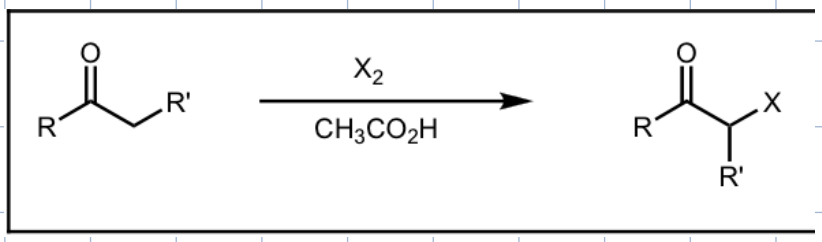
Les Énols

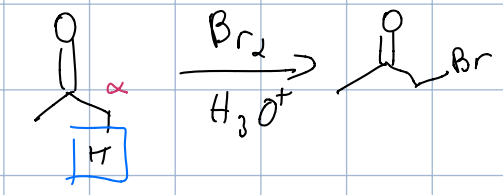
- Halogenation acide



Halogenation alpha → 1 carbone away from the carbonyl group

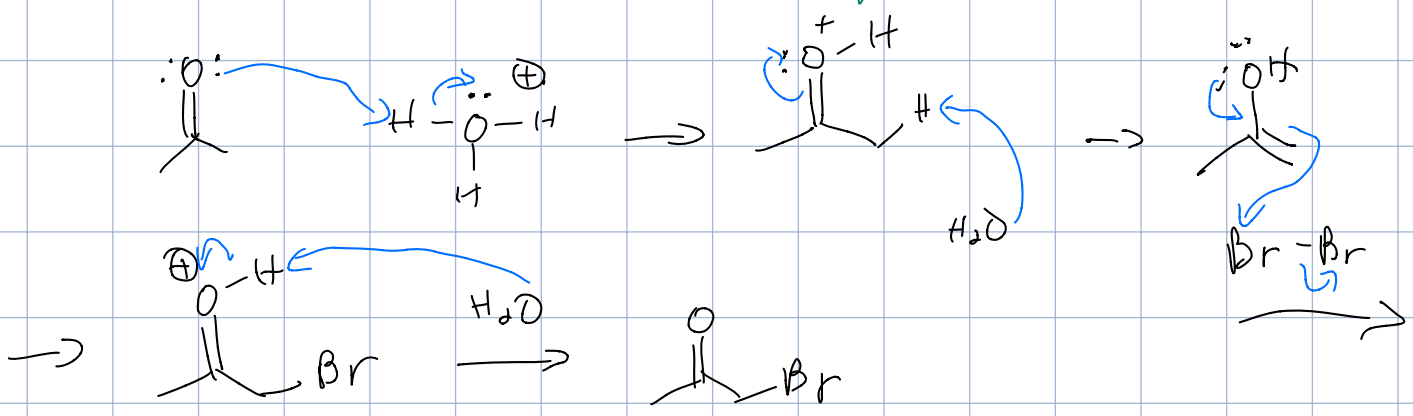
acide → un seul carbone alpha se fait remplacé

cétone

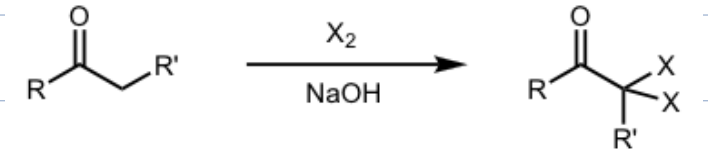


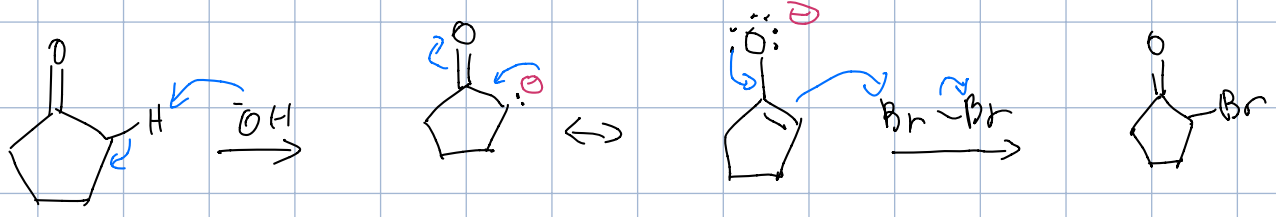
Mécanisme

transformer en énol

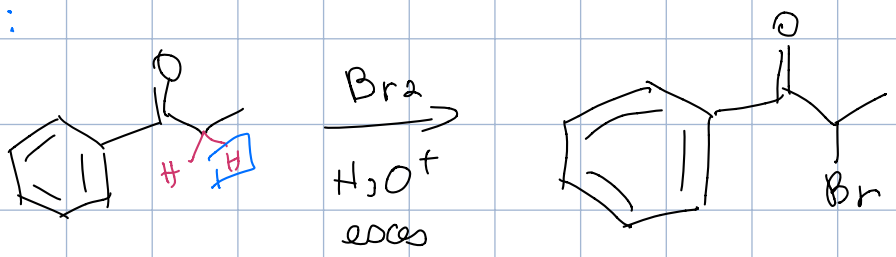


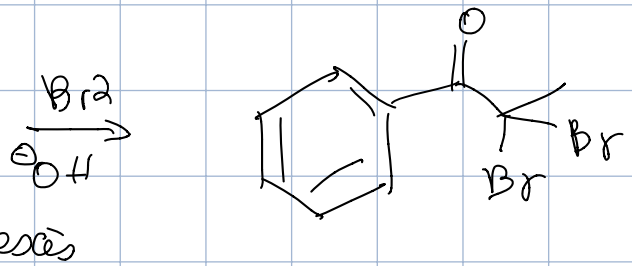
- Halogénation basique



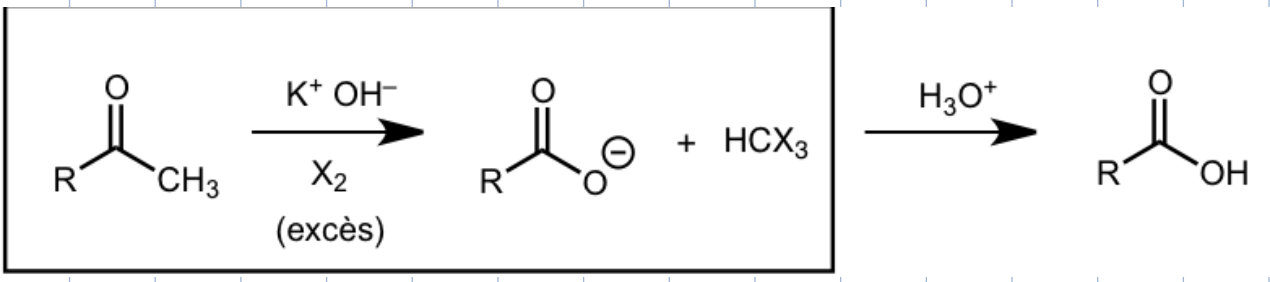


exo 1 :

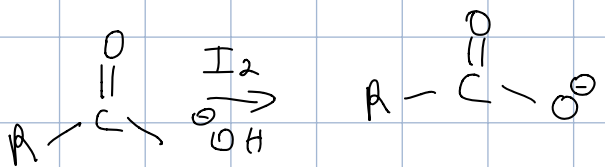




– Réaction haloforme

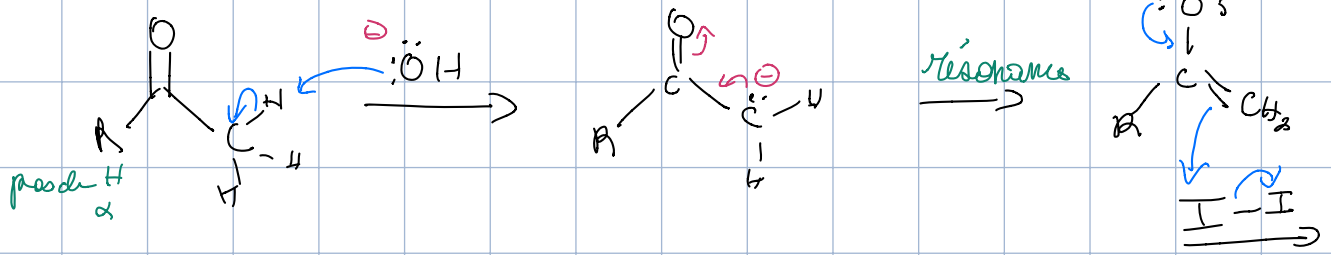


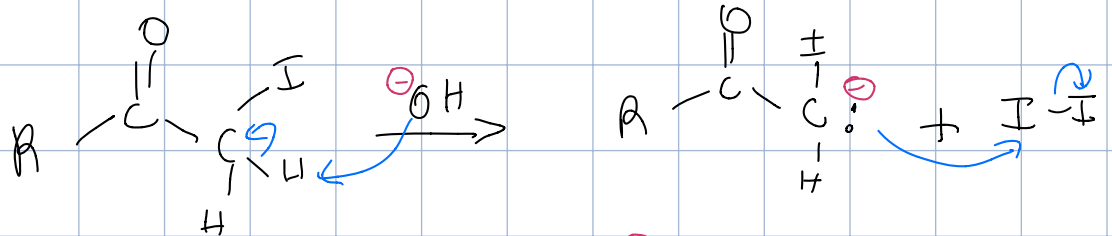
Iodoform test

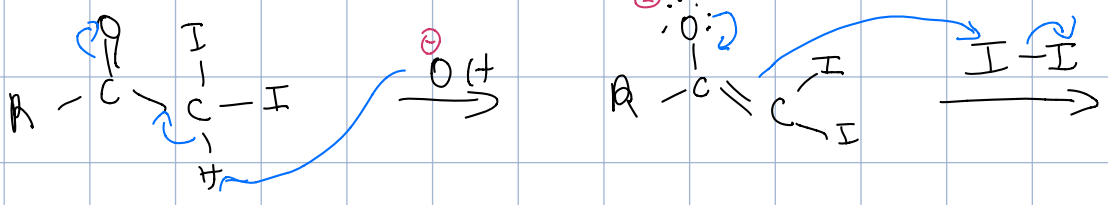


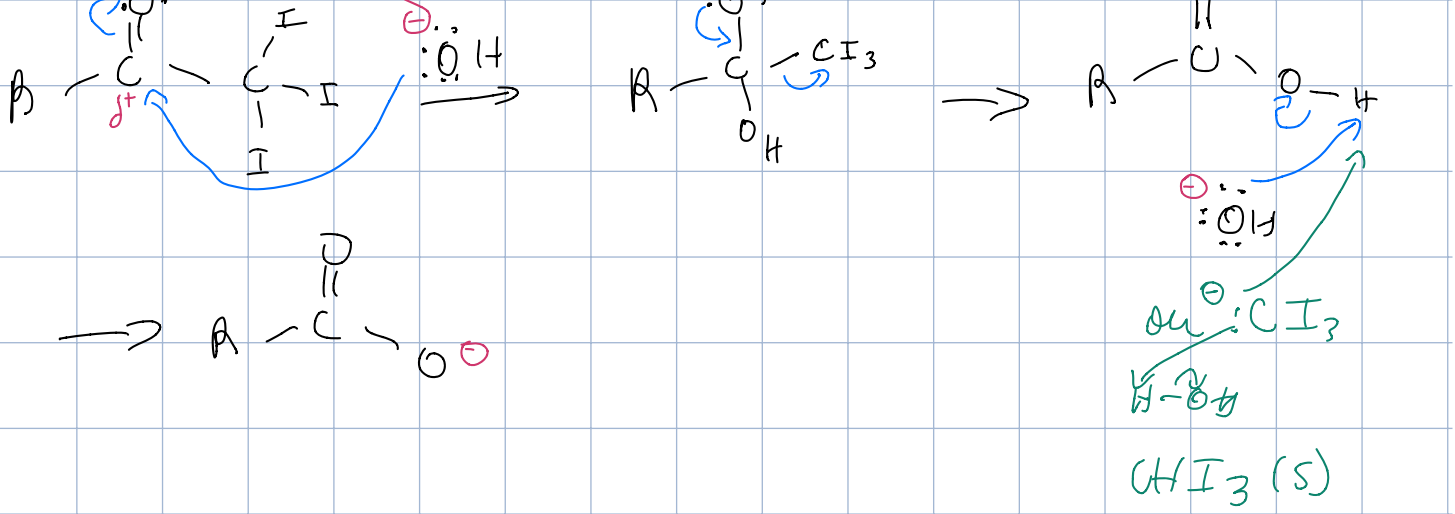
CHI_3 (S)

Mécanisme

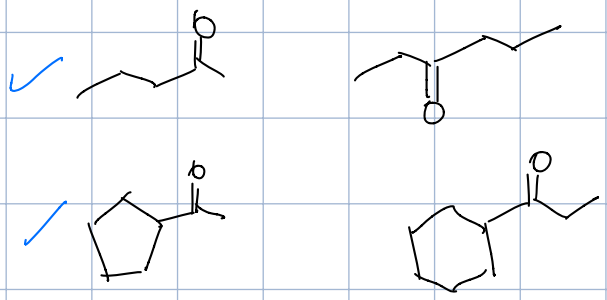


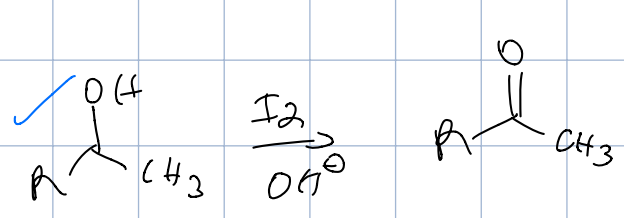




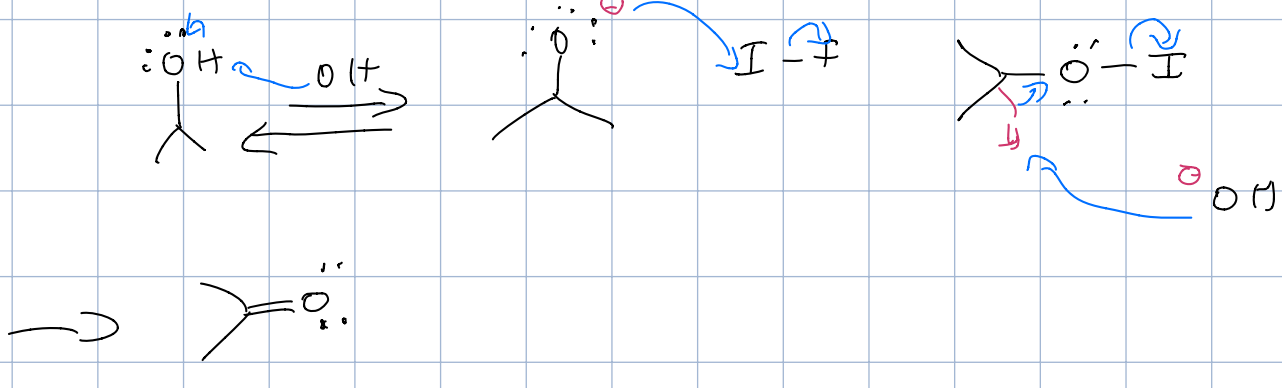


ex 1 : positif idoform test

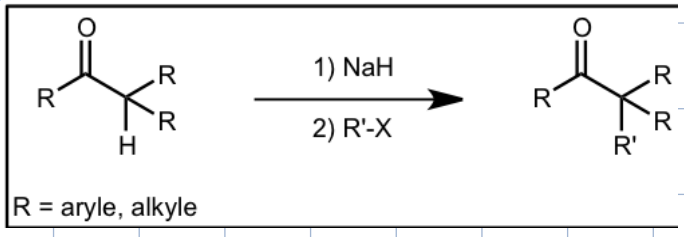


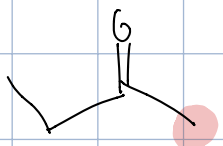


alcool (2°) et aldéhyde (tous les halogène I, Br, Cl



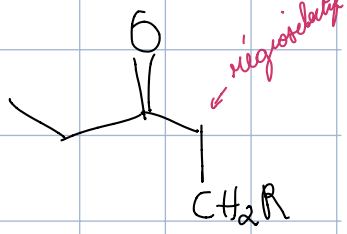
- Alkylation α des aldehydes et des cétones

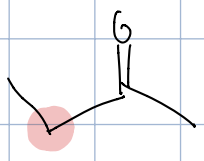




(base encombré)
1. LDA -78°C
2. RCH_2Br
(CH_3I) (I)
(1°) ou méthyle car SN2

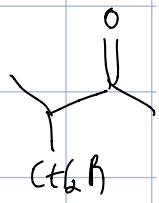
retire un proton α
ajoute la partie alkyl

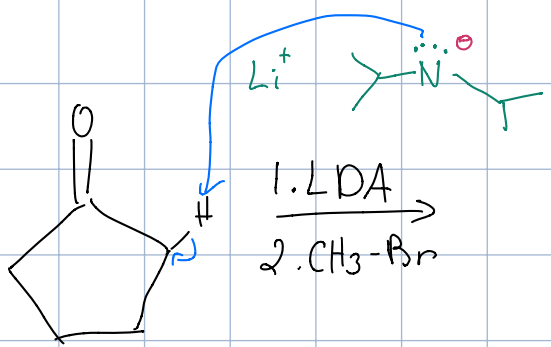




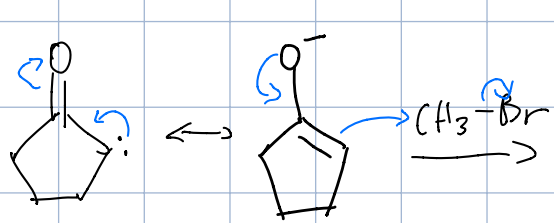
1. NaH 25°C
2. RCH_2Br
(CH_3I) (I)

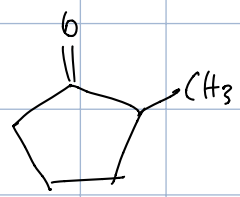
substitution au carbon plus substitué

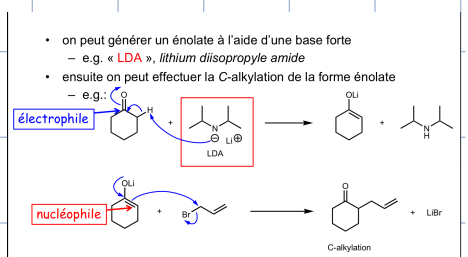




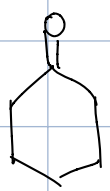
1. LDA
2. CH_3-Br



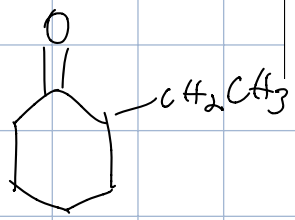




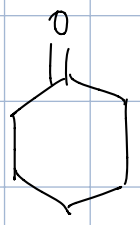
esc 1 :



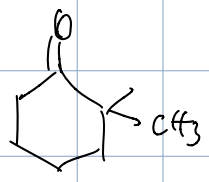
1. LDA
2. CH_3CH_2-Br



ex 2 :



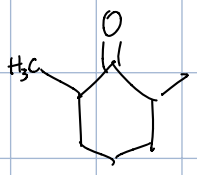
1. NaH 23°C
2. CH_3Br



produit thermodinamique

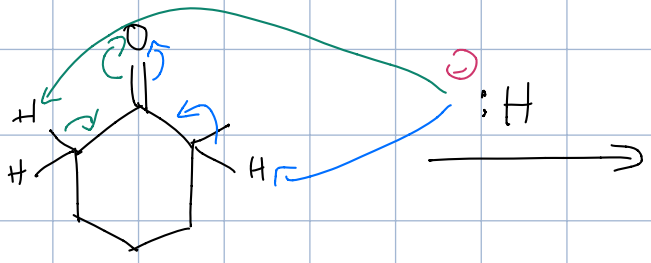
ex 3 :

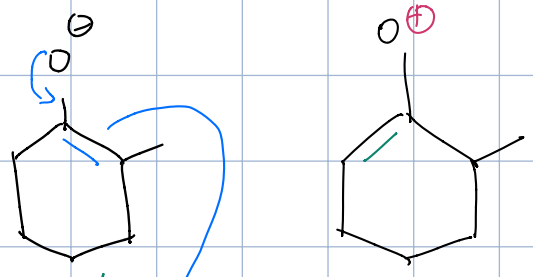
1. LDA -78°C
2. CH_3Br



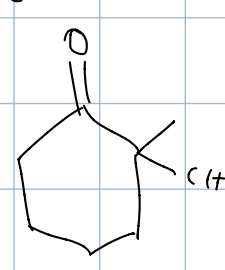
produit kinétique

ex 2 : mécanisme



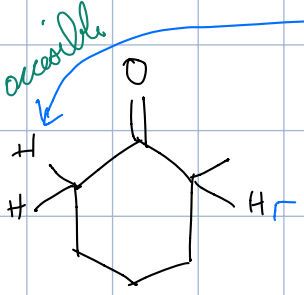


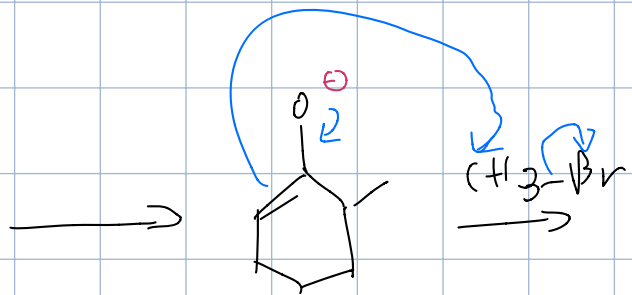
plus stable

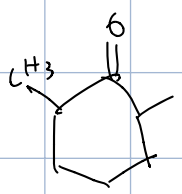


ex 3 : mécanisme

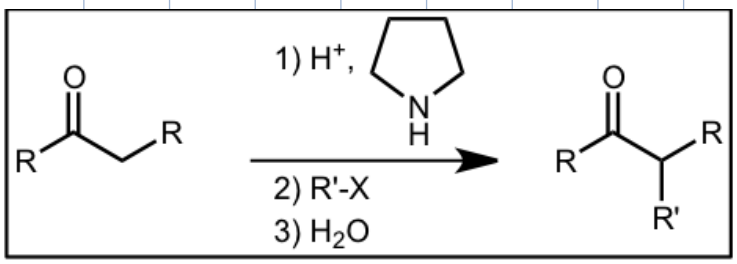
plus accessible





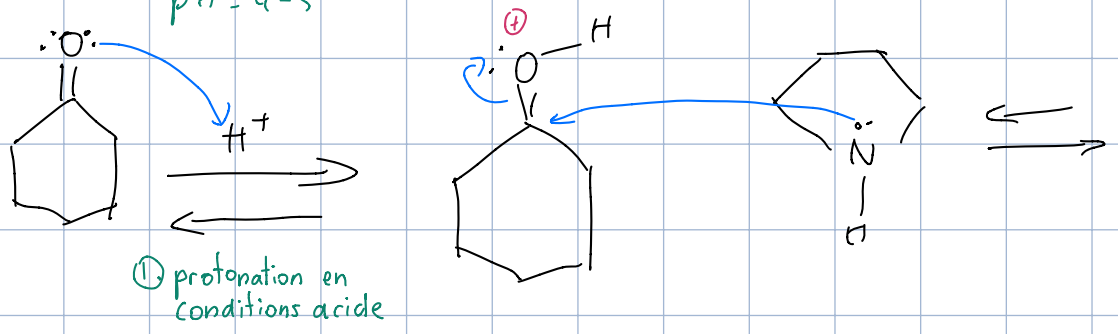


- Énamine

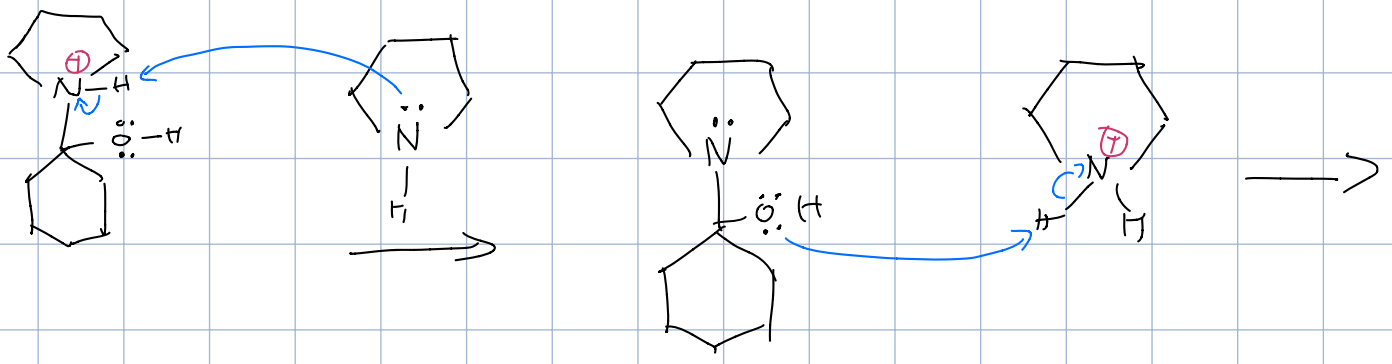


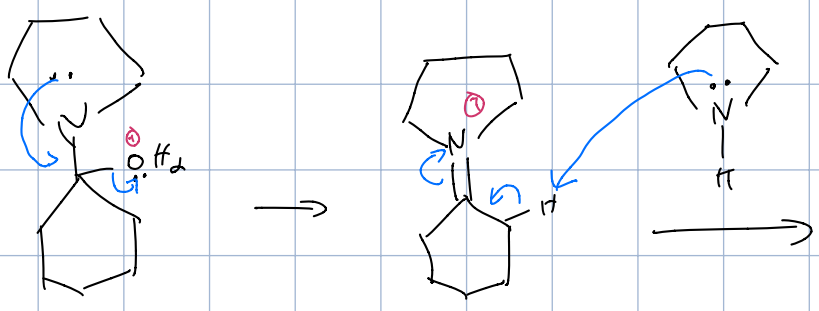
mécanisme : formation d'un énamine

pH = 4-5

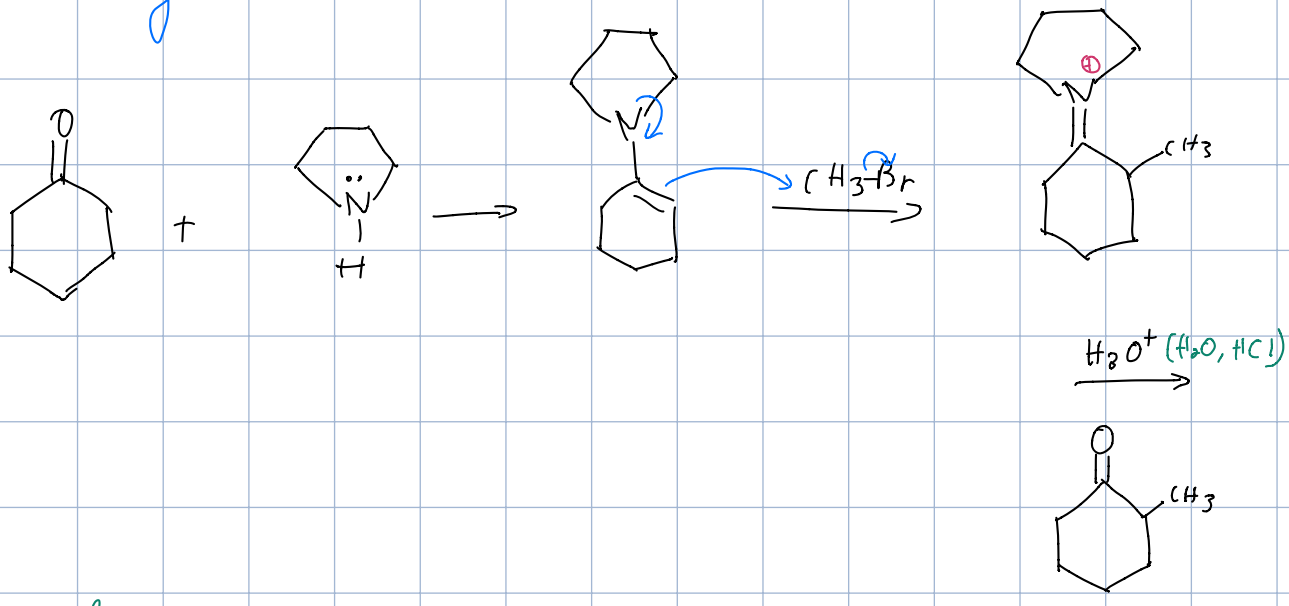


① protonation en conditions acide

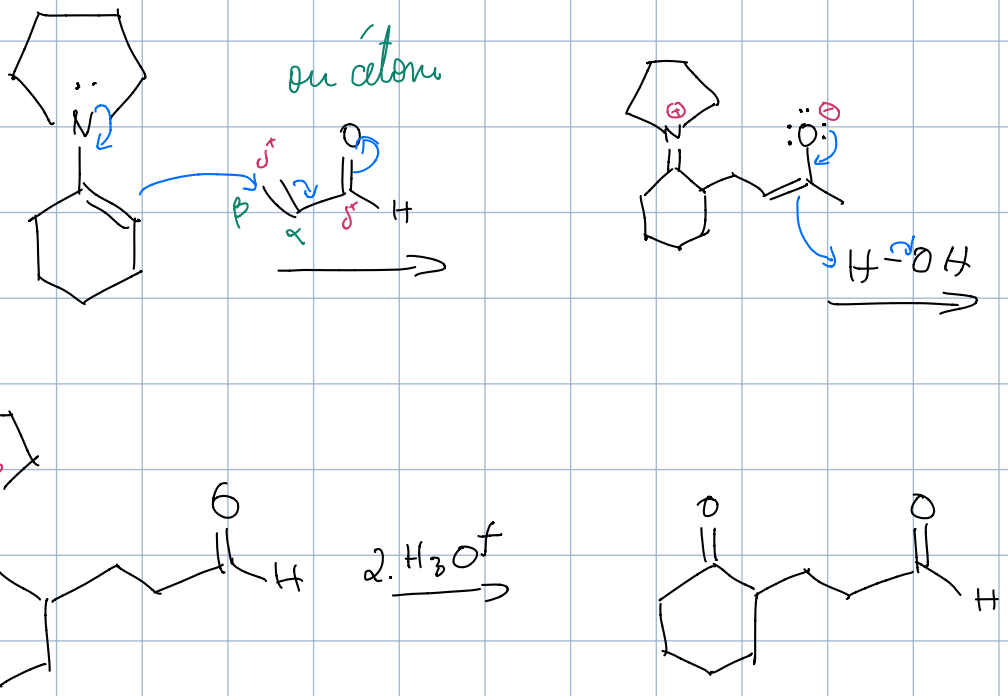




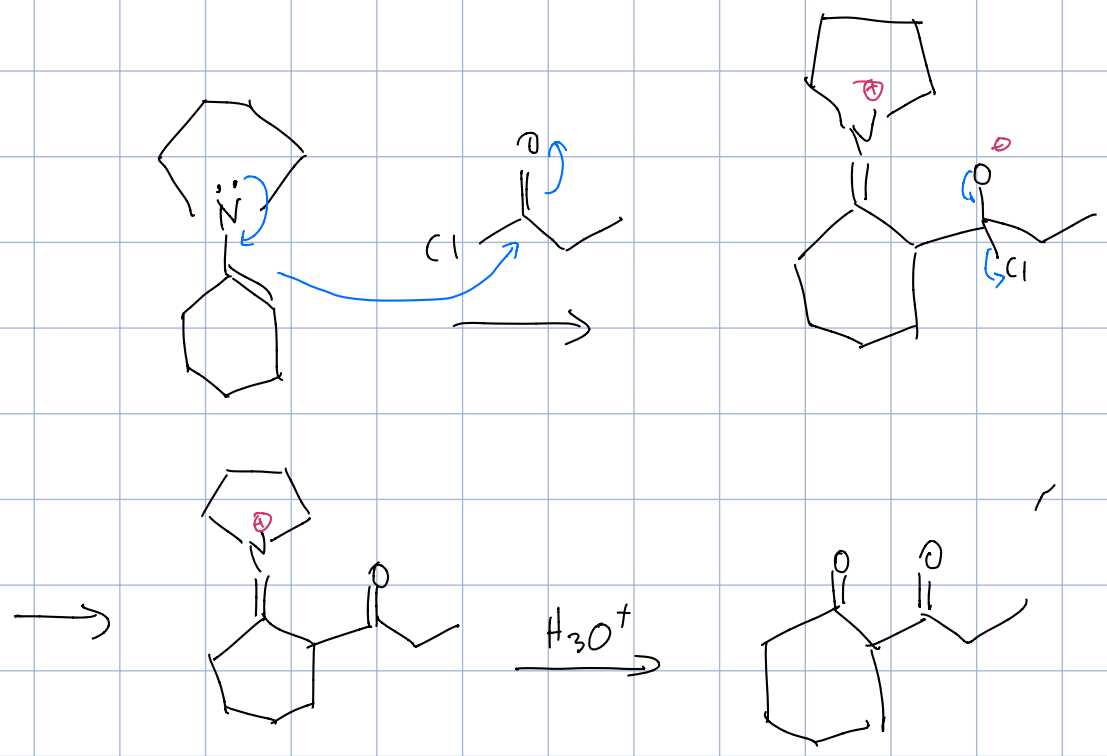
ex 1 : Alkylation des cétones en utilisant énamine



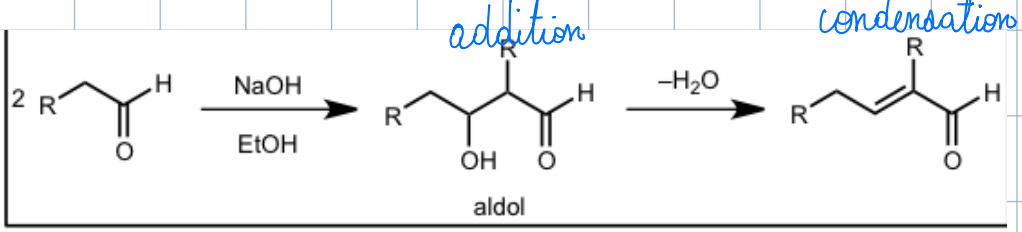
ex 2 : base faible préfère attaché le carbone β



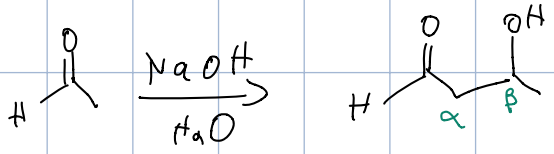
ex 3 :



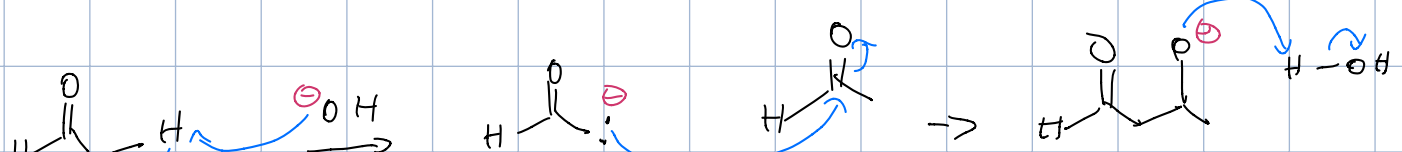
- Énols Condensation aldolique

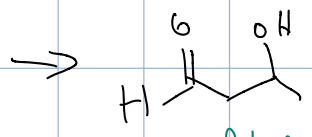


addition



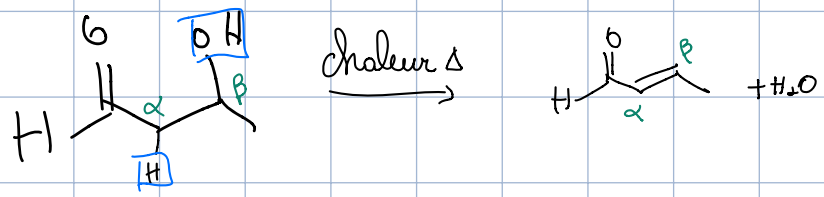
mécanisme : addition



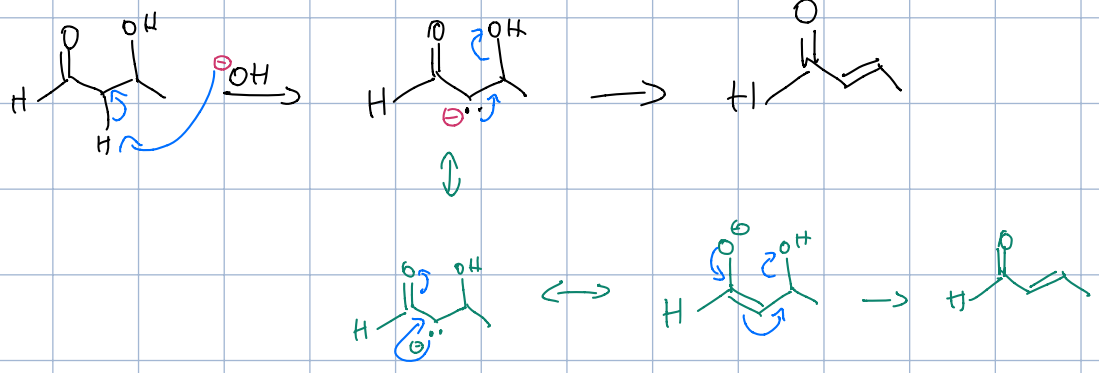


aldol

Condensation

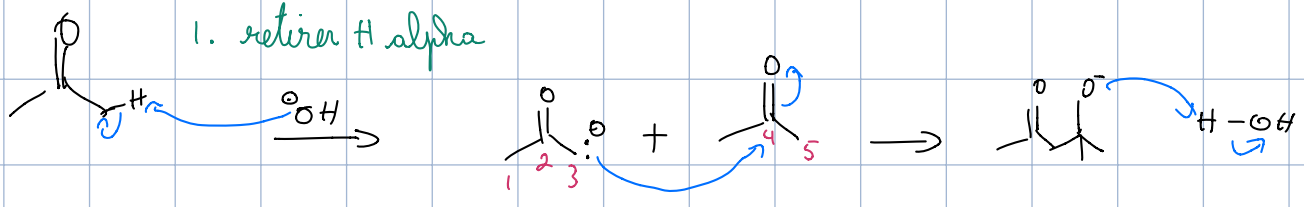


Mécanisme : condensation

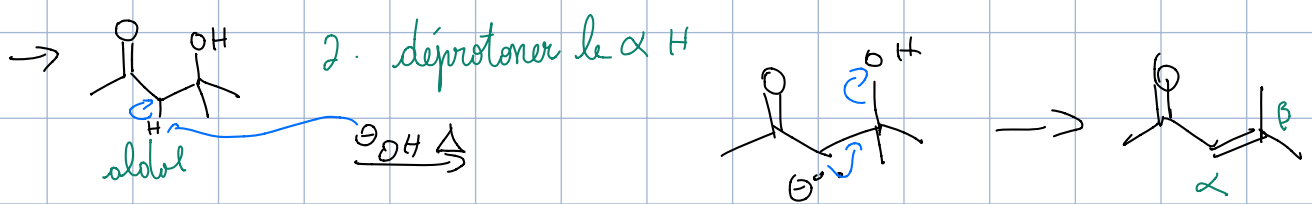


ex 1 :

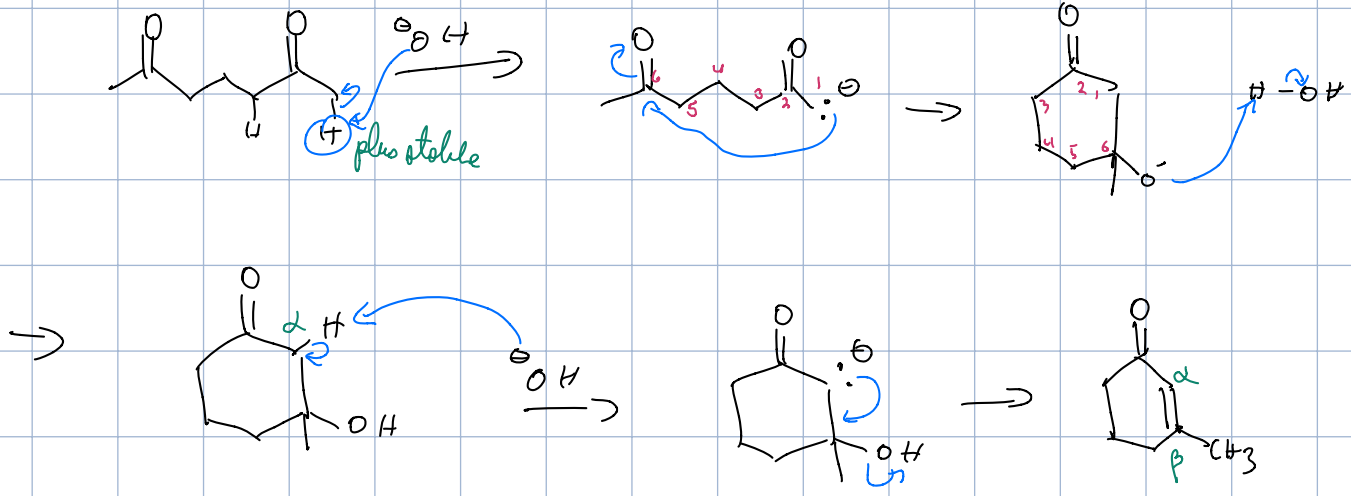
1. retirer H alpha



2. déprotoner le α H

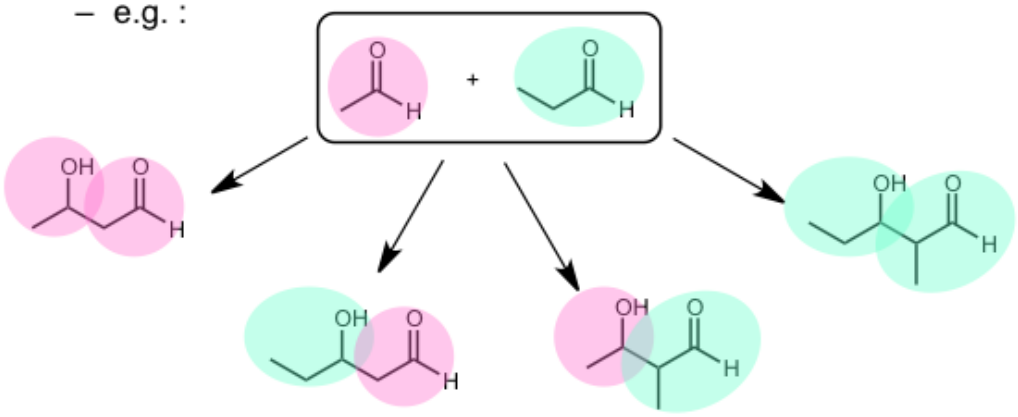


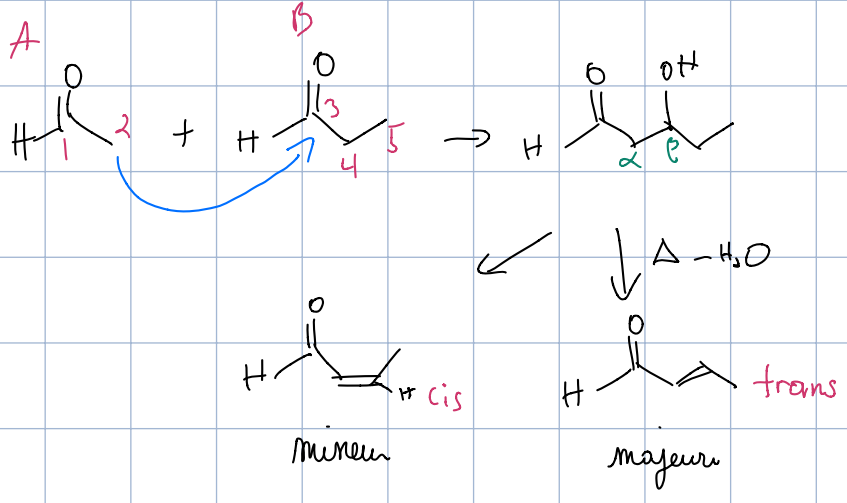
ex 2



Condensation aldolique croisée

- à partir de deux différents aldéhydes (ou cétones), la condensation aldolique donne un mélange de quatre différents produits
  - e.g. :

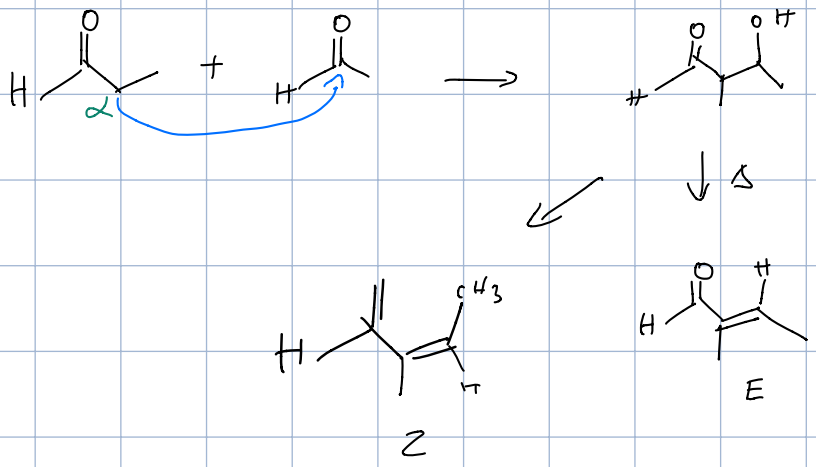




A + B
B + A
A + A
B + B

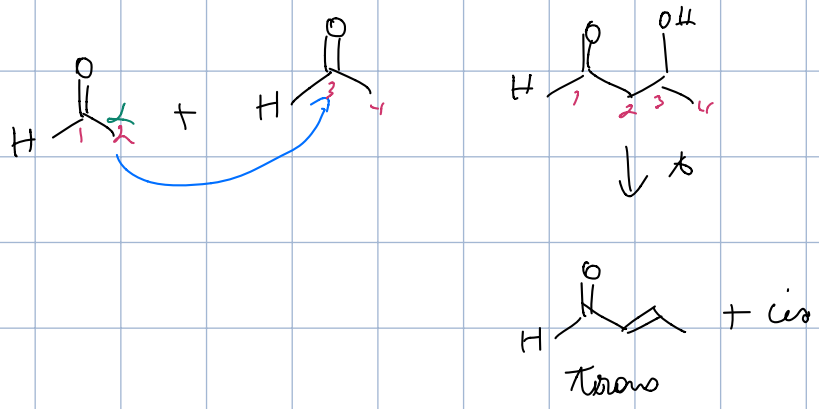
Isomères → cis / trans
E / Z

B A



Z E

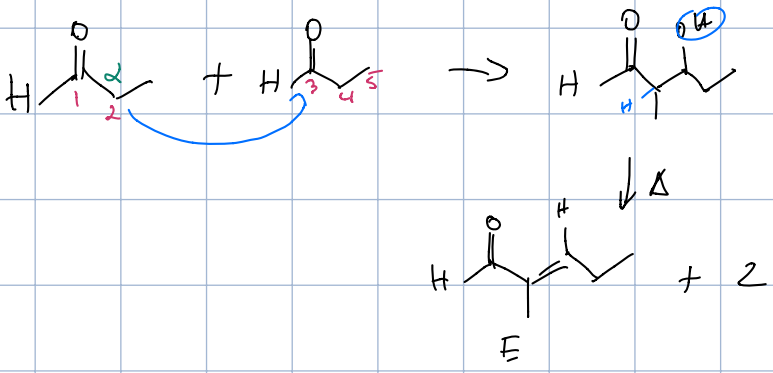
A A



+ cis

Trans

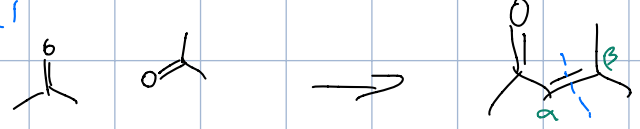
B B



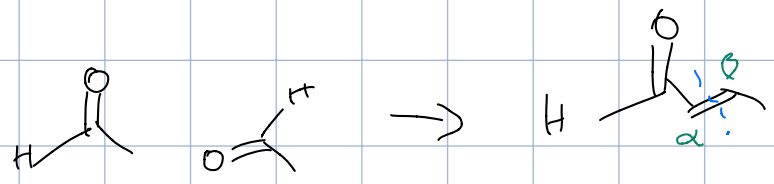
E + Z

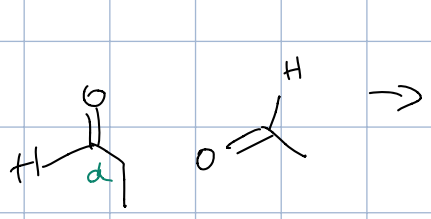
déterminer les réactifs

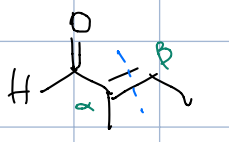
ex 1

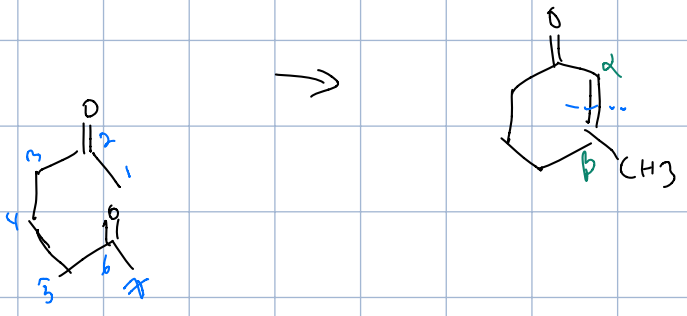


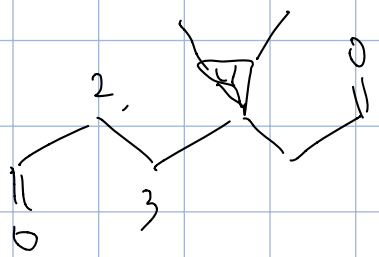
ex2

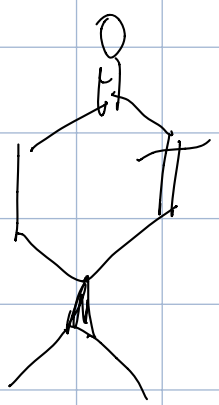


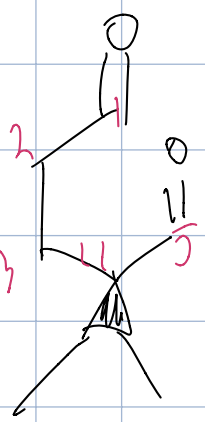


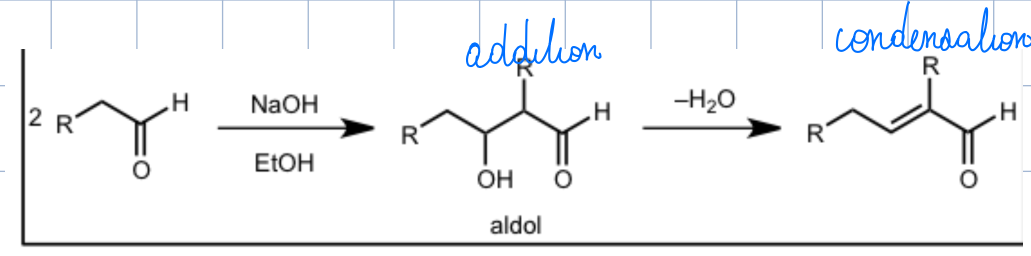






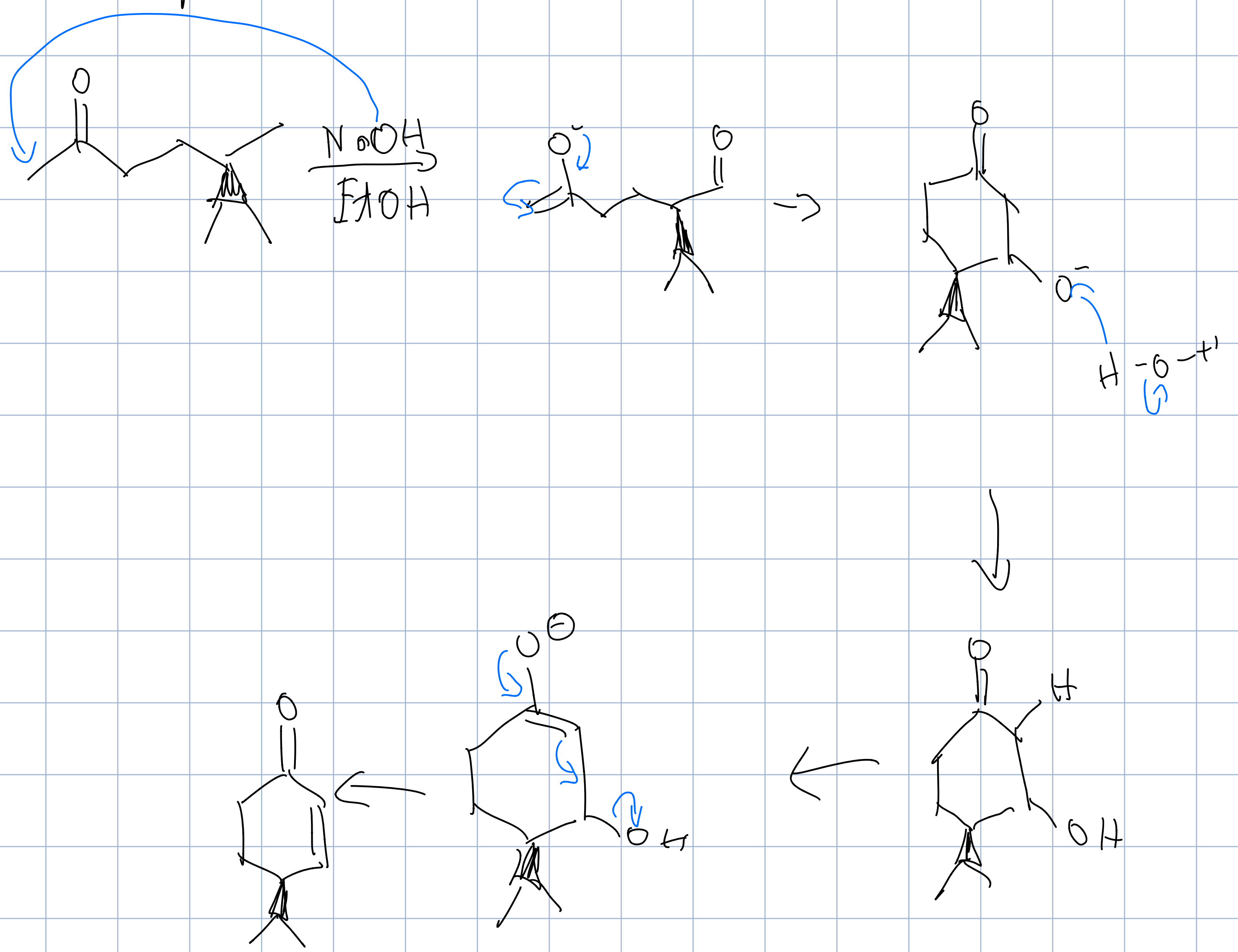






addition
condensation
2
R
H
O
NaOH
EtOH
R
OH
O
H
aldol
$-H_2O$

question 9



NaOH
EtOH
OH