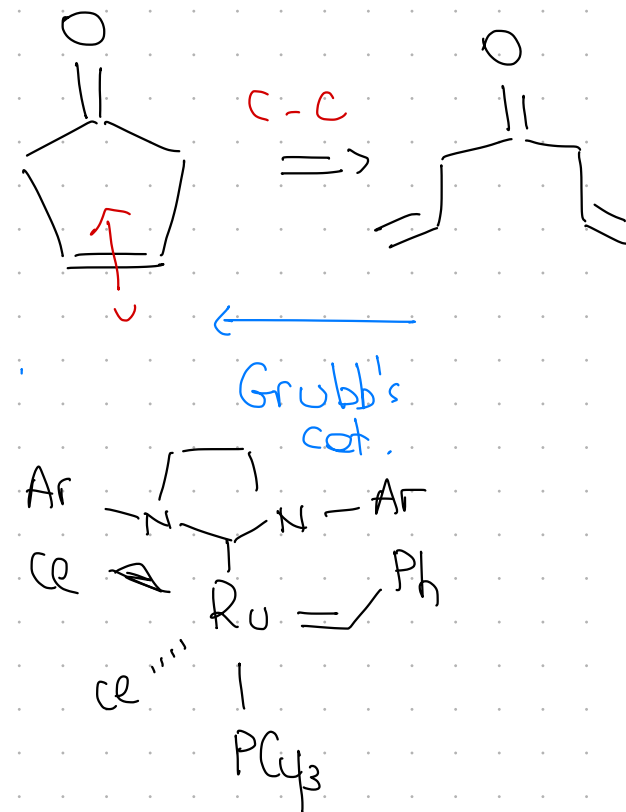
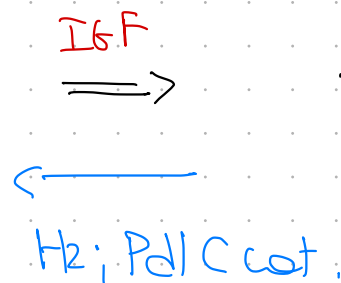
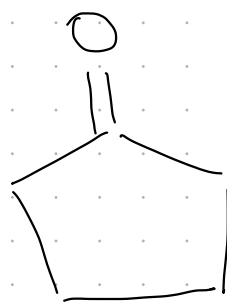
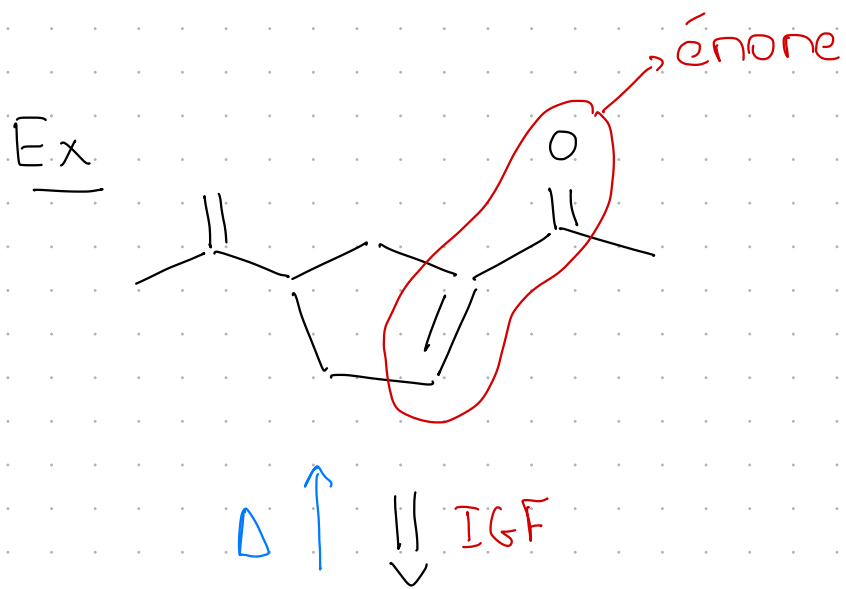
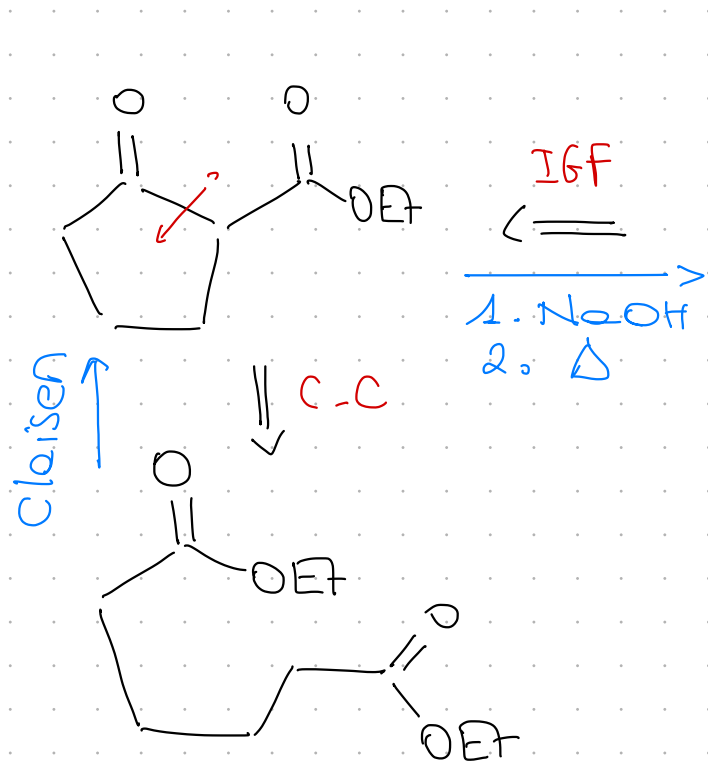


L, chélation d'atomes porteurs de doublets non liants

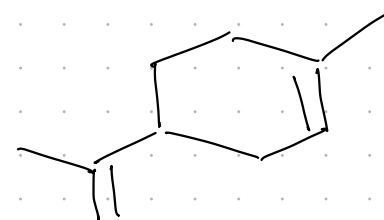


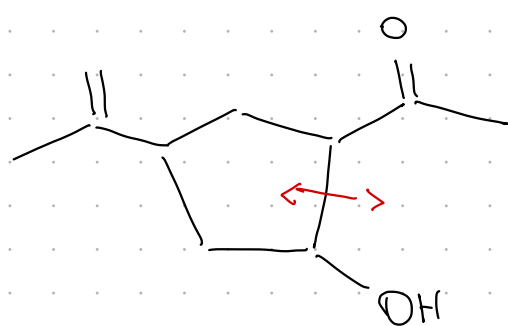
II - Cycles & Schémas

3

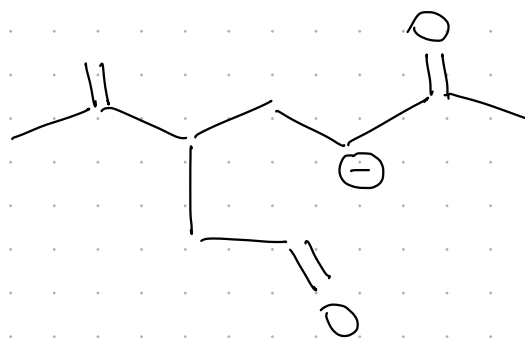


produit de départ





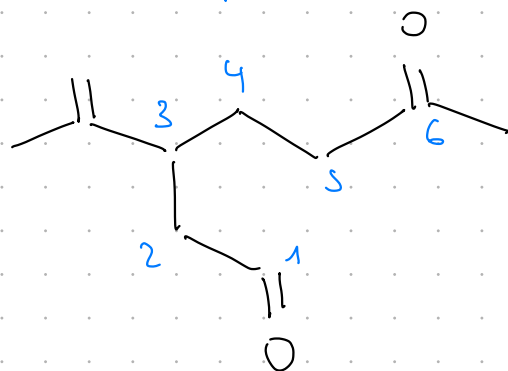
C-C
=>



IGF
=>

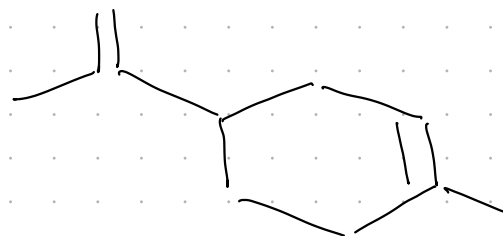
14

↑ NaOH



reconnection

=>

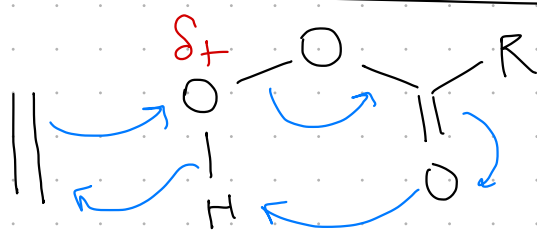


←

1. OsO₄ cat.; NMO

2. Pb(OAc)₄ ou

1. mCPBA, 0°C
2. NaOH
3. NaIO₄

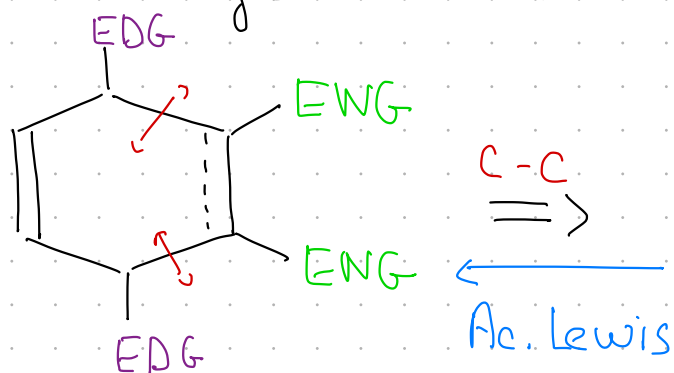


III - Cycles à six chaînons

/5

1) Stratégies correspondant aux cycloadditions de Diels-Alder

- ↳ IGFs jusqu'à retomber sur un cyclohexène / cyclohexadiène
- ↳ 2x C-C (cycloaddition de Diels-Alder)



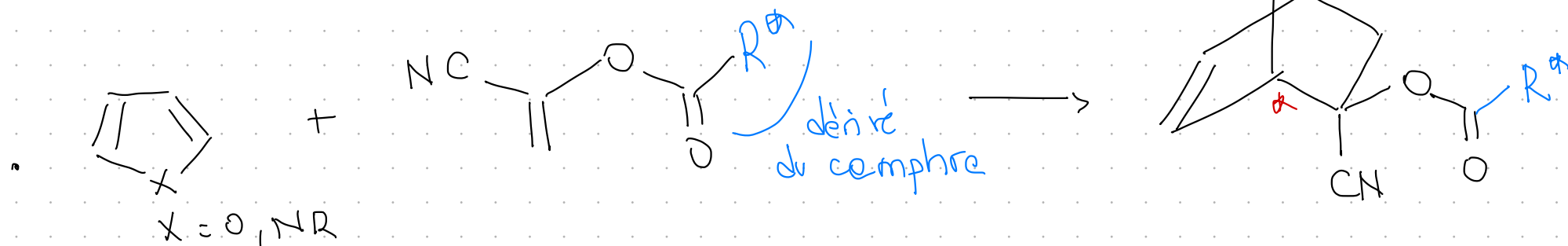
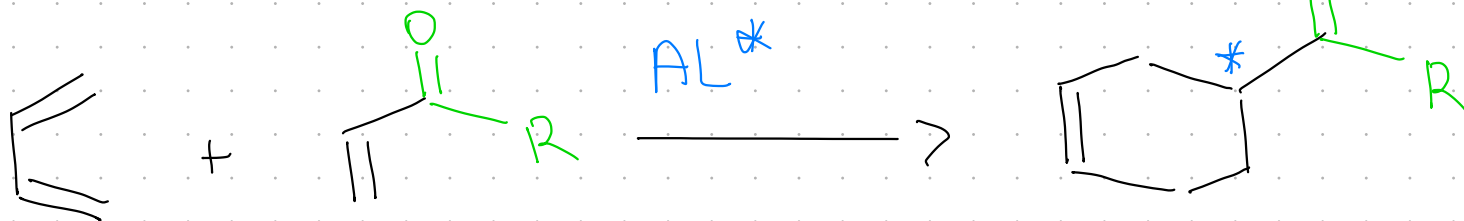
EWG

EWG

- CO_2R
- C(=O)R
- CN
- NO_2

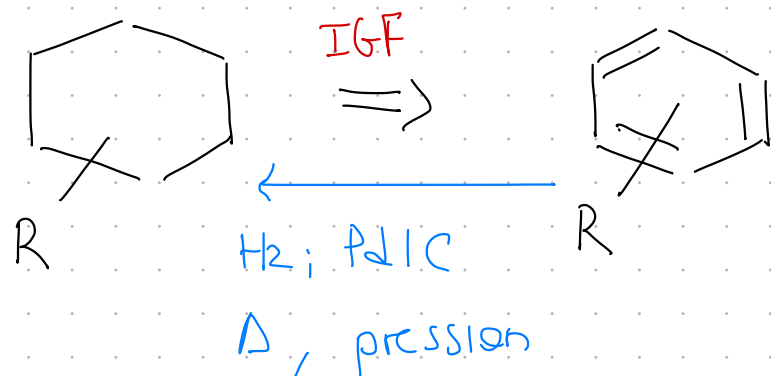
Conservation de la géométrie des produits de départ

Versions asymétriques

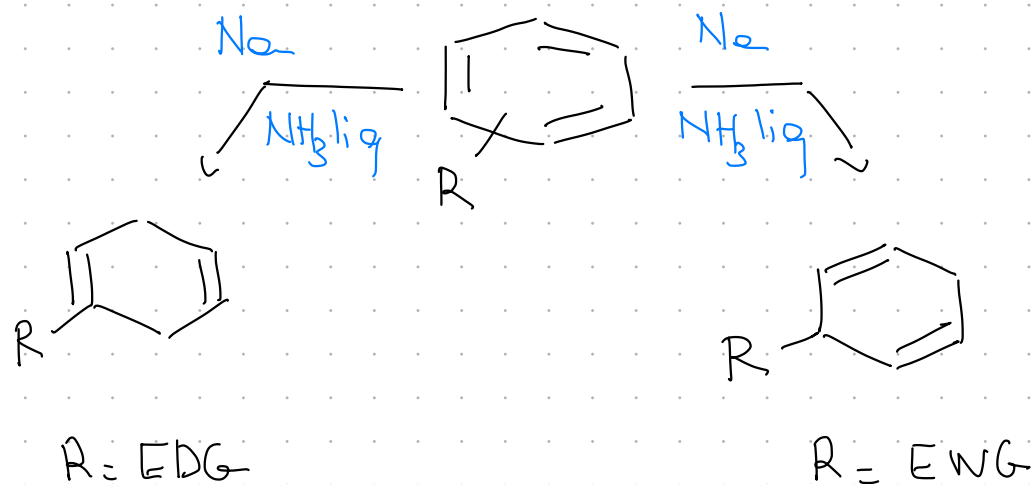


2) Réduction / semi-réduction de composés aromatiques

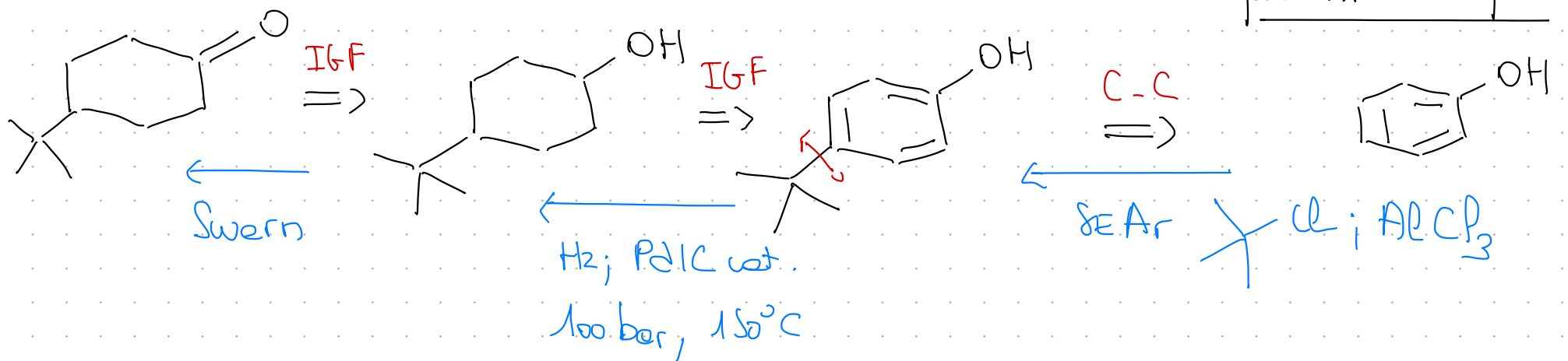
6



Réduction partielle



Ex



IV - Macrocycles

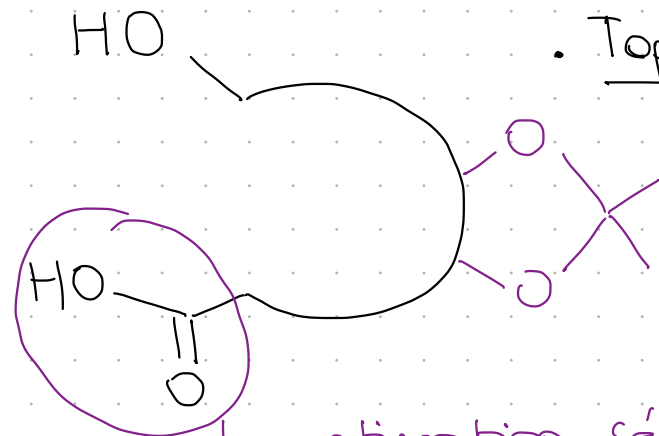
↳ jusqu'à 30 chaînons

1) Macrocyclisation: macrolactonisation

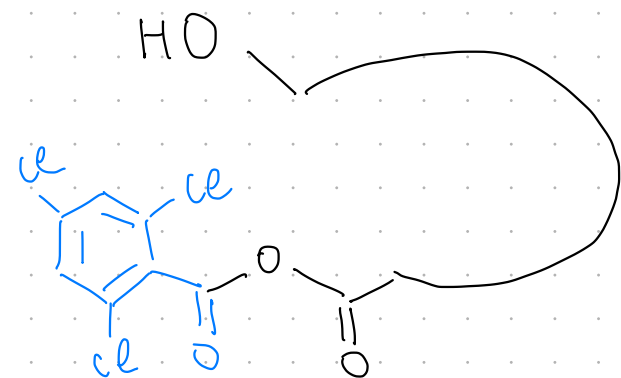
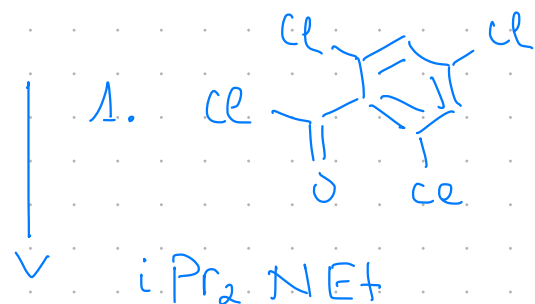
• Topologie : rapprocher les 2 fonctions réactives

- insaturations
- acétals cycliques

• Dilution : $\sim 10^{-4} M$



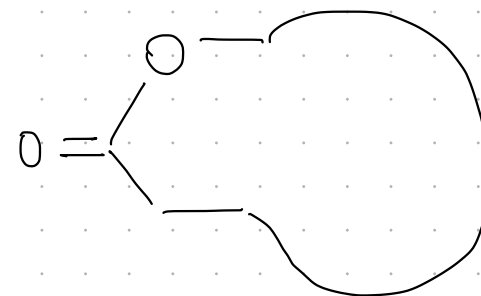
↳ activation sélective



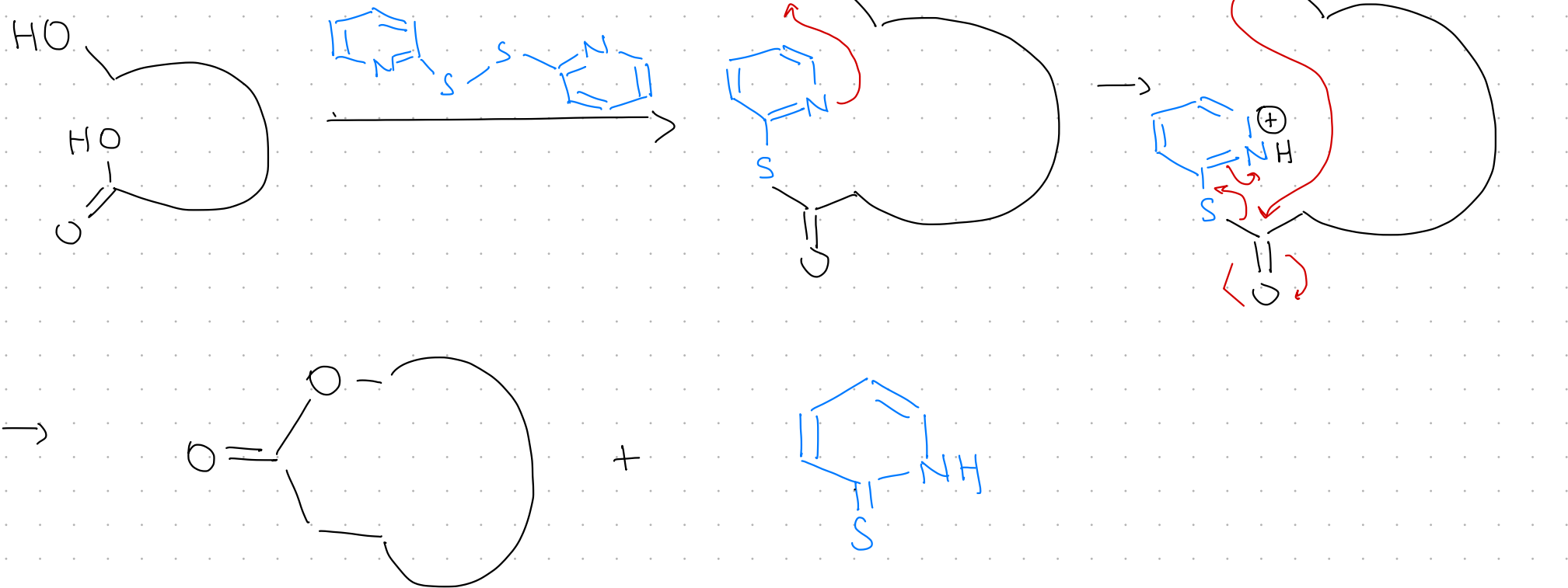
Dilution
(PhMe)

Addition lente
sur une solution
de DMAP

PhMe, reflux

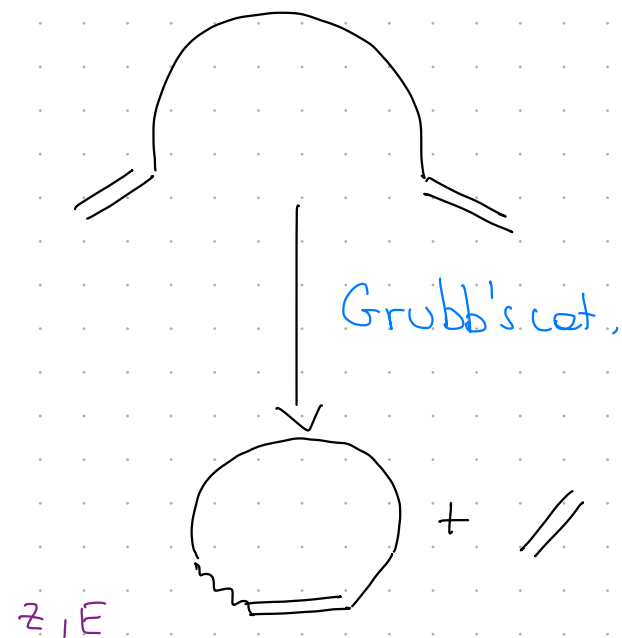


Double activation



2) Métathèse cyclisante

taille de cycles $\left. \begin{matrix} 5-6 \\ 7-9 \end{matrix} \right\} \rightarrow$ double liaison Z
 ≥ 10 : mélange Z/E



Cat:

