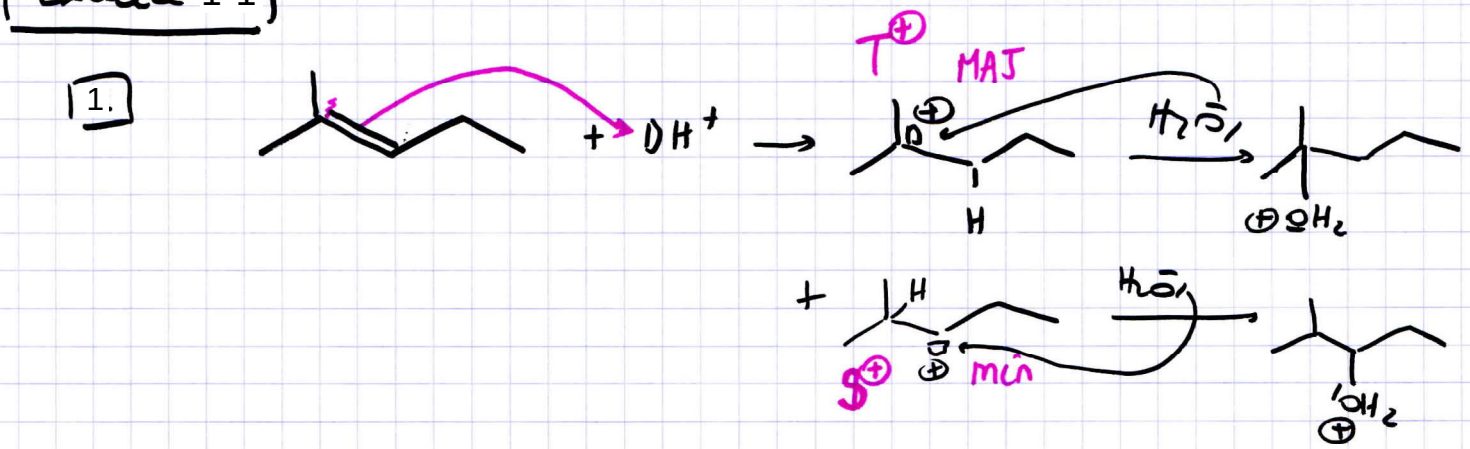
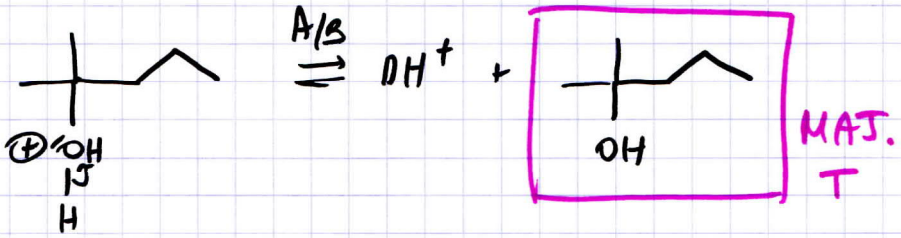
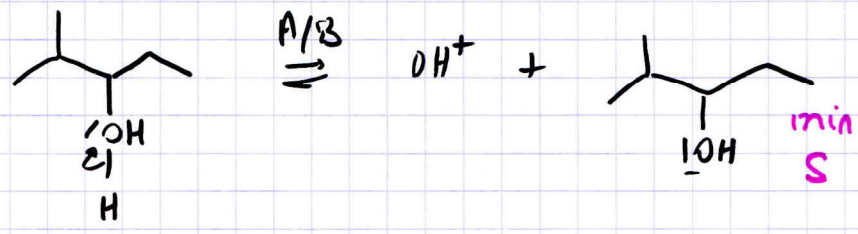
CORRECTION EXERCICES à partir des alcènes

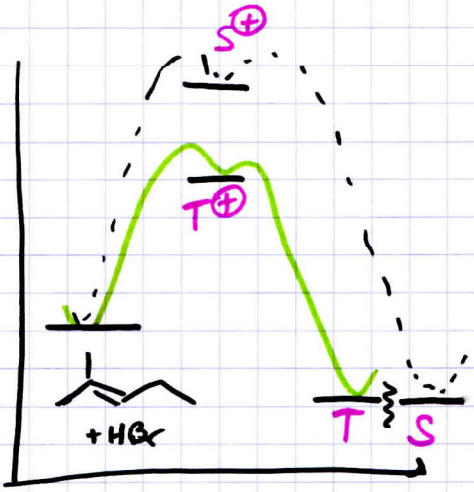
Exercice 1-1

1.



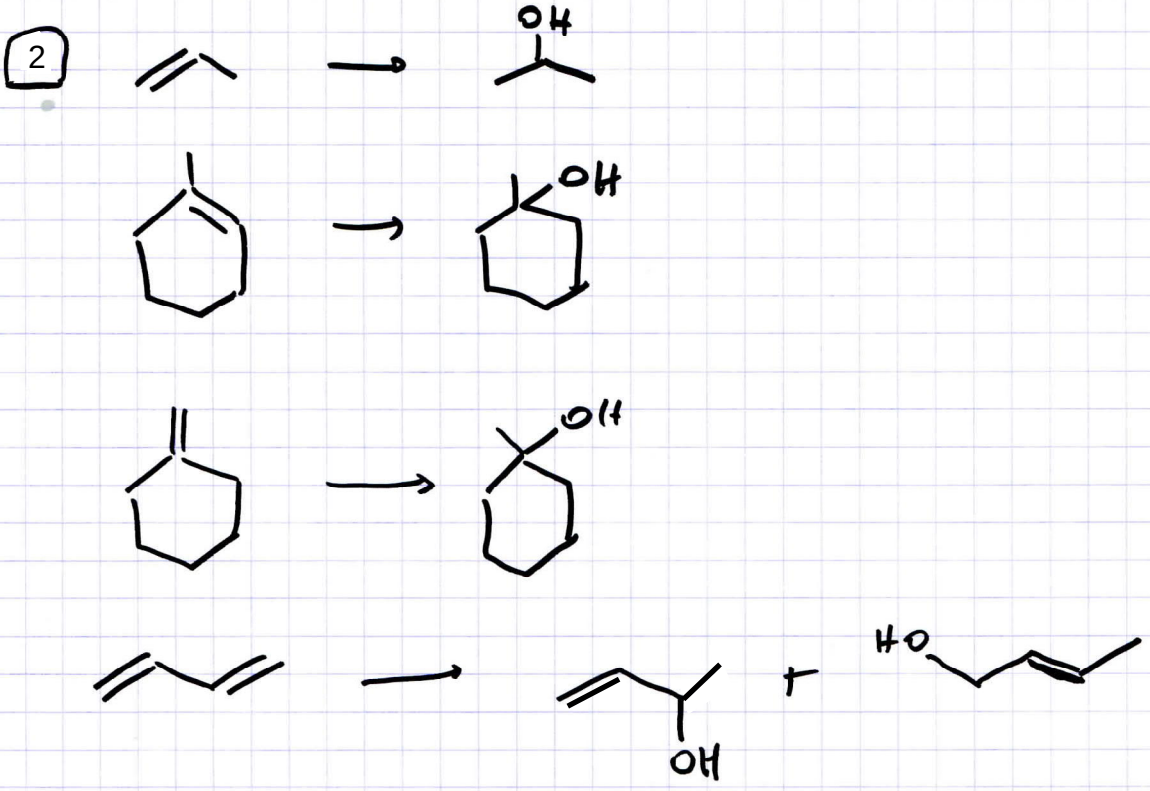






d'hydratation acide conduit à l'alcool issu du carbocation le plus stable, sous contrôle cinétique (Règle de Markownikoff).

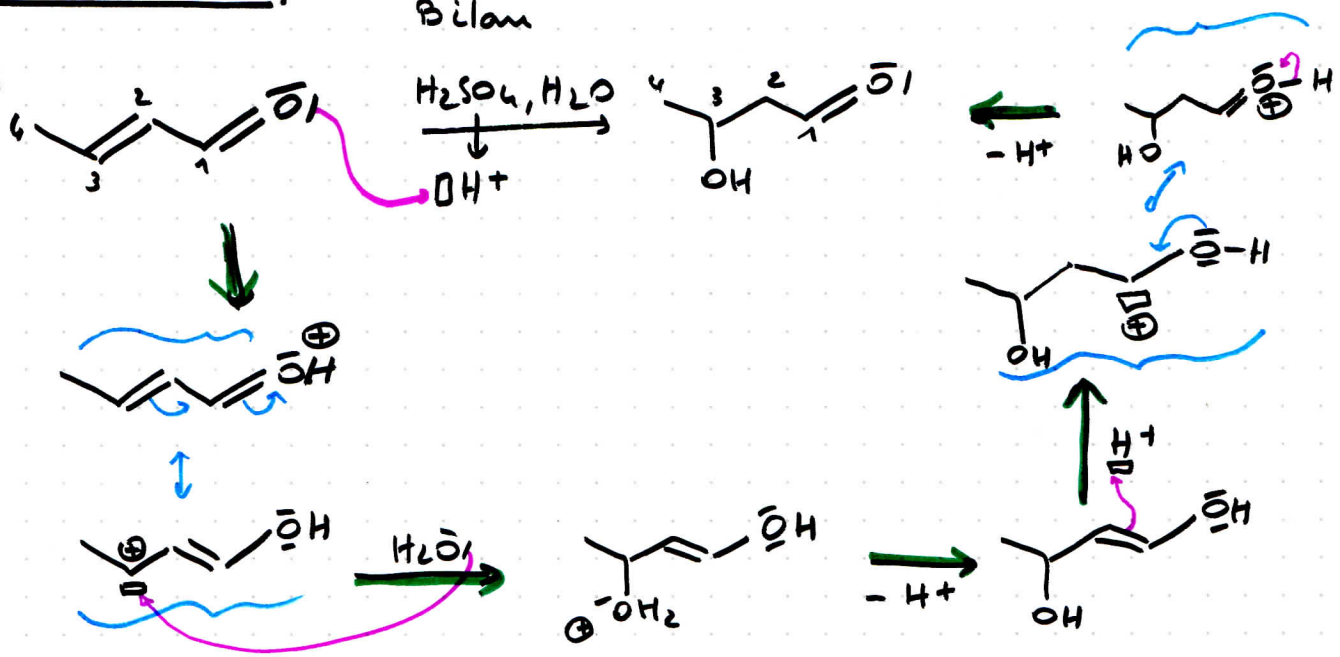
2



Exercice 1-2

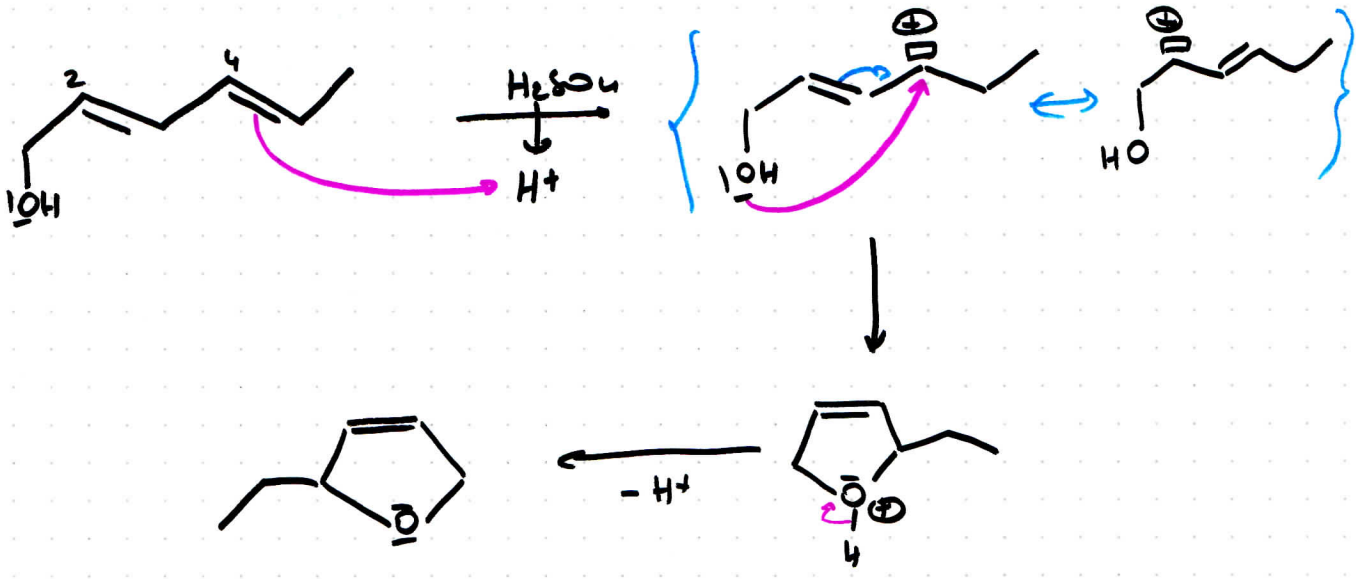
Bilan

1

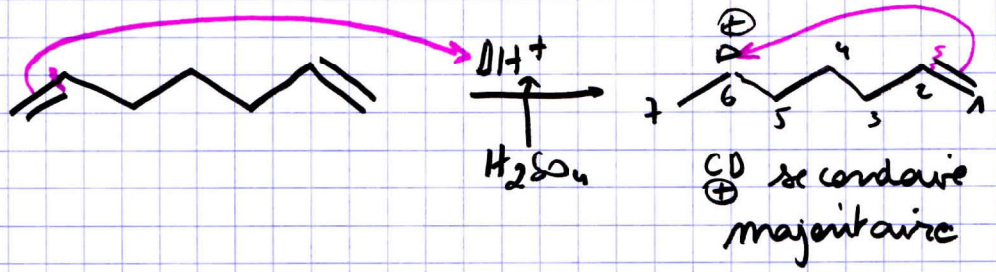


→ → → (mécanisme).

2

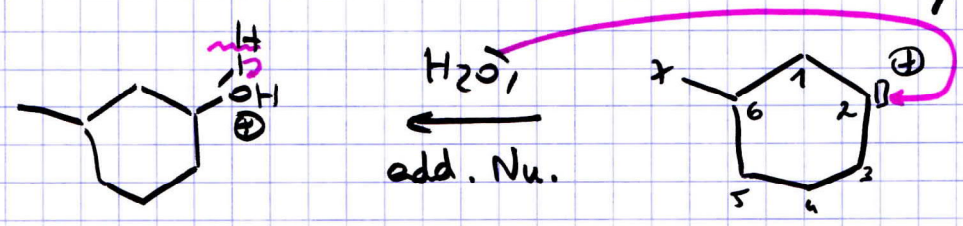


3.

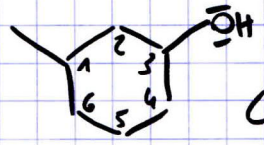


CD ⊕ secondaire majoritaire

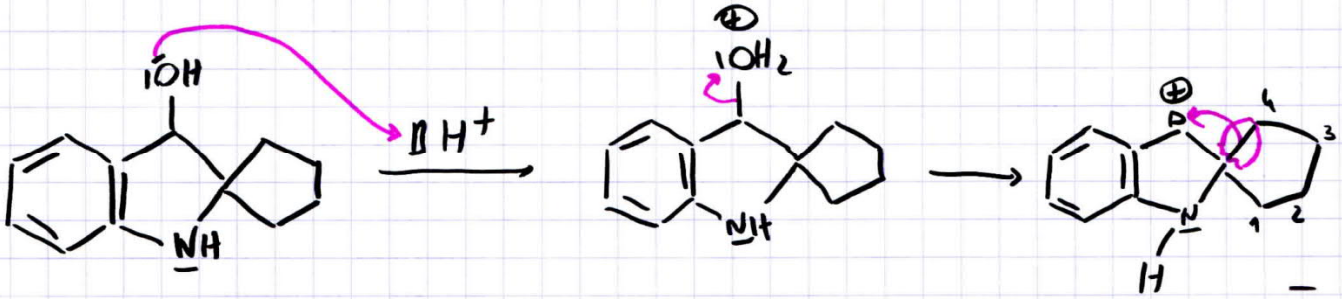
↓ cyclisation intramoléculaire ≠ réarrangement.

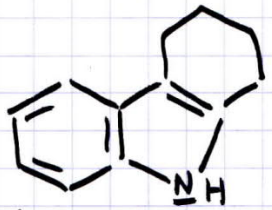


⇅ A/B.

H+ catalyseur régénéré +  CQFD.

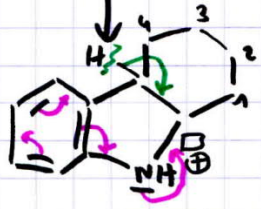
4.





molécule conjuguée sur l'ensemble des 2 cycles. (très stable).

Δ élimination

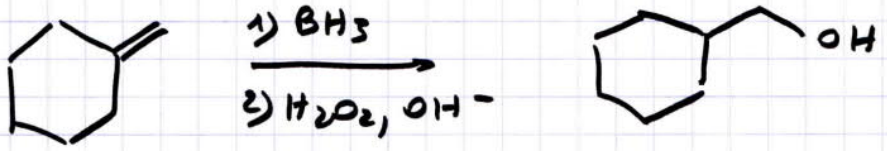


↕

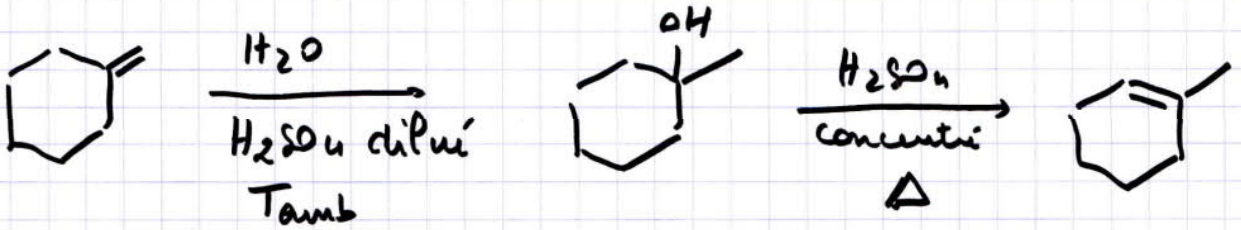
....

conjugaison = longue chaîne + cycle à 6 C plus stable.

Exercice 2 - 1

- 

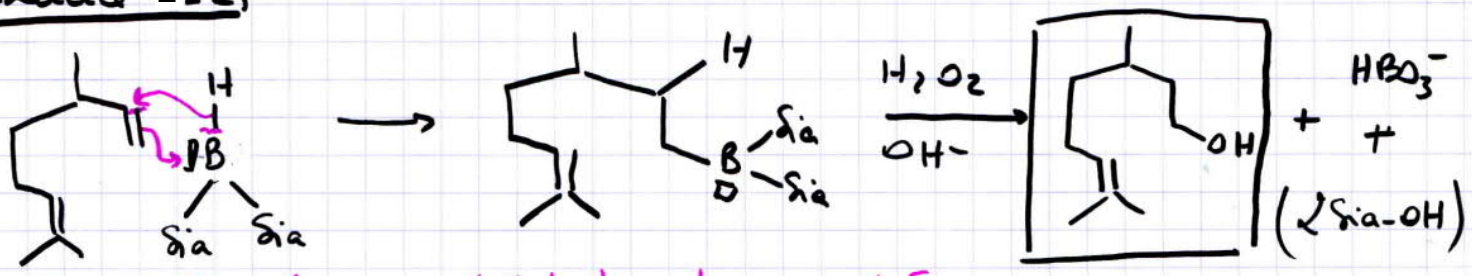
hydroboration sous contrôle stérique



hydratation acide sous contrôle cinétique

déshydratation sous contrôle thermodynamique

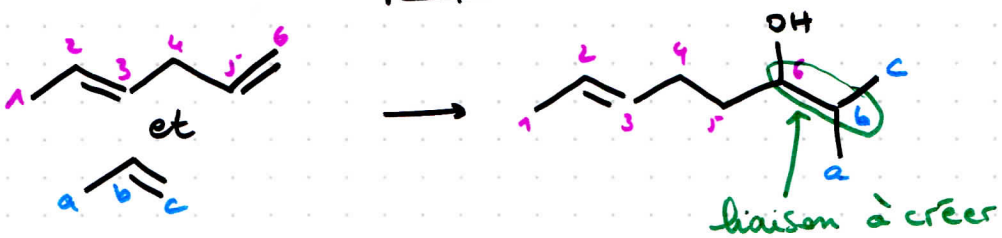
Exercice 2 - 2



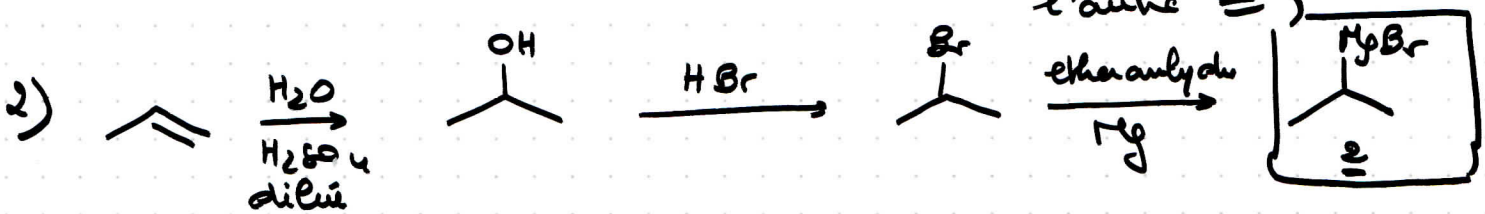
B se place près du C le - encombré de la = la - encombrée

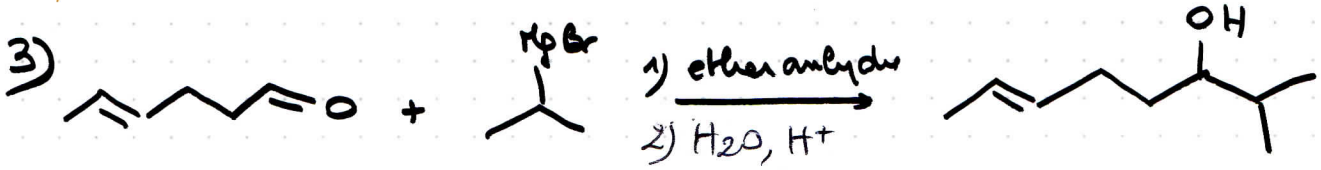
Exercice 2.3

Séquence 1

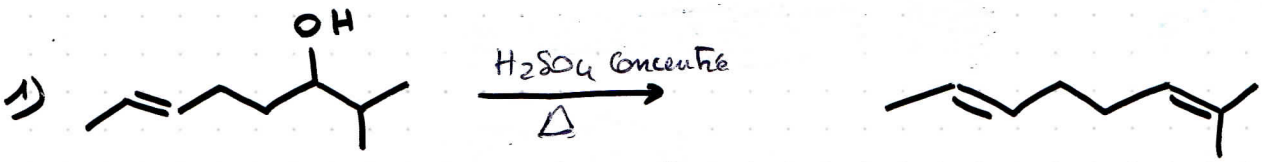


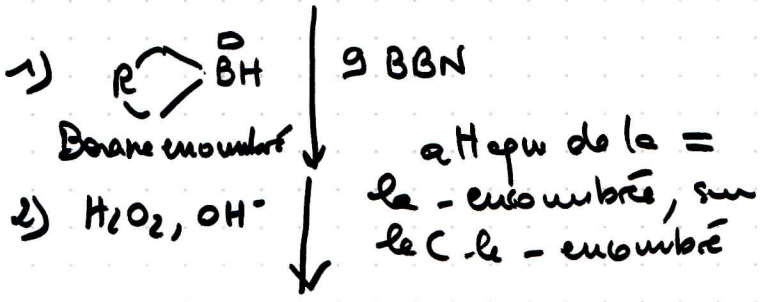
1) 

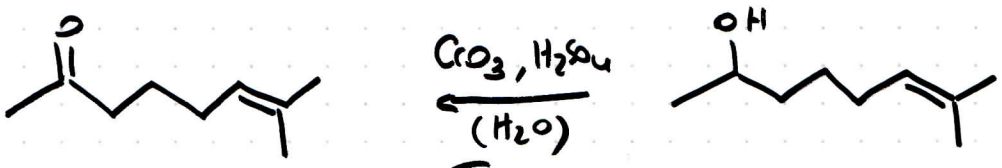
2) 

3) 

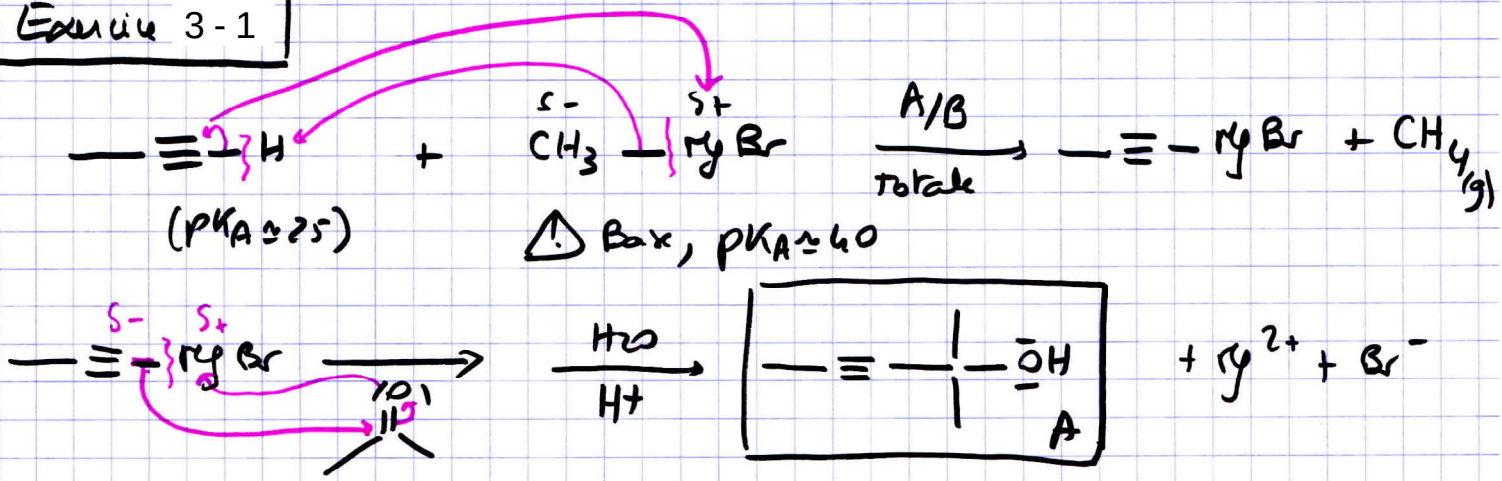
Séquence 2

1) 

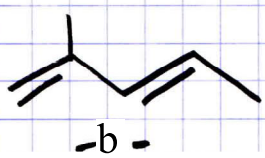




Exercice 3-1

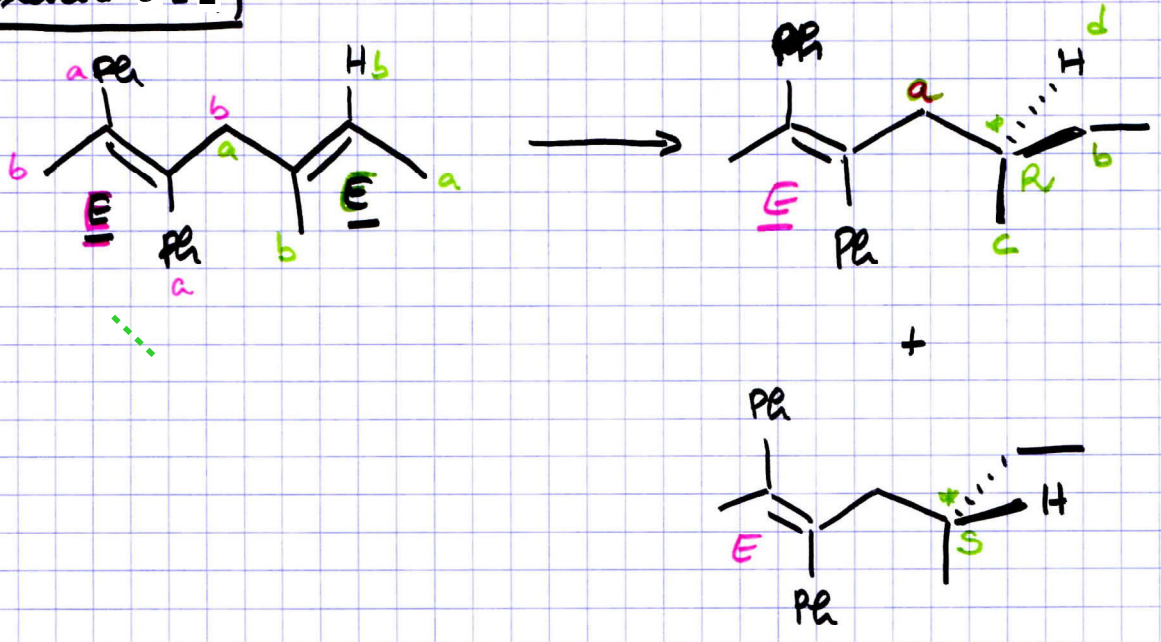


-  -a- : A $\xrightarrow[\text{Concentré chaud}]{H_2SO_4}$  -I- $\xrightarrow[\text{1 Bar Tamb.}]{H_2,\ Pd/C}$ -a-

-  -b- : -I- $\xrightarrow[\text{Pd/C + quinoléine (= catalyseur de Lindlar)}]{H_2}$ -b-

Exercice 3 - 2

(1)



+

Définition de l'excès énantiomérique :

$$ee = \frac{(E,R) - (E,S)}{(E,R) + (E,S)} = 0,9 = \frac{(E,R)}{(E,R)+(E,S)} - \frac{(E,S)}{(E,R)+(E,S)}$$

$= \%(E,R)$ $\qquad = \%(E,S)$.

→ **On cherche** $\%(E,R) = \dfrac{(E,R)}{(E,R)+(E,S)}$

or $\%(E,S) = 1 - \%(E,R)$.

$\Rightarrow 0,9 = \%(E,R) - 1 + \%(E,R)$

$\Rightarrow 0,9 = 2\%(E,R) - 1.$

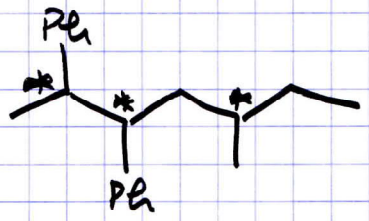
$\Rightarrow \%(E,R) = 1,9/2$

$\Rightarrow \%(E,R) = 0,95$

$\Rightarrow$ (E,R) est obtenu à 95 %, (E,S) à 5 %.

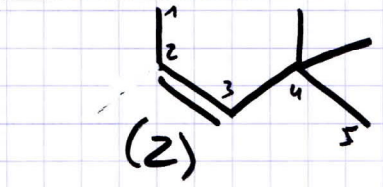
Cette réaction est régiosélective (1 alcène intact) ET énantiosélective (1 énantiomère privilégié).

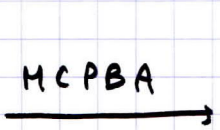
(2)

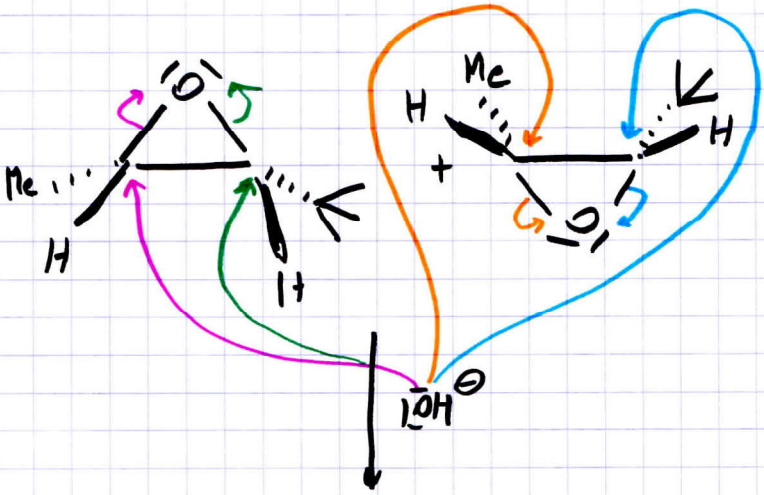


aurait été obtenu en mélange racémique.

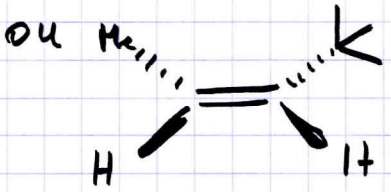
Exercice 4.1

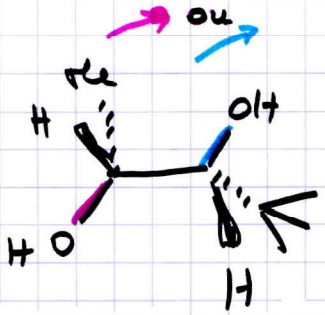




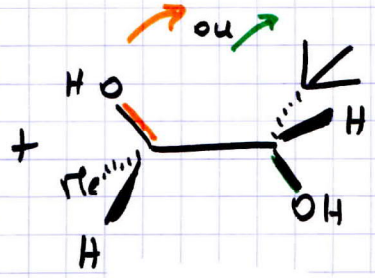


ou

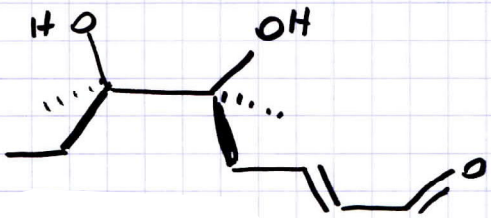


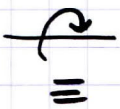


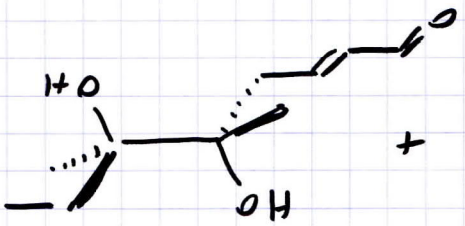
+



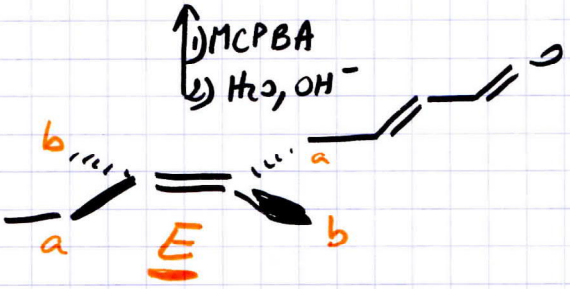
Exercice 4.2





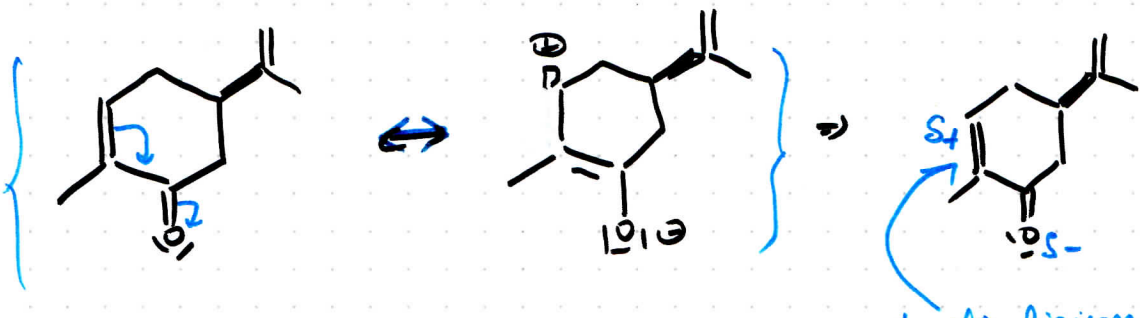


+ énantiomère.



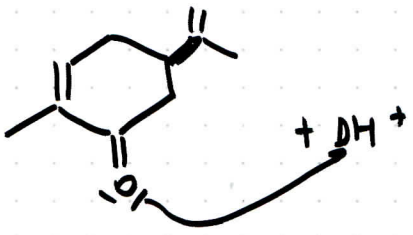
Par cette méthode, le produit souhaité est obtenu EN MÉLANGE avec son ÉNANTIOMÈRE, et non seul.

Exercice 5-1



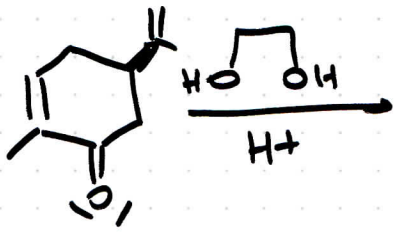
double liaison pauvre en e⁻
=) MCPBA attaquerait plutôt l'autre double liaison.

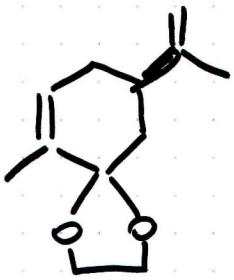
d'hydratation acide pourrait toucher les 2 double liaisons, et en plus :

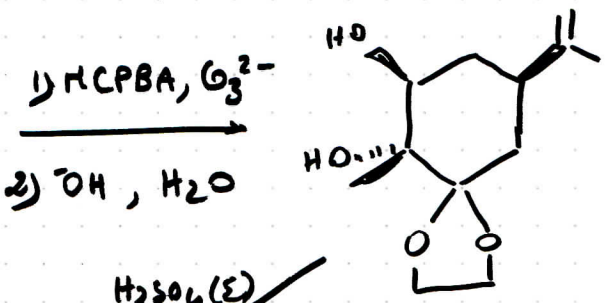


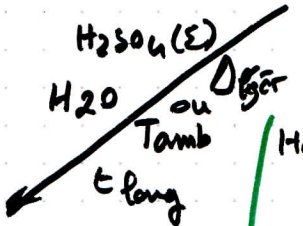
→ évolution qui donne le cation le + stable par résonance

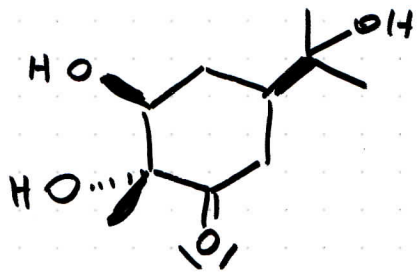
=) Protéger la fonction cétone par acétalisation :



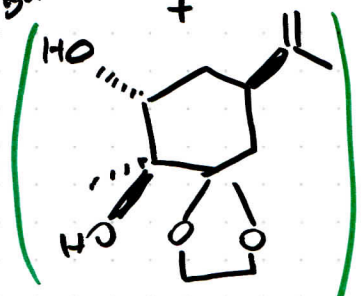








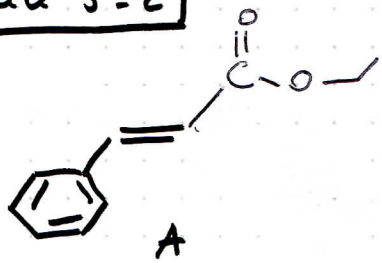
(par hydratation et désacétalisation).



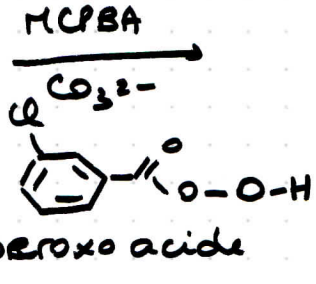
Diastéréoisomères à séparer (cristallisation fractionnée ou Chromatographie colonne).

Exercice 5-2

1)



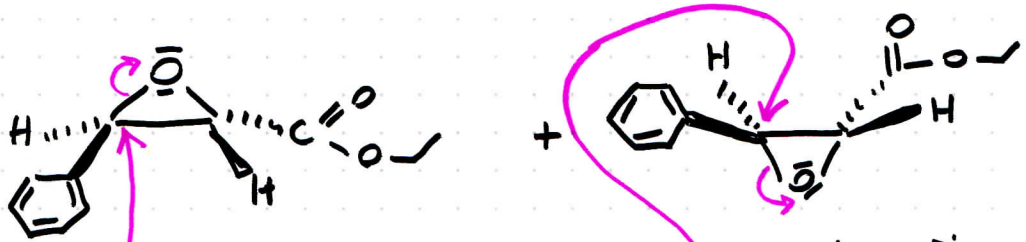
A



B

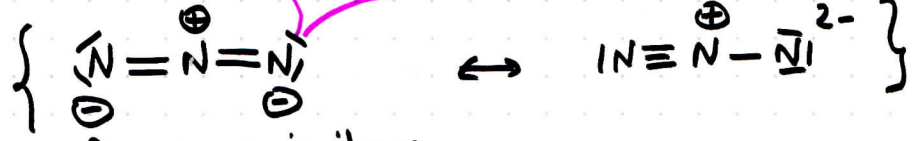
peroxo acide

2)



sont les stéréoisomères, énantiomères entre eux de B.

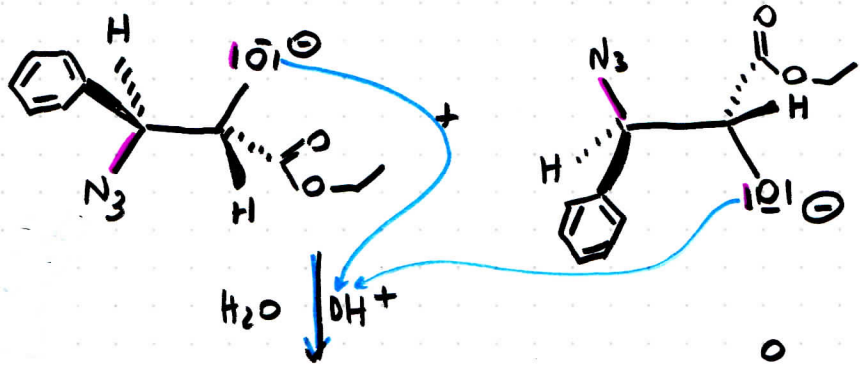
3)

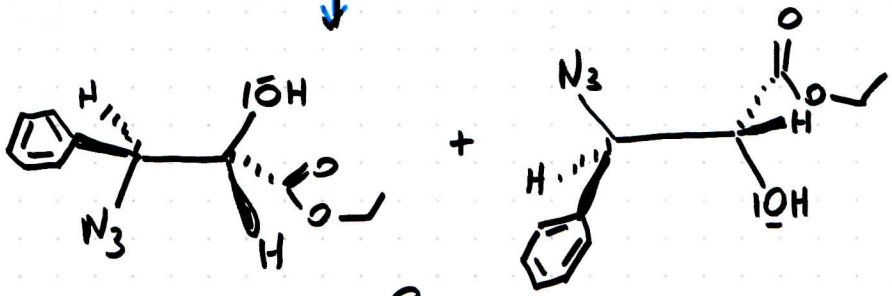


forme majoritaire car symétrique

(3×5+1 = 16 e- de v. ⇒ 8 doublets).

↓ anti addition sur le C le + éloigné de CO_2Et, riche en e-



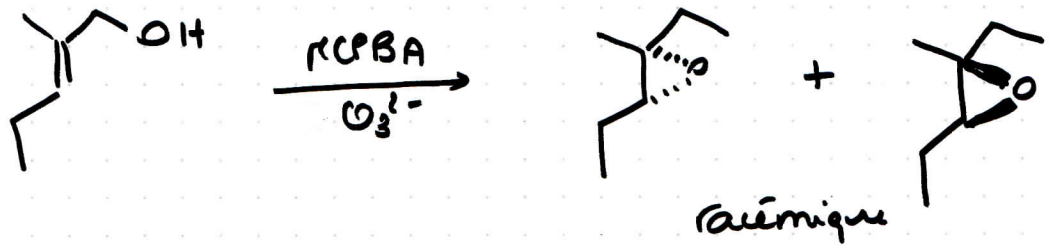


C

(2 énantiomères)

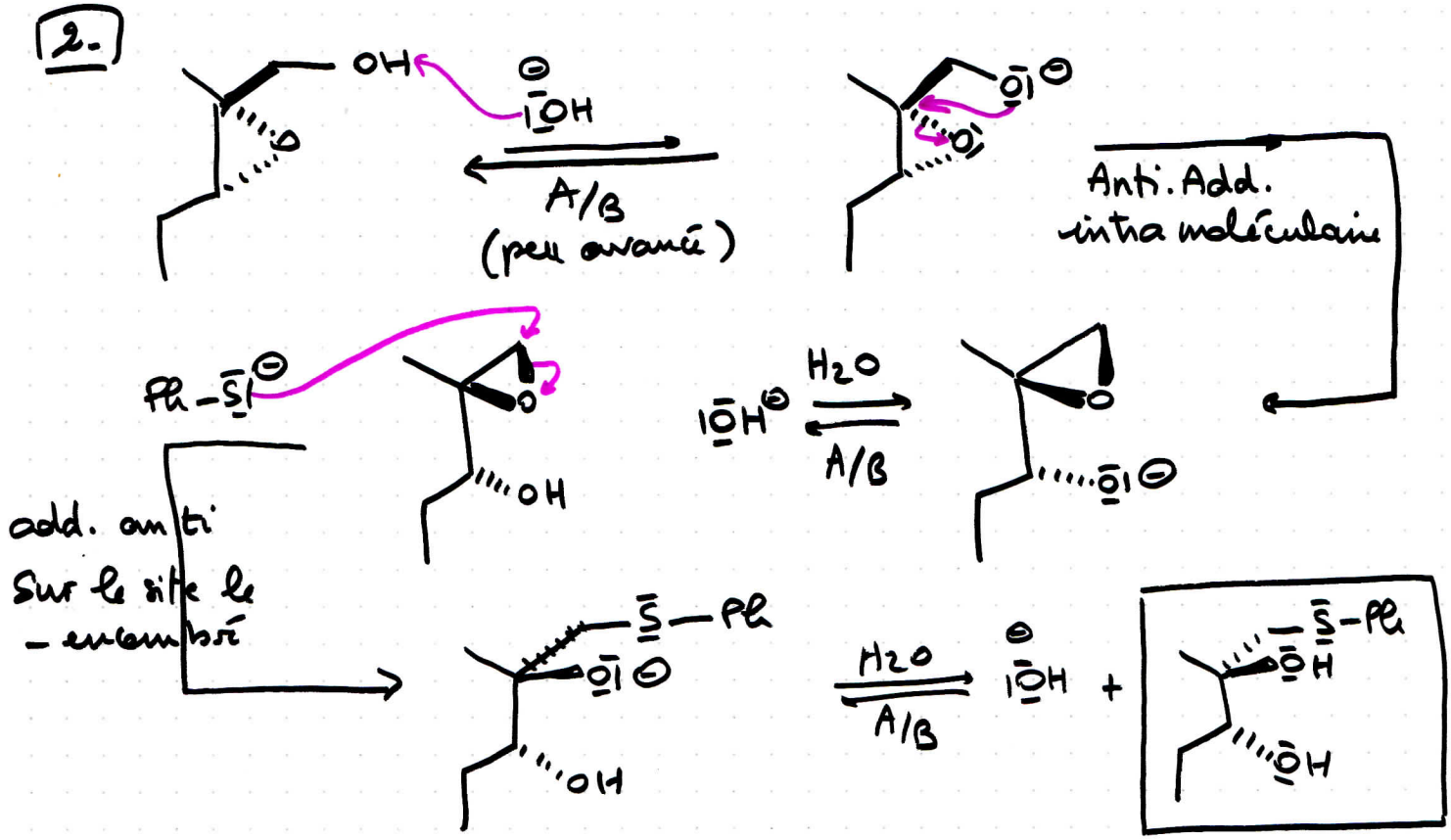
Exercice 5-3

1. En époxydation électrique (c'est-à-dire, en utilisant mCPBA) on obtiendrait les 2 énantiomères de l'époxyde :

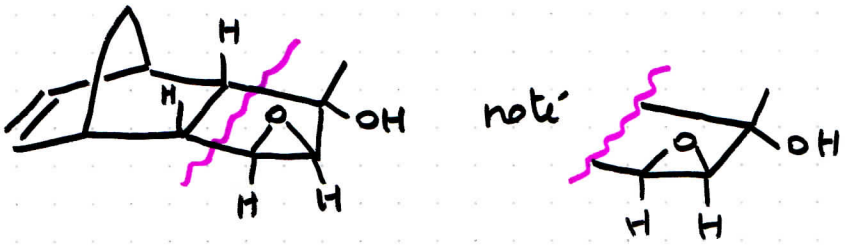


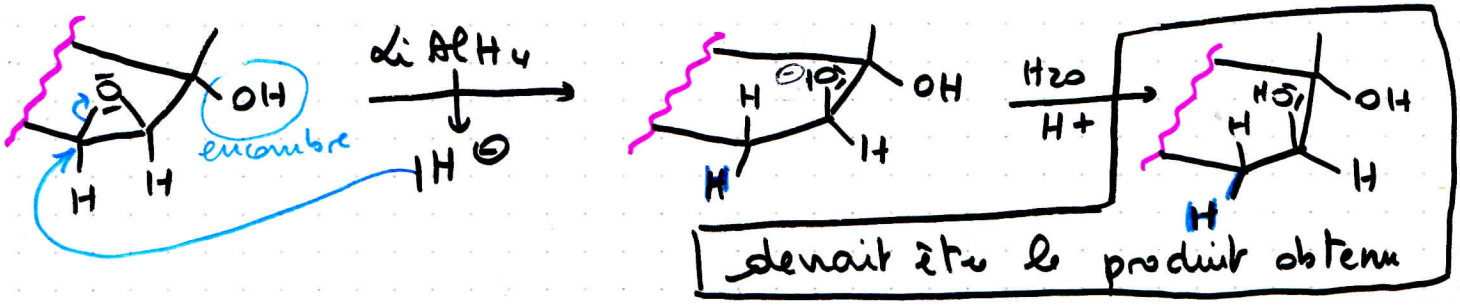
L'époxydation de Sharpless est donc **énantiosélective** (stéréosélective).

2.

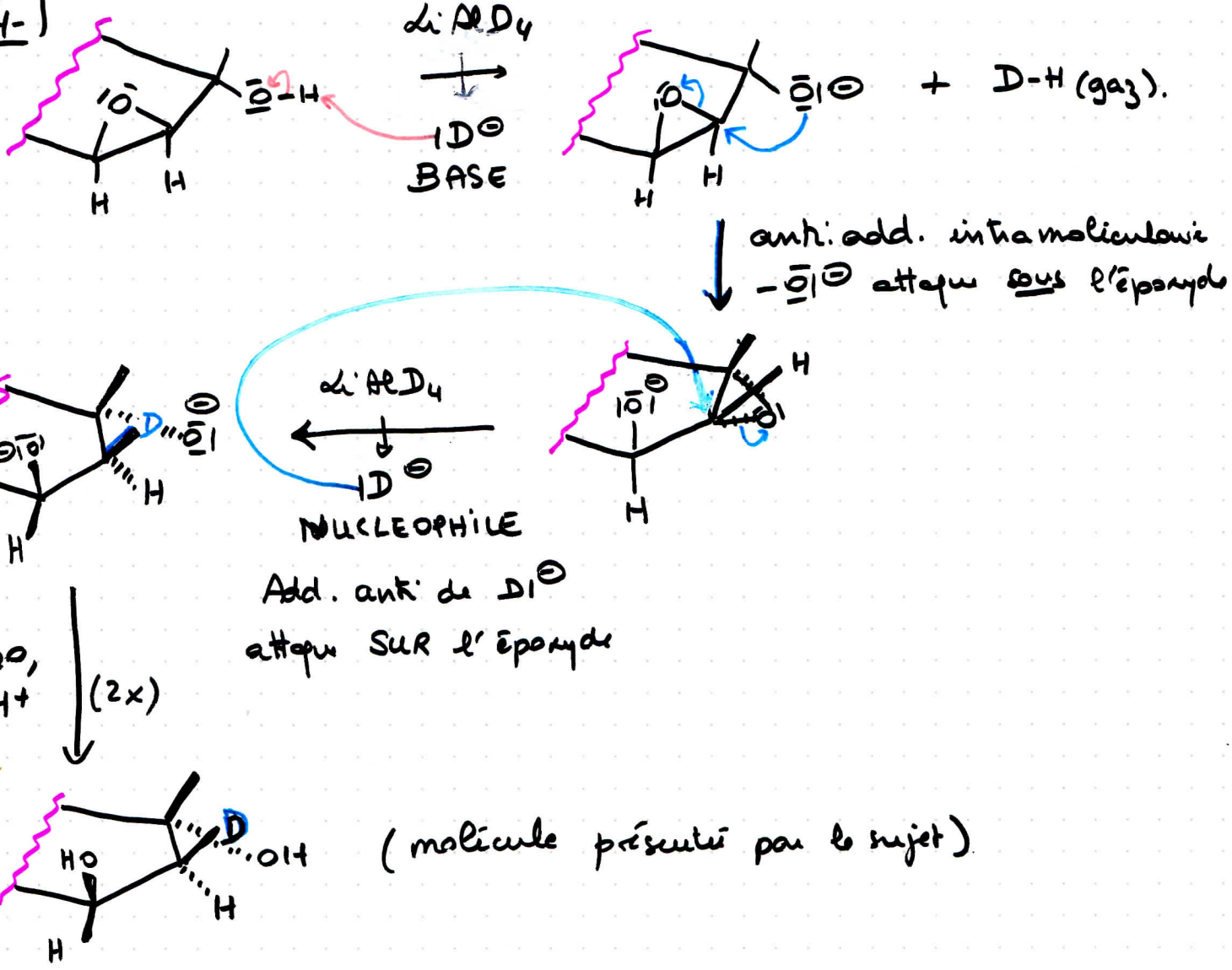


3. Notons le réactif



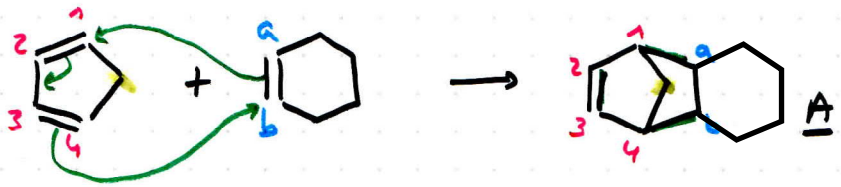


4-

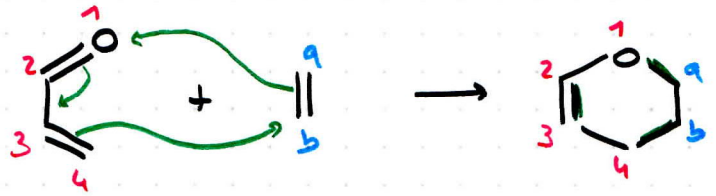

LiAlD4
BASE
+ D-H (gaz).
anti. add. intramoléculaire
- $\bar{O}|^{\ominus}$ attaque sous l'époxyde
LiAlD4
NUCLEOPHILE
Add. anti de $D|^{\ominus}$
attaque SUR l'époxyde
H_2O, H^+
(2x)
(molécule présentée par le sujet)

Exercice 6.1

1

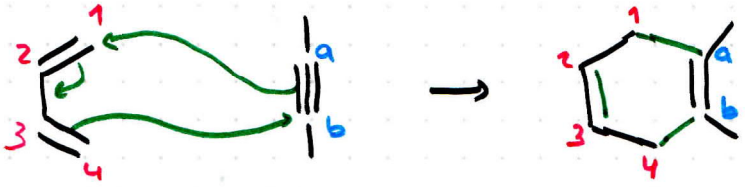


2



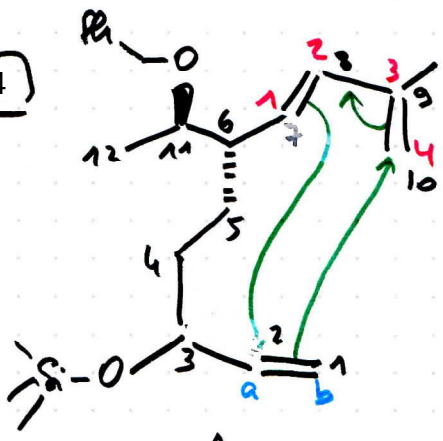
propénal

3



butadiène but-2-yne

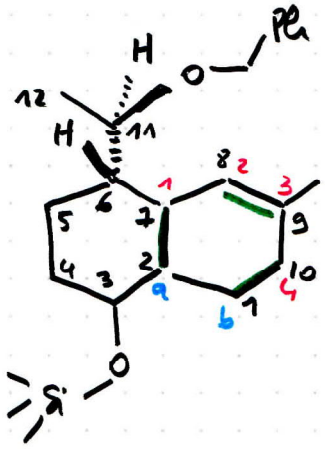
4



A

diène en conformation syn.

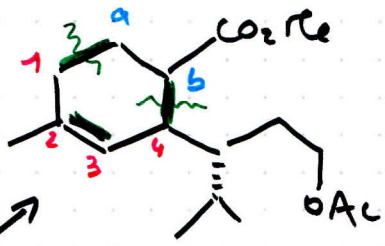
Diels Alder



où les configurations de $_6C$ et $_{11}C$ sont conservés.

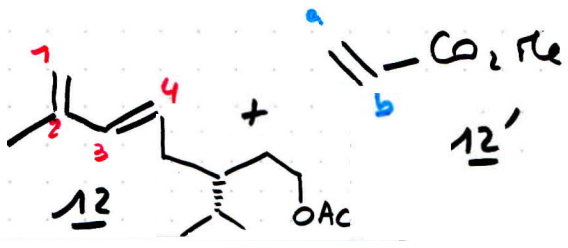
Exercice 6.2

a Rétrosynthèse en Diels Alder :



2 C ont été créés par DA.

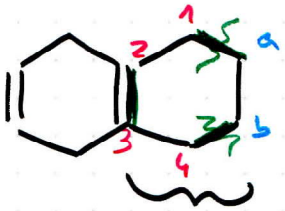
donc



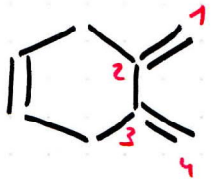
12

12'

b



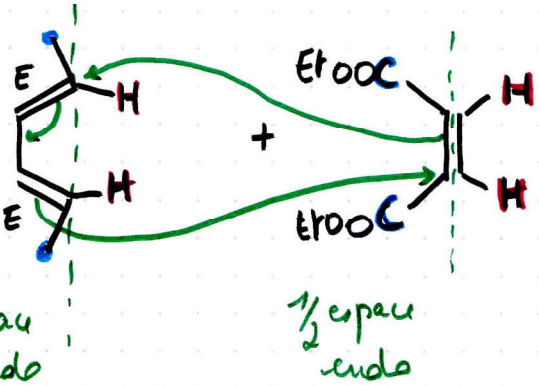
provient de ⟹

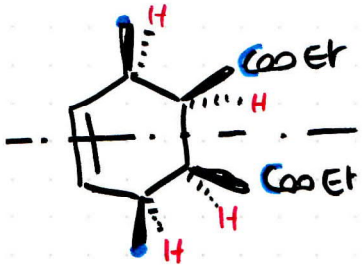


+ éthylène

cycle formé par DA.

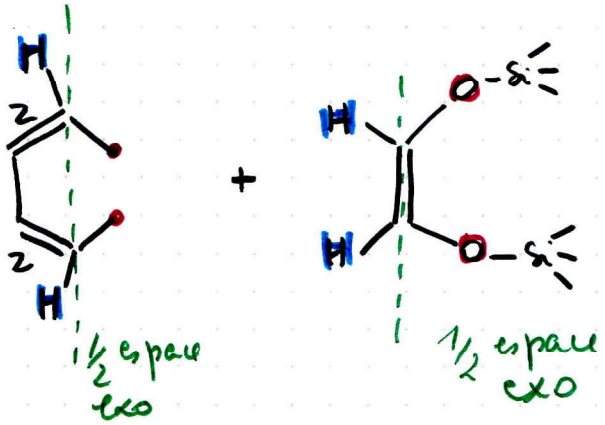
Exercice 7.1

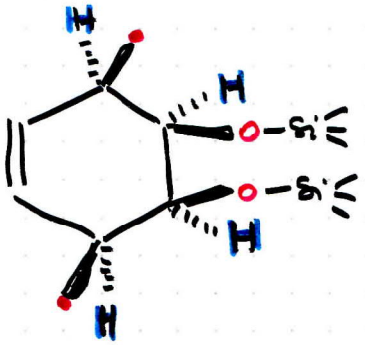


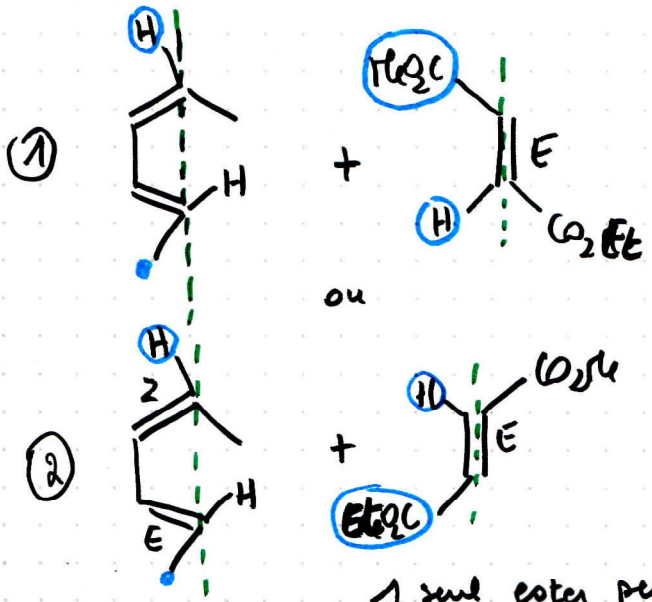


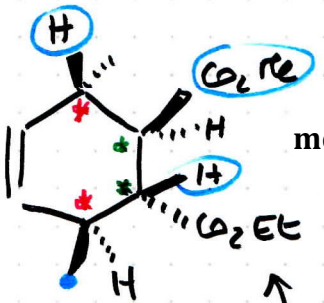
molécule unique car méso.

Tous les gpes dans le même 1/2 espace endo, sont dans le même 1/2 espace / plan moyen du cycle à 6 centres





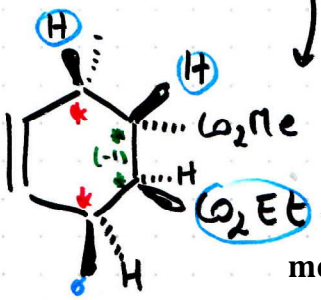




molécule MESO unique

diastéréoisomères

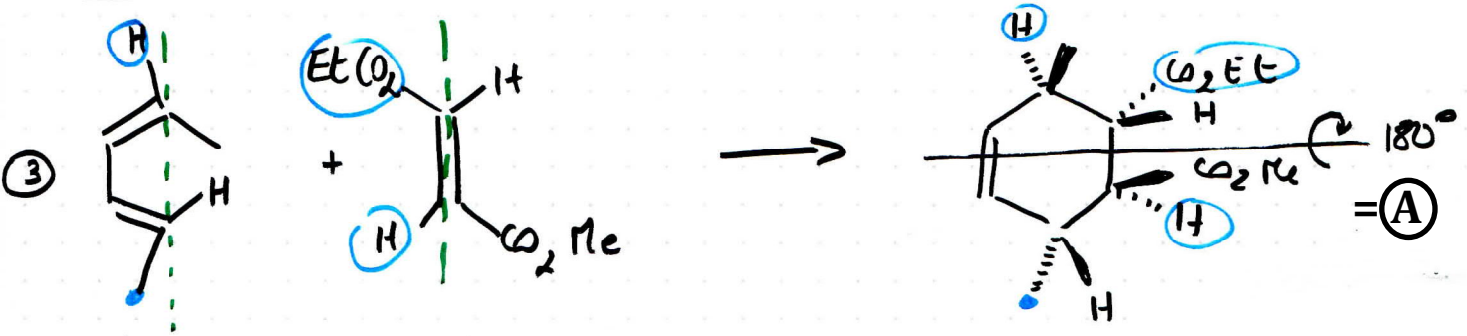
* identique
* inversés



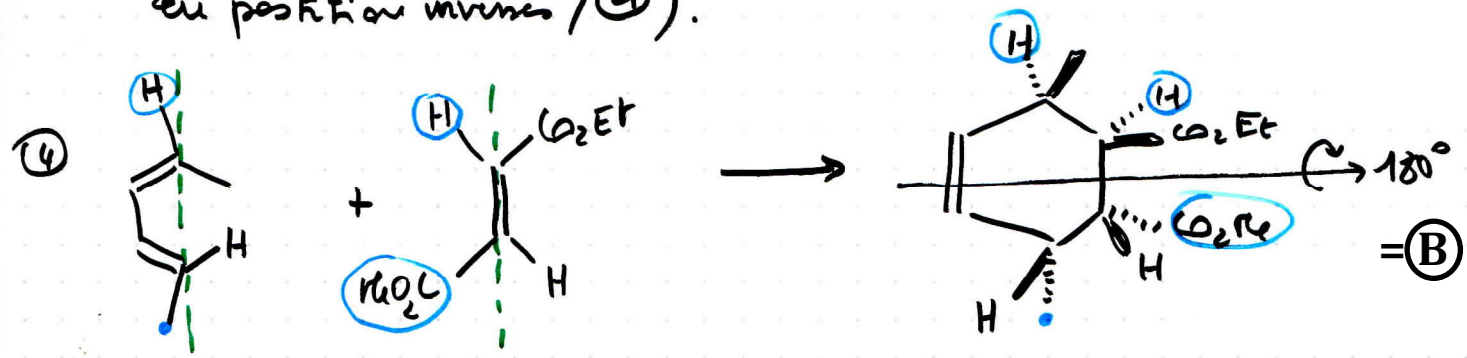
molécule MESO unique

1 seul ester peut être en endo

Mais aussi :

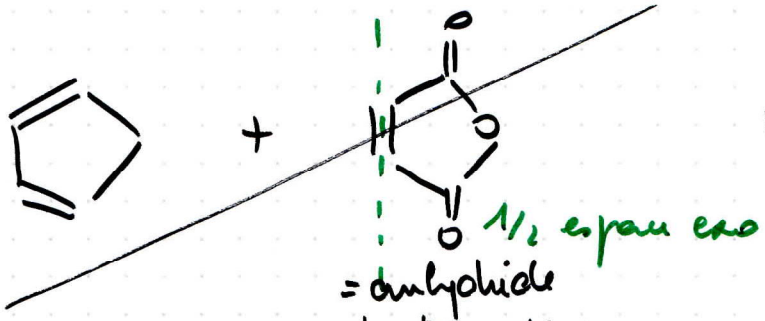


(où Et et Me sont en position inversé / ④).

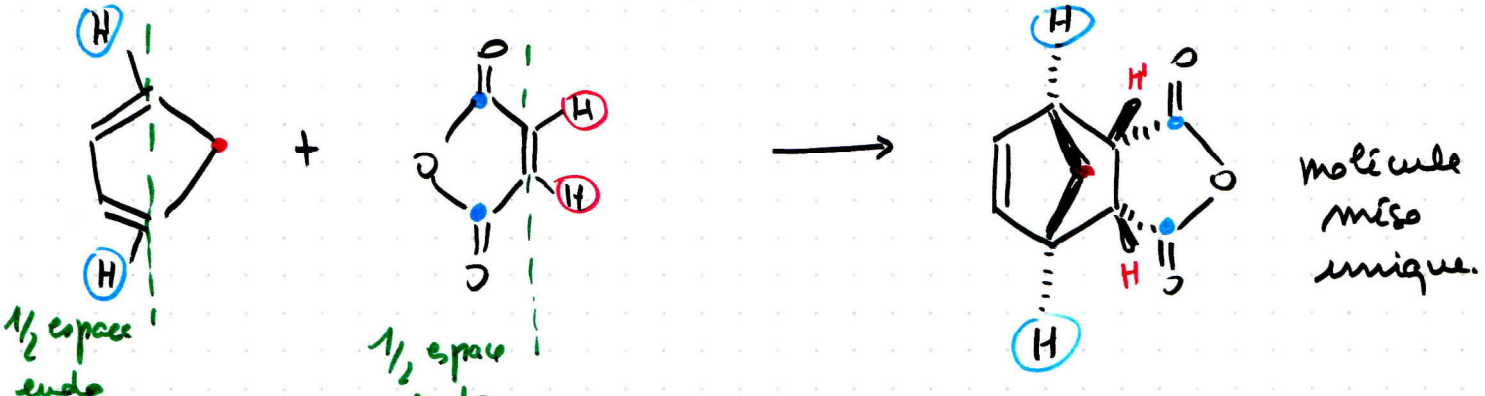


On n'obtient donc que 2 stéréoisomères

Exercice 7.2

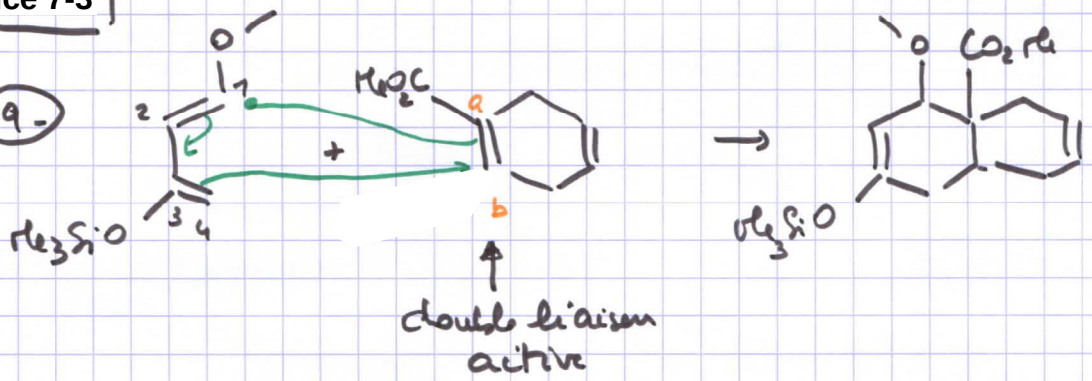


non réalisé d'après le texte



Exercice 7-3

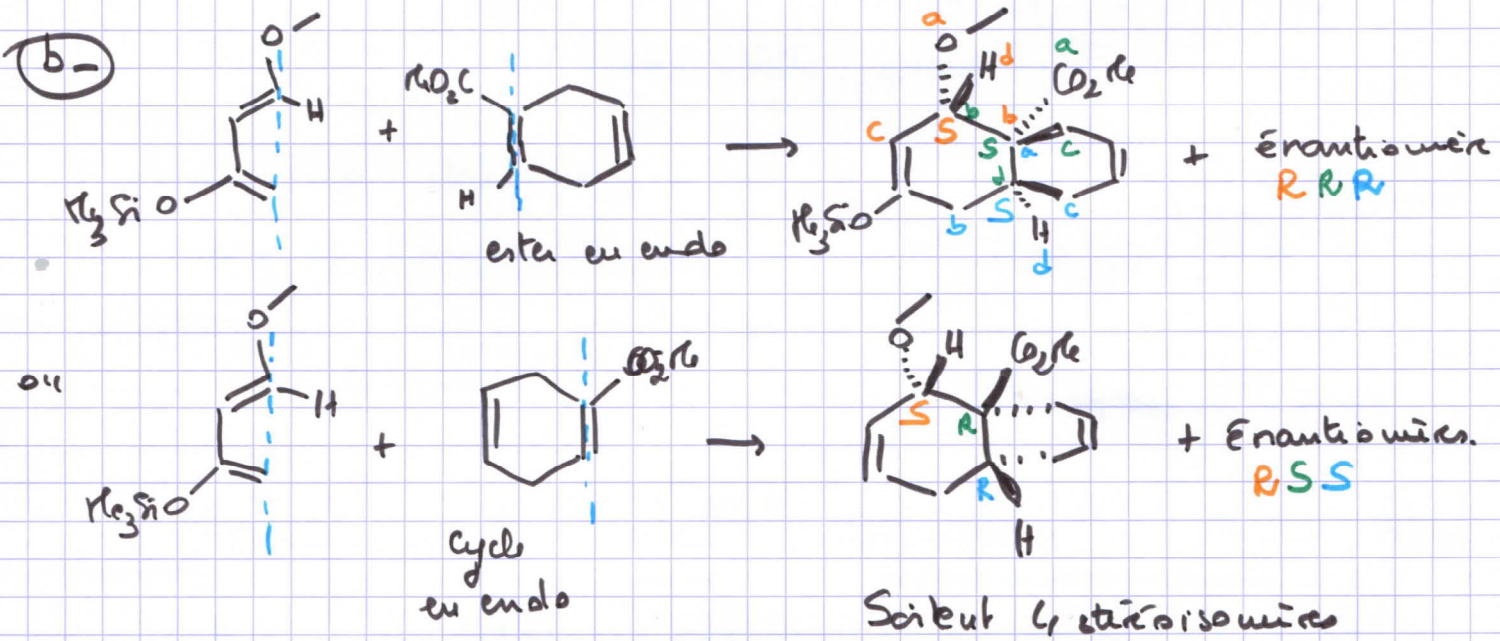
a-



Le carbone a portant l'ester s'est lié au C 1 portant le groupe methoxy. **La réaction est régiosélective.**

---

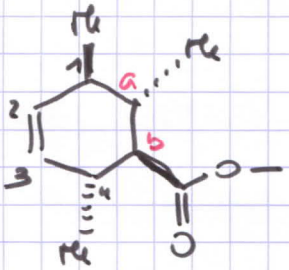
b-



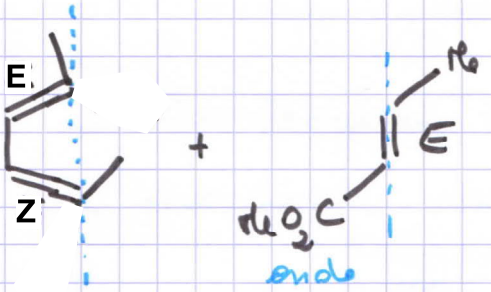
---

c- donc seuls les stéréoisomères SSS et RRR sont obtenus.

Exercice 7-4

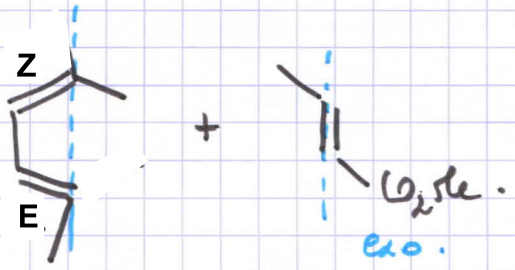


⇒



Situation ①

ou



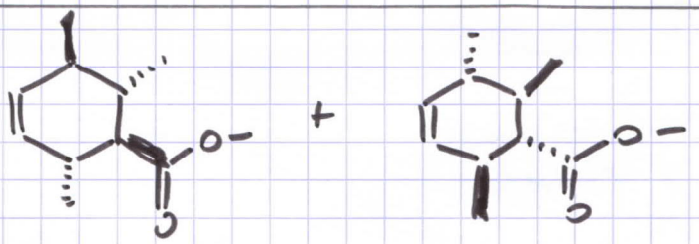
Situation ②

a- Les 2 Me sont en position trans en 1 et 4 ⇒ une alcène Z et l'autre E

Me et CO_2Me sont en position trans en a et b ⇒ alcène E.

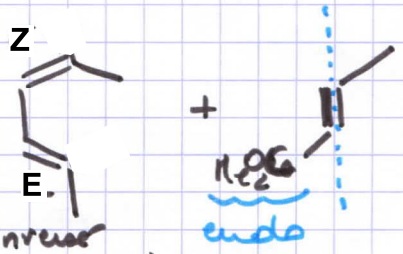
---

b- On obtient des :



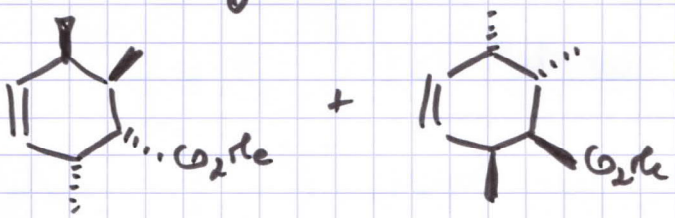
en situation ①

mais aussi, provenant de



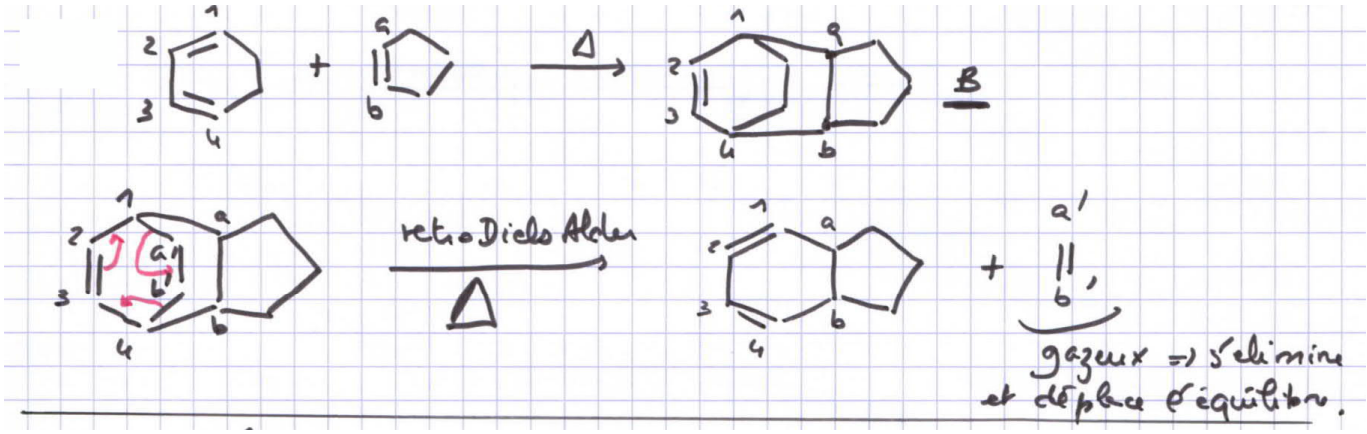
alcène inverse

Situation ③

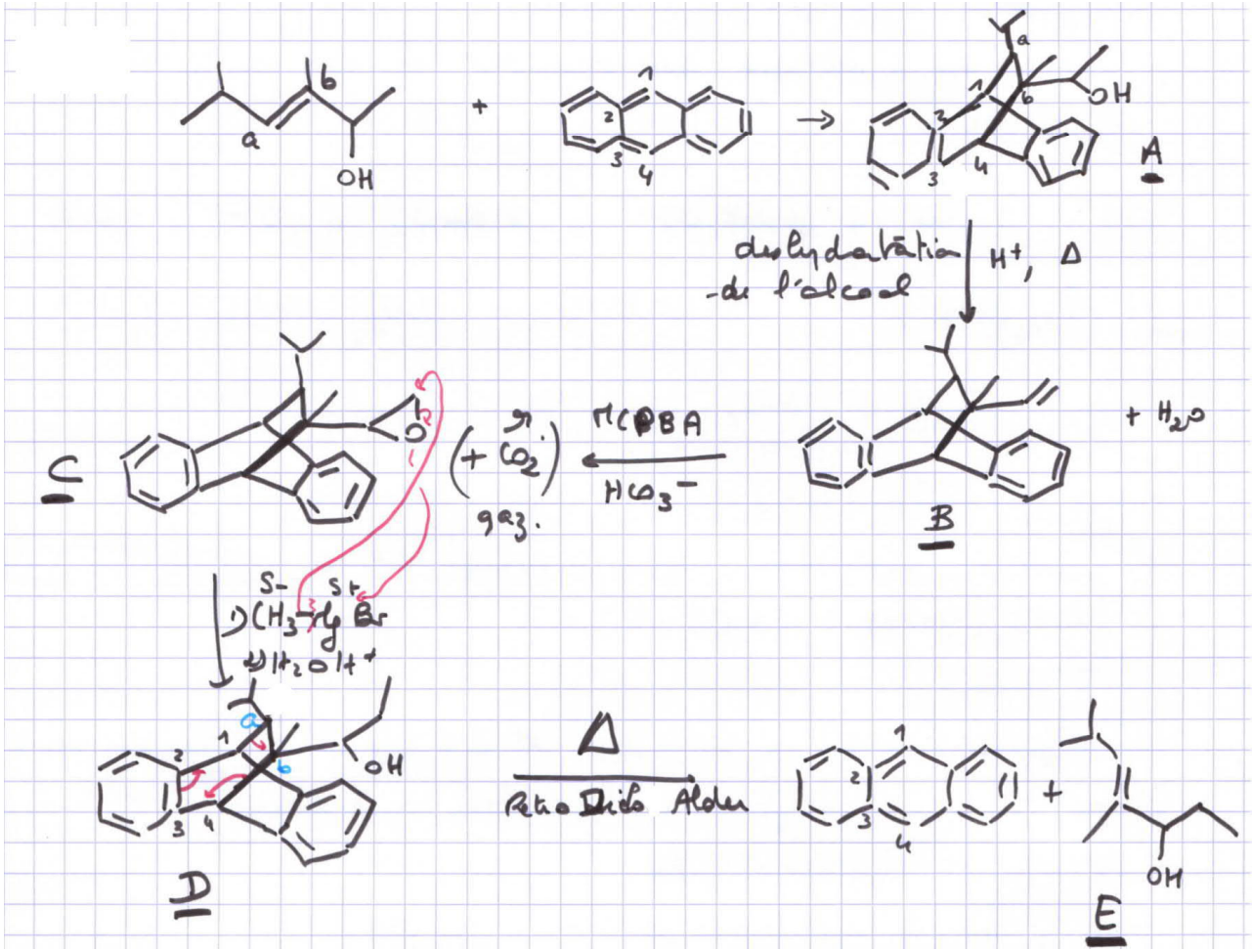


non souhaités.

Exercice 8-1

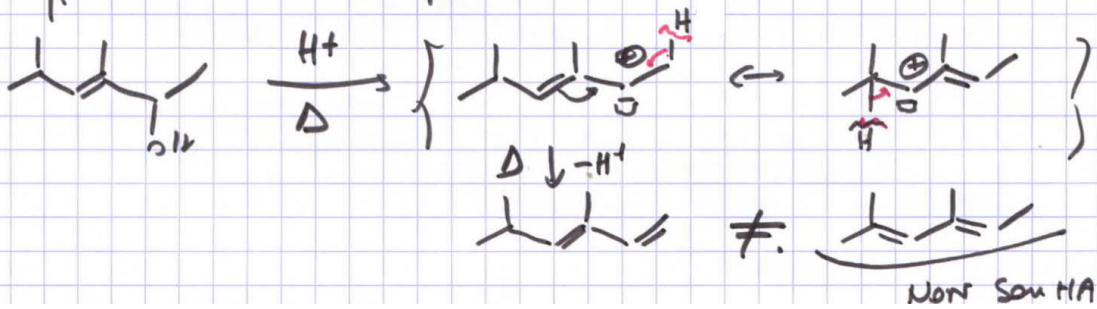


Exercice 8-2



L'anthracène a permis 1°) de protéger la double liaison lors de la déshydratation de l'alcool.

En effet, sans cette protection :



et aussi 2°) protéger la double liaison initiale de l'action du mCPBA lors de l'étape B → C.