CH-335 / Séance de révisions

S. Nicolai
S. Gerber

11.06.2025

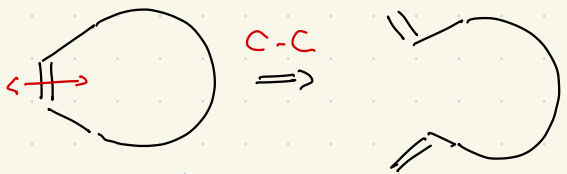
I - Double liaisons

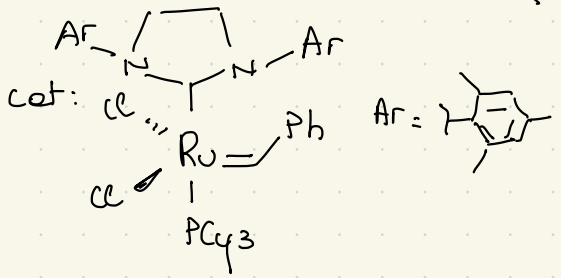
1) Isolées

. Dans un cycle

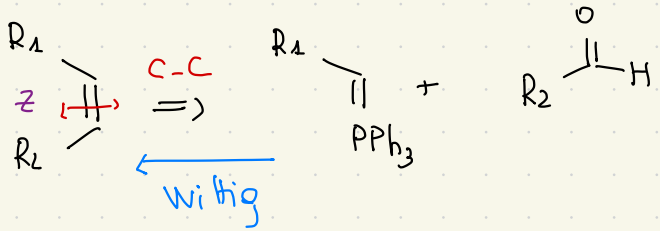
cycles petits/moyens : Z

macrocycles : Z / E



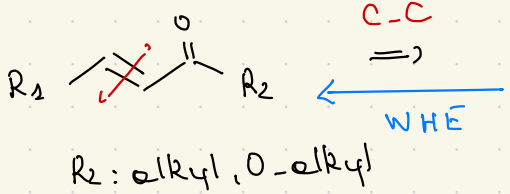


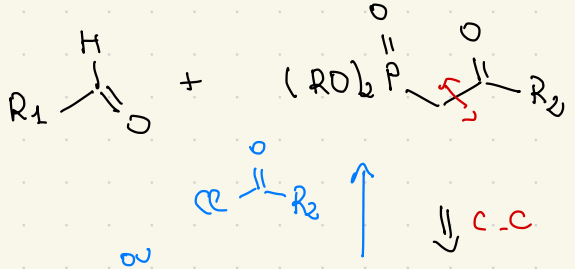
. Dans un système acyclique



E : variant de Wittig - Schlosser

2) Conjugués

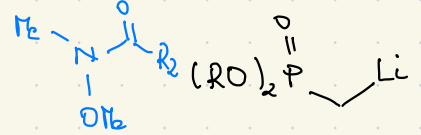




R2 : OMe, OEt commerciaux

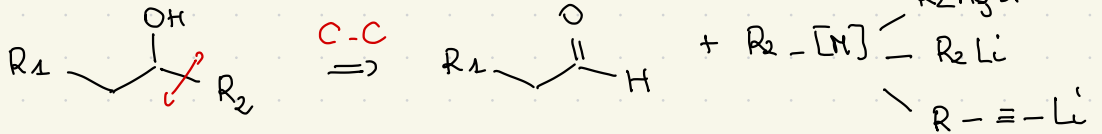
R = Me, Et, tBu

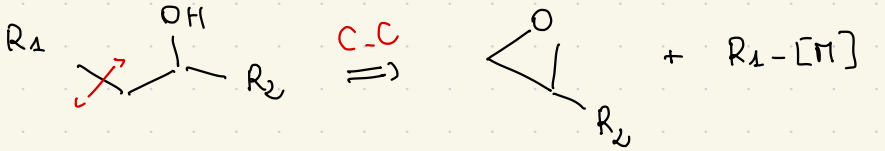
R2 : alkyl



II - Fonctions alcools

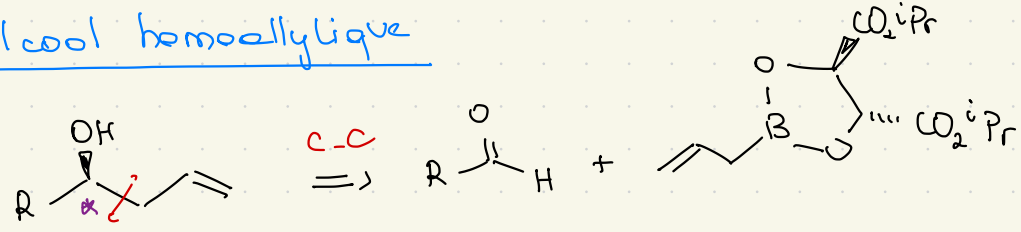
1) Alcool isolé

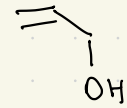




⚠ régiosélectivité de l'ouverture nucléophile

2) Alcool homoallylique

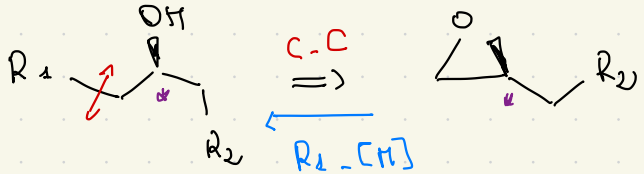




C-O

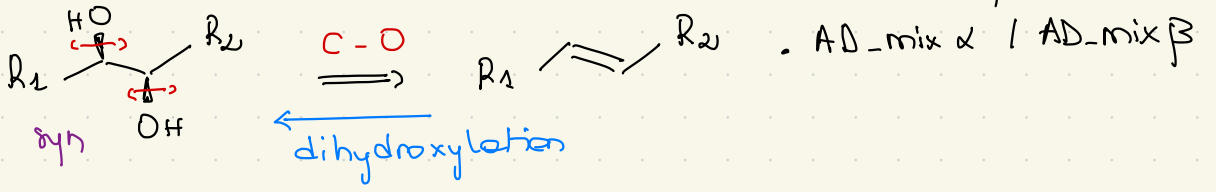
SAE
tBuOOH
Ti(OiPr)4
(+) ou (-)-DET

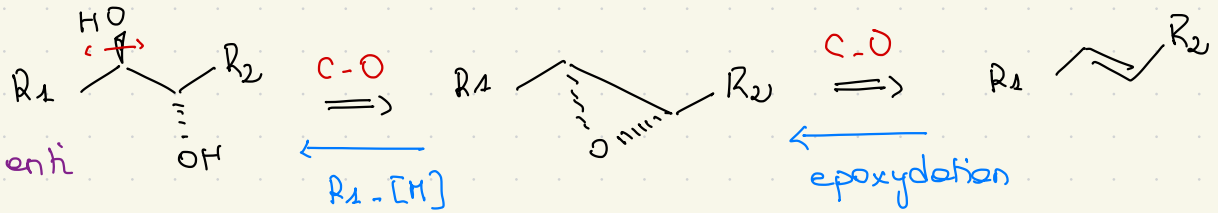
3) Alcool chiral



4) Diols - 1,2

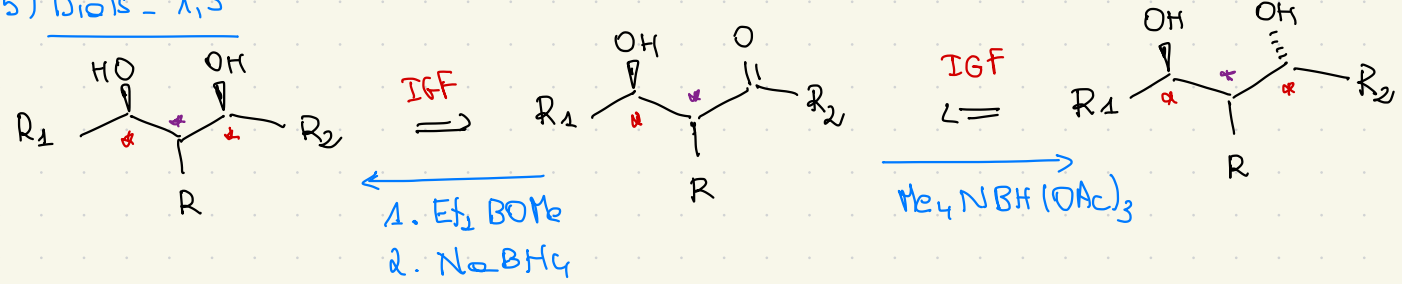
- OsO_4 cat. ; NMO
- AD-mix α / AD-mix β (asymétrique)



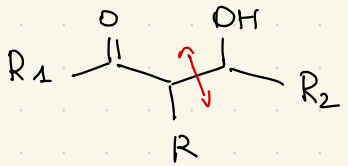


⚠ régiosélectivité de l'ouverture nucléophile

5) Diols - 1,3

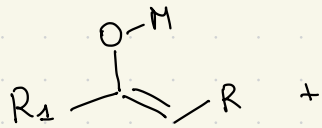


6) β-hydroxycétones

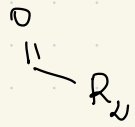


C-C

aldolisation

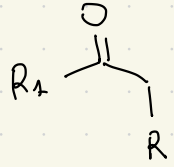


+

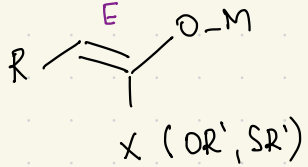


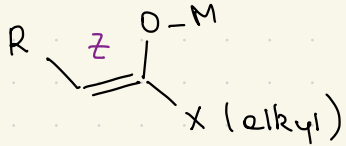
énolisation

|| IGF



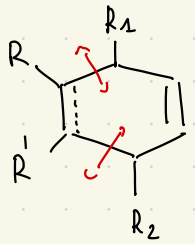
Enolisation
- cinétique
- thermodynamique





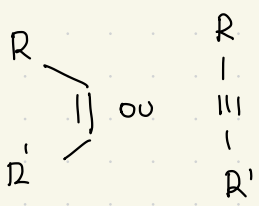
III - Cycles à 6 chaînons

↳ on fait des IGFs jusqu'à atteindre un
- cyclohexène
- cyclohexadiène

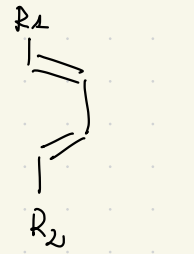


2x C-C

Diels Alder



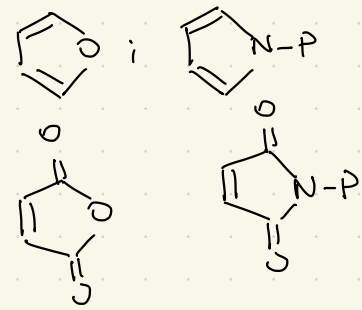
$R, R' = EWG$



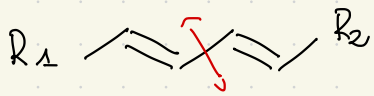
$R_1, R_2 = EDG$

produits de départ cycliques

/5



IV - Couplages croisés

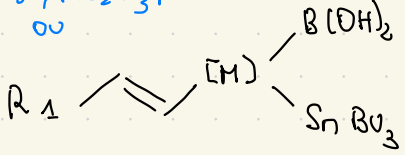


$Pd(PPh_3)_4$ cat.

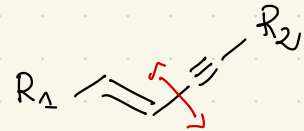
NEt_3 ; Na_2CO_3

ou

|| C-C



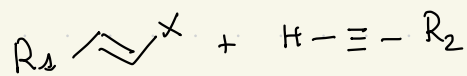
$X = OTf, I, Br$



$Pd(PPh_3)_4$ cat.

CuI ; NEt_3

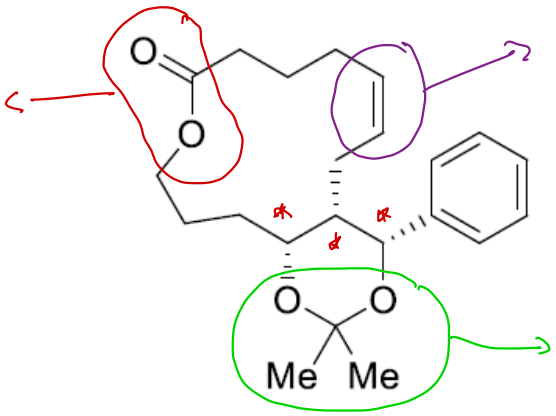
|| C-C



Exemple de Rétrosynthèse

1. Fonctions principales
2. Stéréochimie
3. Disconnection des liaisons les plus fragiles en premier

Procédez à l'analyse rétrosynthétique de la molécule cible dessinée ci-dessous et proposez-en une synthèse.

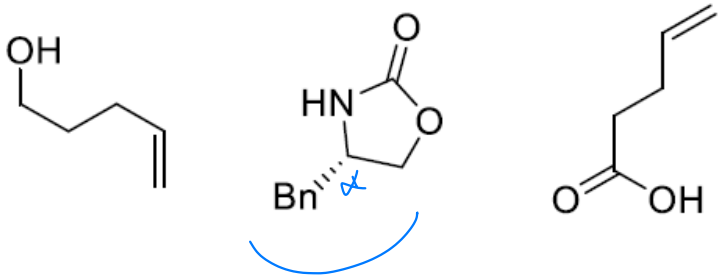


Lactone

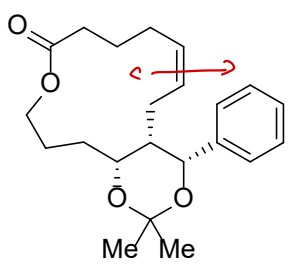
double liaison isolée

acétal ⇒ diol (stéréochimie !)

Composés de départ et réactifs proposés :

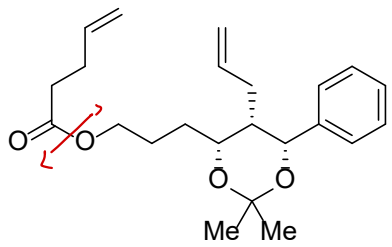


auxiliaire chiral



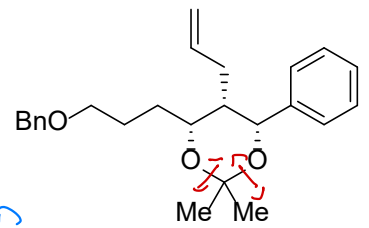
C-C

métathèse cyclisante cat. Grubbs



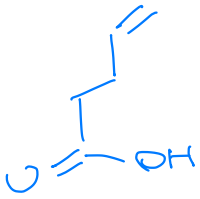
C-O IGF

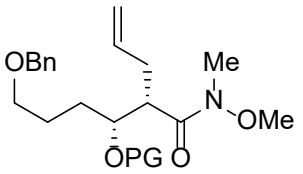
1. déprotection
2. estérification (agent de couplage)



C-O

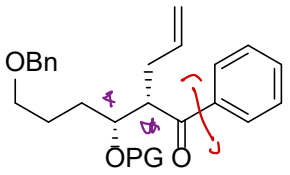
acétalisation ; p-TsOH cat.





C-O

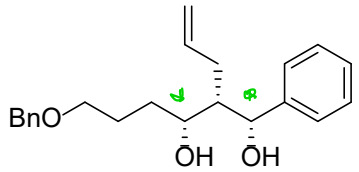
PhMgBr



IGF

[rd] diastéréosélective

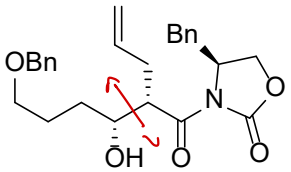
1. Et_2BOMe
2. $NaBH_4$



diol-1,2-syn

1. $ClSi^{i}Pr_2H$
2. $MeNH(OMe)$, $AlMe_3$

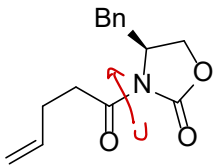
IGF O-Si



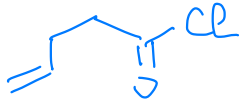
C-C

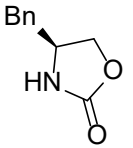
syn-Evans

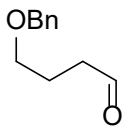
1. Bu_2BOTf, NEt_3
2. RCH



C-N



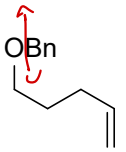




IGF

ozonolyse

1. O_3, -78°C ; 2. Me_2S



C-O

protection

1. NaH
2. BnCl