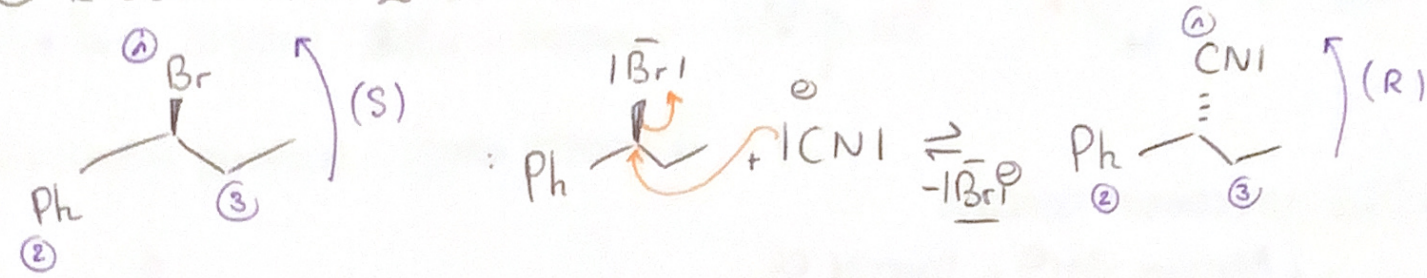
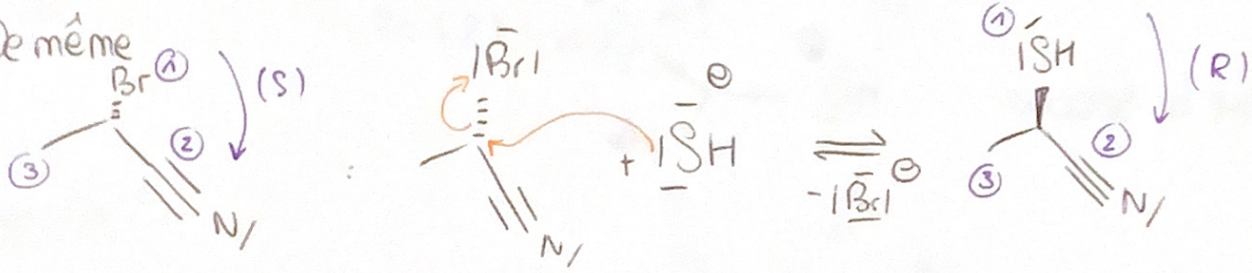
Correction TD CG 3 - S_N1/S_N2 - TB1.

* Exercice 1 :

① Réaction ordre 2 => S_N2 => inversion Walden

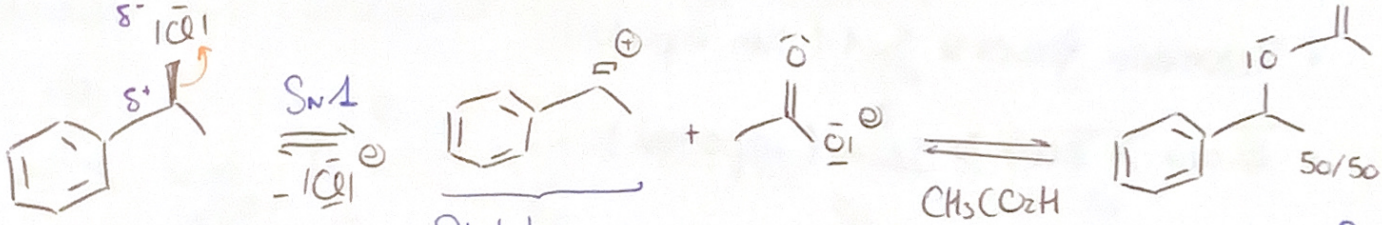


② De même



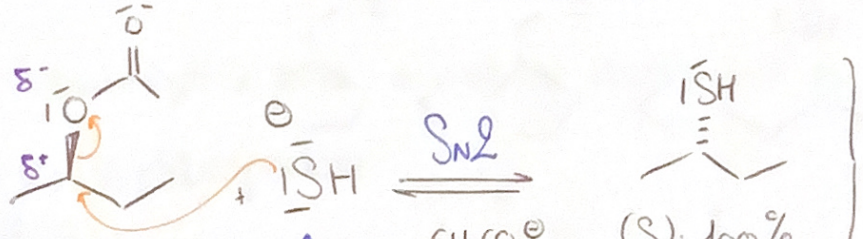
* Exercice 2 :

①



↖ polaire protique : S_N1 ✓

②

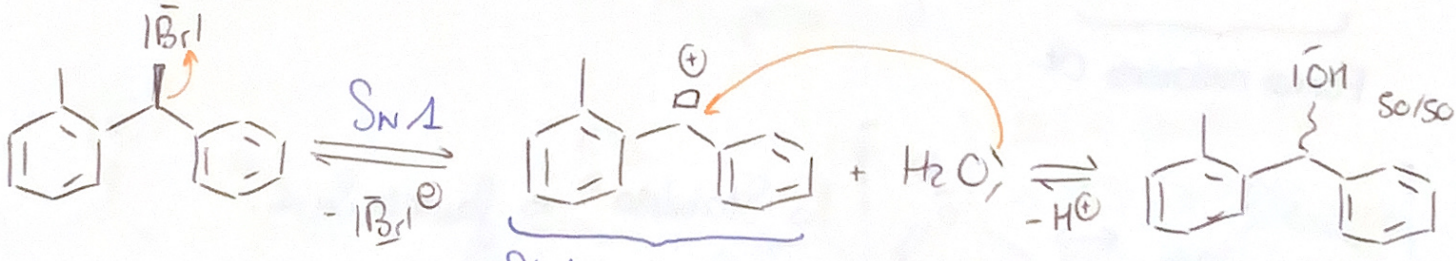


Il faire : pas info

Nu fort => S_N2

S_N2 : Solvant Et_2O { peu polaire, aprotique

③

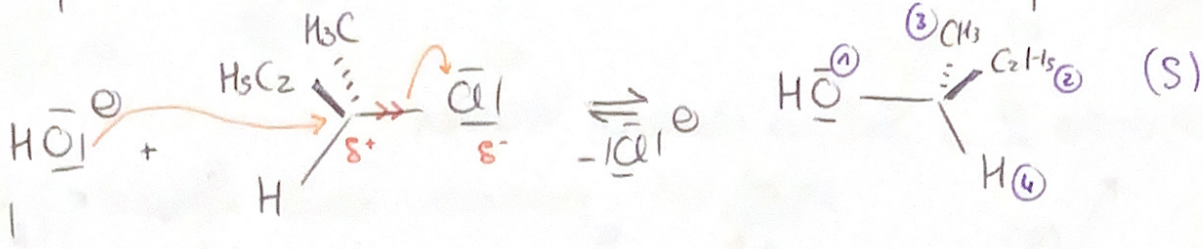


Stabilisé : mesomérie

S_N1 solvant : EtOH

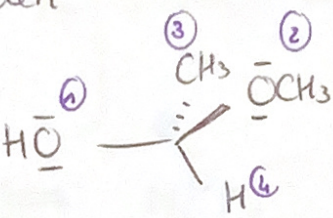
* Exercice 3

① Unique stéréoisomère => S_N2. ($OH^\ominus$ bon nucléophile)



L. S_N2 : mécanisme concerté
Attaque $OH^\ominus$ à l'opposé de Cl
Inversion Walden

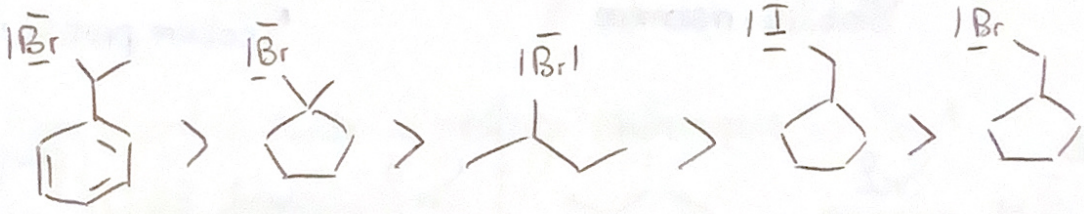
Idem pour le second :



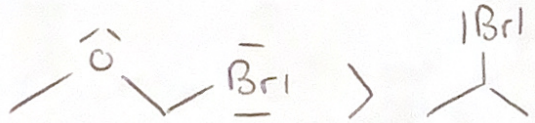
* Exercice 4 :

① • I plus réactif que Br (moins important)
• Mésomérie favorise S_N1 (très important)
• III aire > II aire > I aire (important)

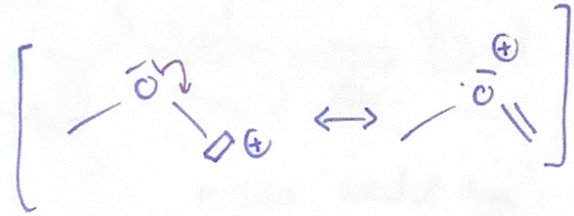
=>



②



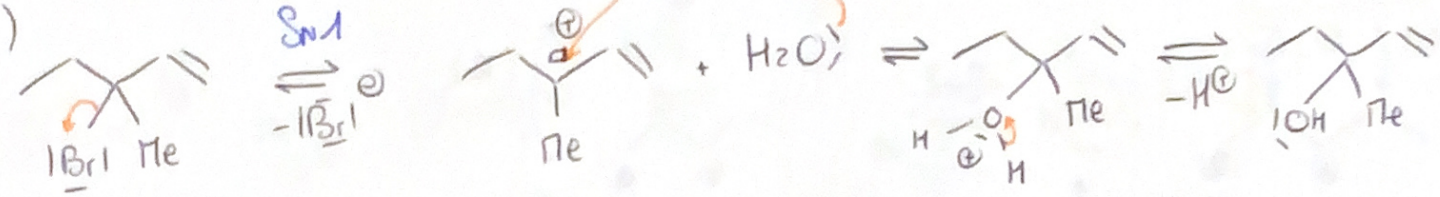
Formes mésomères de



=> Stabilisa° => favorise S_N1.

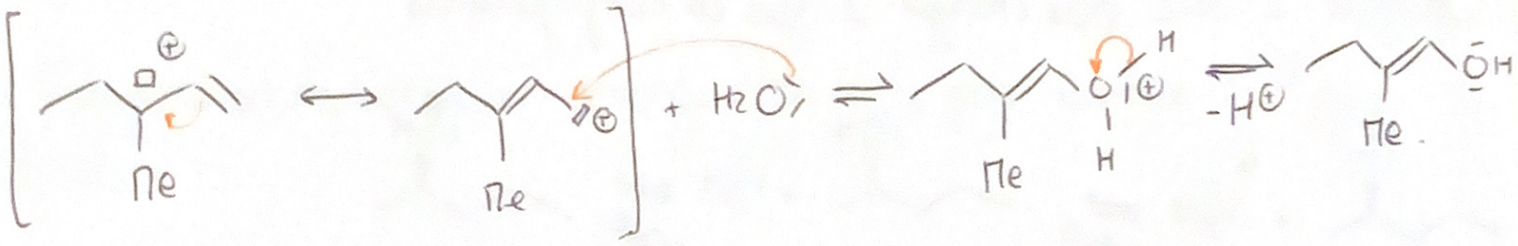
③

a)



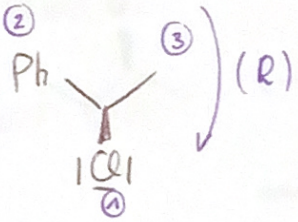
↳ SN1 : substrat IIIaire + mesomerie + Nu faible

b) Alcool primaire : formes mesomères

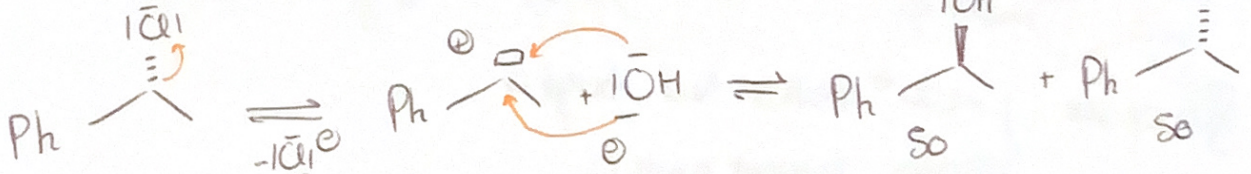


* Exercice 5 :

① a). (S)-1-chloro-1-phénylethane :

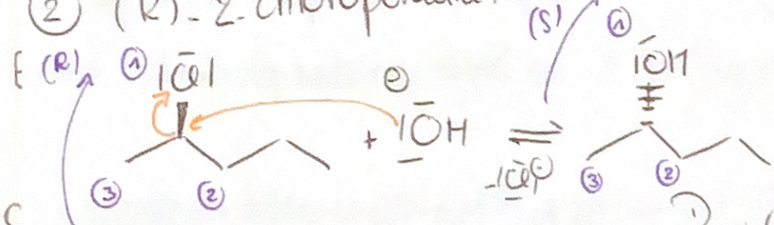


b). Mécanisme SN1 : Carbocation stabilisé par mésomérie



! ↳ Activité optiQ nulle => mélange racémique => SN1

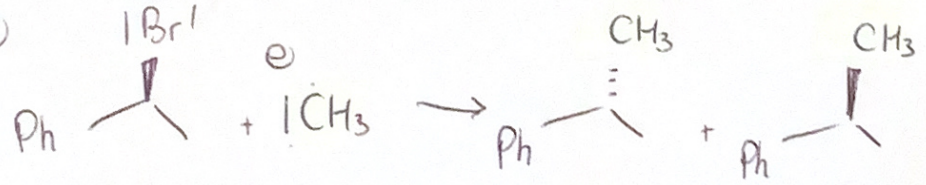
② (R)-2-chloropentane :



Activité optique => chiral non racémiQ
=> SN2

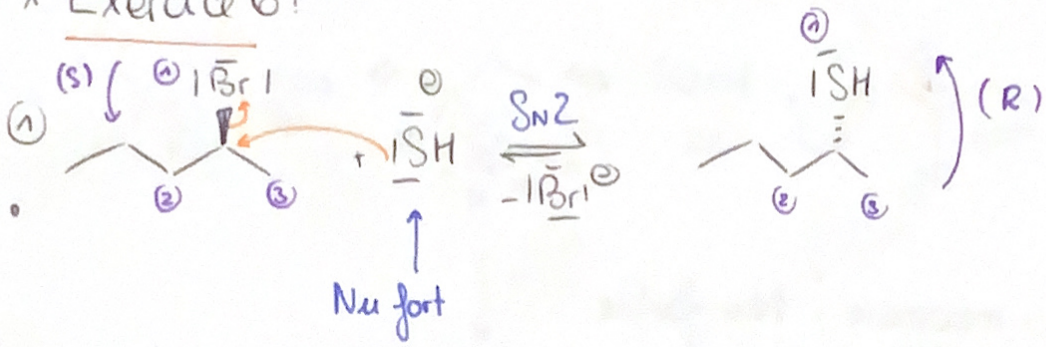
: (S)-pentan-2-ol.

③

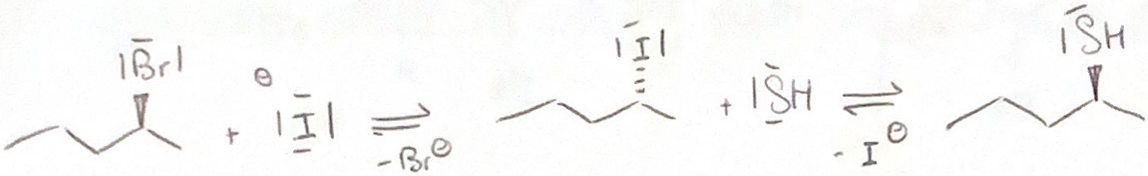


22,5% produit (R)
=> 45% SN1
=> 55% SN2
} mélange

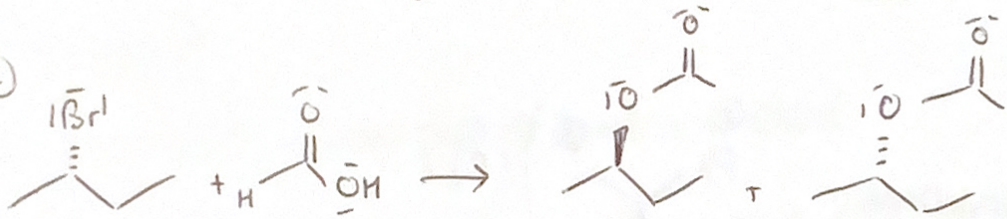
* Exercice 6 :



. On fait 2 SN2 pour changer 2 fois de configurations.

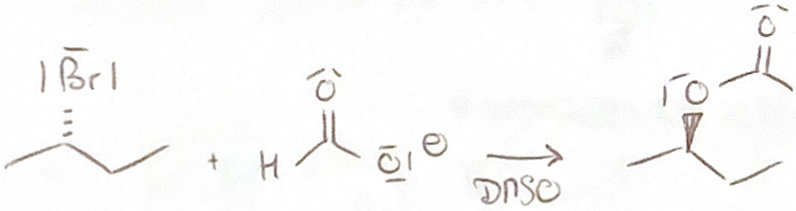


(2)



optiquement inactif

SN1

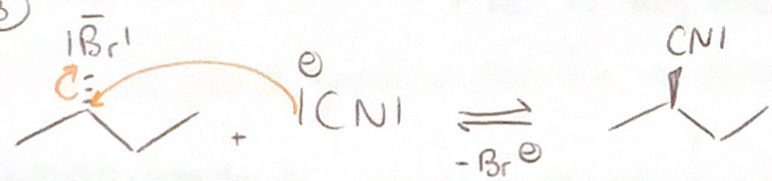


un seul produit : SN2

↳ SN2 favorisée : HCOO⊖ meilleurs Nu : chargé ⊖

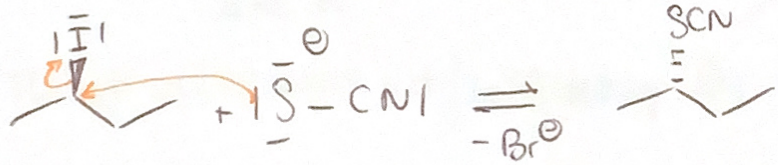
DMSO : Solvant aprot. Q

(3)



CN⊖ bon Nu : petit et chargé

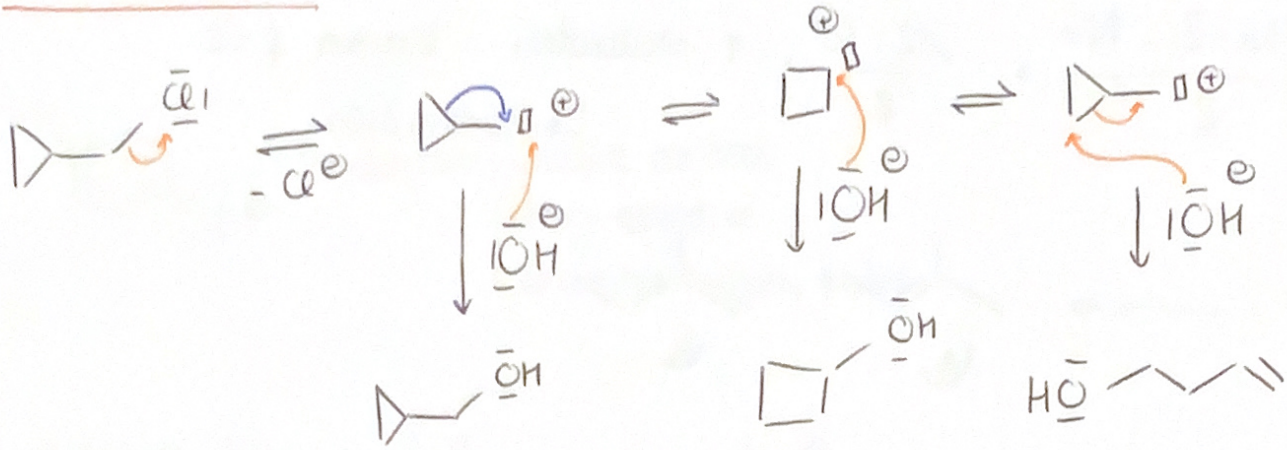
=> SN2 : un seul produit



SCN⊖ bon Nu : petit et chargé

=> SN2 : un seul produit

* Exercice 6 (bis)



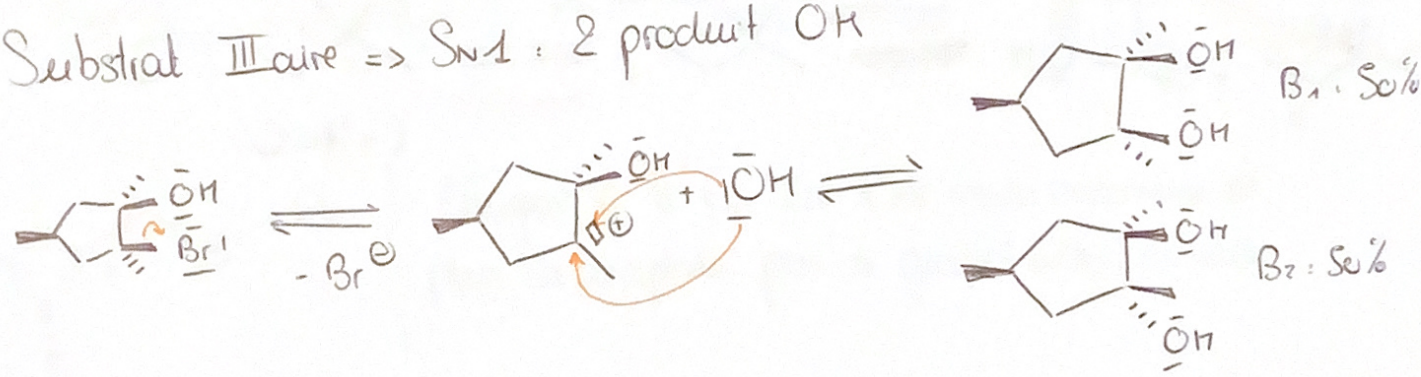
• Transposition carbocation : echange d'un CH_3 pour avoir un $C^{\oplus}$ plus stable.

* Exercice 7 :

① A à 3 C* : aucun plan de symetrie => chiral

② Substrat IIIaire => SN1 : 2 produit OH

a)



B_1 : 50%

B_2 : 50%

b)- Plan de symetrie dans B_1 => achirale : compose méso

Pas de plan de symetrie dans B_2 => chirale

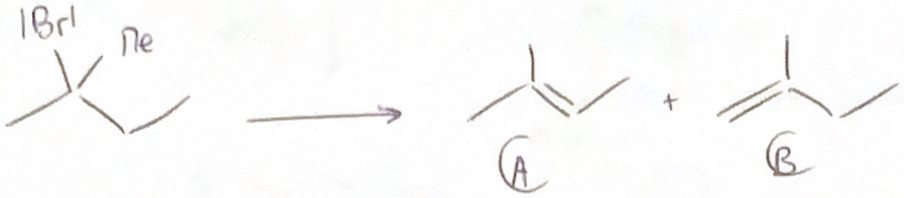
Entre B_1 et B_2 changement de 1 configuration sur 3 => diastéréoisomeres

c)- Melange optiquement actif : seulement B_2 chiral, et pas son enantiomere

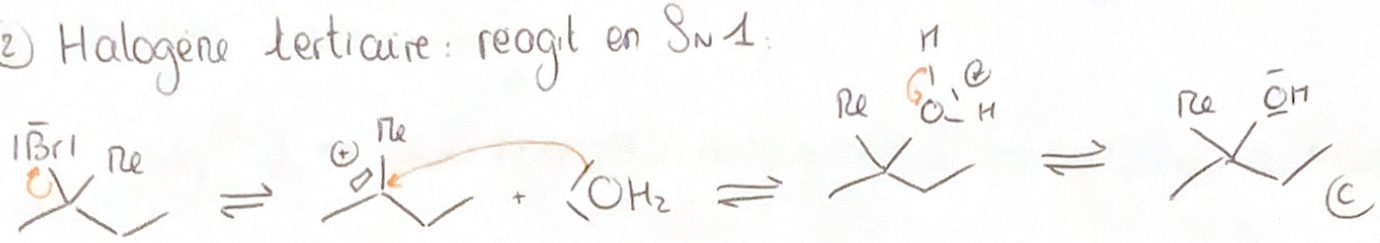
* Exercice 8

① $N_i = \frac{2N_C + 2 - N_H}{2} = \frac{12 - 10}{2} = 1$ insaturation : liaison C=C

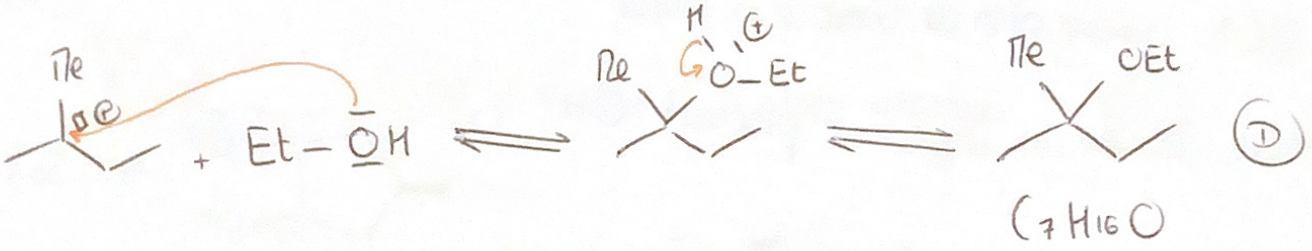
La elimination



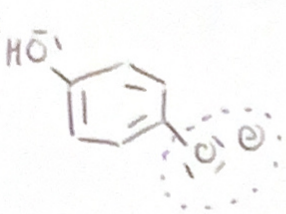
② Halogène tertiaire : reagit en S_N1 :



③ L'ethanol peut aussi jouer le rôle de nucléophile

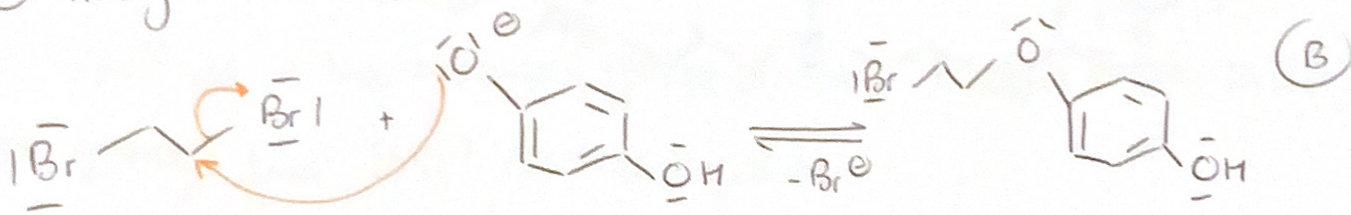


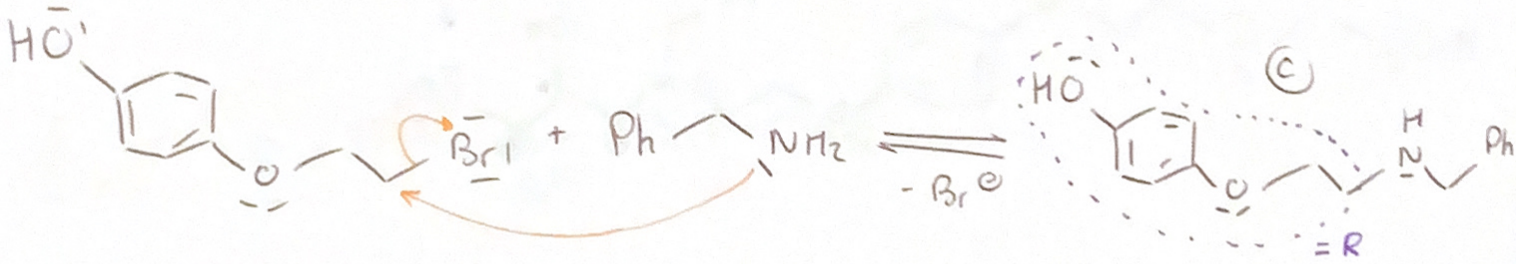
* Exercice 9

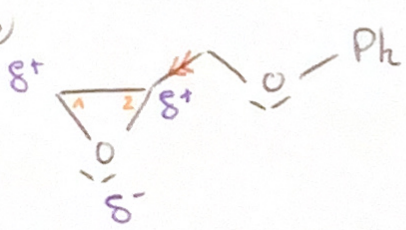
① 

Nucléophile : { Doublet non liant
charge négative
encombrement assez faible

② Halogéné Iaire => S_N2

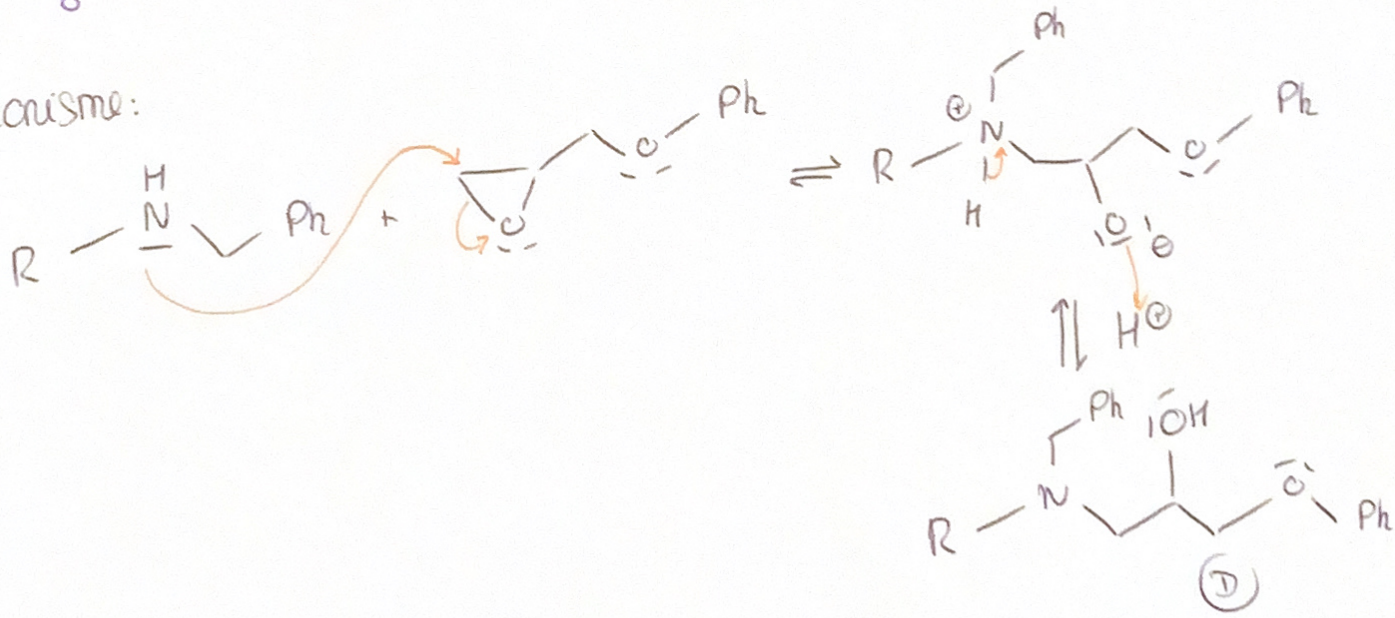




③ 

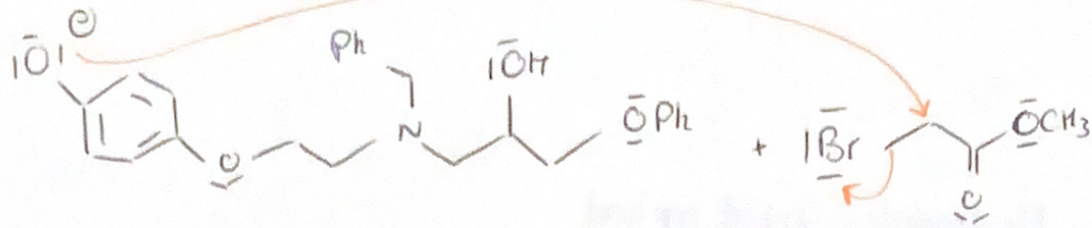
{ Attaque sur le C_1 car il est moins encombré et plus électrophile : pas de groupement alkyl donneur

Mécanisme :

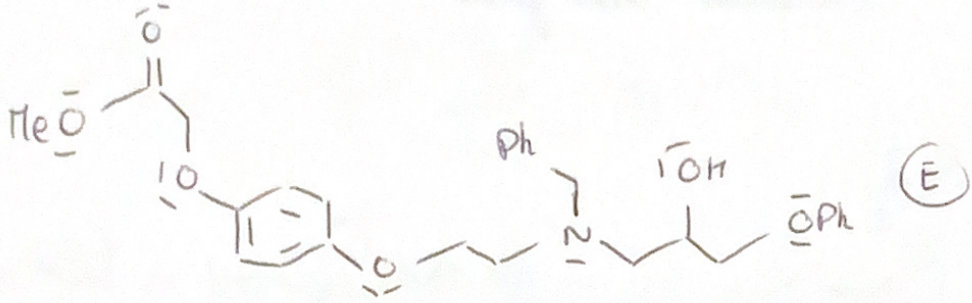


(4)

D' :

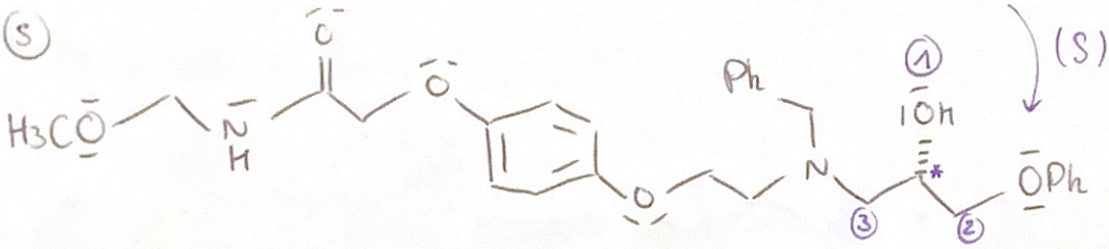


$-Br^{\ominus}$ ⇅ S_N2 (1aire)



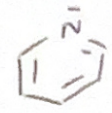
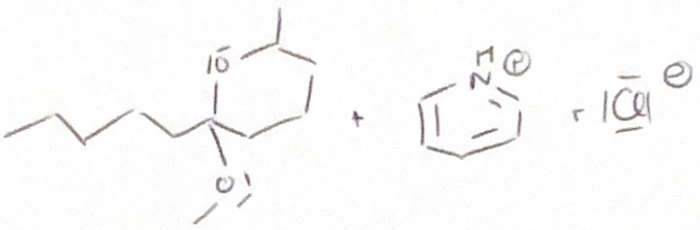
(E)

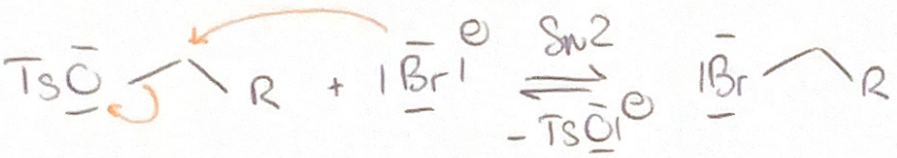
(5)



(S)

Exercice 10

① A + TsCl +  (pyr) = 

② 

③ $OH^{\ominus}$ est un trop mauvais groupe partant : basique => peu nucléofuge
Sans passage par $TsO^{\ominus}$ réaction impossible.

④ Br Iode => S_N2