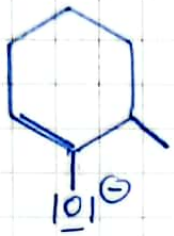
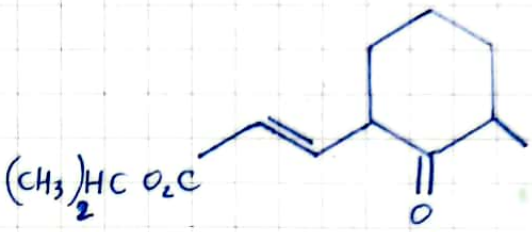
TMC01 - Exercices - corrigé

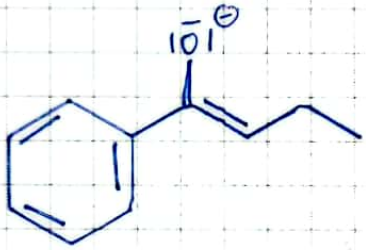
* Uniquement s'il s'agit d'un examen.

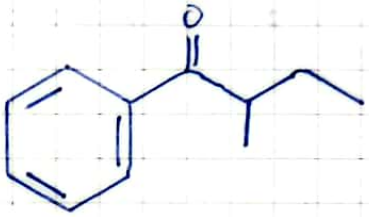
Applications directes du cours

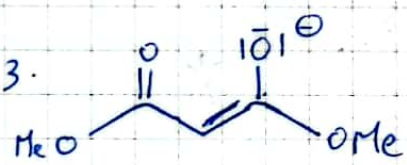
Ex 1

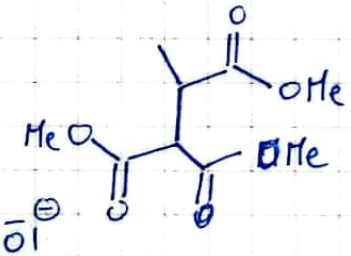
1.  énolate cinétique

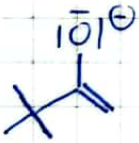
 C-alkylation

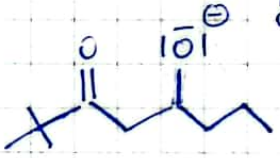
2. 

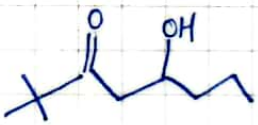
 C-alkylation

3. 

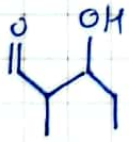
 Réaction de Michael

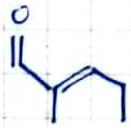
4. 



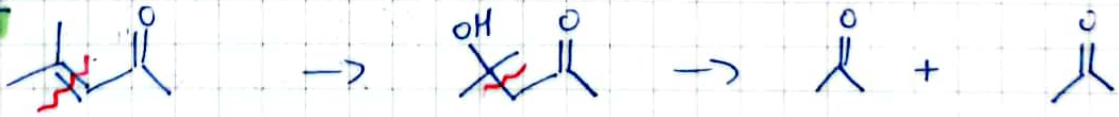


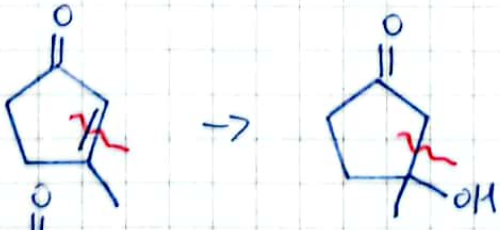
aldolisation croisée dirigée

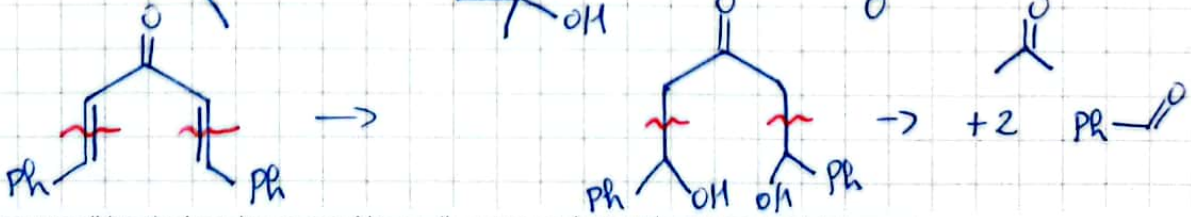
5. 

 condensation aldolique

Exercice 2

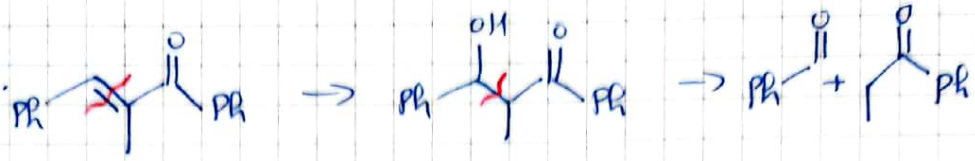
1. 

2.  intramoléculaire

3. 

N° .../...

4. 

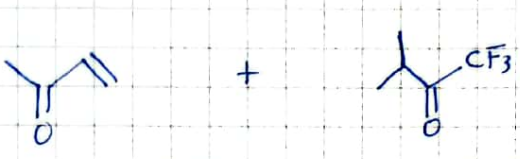
5. 

Conditions operatoire ; 1,2,3,5 : NaOH et Δ

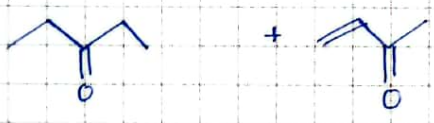
4 : aldolisation croisée dirigée

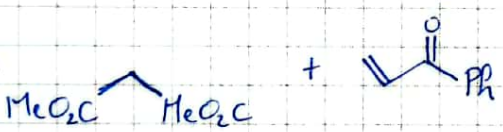
→ 1) LDA, THF 2)  3) NH_4Cl 4) NaOH, Δ.

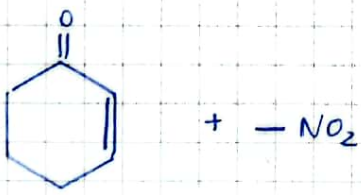
Ex3

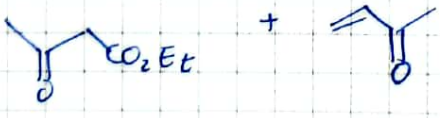
1. 

accepteur de Michael donneur de Michael

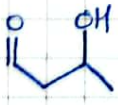
2. 

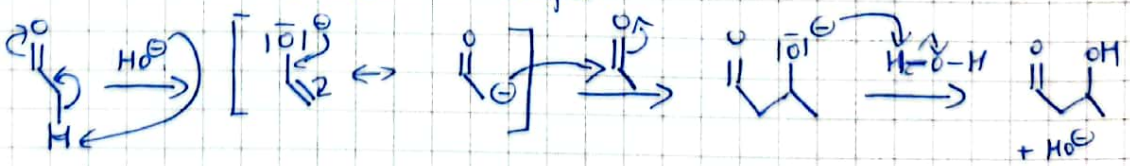
3. 

4. 

5. 

Ex4

1. a.  aldolisation simple



1. b. on obtient le produit de la crotonisation 

on peut se mettre en milieu basique, à chaud pour obtenir le même produit

N° .../...

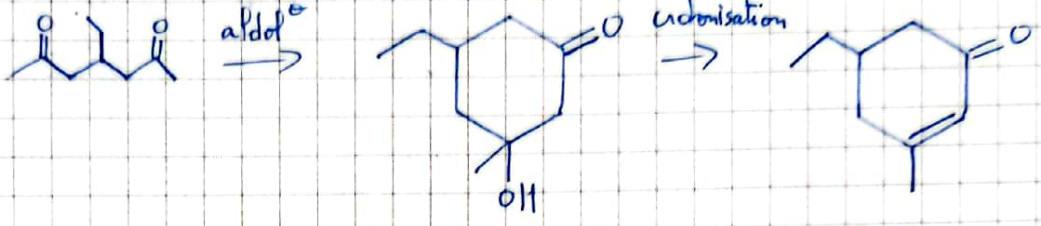
1. c. Le benzaldéhyde n'est pas énolisable

2 on doit faire une aldolisation croisée dirigée

1) LDA, THF

2) éthanal

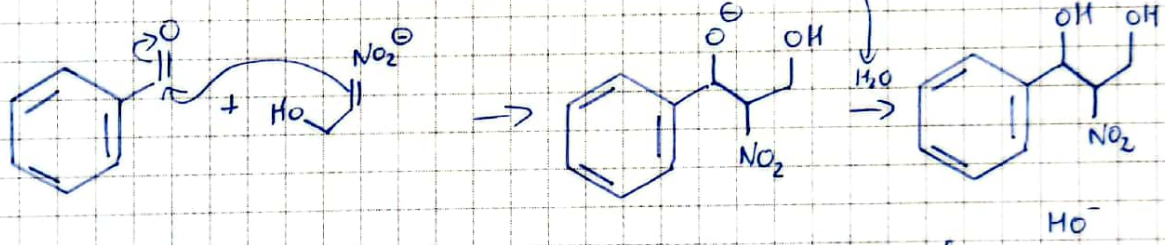
3) NH_4^+ ; Cl^-

3. 

condensation aldolique intramoléculaire $C_9H_{14}O$

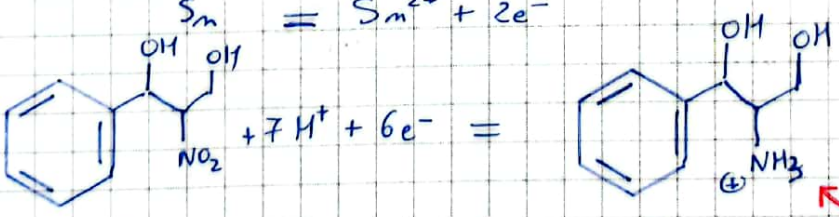
Ex 5

1. H labile car la base conjuguée est très stable par mésomérie

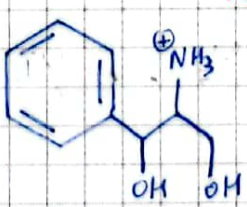
2 

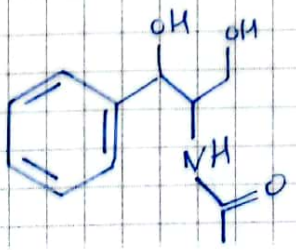
3. même méthode que pour obtenir A mais avec du méthanal

4. $Sn = Sn^{2+} + 2e^-$



⚠ ce n'est pas B, c'est l'intermédiaire avant action de la soude

$3\,Sn + A + 7H^+ = 3\,Sn^{2+} + 2H_2O$ + 

5. 

amide.

l'amine est plus nucléophile que l'alcool → N réagit sur le chlorure

N° .../...

S'entraîner

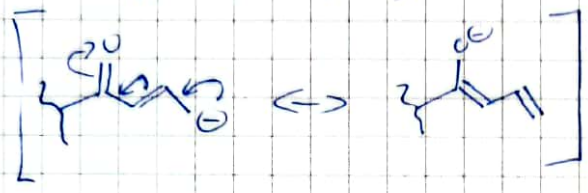
ne rien écrire dans la partie barrée

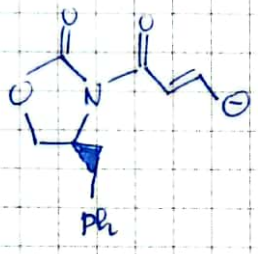
Ex 1

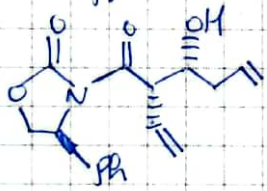
1. Configuration S

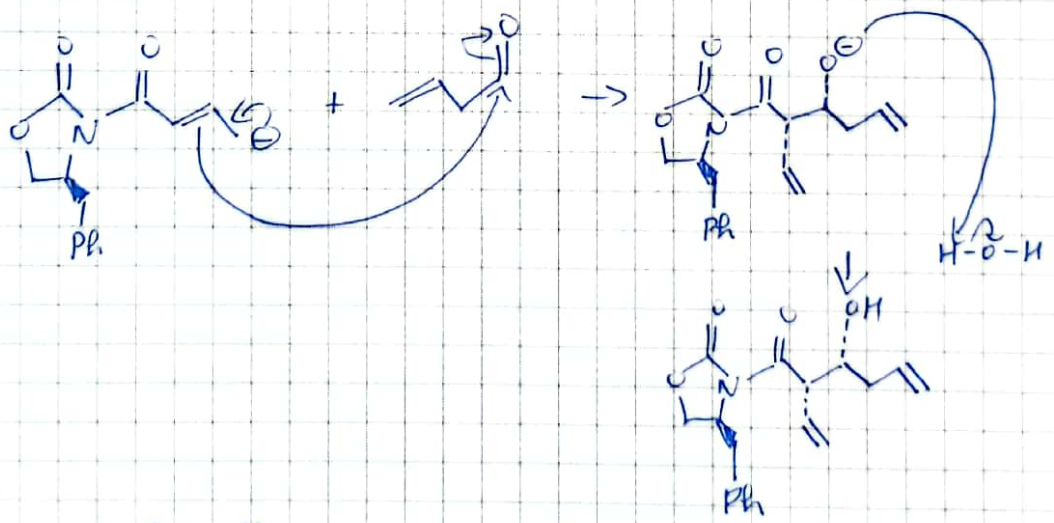
2. Il s'agit surement d'éthanol. Distille. permet de déplacer l'équilibre pour produire B

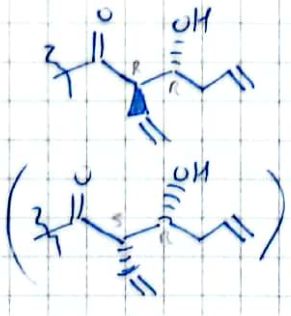
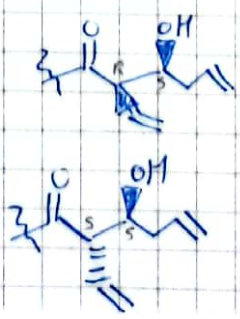
3. On peut utiliser du chlorure de thionyle
le chlorure d'acyle est plus réactif que l'acide carboxylique
(c'est plus électrophile)

4.  ⇒ H au bout du groupe éthyle

5. 

6. On s'appuie sur le document de fin d'exercice.


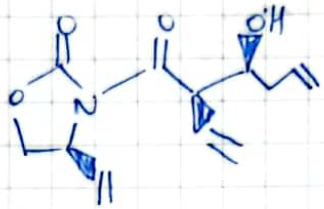
7. 

8. 

ils sont tous diastéréoisomères

N° .../...

* Uniquement s'il s'agit d'un examen

9- On obtient majoritairement l'énantiomère de K



Ex2.

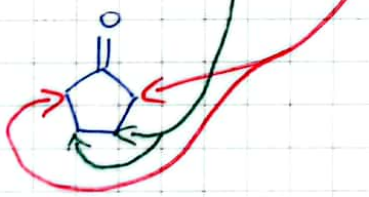
1. Bande IR à 1745 cm^{-1} => C=O

nb insaturations $n = \frac{(2\times5+2)-8}{2} = 2$ => autre insaturation en plus de C=O, on peut soupçonner un cycle

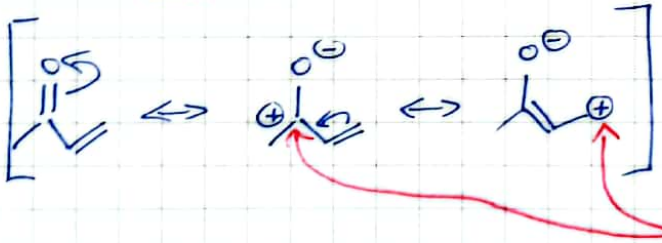
4 H avec deux voisins

4 H avec plus de voisins

=>



2.



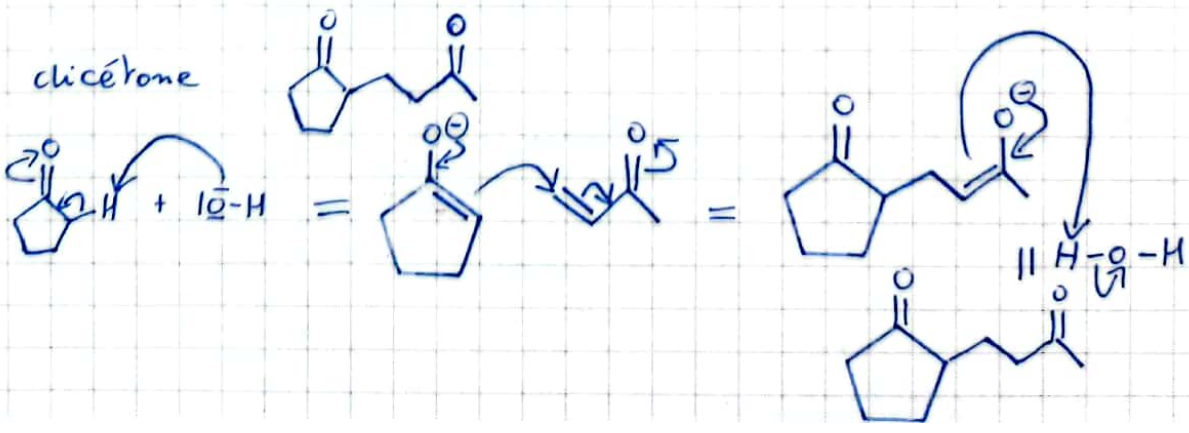
sites électrophiles

3. L'addition Nu se fait sur la BV de B, c'est à dire Ψ_4

=> le plus gros coefficient est sur C_{i4}.

4.

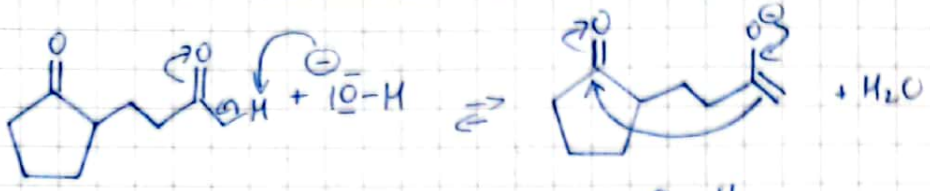
clicétone



N°

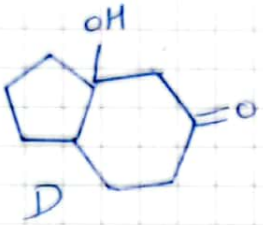
.../...

5.

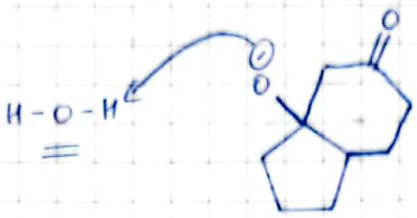


+ H_2O

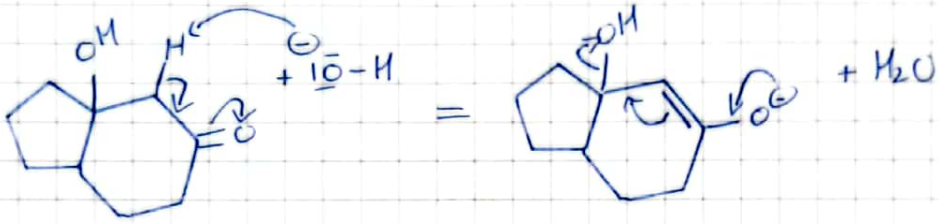
II



D



6

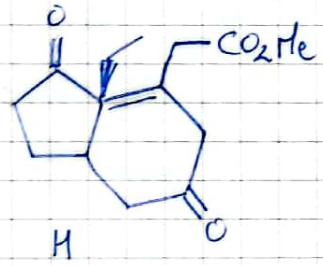


+ H_2O

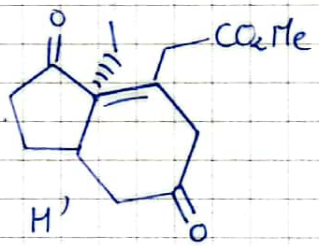
II

E

7.



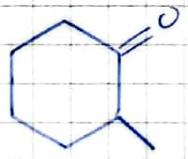
H



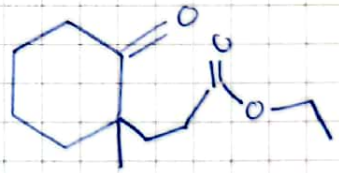
H'

Ex3

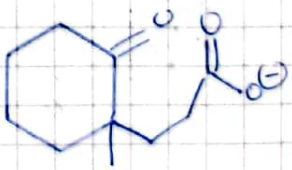
1. A' → (étape a : C-alkylation sur énolate cin)



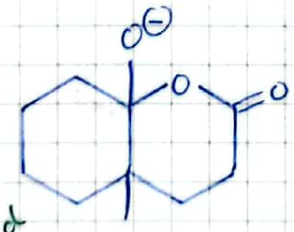
→ (étape b : C-alkylation sur énolate thermo) ⇒ étape régiosélective



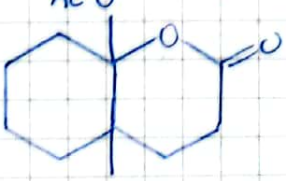
→ (étape c : saponification)



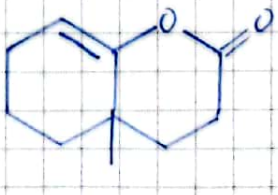
→ (étape d : addition Na)



→ (étape d : AN/E sur Ac_2O)

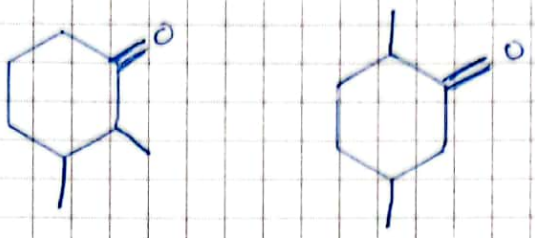


→ (étape d : Elimination AcO^-)

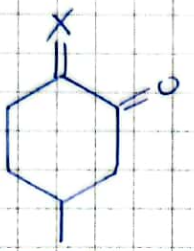


N° .../...

2. Pour l'étape 1, on peut obtenir 2 régioisomères

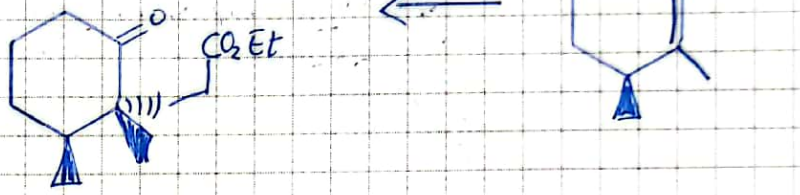


3. Etapes 1 et 2 pour protéger un carbone en α de C=O



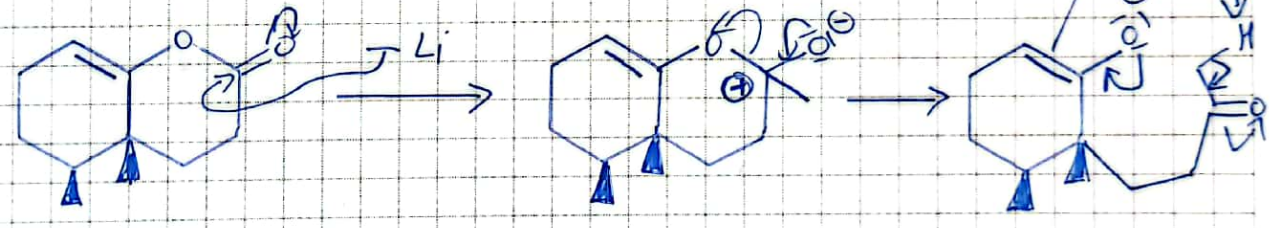
cétone protégée

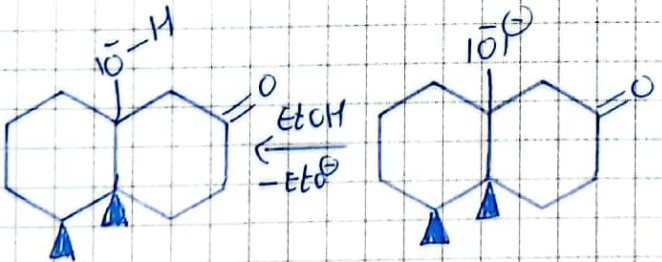
A l'étape 4, le dérivé bromé attaque la face la moins encombrée de l'énolate, en anti du méthyle

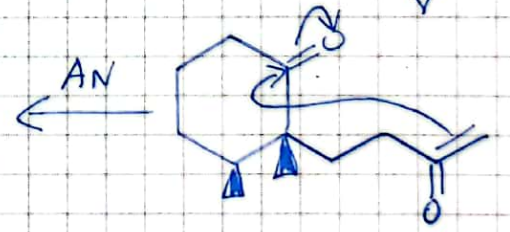


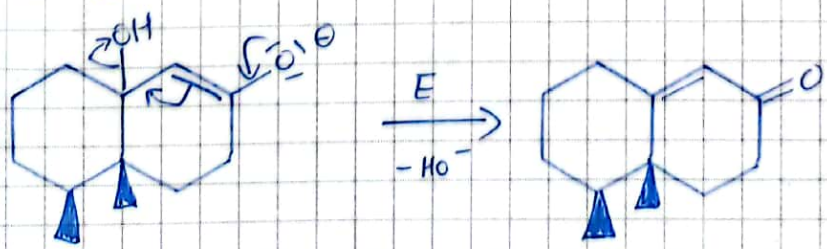
Etape 5 : déprotection

4.



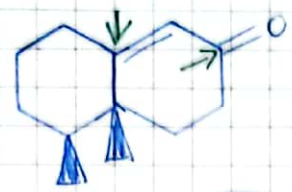






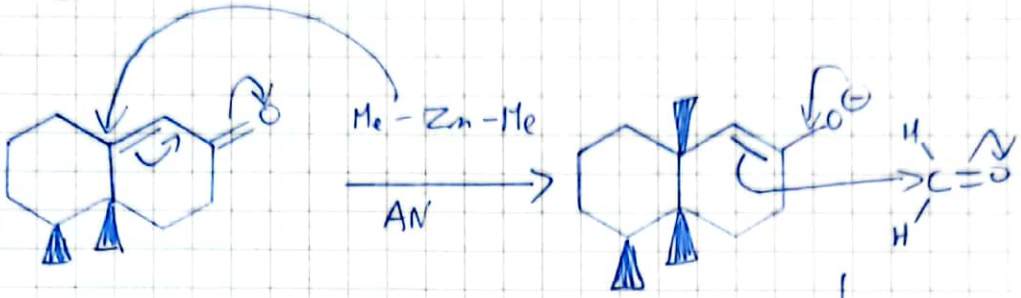
N° .../...

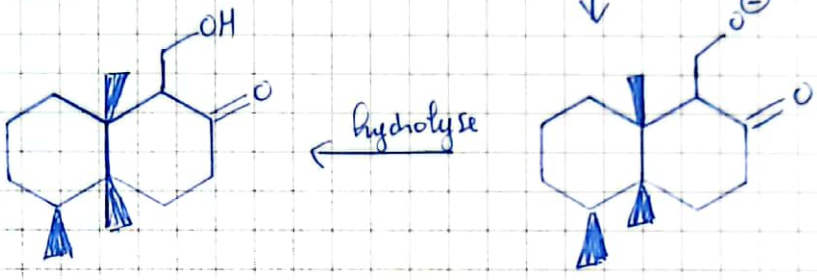
5- C comple e site électrophiles



Me - Zn - Me comporte

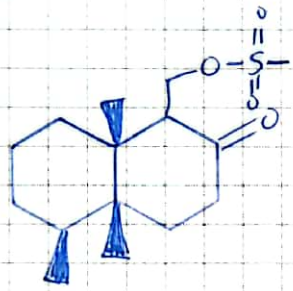
2 groupes Me nucléophiles





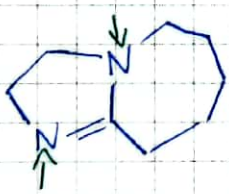
ne rien écrire dans la partie barrée

6.

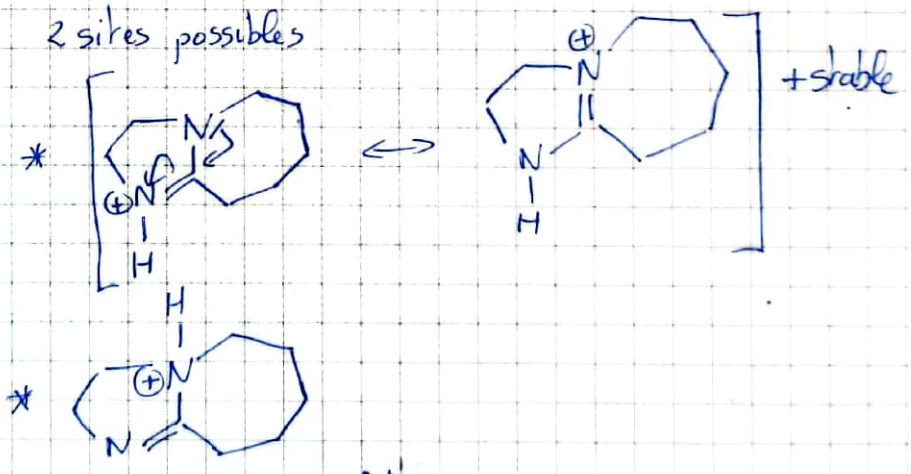


iPr_2EtN est une base qui piège le produit HCl (iPr_2EtNH^+, Cl^-)

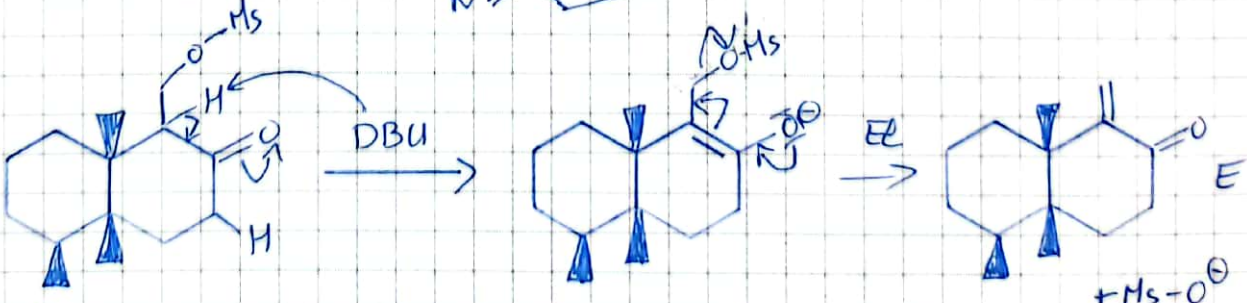
7.



2 sites possibles



8



D'

attaque sur ce H car carbanion stabilisé par mesomerie

N° .../...

Note : /20

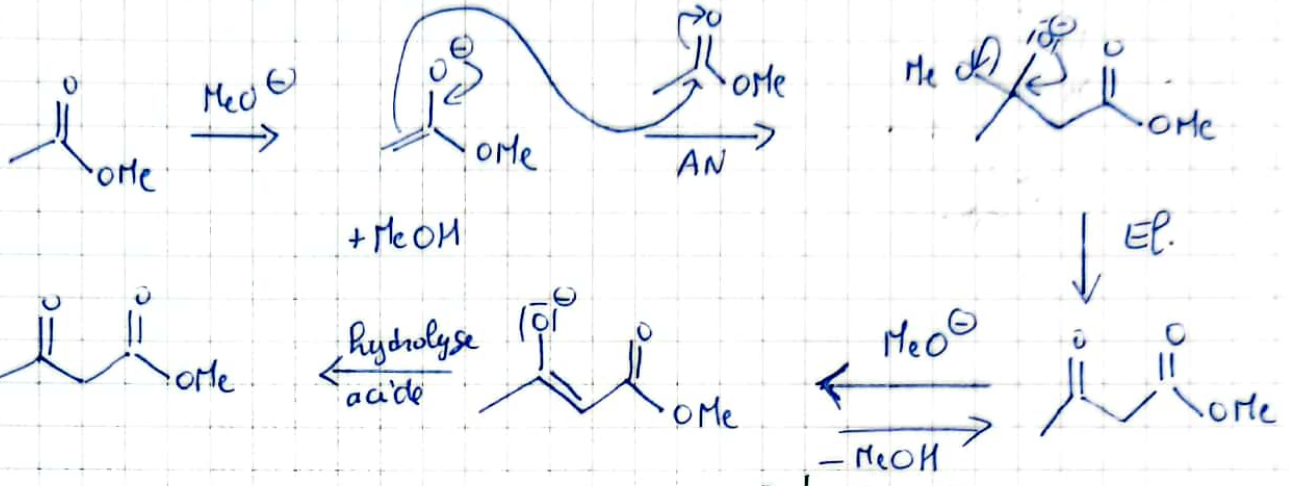
Appréciation du correcteur (uniquement s'il s'agit d'un examen) :

TMCO1 - Exercices - Corrigé.

* Uniquement s'il s'agit d'un examen.

Ex 4.

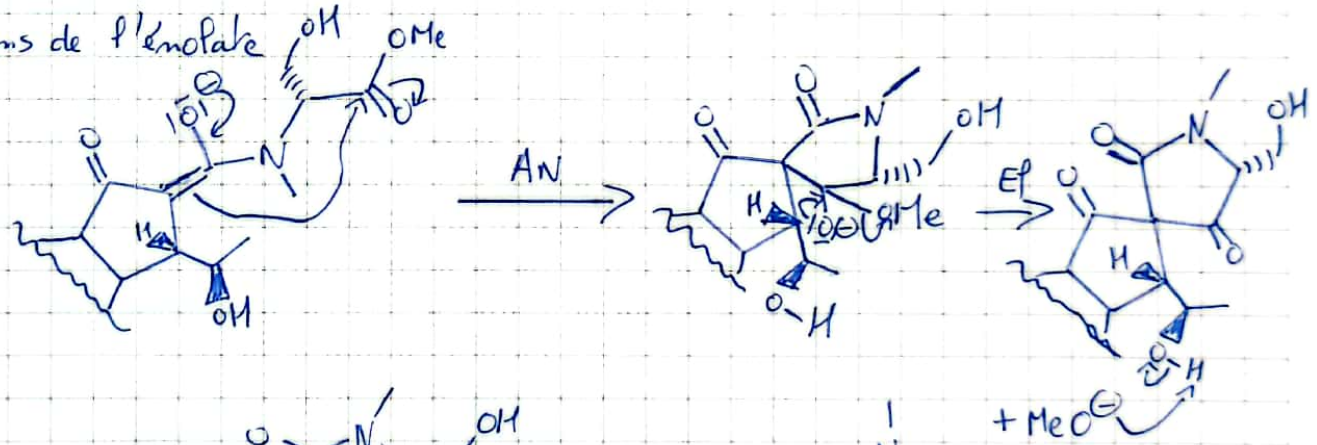
1.

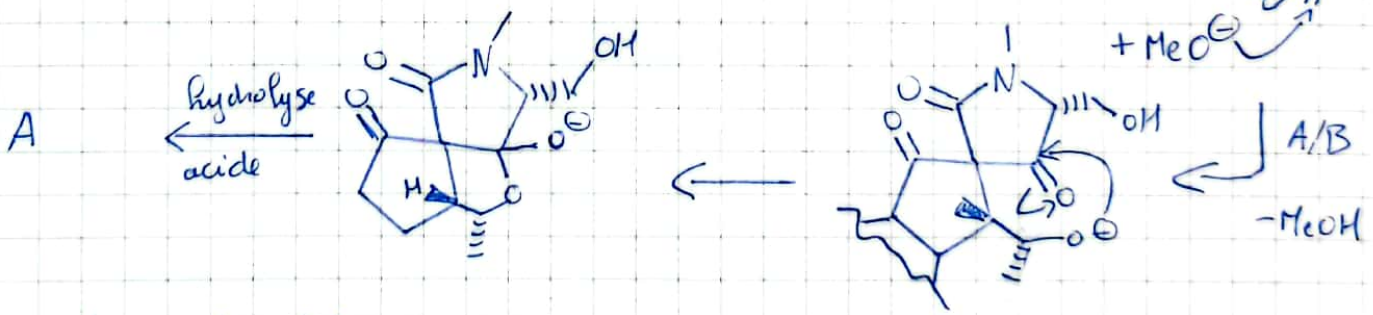


Tant que pas hydrolyse acide (déplacé sens 1)

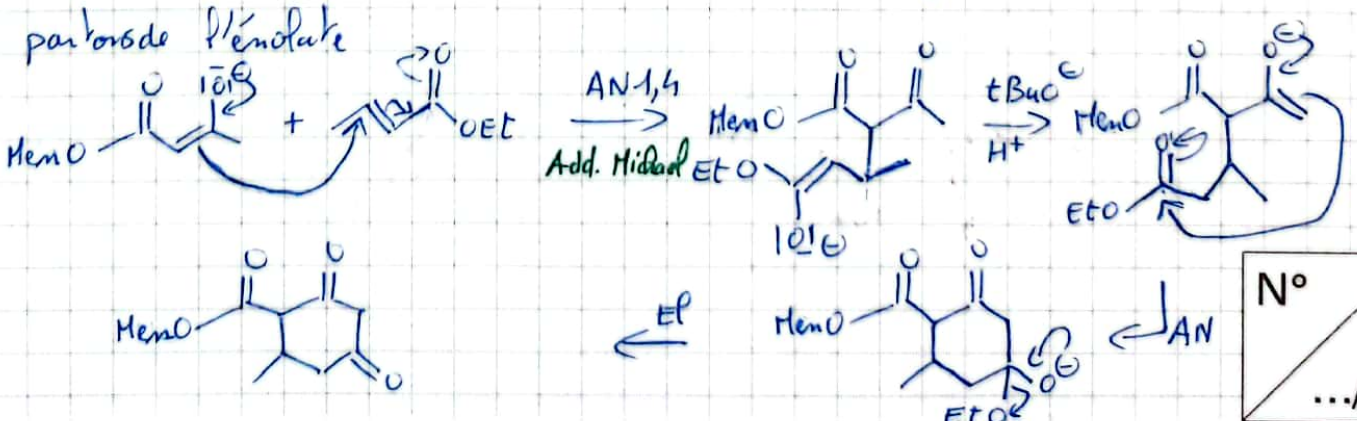
2. Le H central est très labile => énolate favorisé fortement.

3. Partons de l'énolate





4. partons de l'énolate

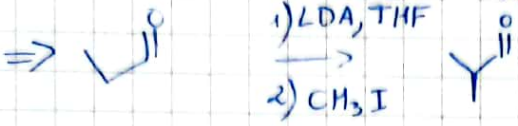


N° .../...

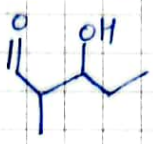
Ex5

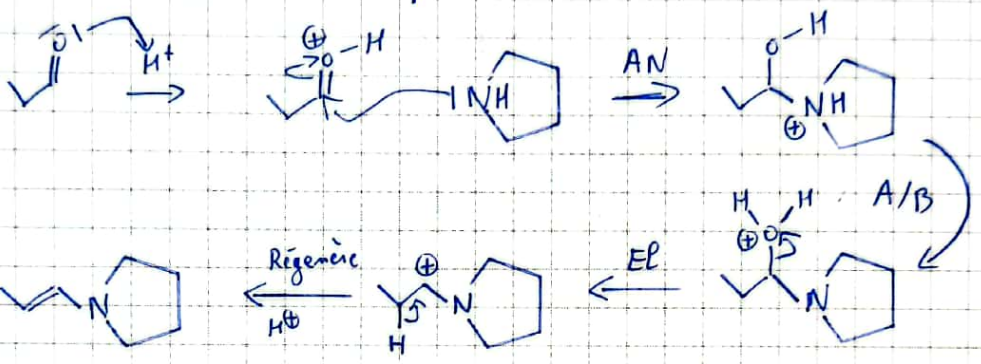
1.  il s'agit d'une C-alkylation

⇒ milieu basique pour produire l'enolate puis réaction sur halogénoalcane

⇒ 

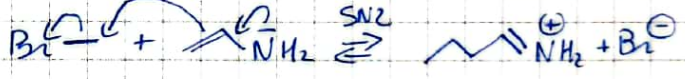
2. Il s'agit d'une aldolisation simple (les aldéhydes font plus facilement une aldolisation qu'une C-alkylation)

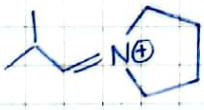
A 

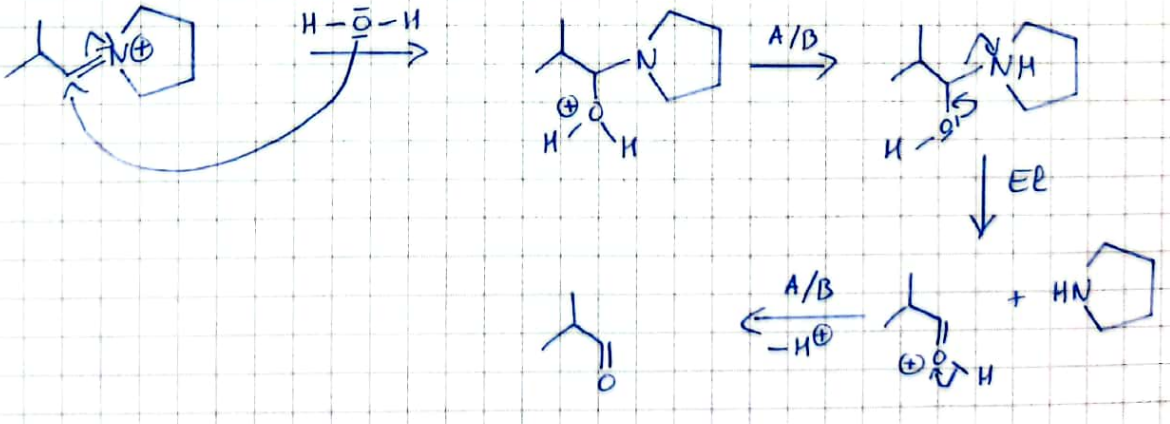
3. 

4. L'énamine joue le rôle de nucléophile, on étudie l'orbitale frontalière HO.

5. Le site de fixation est C_1. 

6. Il se produit une SN2 

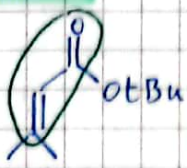
7 

8. 

N° .../...

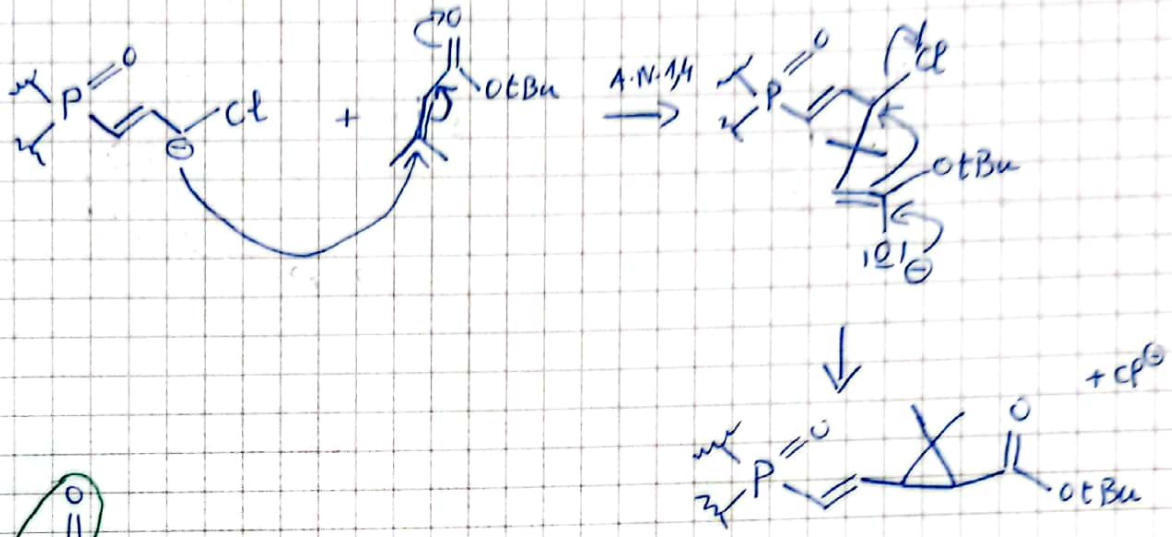
Approfondir

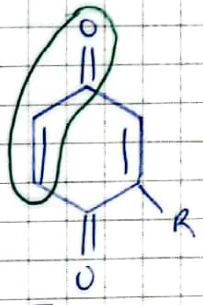
Ex1

1. 

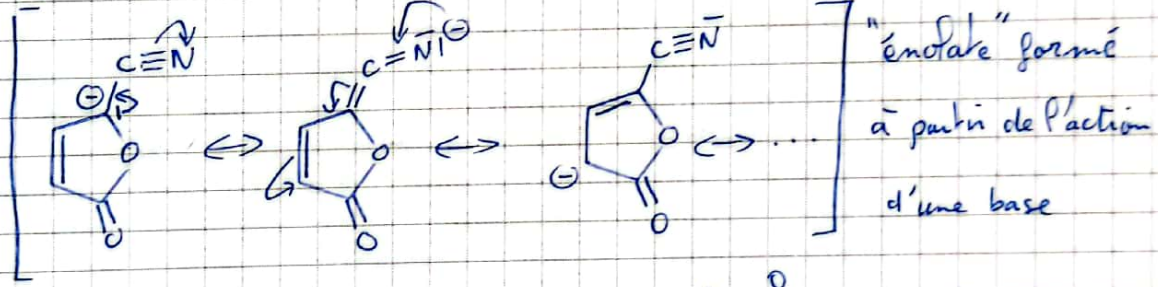
ne fait pas d'énolate (pas de H en α) donc il joue le rôle d'accepteur de Michael + α-énone

Mécanisme (à partir du carbanion de l'énolate)

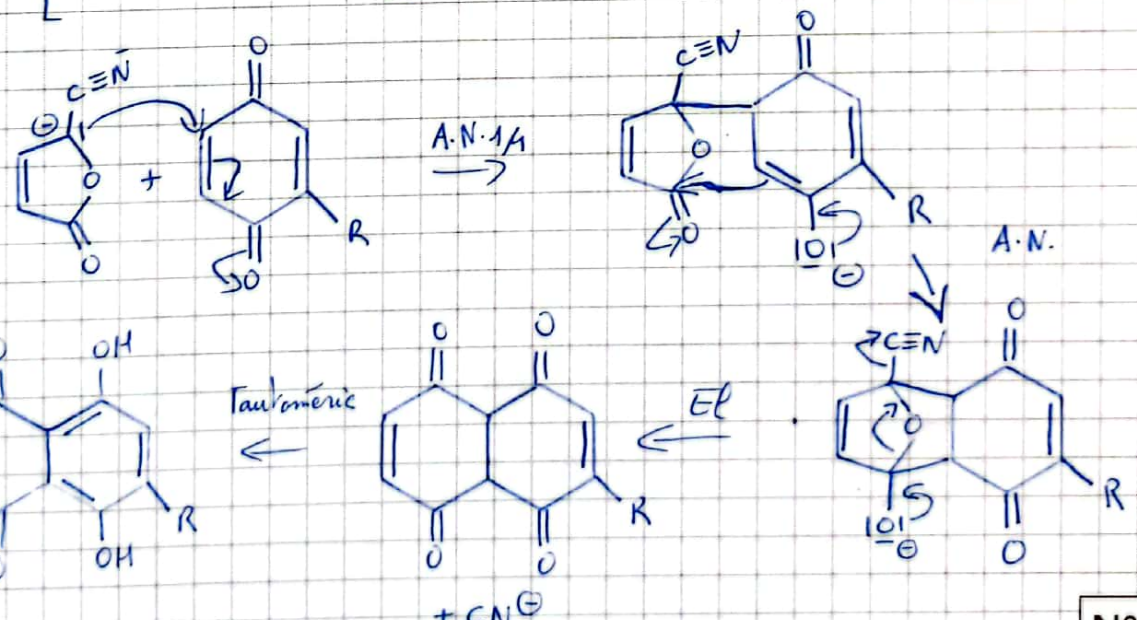


2. 

joue le rôle d'accepteur de Michael (α-énone + pas d'énolate)



"énolate" formé à partir de l'action d'une base

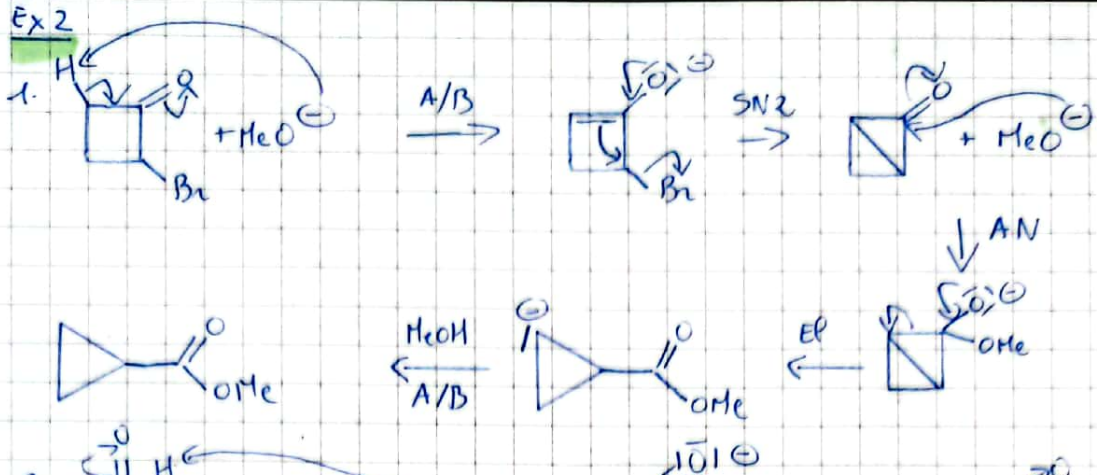


N° .../...

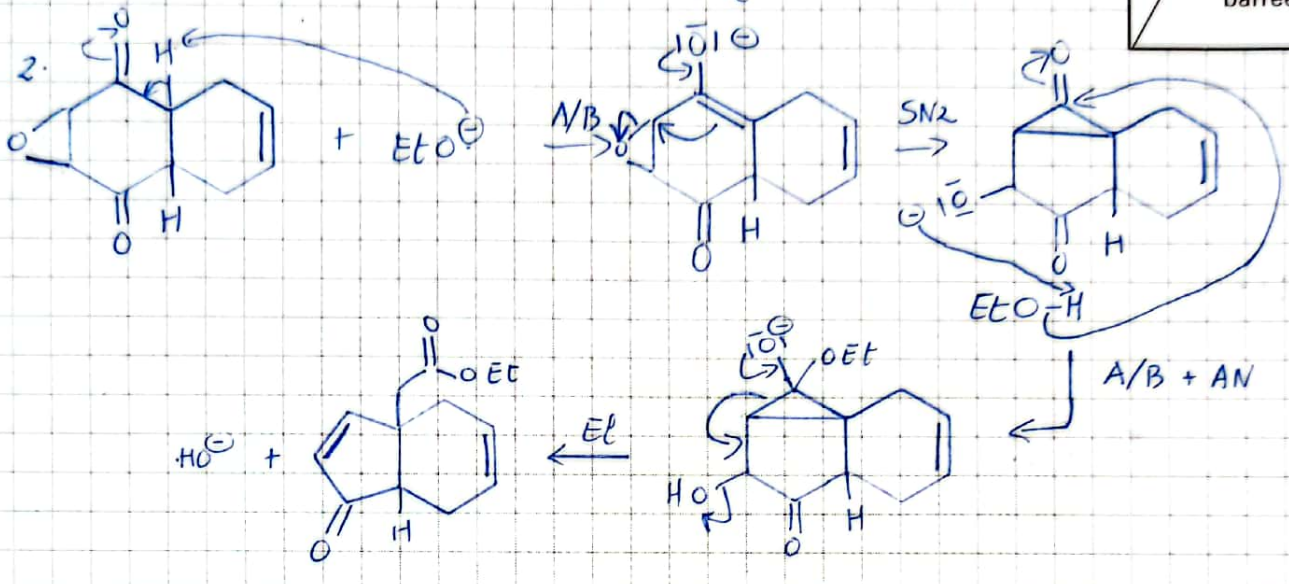
ne rien écrire dans la partie barrée

Ex 2

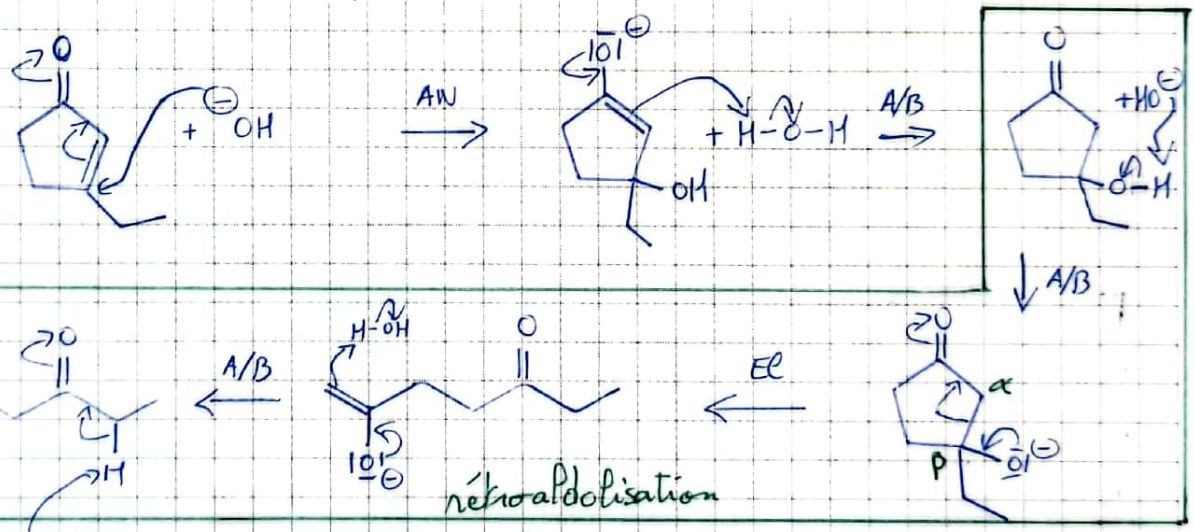
1.

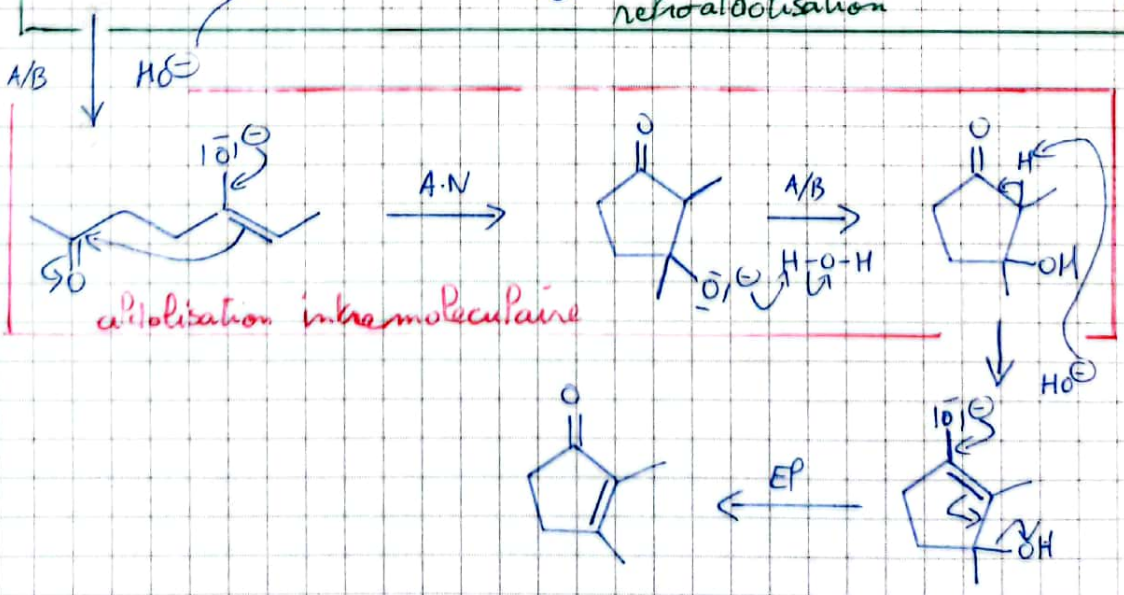


2.



Ex 3





N° .../...