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Université de Batna 2005/2006

Faculté de Médecine

Département de Pharmacie

Cours de Chimie Générale

1ère Année Pharmacie

Chimie Organique Descriptive

Chapitre VII : Les aldéhydes et cétones

D'après le cahier de :

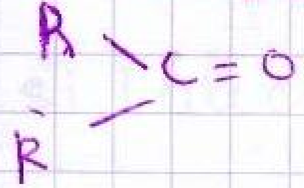
I. Hadef

Created by: T. Djebaili

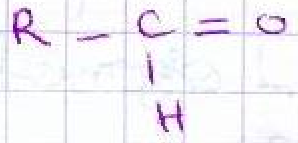
ALDEHYDES Et CETONES

(derivés carbonyles $>C=O$)

I - Nomenclature:

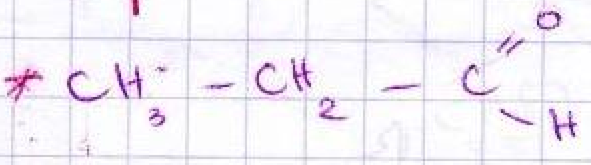


$RR'C=O$ one (cétone),

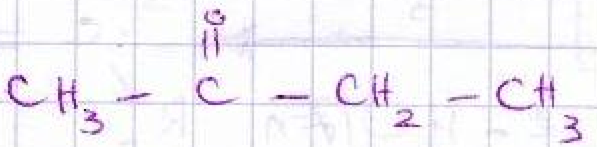


$R-CH=O$ al (Aldehyde)

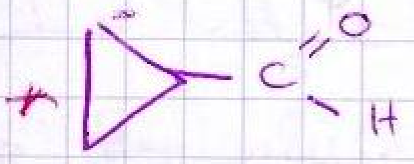
exp

* 

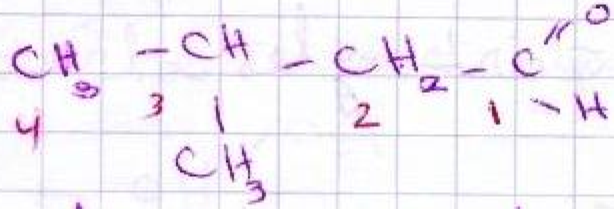
CH_3-CH_2-CHO propanal,

* 

$CH_3-CO-CH_2-CH_3$ Butan-2-one

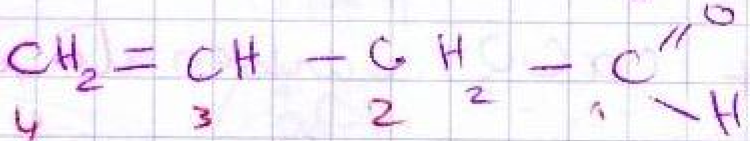
* 

cyclopropyl methanal.

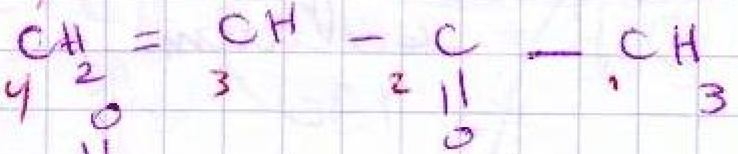
* 

$CH_3-CH(CH_3)-CH_2-CHO$ 3-methyl Butanal.

on donne au carbonyl l'indice le plus faible

* 

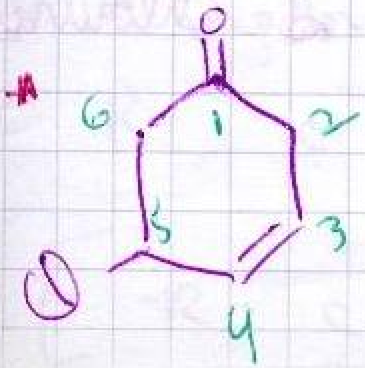
$CH_2=CH-CH_2-CHO$ But-3-énal.

* 

$CH_2=CH-CO-CH_3$ But-3-èn-2-one.

* 

2 methyl cyclopentanone.

* 

5 chlorocyclohex-3-enone.

II - préparation :

1- R^{on} d'oxidation :

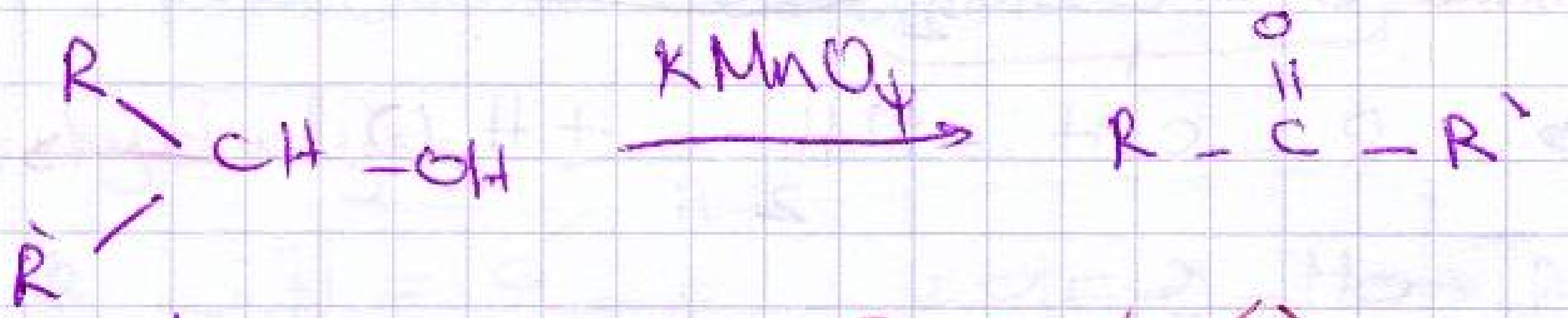
a - à partir des Alcools :

Alcool I $\xrightarrow[200-300°c]{O_2, Cu}$ Aldehyde.

$R-CH_2-OH \xrightarrow{//} R-\overset{\overset{O}{\|}}{C}H$

$KMnO_4$ continue l'oxydation à l'acide (oxydation forte) :

$R-CH_2OH \xrightarrow{KMnO_4} RCOOH$



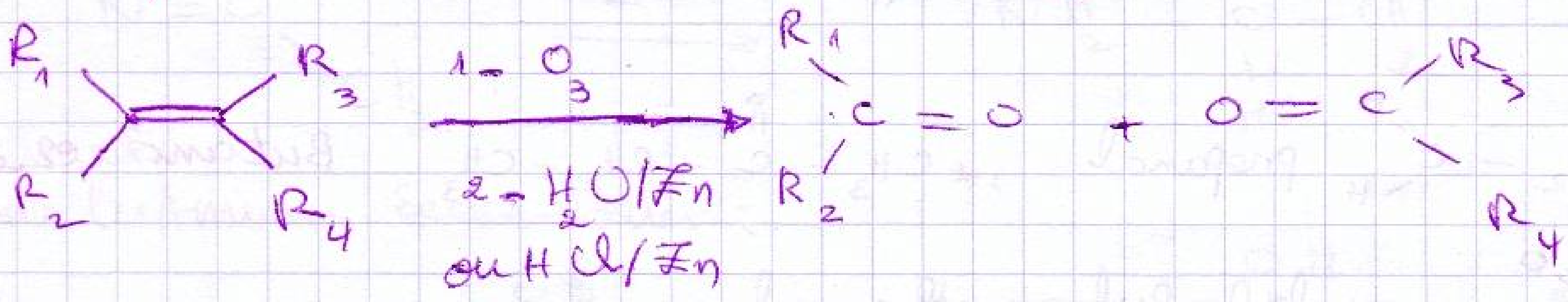
$R(R')CH-OH \xrightarrow{KMnO_4} R-\overset{\overset{O}{\|}}{C}-R'$

* autre oxydants : CrO_3 /  réactif plus selectif que $KMnO_4$ ⇒ on s'arrête au stade de l'aldehyde $RCH_2OH \xrightarrow{CrO_3/Pyr} R-C(=O)H$.

conclusion : pour préparer les Aldehydes soit utiliser [O] par (O_2, Cu) ou CrO_3/  à partir d'Alcool I.

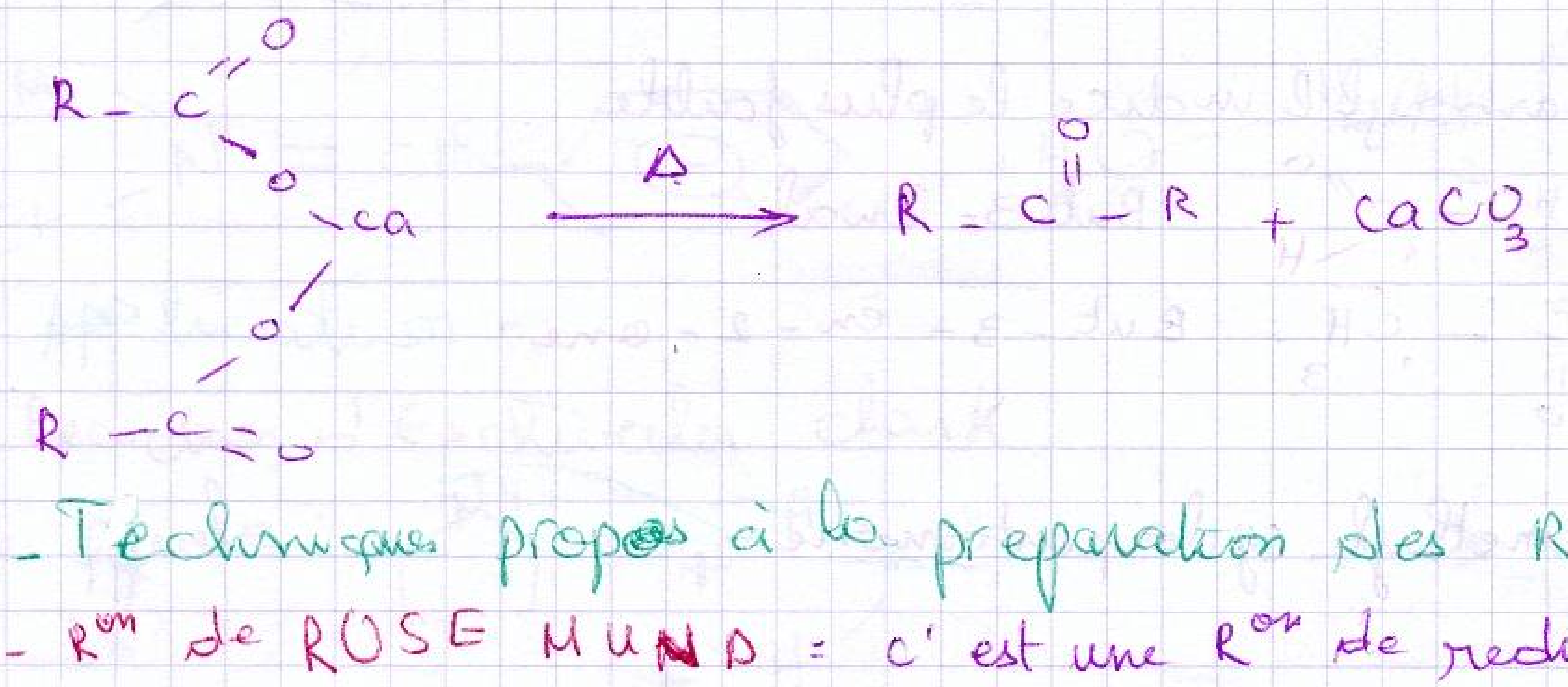
. pour les cétone on utilise $KMnO_4$ avec un Alcool II

b- à partir des alcènes : - ozonolyse :



2- R^{on} de Pyrolyse :

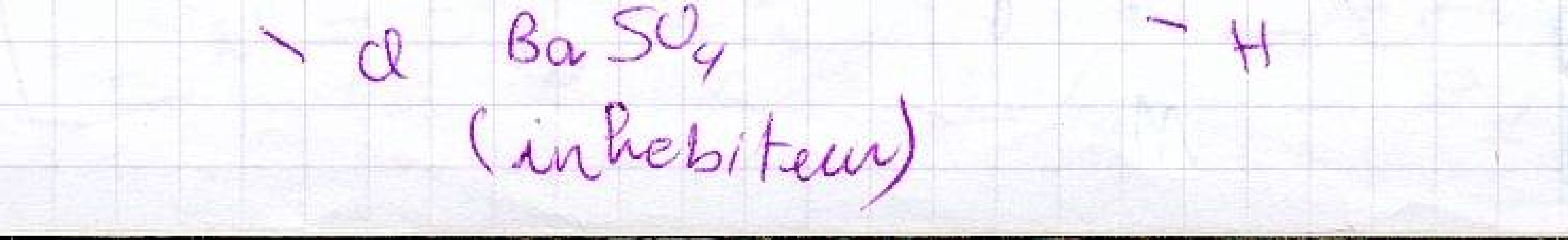
pyrolyse des sels de Ca ⟶ dérivés carbonyles



carbonate de calcium

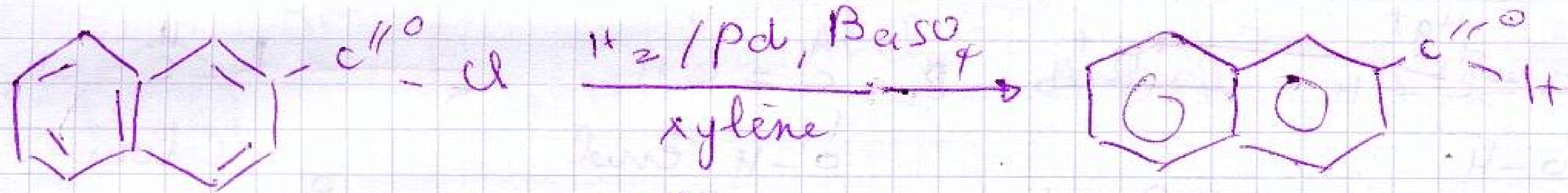
3- Techniques propres à la préparation des $R-C(=O)H$

a- R^{on} de ROSEMUND : c'est une R^{on} de réduction de chlorures d'acides :

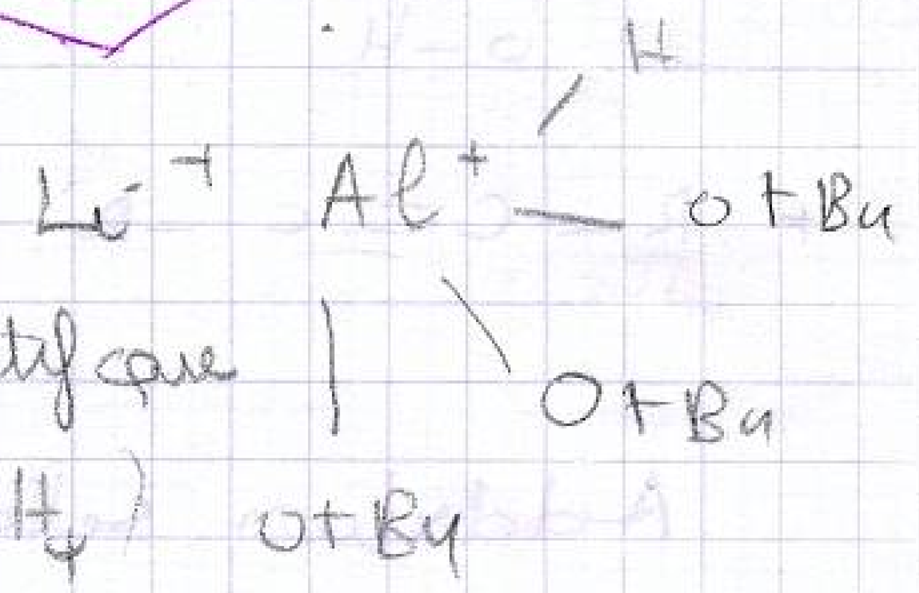


$R-C(=O)Cl \xrightarrow[BaSO_4]{H_2/Pd} R-C(=O)H + HCl$

(inhebiteur)



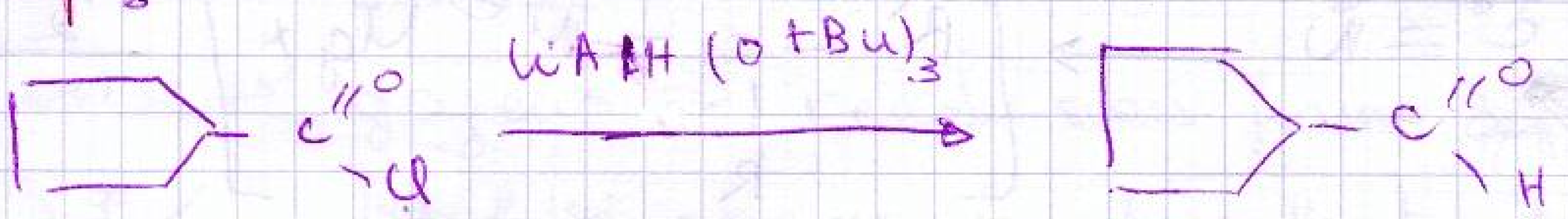
$$R-C(=O)Cl \xrightarrow{LiAlH(OtBu)_3} R-C(=O)H$$



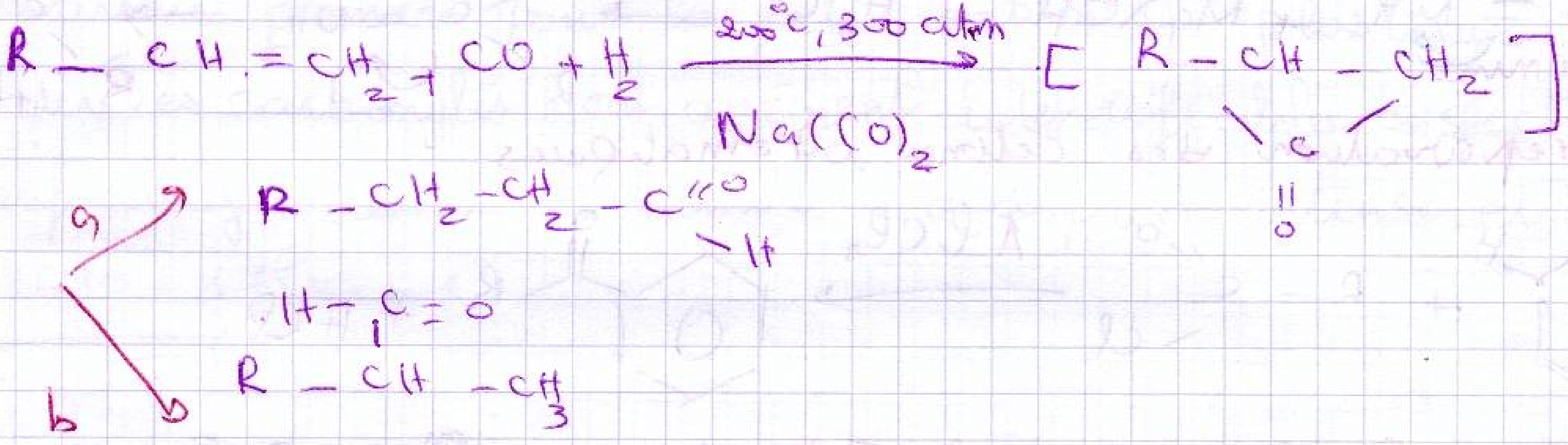
- réactif que

$$LiAlH_4 \xrightarrow[Ether]{+BuOH} LiAlH(OtBu)_3 \ (LiAlH_4)$$

exp :



b - R^{on} Oxo ou reduction de REPPE



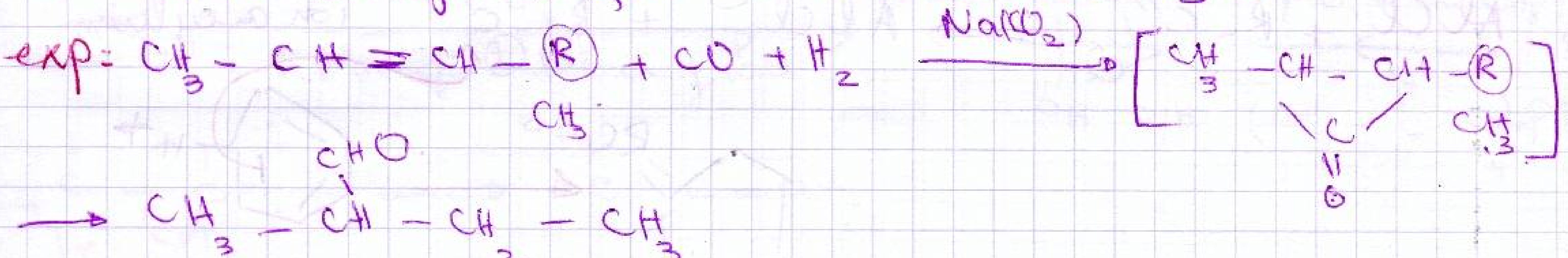
$$R-CH=CH_2 + CO + H_2 \xrightarrow[Na(CO)_2]{200°C,\ 300\ atm} [R-CH-CH_2\ (C=O)]$$

a → $R-CH_2-CH_2-C(=O)H$

b → $R-CH(CHO)-CH_3$

si l'alcène est symetrique → 1 seul aldehyde.

exp :



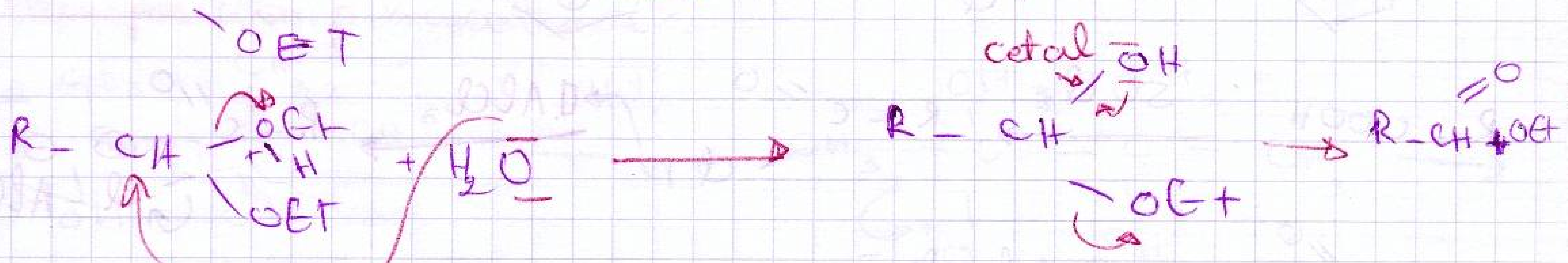
$$CH_3-CH=CH-(R)(CH_3) + CO + H_2 \xrightarrow{Na(CO_2)} [CH_3-CH-CH-(R)(CH_3)\ (C=O)]$$

$$\rightarrow CH_3-CH(CHO)-CH_2-CH_3$$

b- hydrolyse acide d'acetals

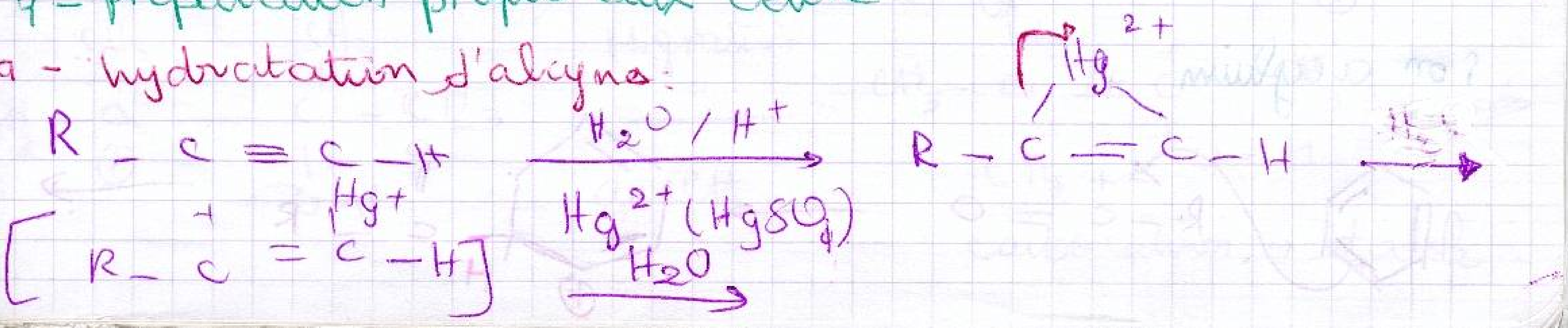
acétal → equivalent d'un diéther

$$R-CH(OEt)_2 \xrightarrow{H_2O/H^+} R-CHO + 2EtOH.$$



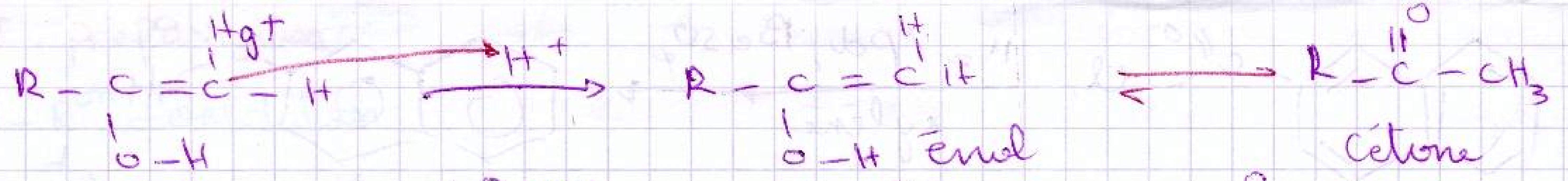
4 - preparation propos aux cétone

a - hydratation d'alcynes

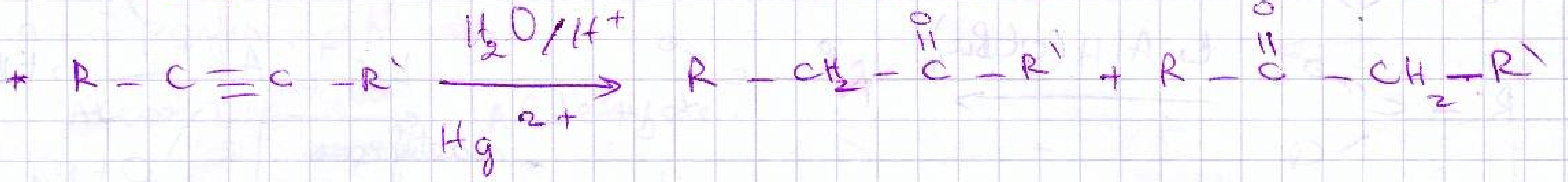


$$R-C\equiv C-H \xrightarrow{H_2O/H^+} R-C=C-H\ (Hg^{2+}) \rightarrow$$

$$[R-\overset{+}{C}=\overset{Hg^+}{C}-H] \xrightarrow[H_2O]{Hg^{2+}(HgSO_4)}$$



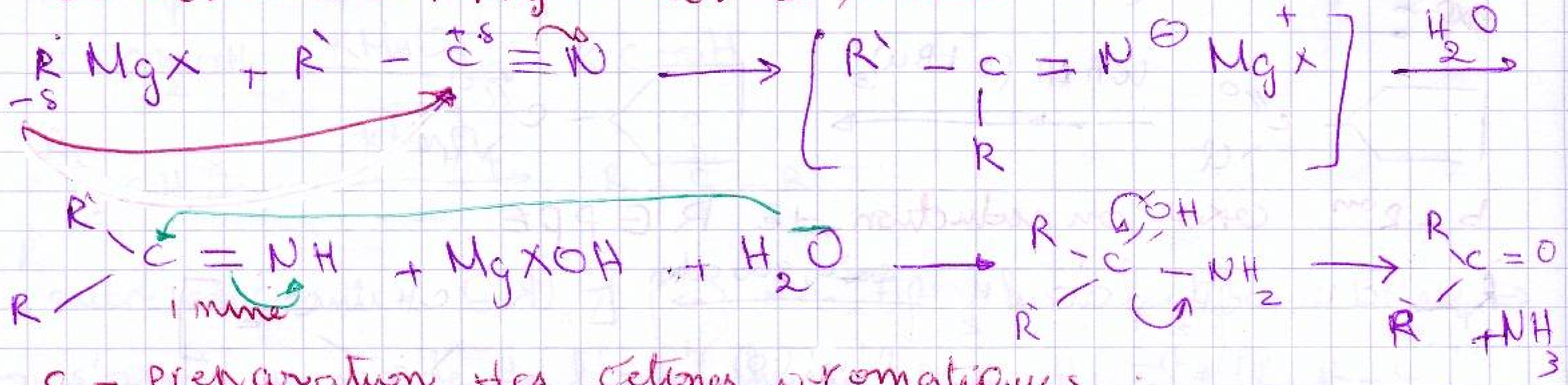
$R-C(OH)=C(Hg^+)-H \xrightarrow{H^+} R-C(OH)=CH_2$ énol $\rightleftharpoons R-CO-CH_3$ cétone



$* \; R-C\equiv C-R' \xrightarrow[Hg^{2+}]{H_2O/H^+} R-CH_2-CO-R' + R-CO-CH_2-R'$

Addition selon Marcovnicov.

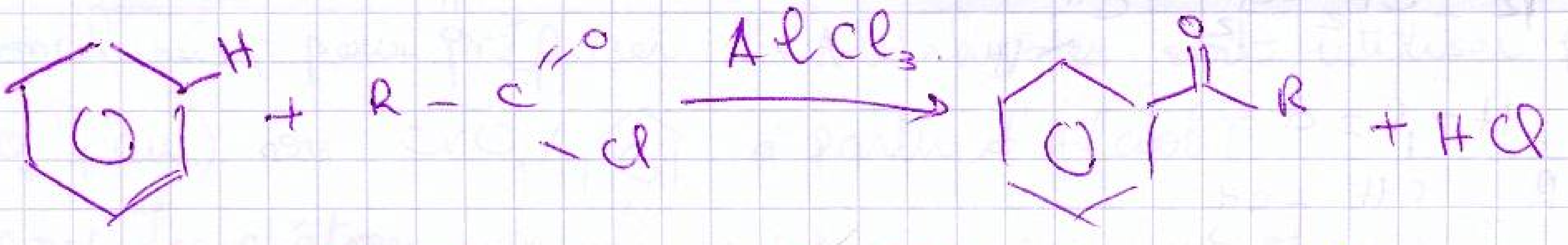
b- action de RMgX sur les nitriles ·



$\overset{-\delta}{R}MgX + R'-\overset{+\delta}{C}\equiv N \longrightarrow [R'-C(R)=N^{\ominus}\,Mg^{+}X] \xrightarrow{H_2O}$

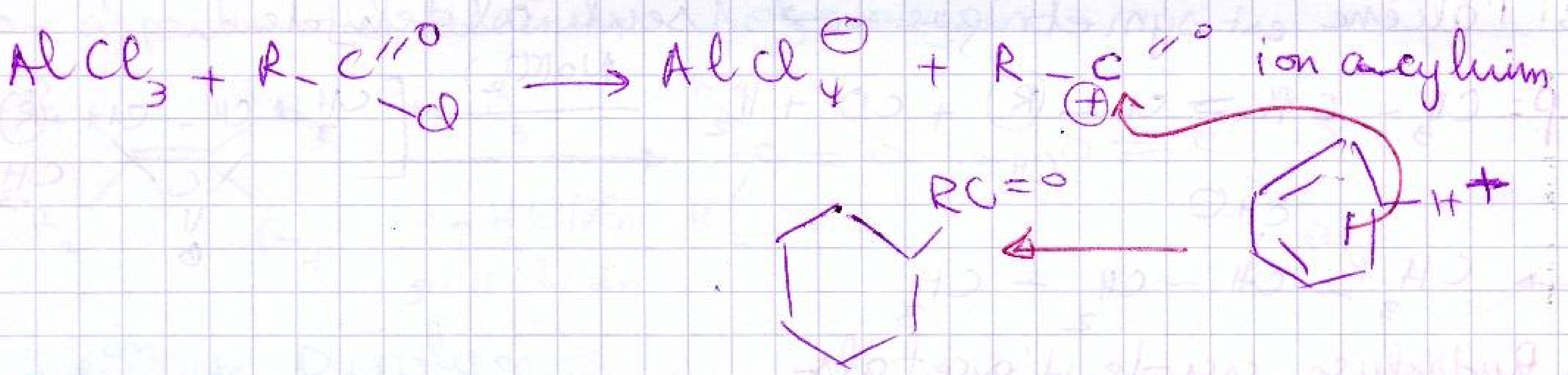
$R'(R)C=NH$ imine $+ MgXOH + H_2O \longrightarrow R(R')C(OH)-NH_2 \longrightarrow R(R')C=O + NH_3$

c- preparation des cétones aromatiques



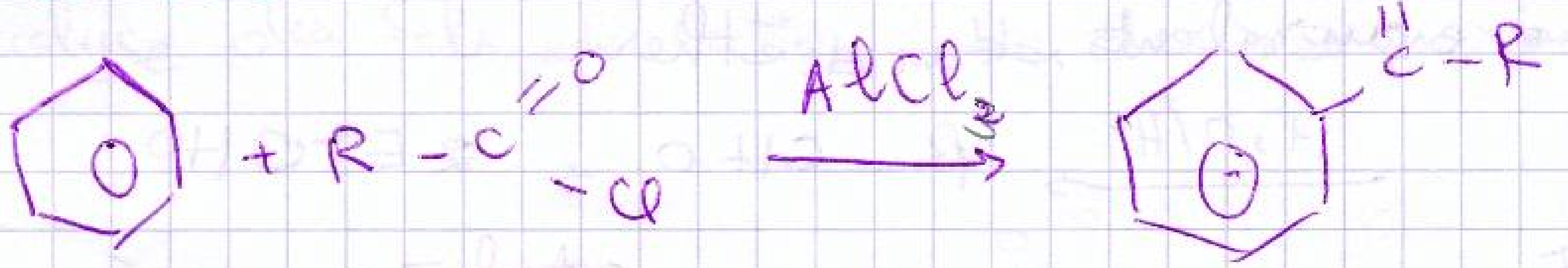
$C_6H_5-H + R-COCl \xrightarrow{AlCl_3} C_6H_5-CO-R + HCl$

la R^{on} de FRIEDEL-CRAFT c'est une R^{on} de S.E

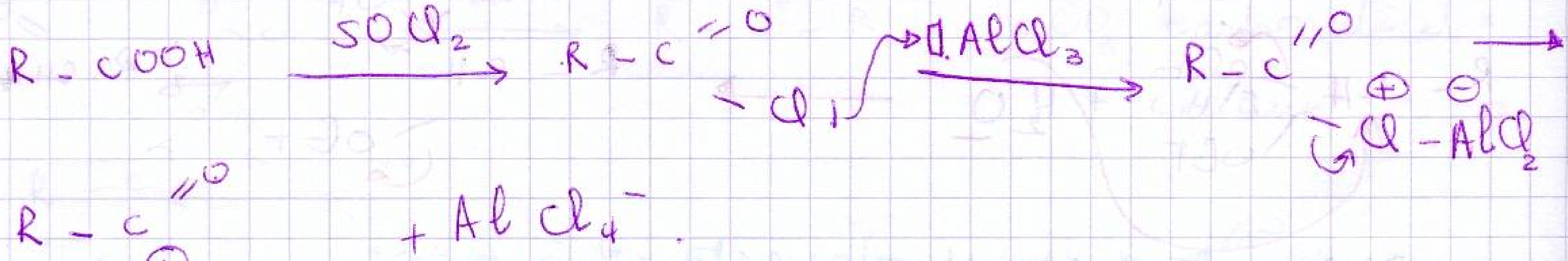


$AlCl_3 + R-COCl \longrightarrow AlCl_4^{\ominus} + R-\overset{\oplus}{C}=O$ ion acylium

Mecanisme :



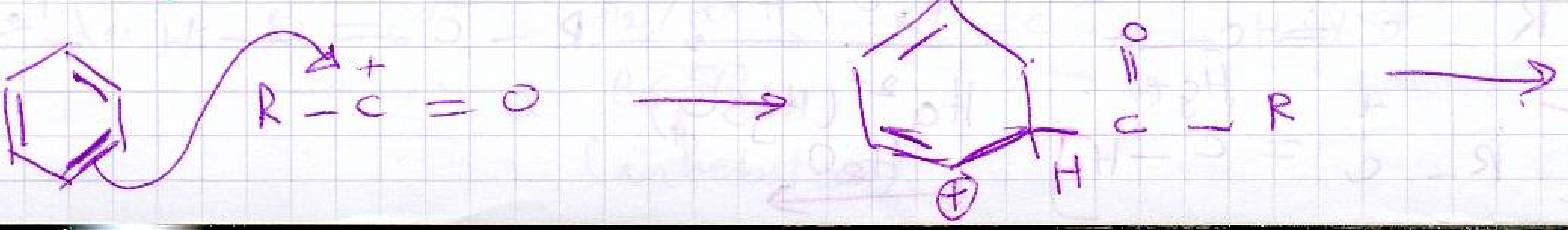
$C_6H_6 + R-COCl \xrightarrow{AlCl_3} C_6H_5-CO-R$



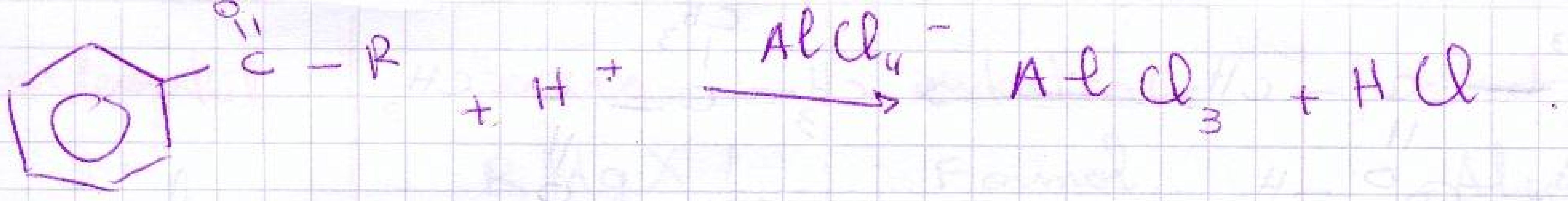
$R-COOH \xrightarrow{SOCl_2} R-COCl \xrightarrow{AlCl_3} R-CO-\overset{\oplus}{Cl}-\overset{\ominus}{Al}Cl_3 \longrightarrow$

$R-\overset{\oplus}{C}=O + AlCl_4^-$

ion acylium +



$C_6H_6 + R-\overset{+}{C}=O \longrightarrow [C_6H_5(H)-CO-R]^{\oplus} \longrightarrow$



Propriétés physiques -

HCHO : Formaldehyde (Formol).

Dans l'industrie.

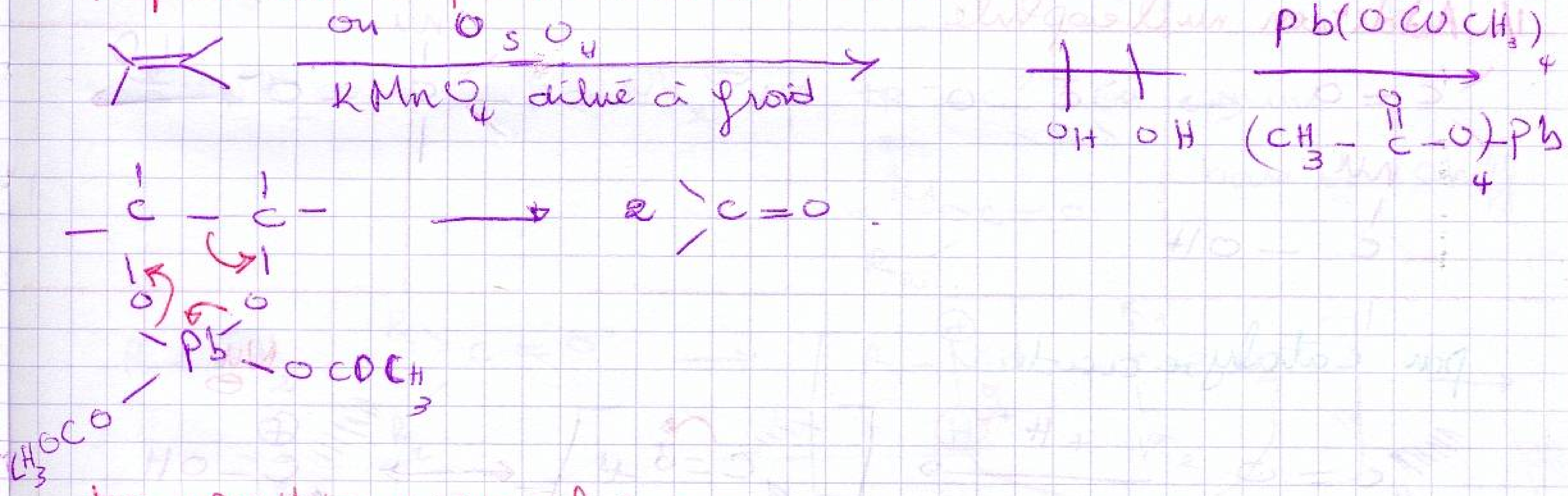
$$CH_3OH \xrightarrow[600-700°c]{Ag} CH_2=O + H_2 \uparrow$$

HCHO est gazeux ⇒ rendu sous forme aqueuse en une solution à 37%. Utilisé comme un désinfectant, antiseptique matière première pour la fabrication du plastique ($E_b = 20°c$)

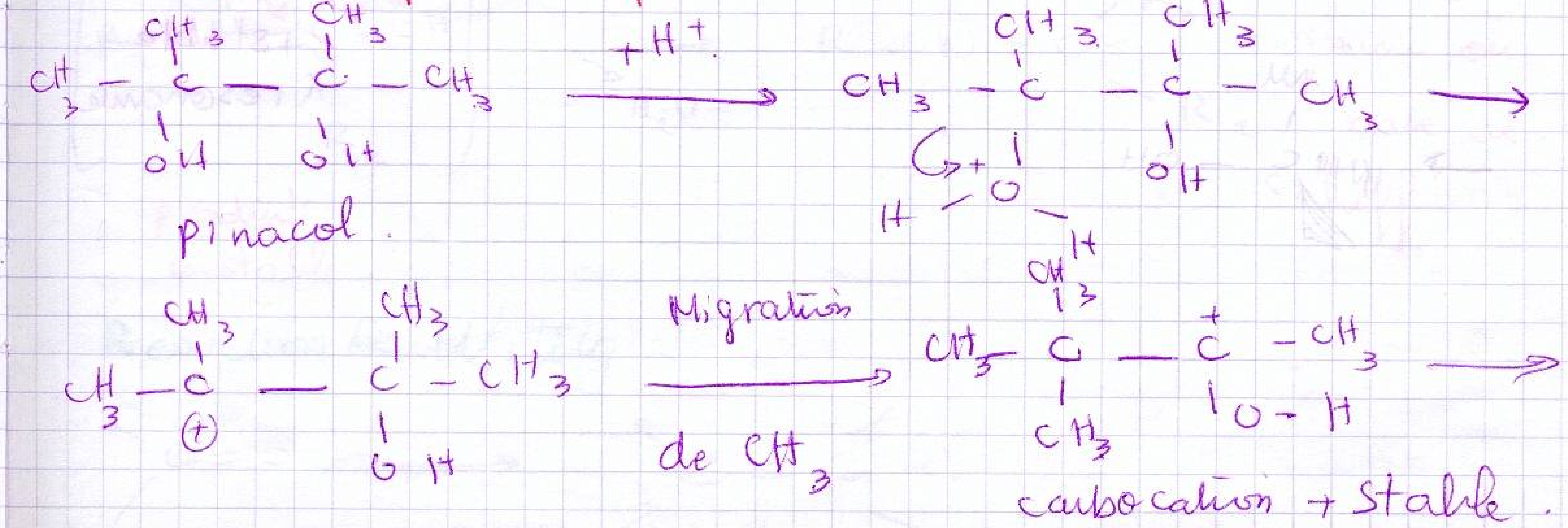
- dérivés carbonylés sont aisément identifiables en spectroscopie infrarouge (IR) ⇒ bande d'absorption intense et fine à

$$\frac{1680 - 1750\ cm^{-1}}{\nu}$$

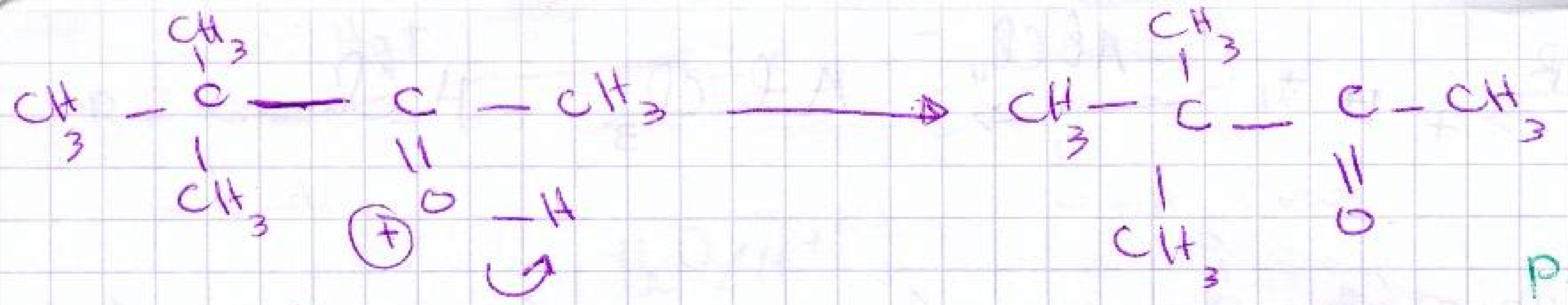
Préparation à partir de diol -1,2-.



transposition pinacolique :

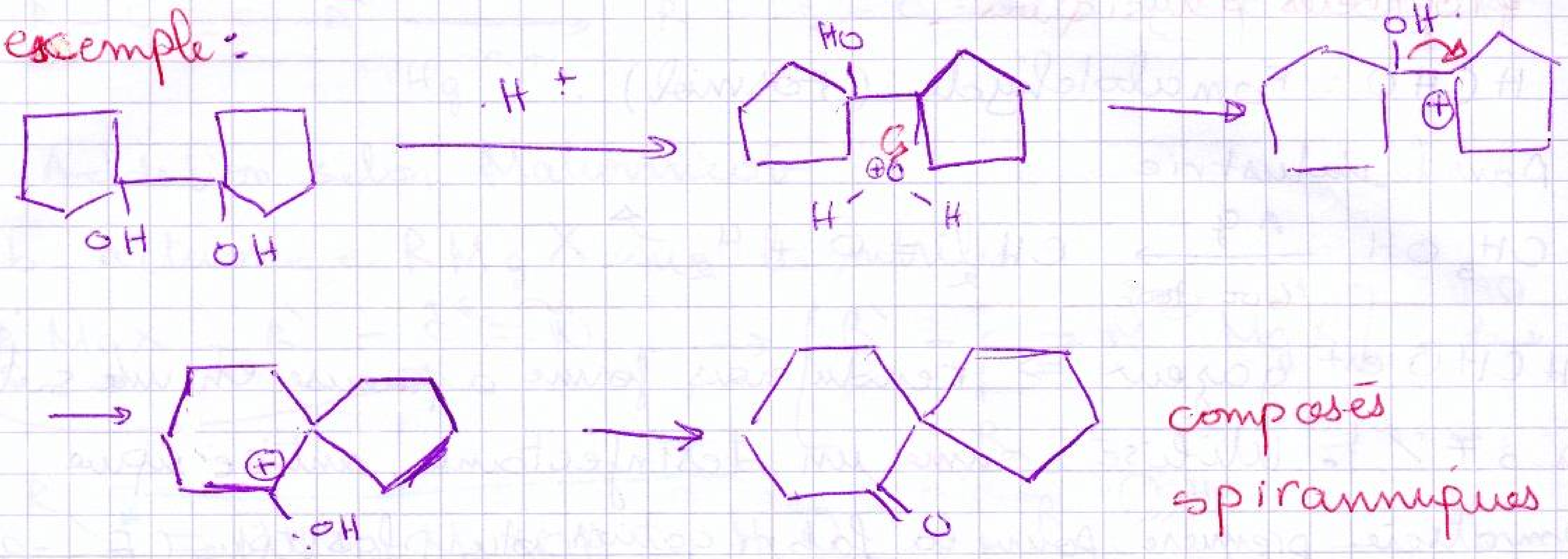


carbocation + stable.



pinacolone.

exemple :



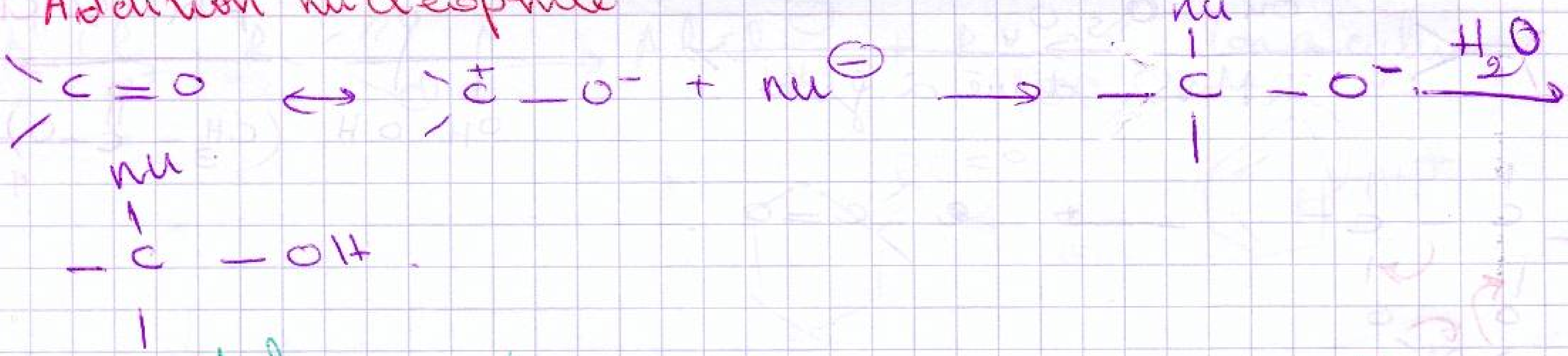
composés spiranniques.

III- propriétés chimiques :

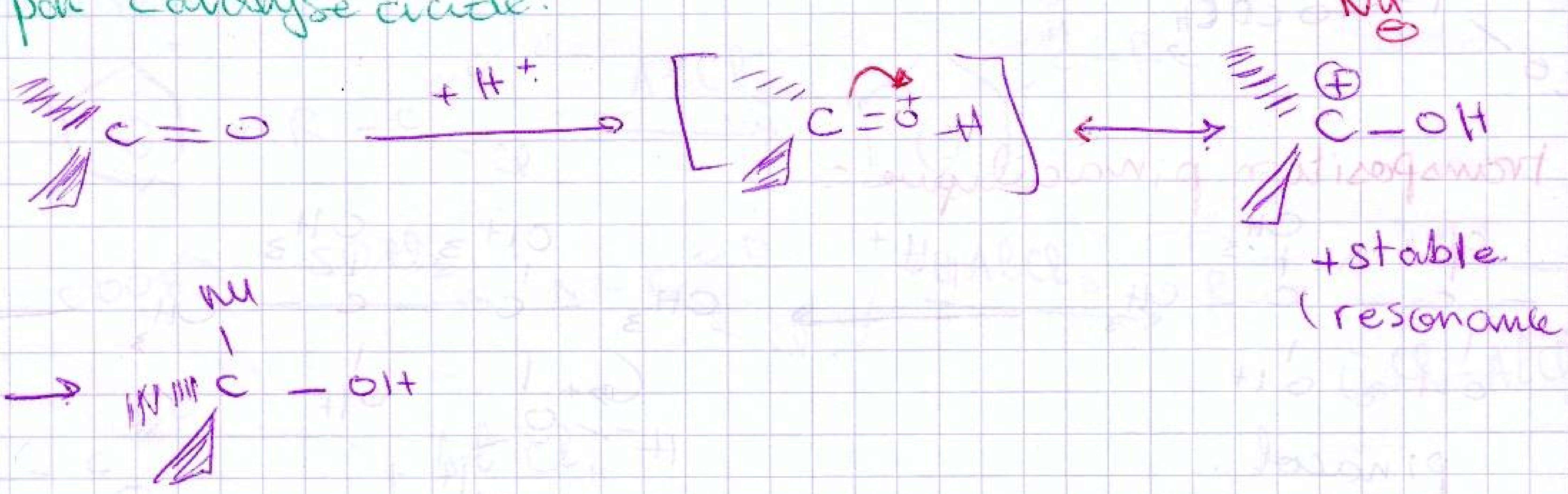
2 formes mésomères

attaque nucléophile sur le carbone = AN

1/ Addition nucléophile

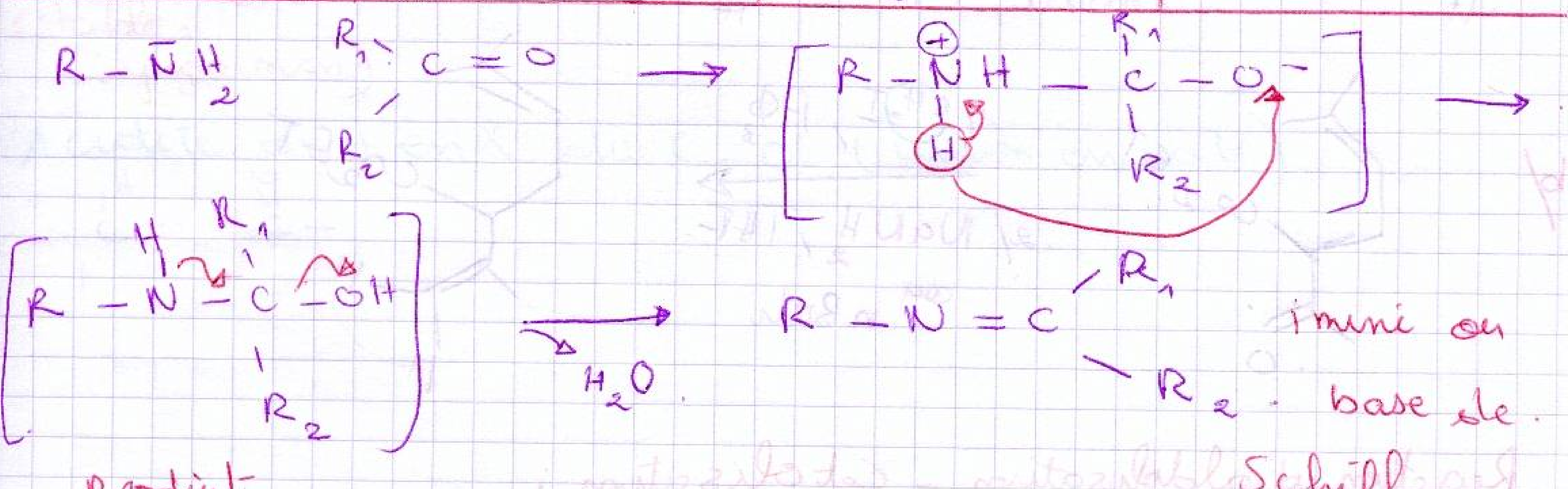


par catalyse acide :



+stable (resonance

nucleophile	Source	Substrat	Produit de la Rᵒⁿ
* $R^{\ominus}$	$RMgX$	Formol. Aldehyde. cétone	Alcool I^{aire} = // II^{aire} = // III^{aire} =
* H^{-}	$LiAlH_4$	aldehyde. cetone	Alcool I^{aire} // II^{aire}.
* $R-C\equiv C^{\ominus}$	$R-C\equiv C-H$ $+ NaNH_2$.	$R-C\overset{/\!/O}{\underset{\setminus H}{}}$ $R_1 \setminus C=O / R_3$	Alcool II^{aire} acétylénique // III^{aire} //.
$^{\ominus}C\equiv N$	HCN + base.	* $R-C\overset{/\!/O}{\underset{\setminus H}{}}$ $R_1 \setminus C=O$ / * R_2	* $R-\overset{OH}{\overset{\mid}{C}}H-CN$ = cyanhydrine * $R_1-\overset{OH}{\underset{R_2}{C}}-CN$.
$R-NH_2$	$R-NH_2$.	$R-C\overset{/\!/O}{\underset{\setminus H}{}}$. ou $R_1 \setminus C=O / R_2$	imine base de Schiff.

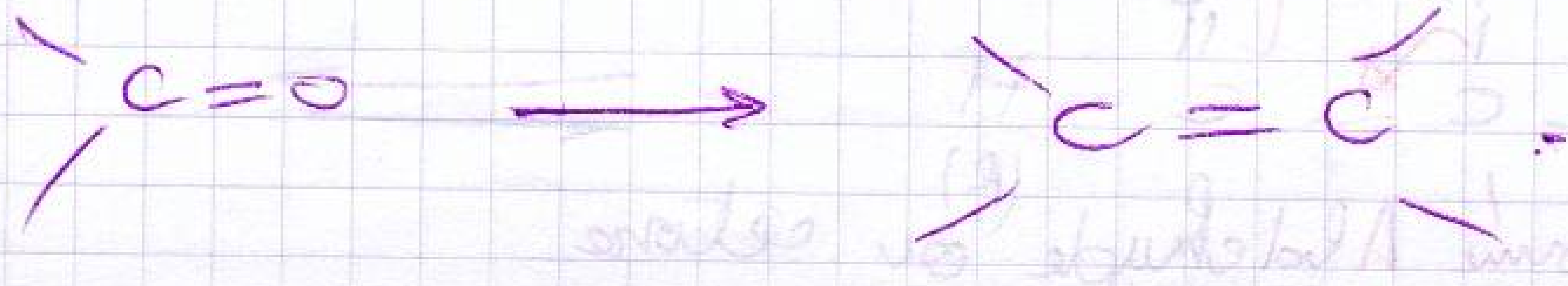


$R-\bar{N}H_2 + \overset{R_1}{\underset{R_2}{}}C=O \longrightarrow \left[R-\overset{\oplus}{N}H(H)-\overset{R_1}{\underset{R_2}{C}}-O^-\right] \longrightarrow \left[R-\overset{H}{N}-\overset{R_1}{\underset{R_2}{C}}-OH\right] \xrightarrow[H_2O]{} R-N=C\overset{R_1}{\underset{R_2}{}}$

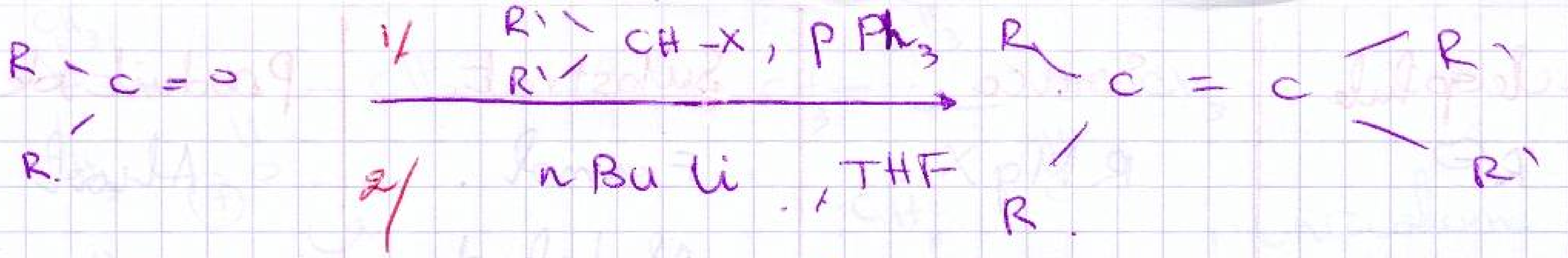
Imini ou base de Schiff

produit instable

Reaction De Wittig :

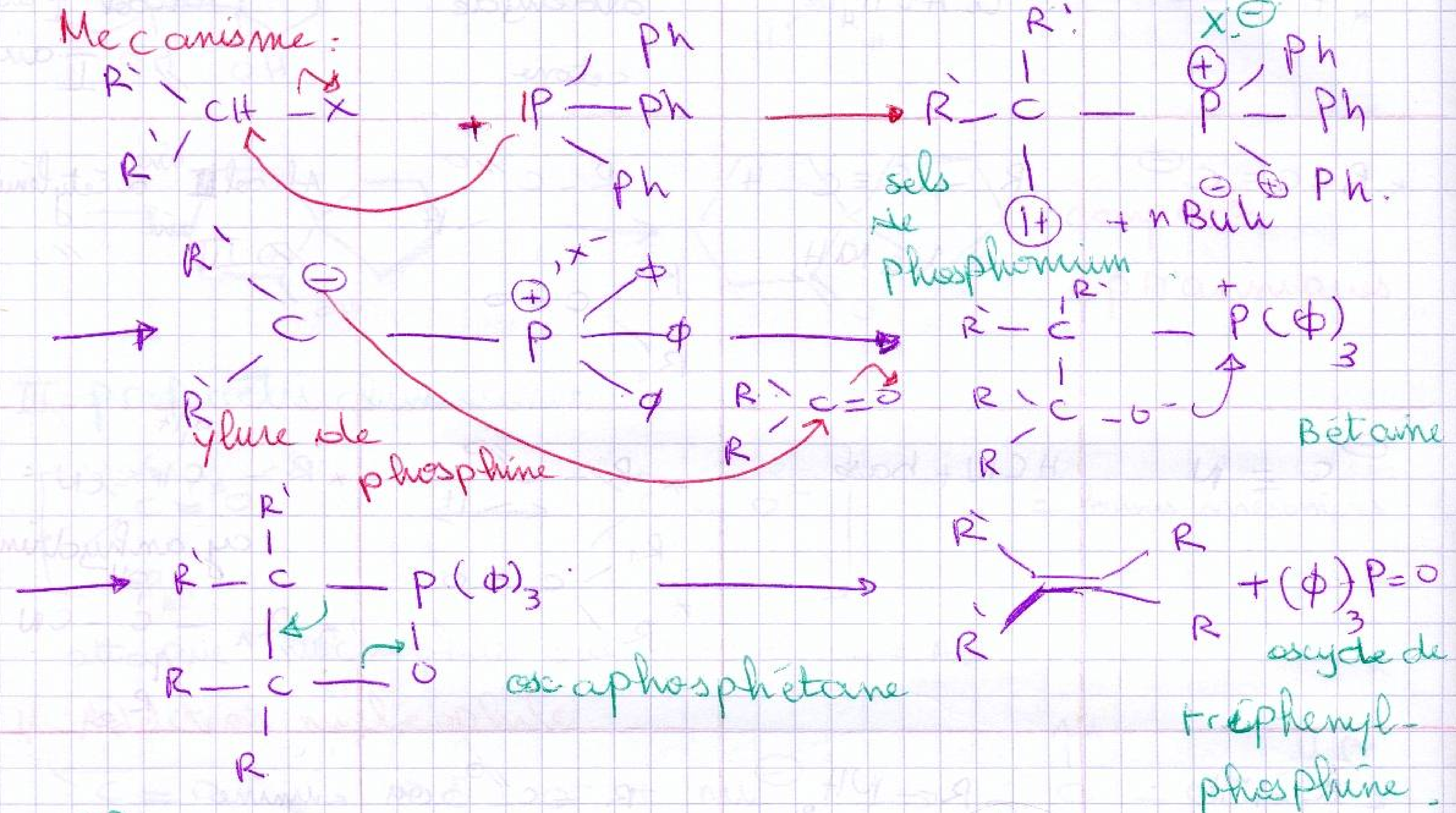


$>C=O \longrightarrow >C=C<$.



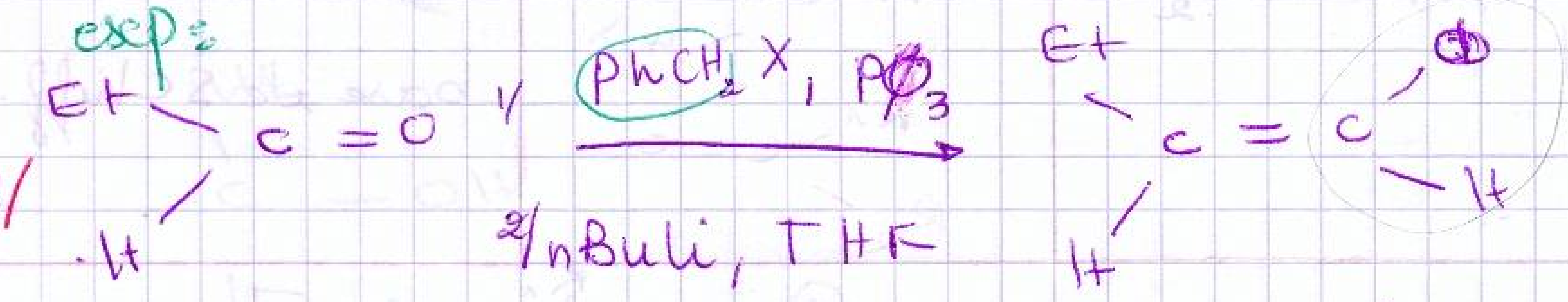
la force directrice de cette R^{on} est l'addition nucleophile d'un ylure de phosphore sur un derivé carbonyle.

Mecanisme :

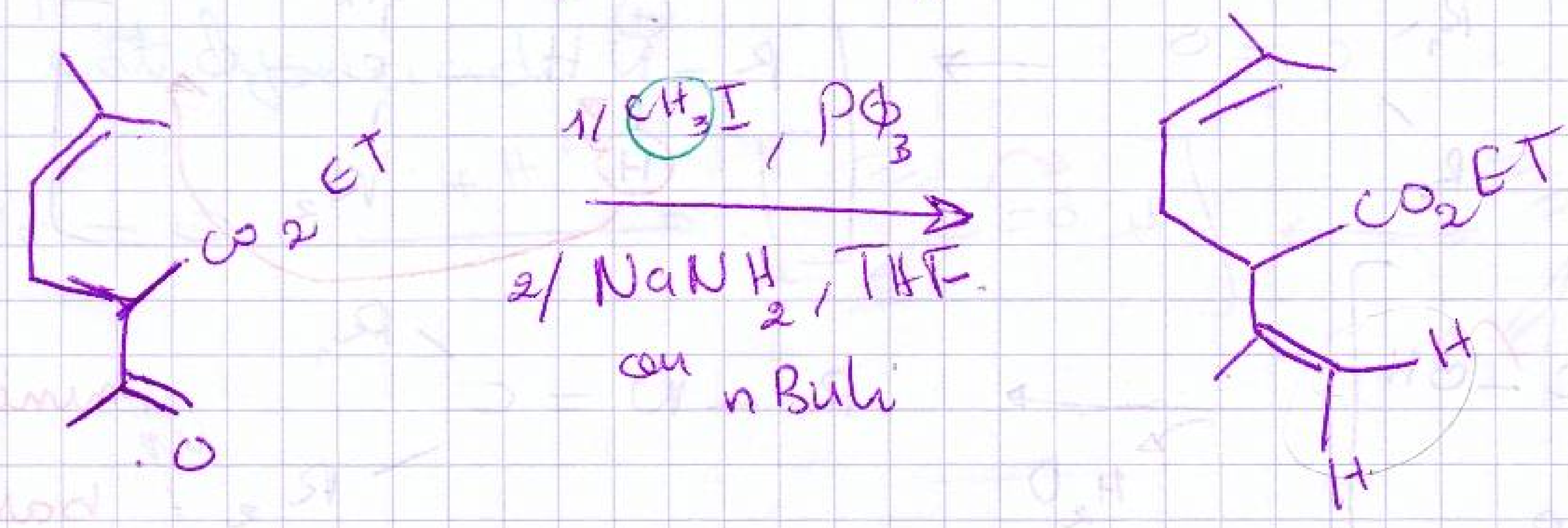


exp :

a/



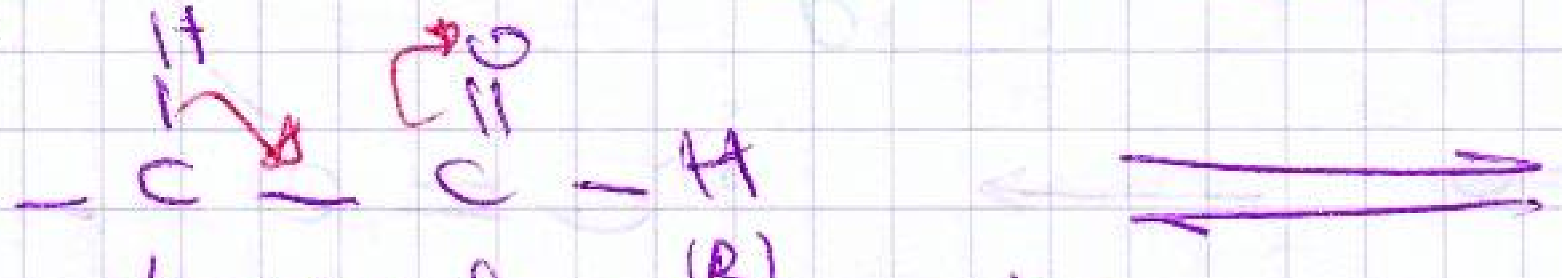
b/



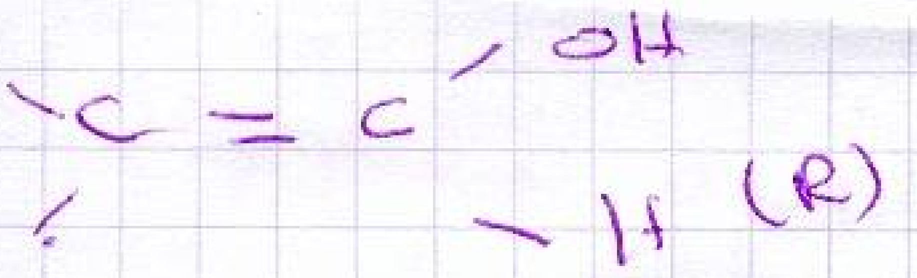
Reaction d'aldolisation – cétolisation :

tautomérie céto-enolique.

$R-C(=O)-H$ ou $R'(R')C=O$ existent la forme d'un melange en equilibre.

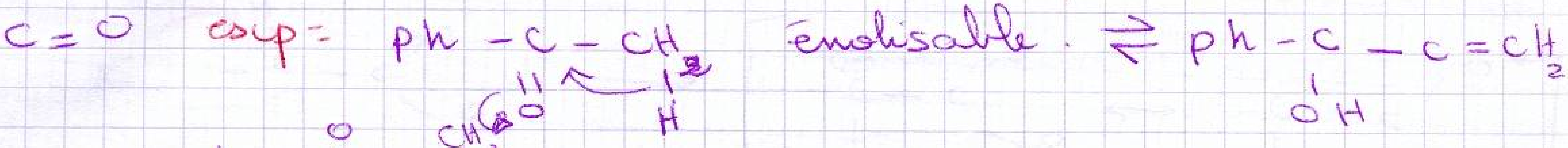


Forme Aldehyde (R) ou cétone

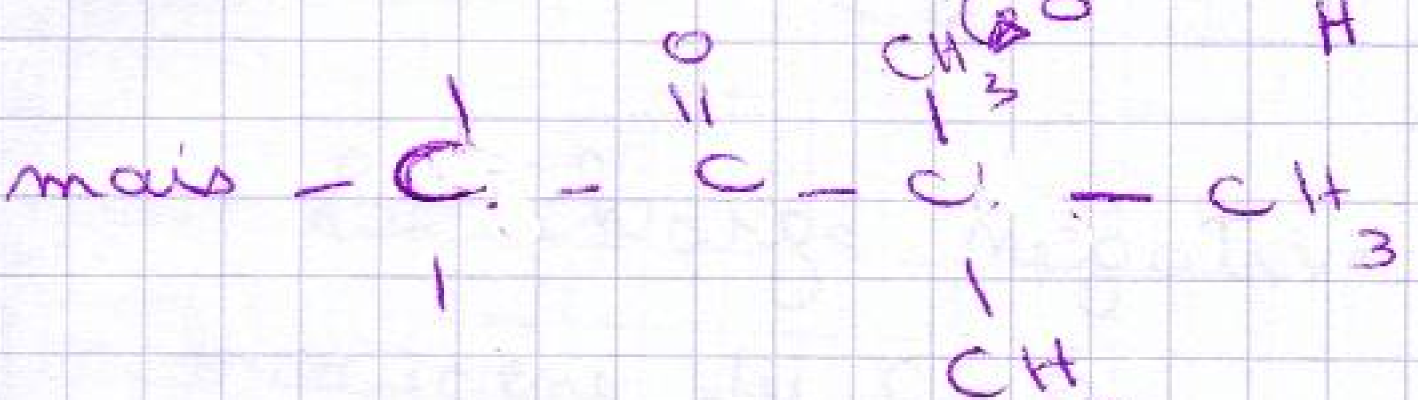


$>C=C<^{OH}_{H\,(R)}$ Forme énol

ces 2 formes sont appelées tautomères. On voit bien qu'un composé n'est énolisable que s'il a au moins un H en α du C=O exp: ph — C — CH énolisable ⇌ ph — C — C = CH



$$Ph-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{|}{CH_2}} \rightleftharpoons Ph-\underset{OH}{\underset{|}{C}}=CH_2$$

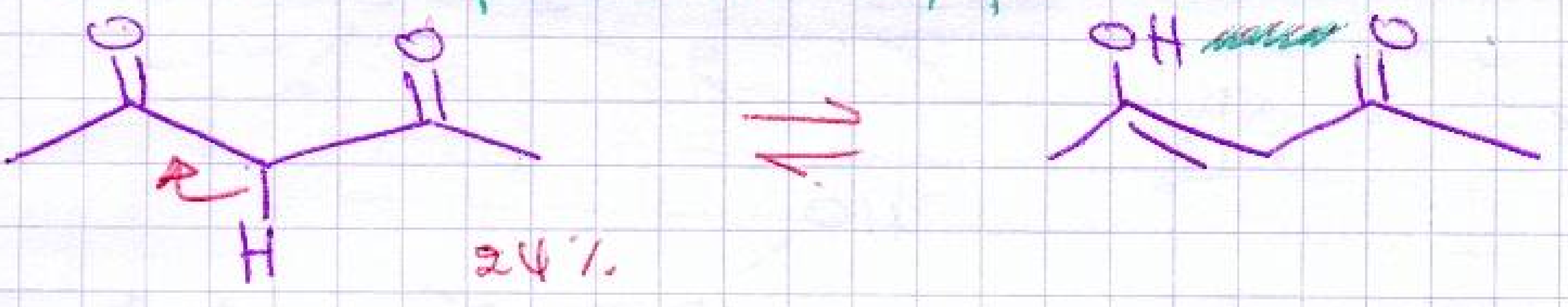


$$\text{mais } -\underset{|}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

en General la forme cetone est maj par rapport à la forme enol (1% enol) ⇌ 99% cetone)

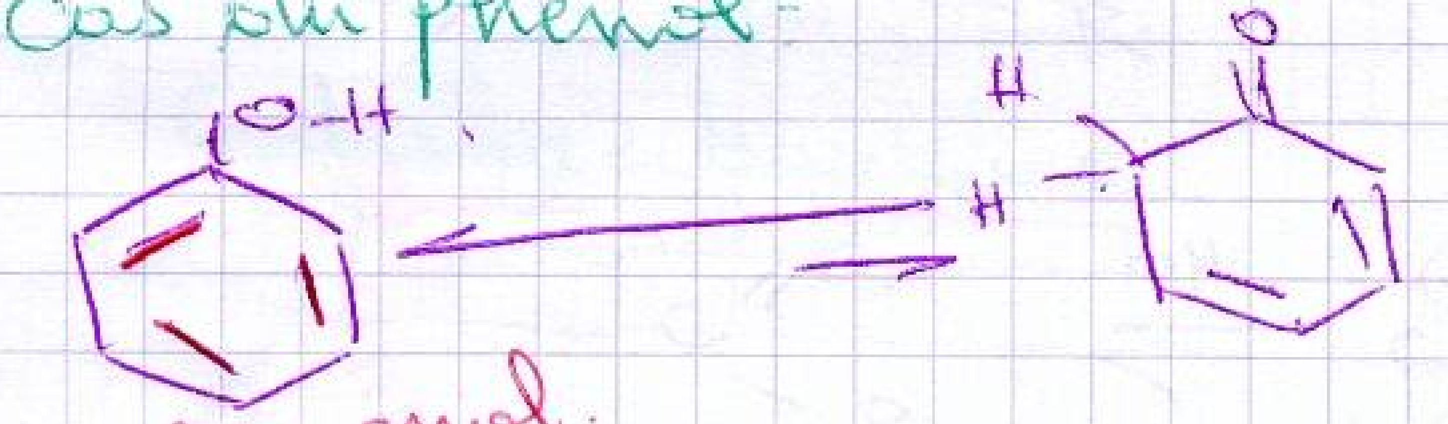
dans certains cas la forme énol peut devenir prepondérante car plus stable. maj

cas de la pentan-2,4-dione.



énol (+stable) 76 %.

cas du phénol.



cetone

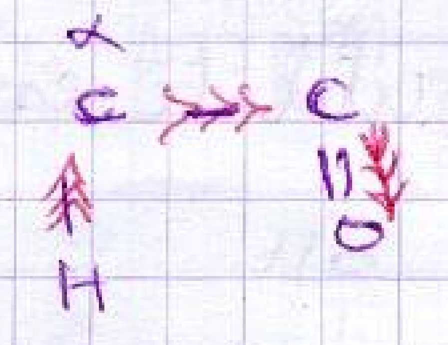
énol

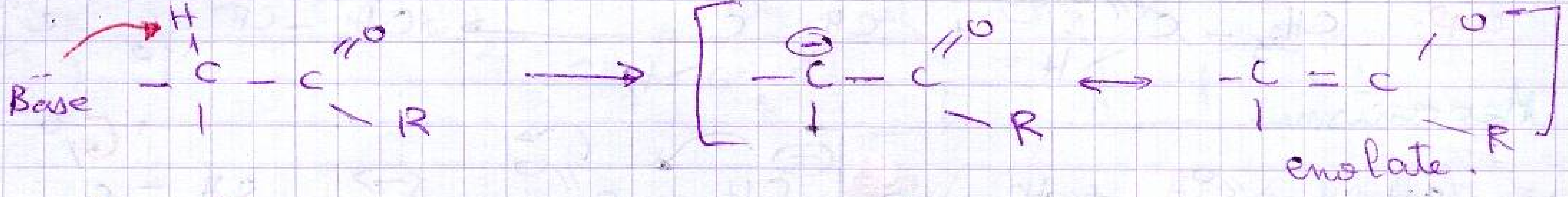
+(stable = conjugaison)

2/ Acidité de H en α du C=O (anion énolate)

$$-\underset{|}{\overset{|H}{C}}-\overset{O}{\overset{\|}{C}}-$$

Acidité du H en α du C=O :



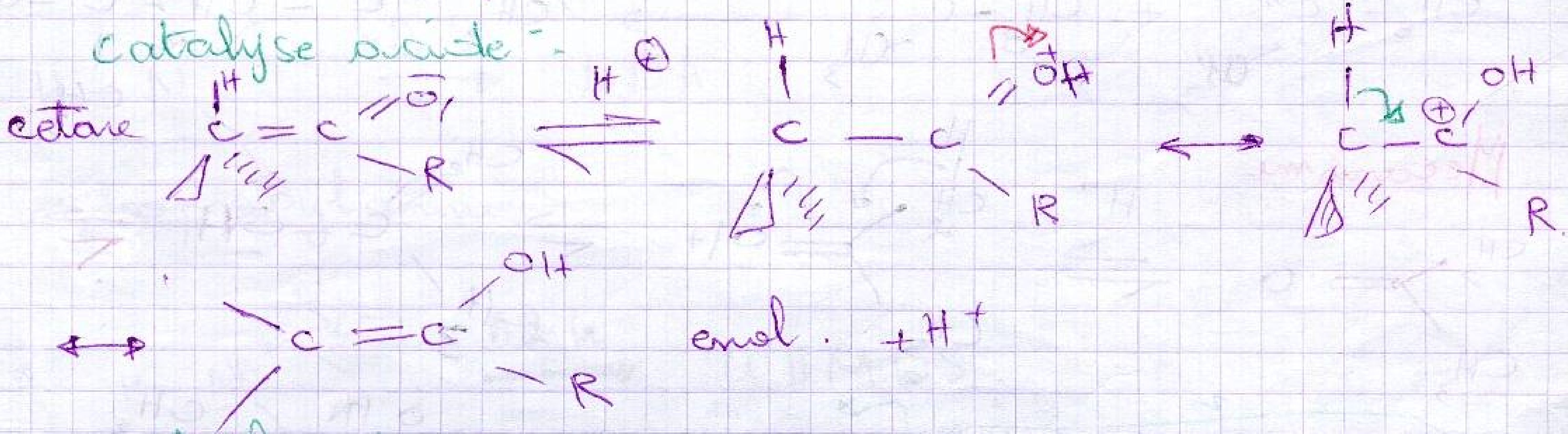


La charge négative est répartie principalement sur l'oxygène du C=O

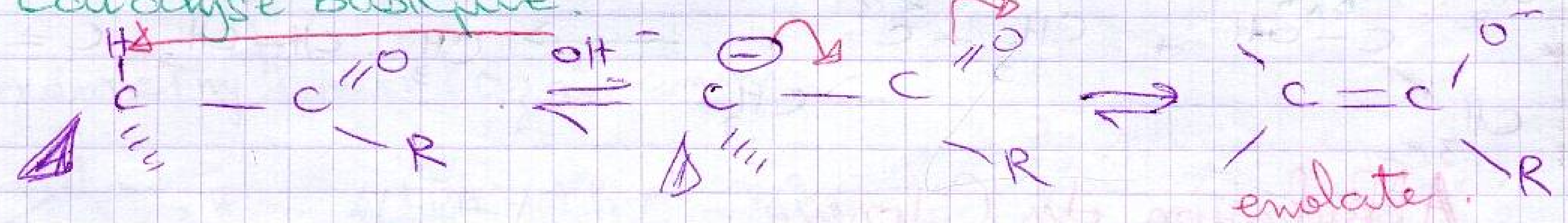
la Tautomerie cetone - enol peut être catalysée

- milieu acide
- // basique.

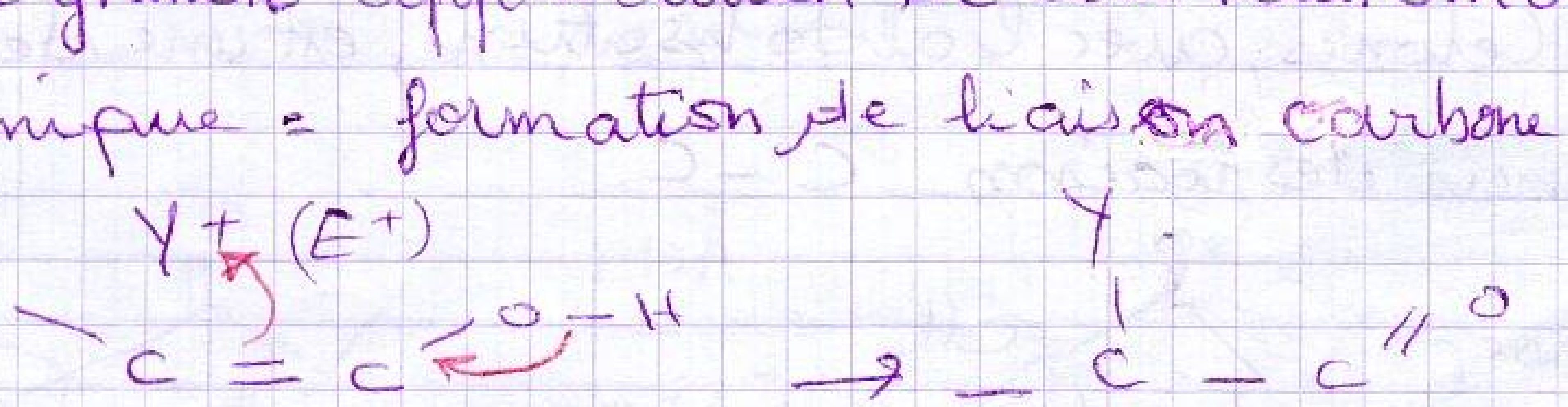
catalyse acide :



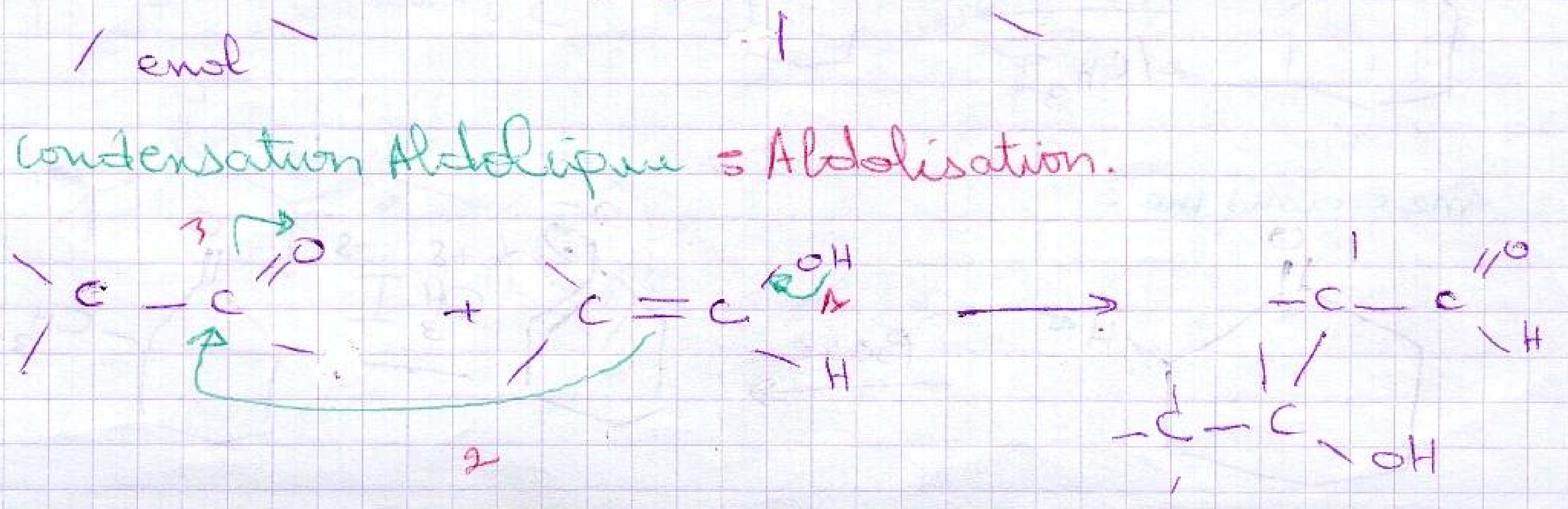
Catalyse basique :



Une grande application de cette tautomerie en synthèse organique = formation de liaison carbone Carbone C–C

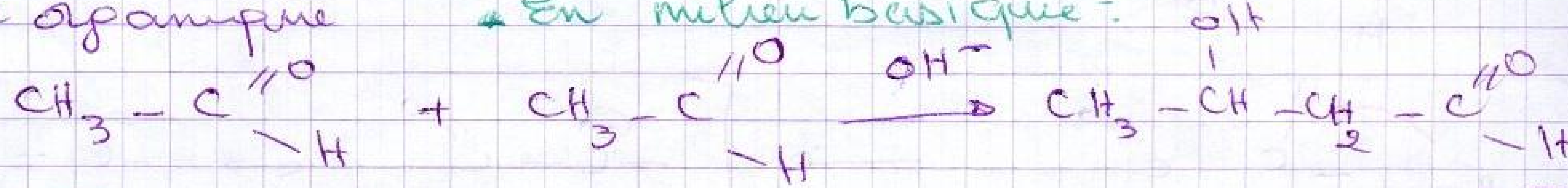


condensation Aldolique = Aldolisation.



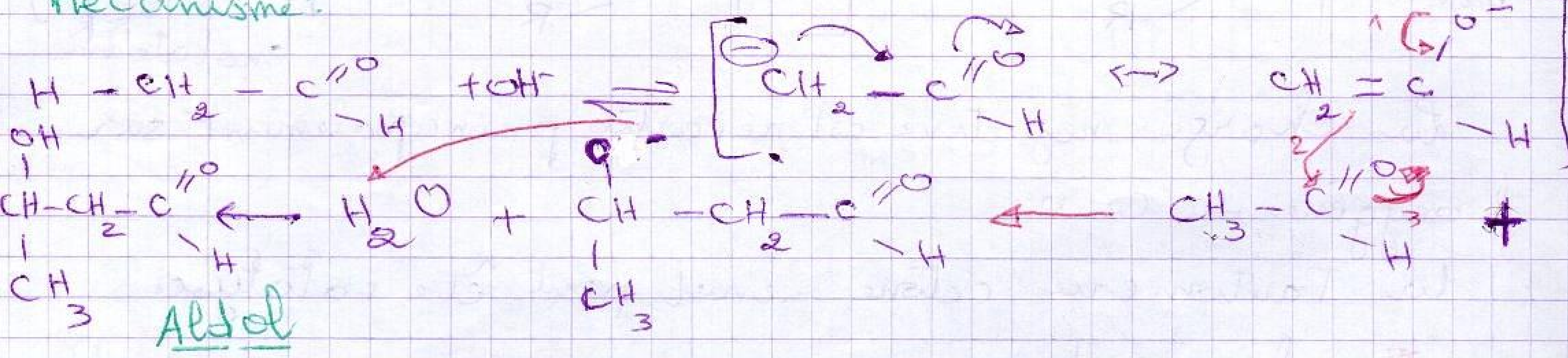
l'addition d'un énol (énolate) sur une double liaison C=O d'une cétone ou un Aldehyde a une grande utilité en synthèse organique * En milieu basique :

esp :

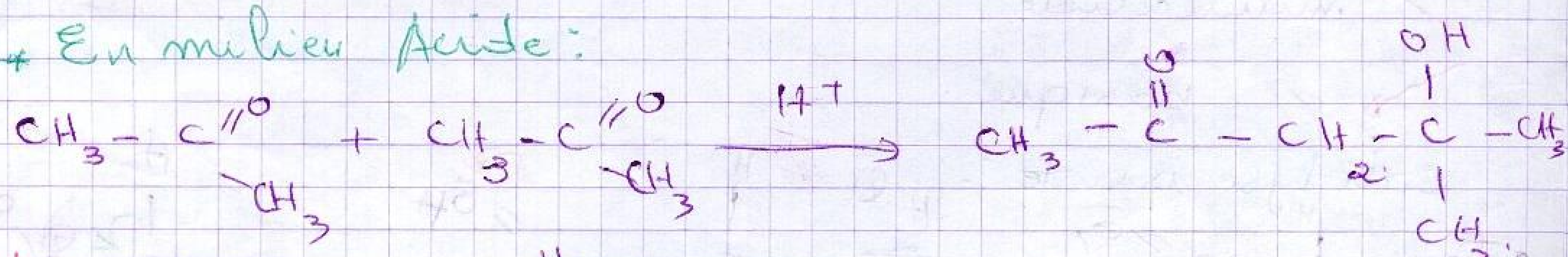


$CH_3-C\overset{O}{\underset{H}{}} + CH_3-C\overset{O}{\underset{H}{}} \xrightarrow{OH^-} CH_3-\overset{OH}{CH}-CH_2-C\overset{O}{\underset{H}{}}$

Mecanisme :

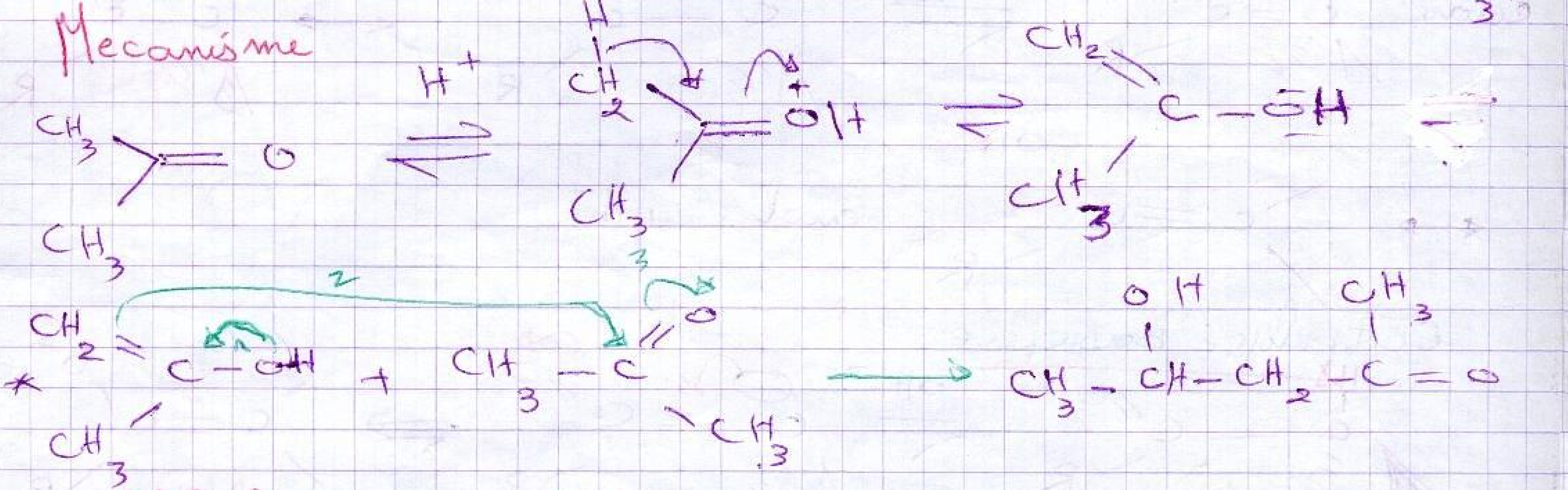


* En milieu Acide :



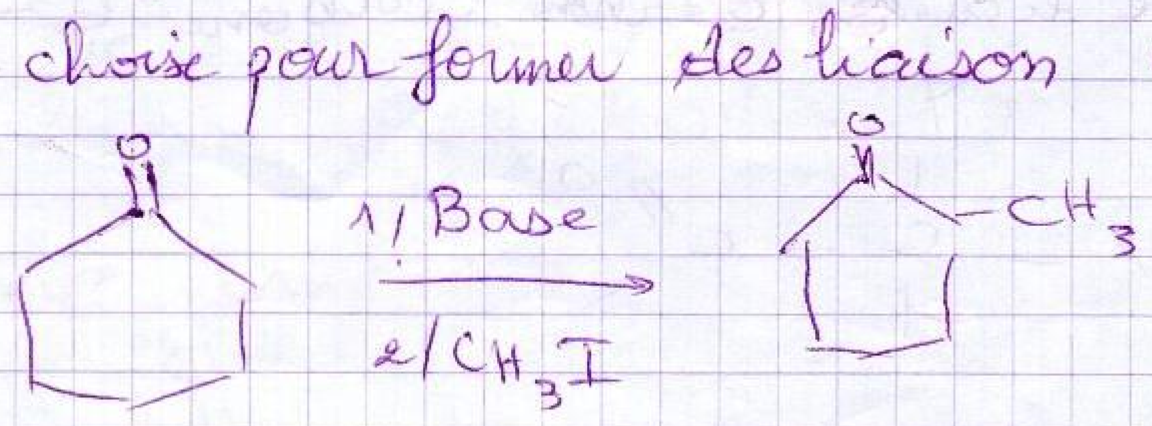
$CH_3-C\overset{O}{\underset{CH_3}{}} + CH_3-C\overset{O}{\underset{CH_3}{}} \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3$

Mecanisme

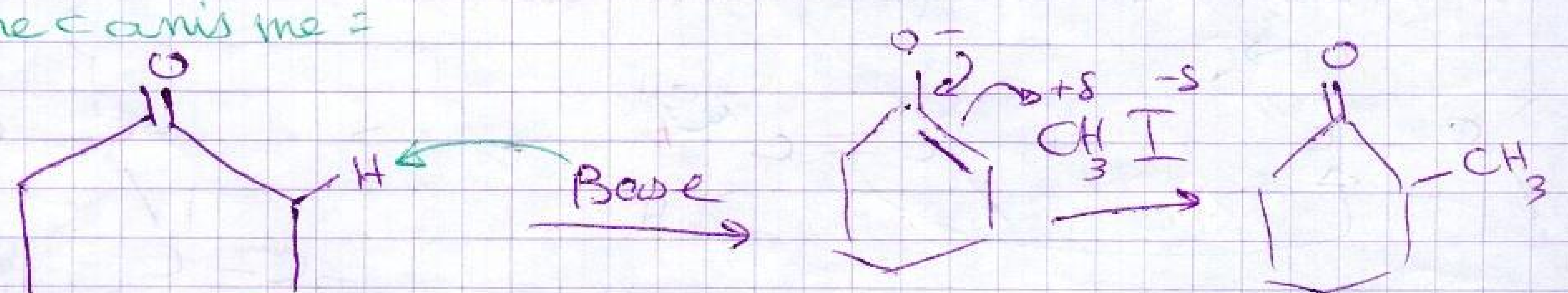


Alkylation des Cétones -

L'Alkylation des Cétones, avec l'aldolisation, est une de R^{on} ple choise pour former des liaison C–C.

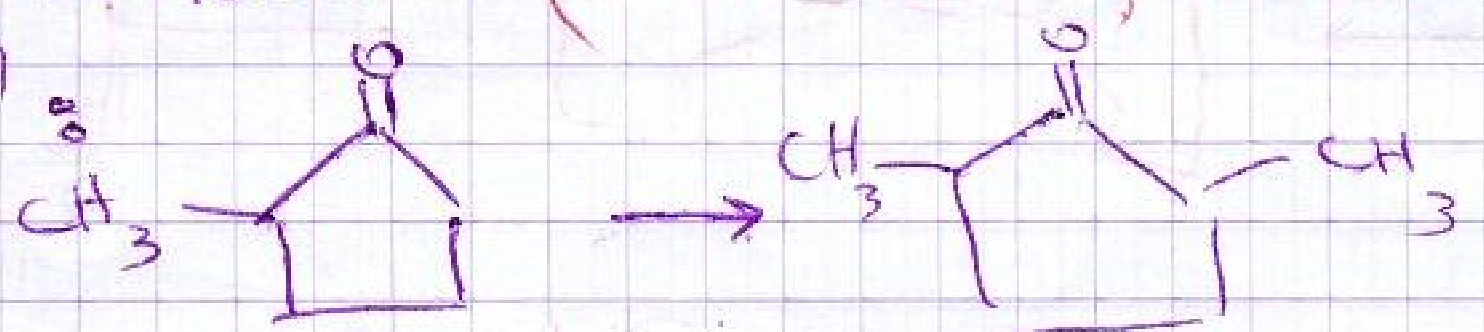


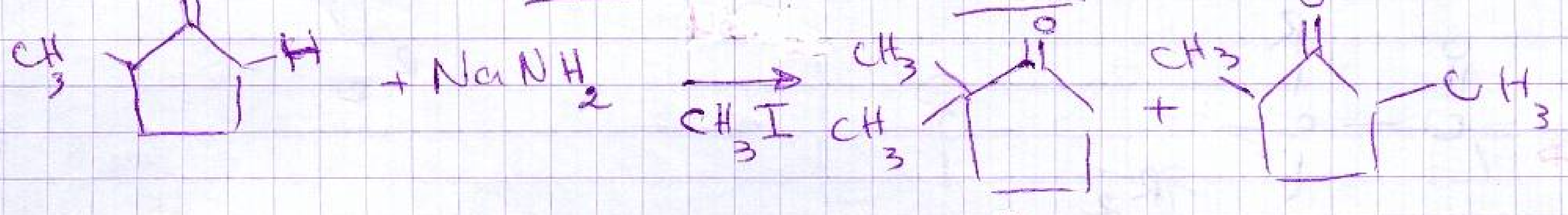
mecanisme :



les Bases utilisées sont : (EtONa, MeONa, NaNH$_2$, BuLi)

soit la R^{on} :

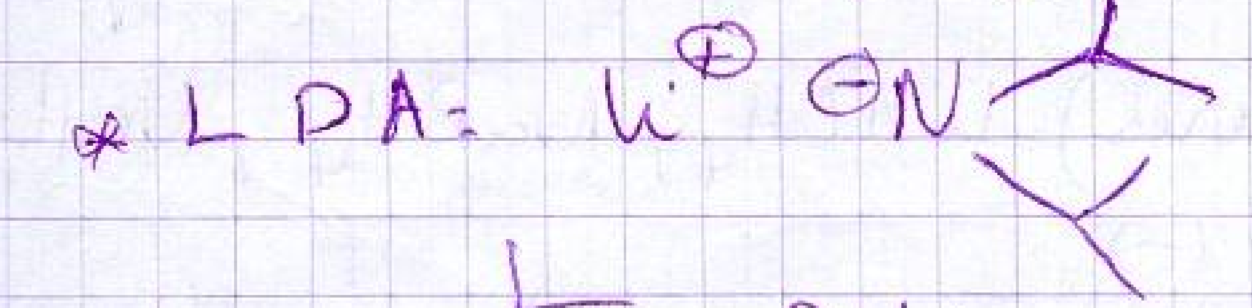


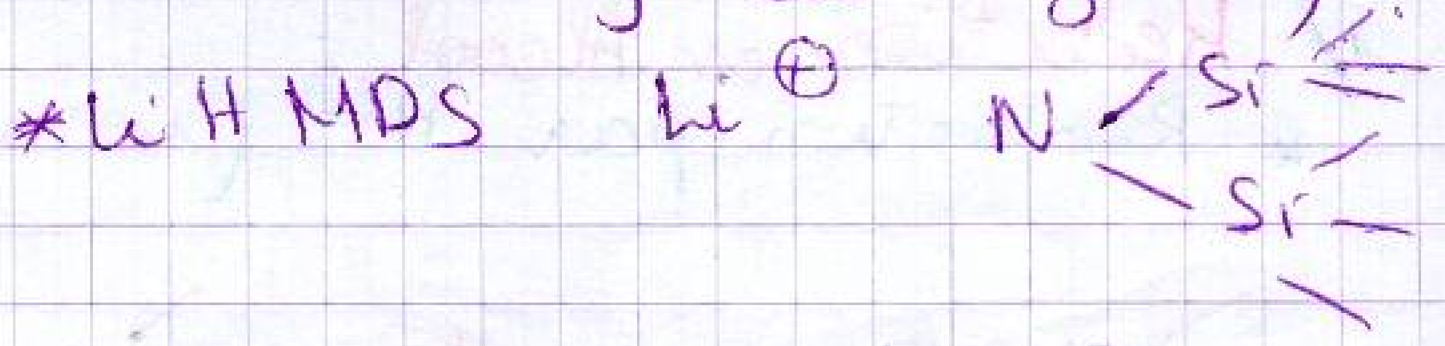


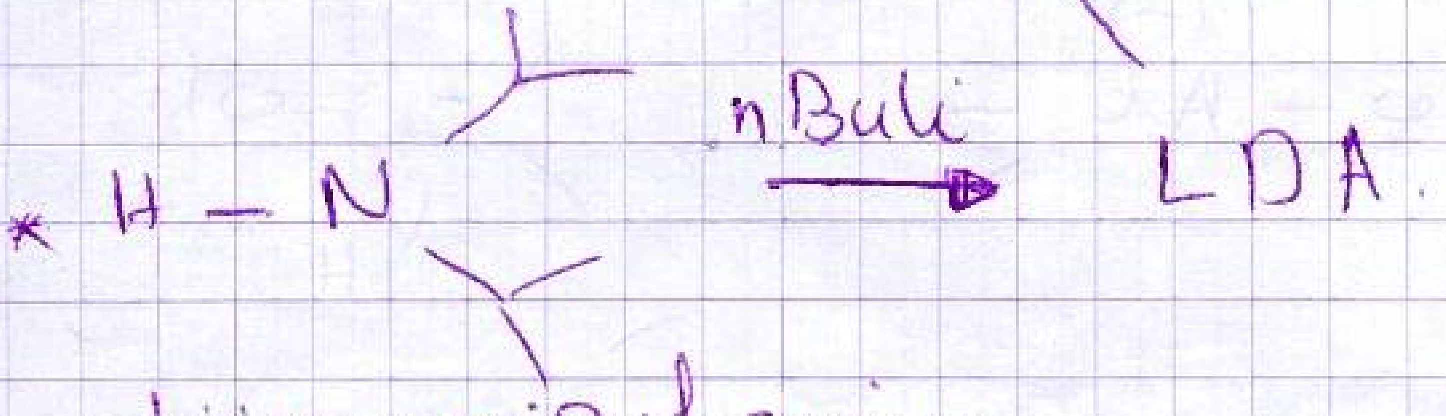
45 % 55 % Produit voulu

Si on veut faire des Alkylations selectives on a recourt aux bases encombrées : * LDA (lithium diisopropyl amidure)

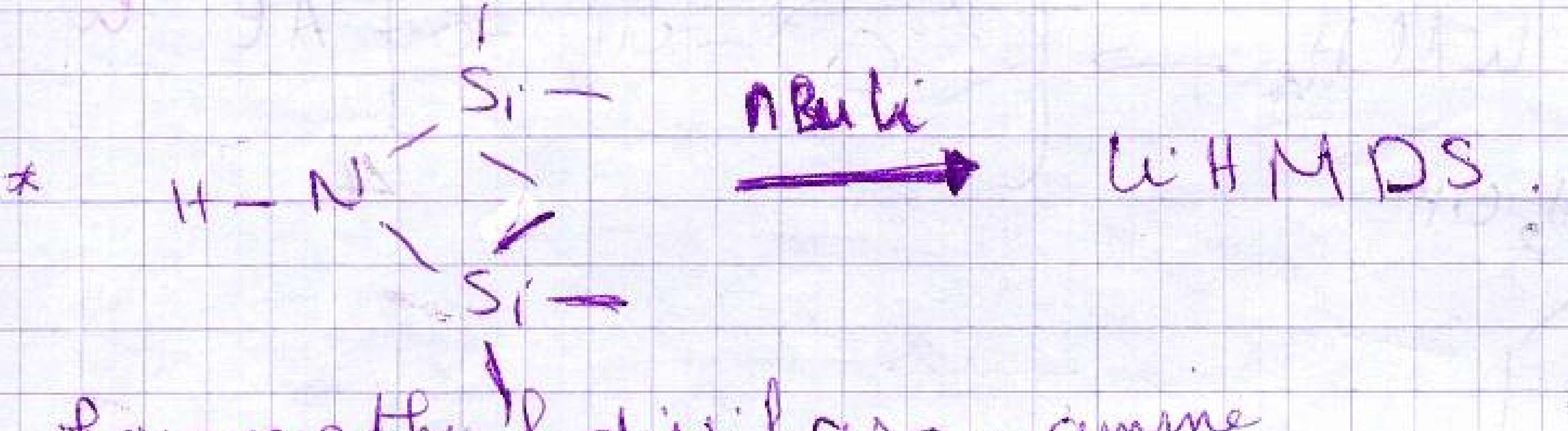
* LiHMDS (// Hexamethyl disilazane)



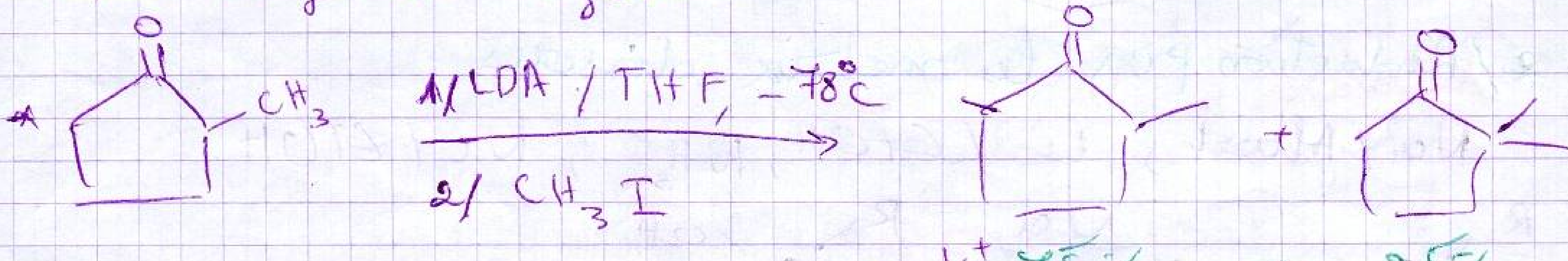




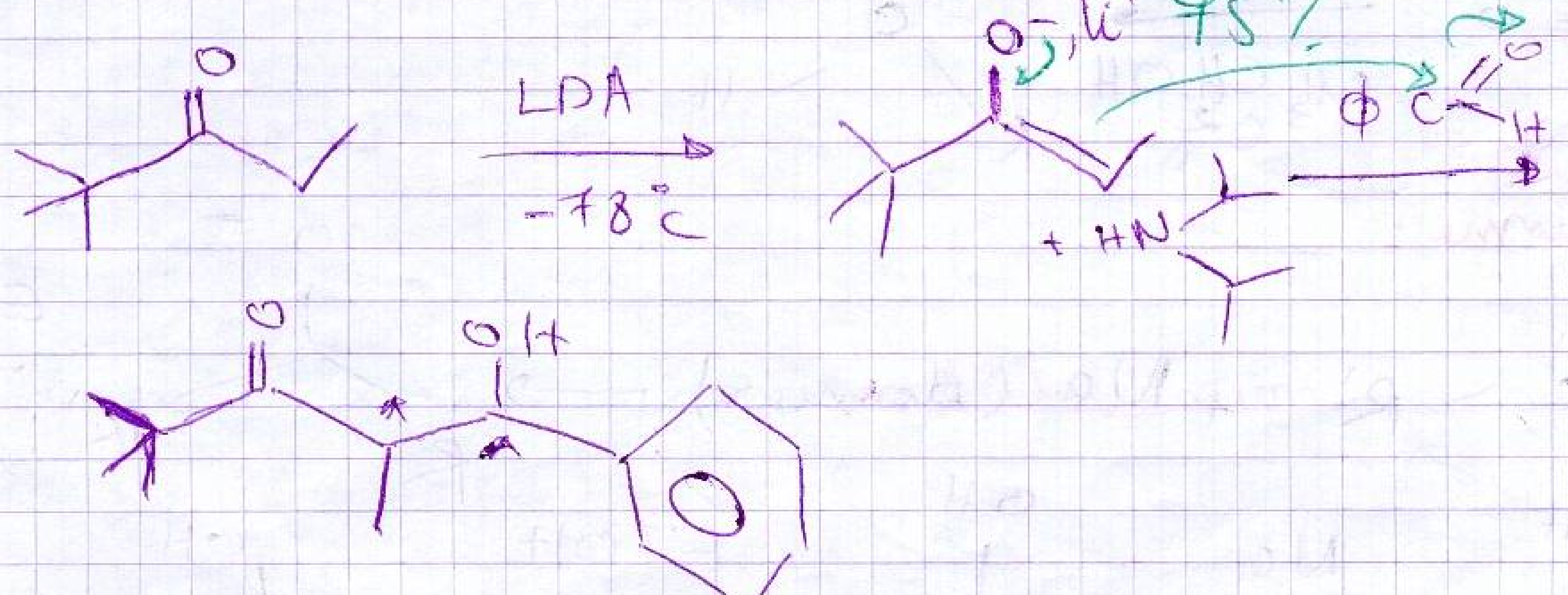
diisopropylamine

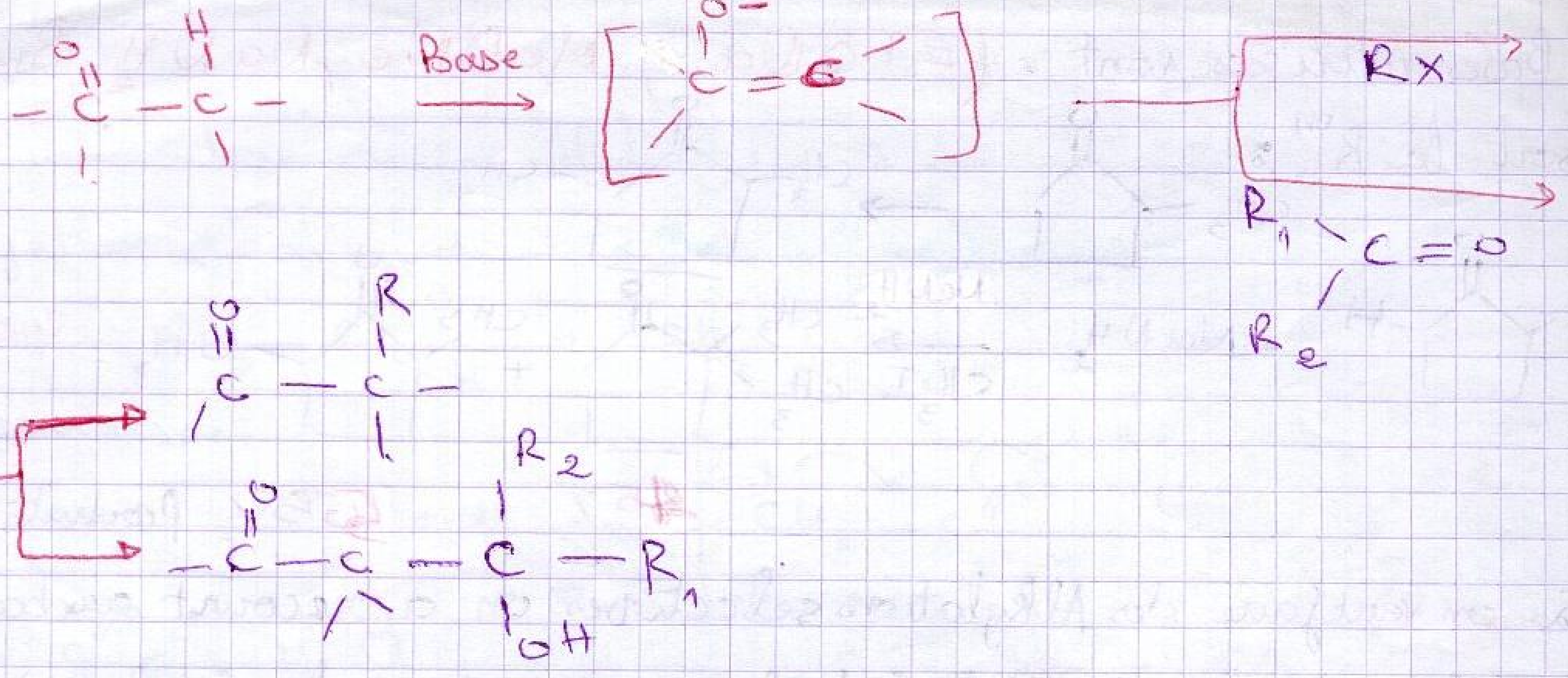


hexamethyl disilazane amine



75 % 25 %



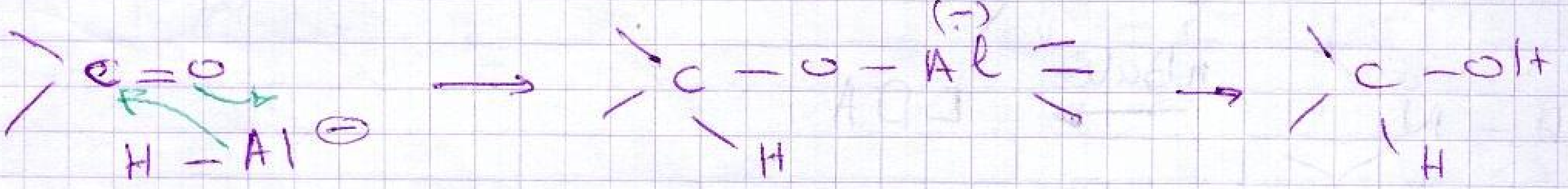


Reduction des dérivés C = O

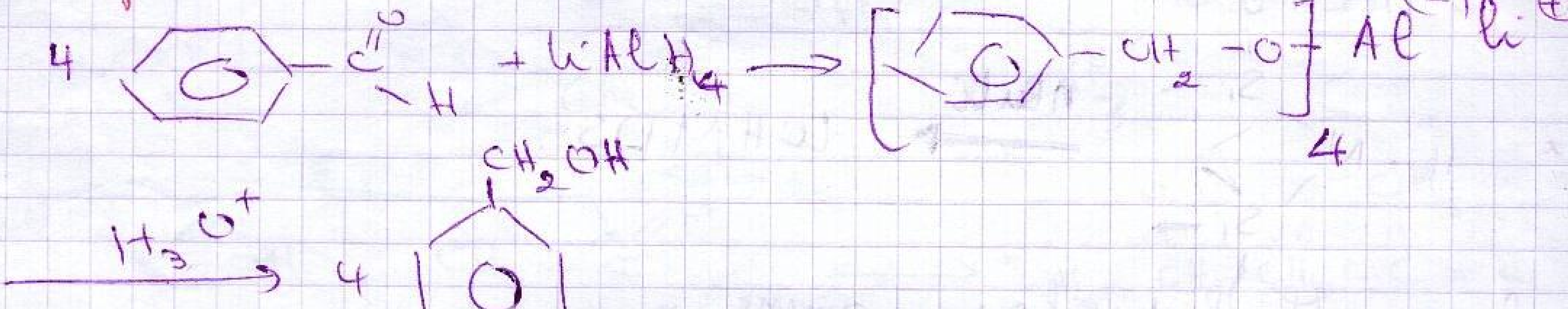
Base forte
↓

1/ Reduction en Alcool :

* Reduction par $H^{\ominus}$ (ions hydrures) $LiAlH_4$, $NaBH_4$, NaH

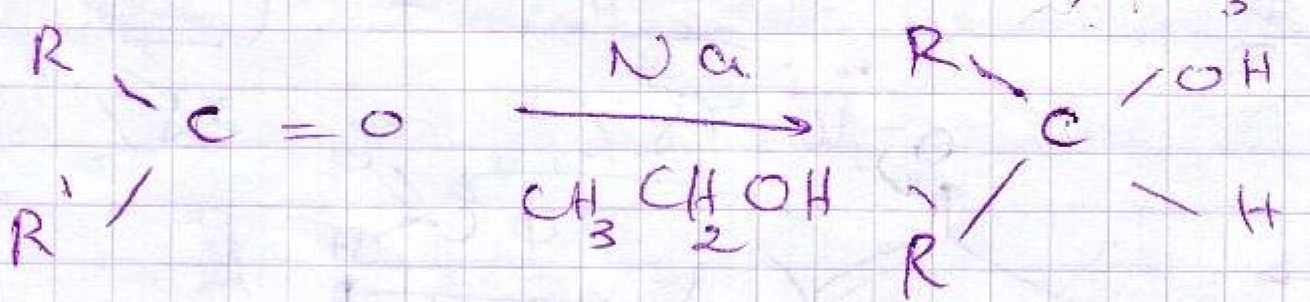


exp :

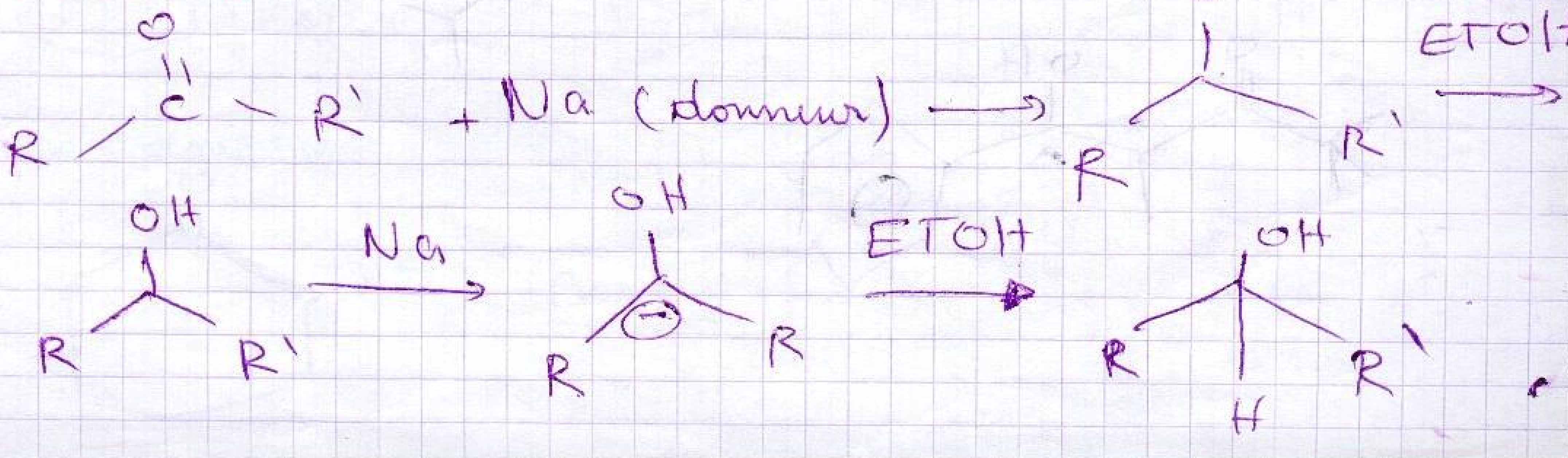


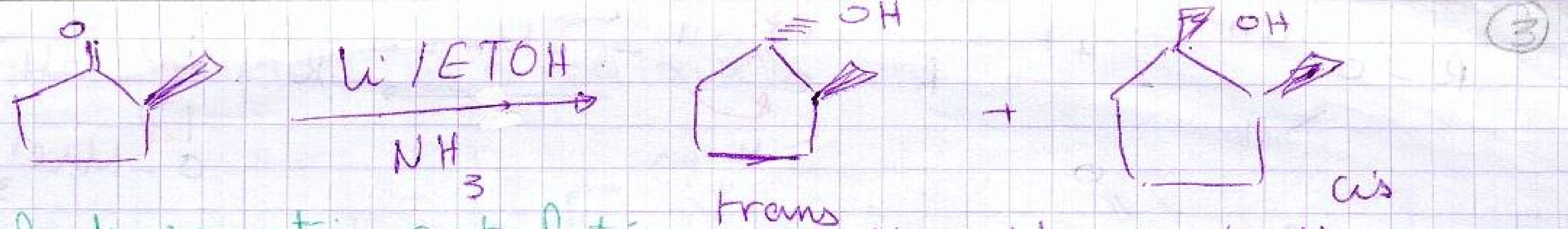
* Reduction par les metaux dissous :

Na / Alcool, Li / EtOH, NH_3, Ni / EtOH.



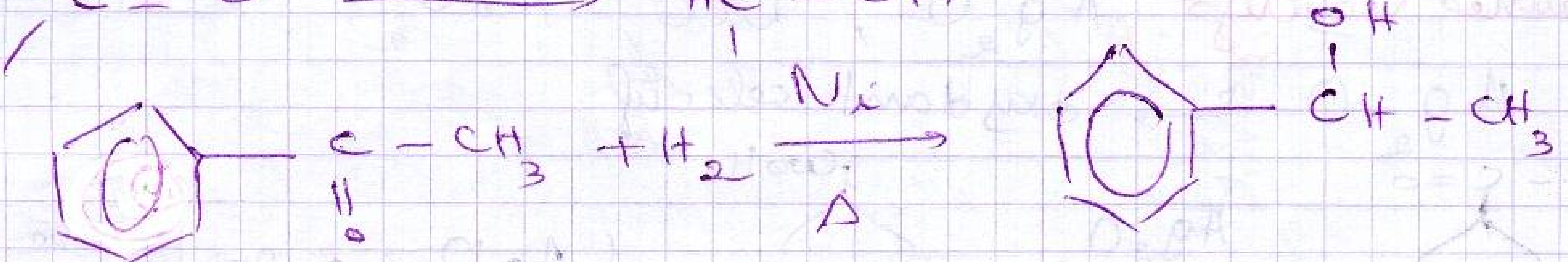
mecanisme :





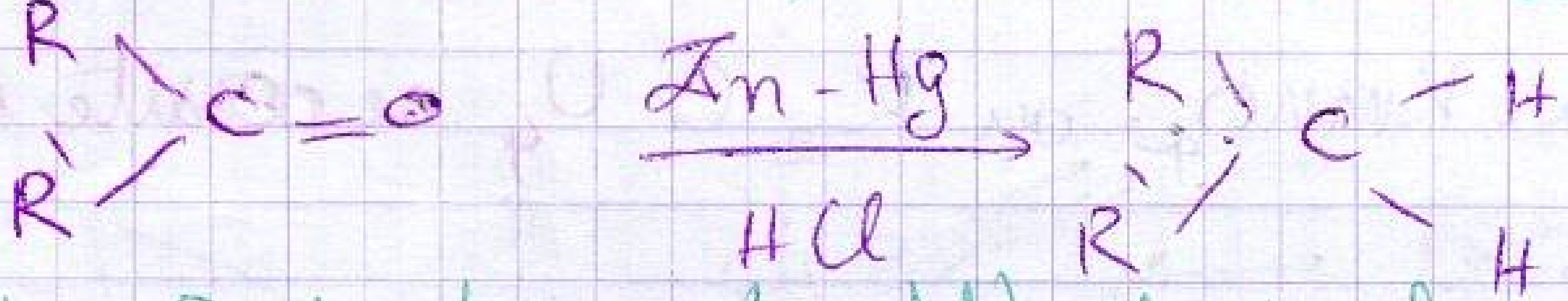
hydrogenation catalytique = H_2 (N_i , H_2/Pd) .

$>C=O \xrightarrow{H_2/Ni} HC-OH$

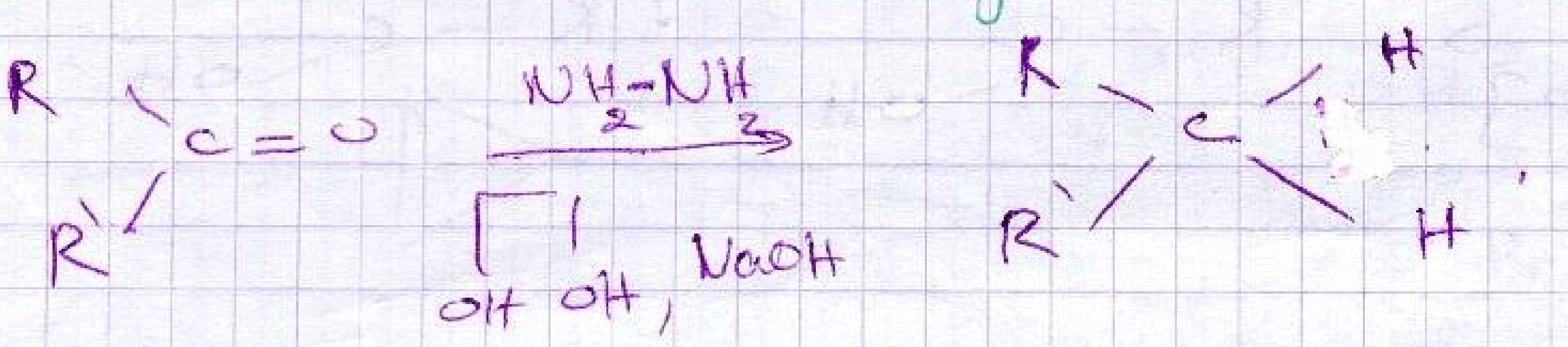


2/ Reduction en Alcanes :

a - Reduction de Clemmensen = On Utilise Zn-Hg / HCl



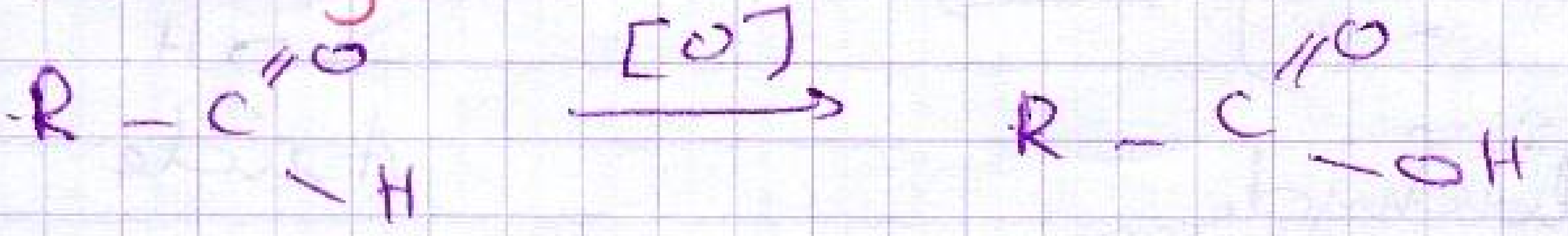
b - Reduction de Wolf Kishner = On Utilise $(NH_2)_2$, $\underset{OH\ OH}{\sqcap}$, NaOH



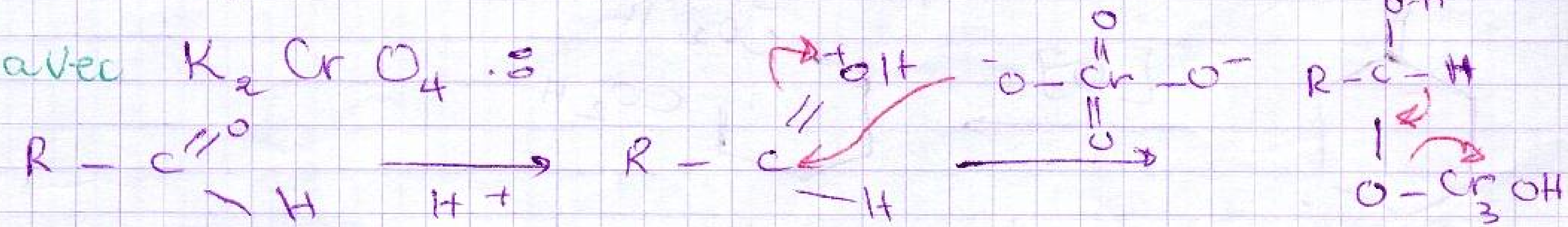
Oxydation des derivés $>C=O$:

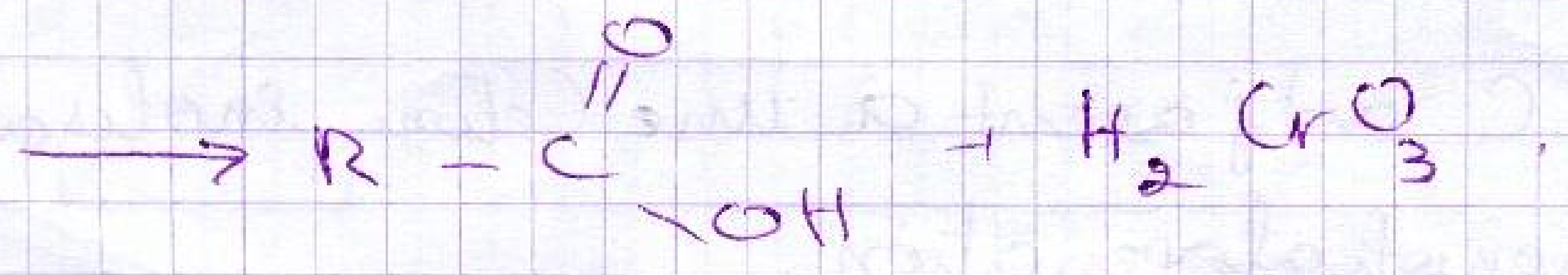
Les Aldehydes s'oxydent plus facilement que les cétones et on obtient les acides correspendant .

1/ Aldehyde =

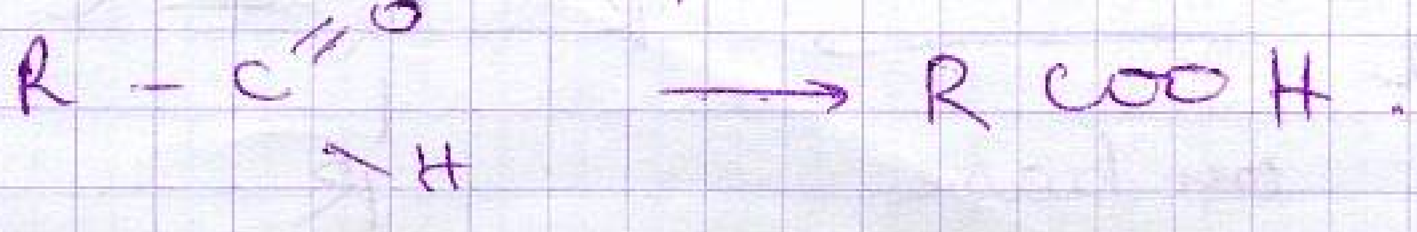


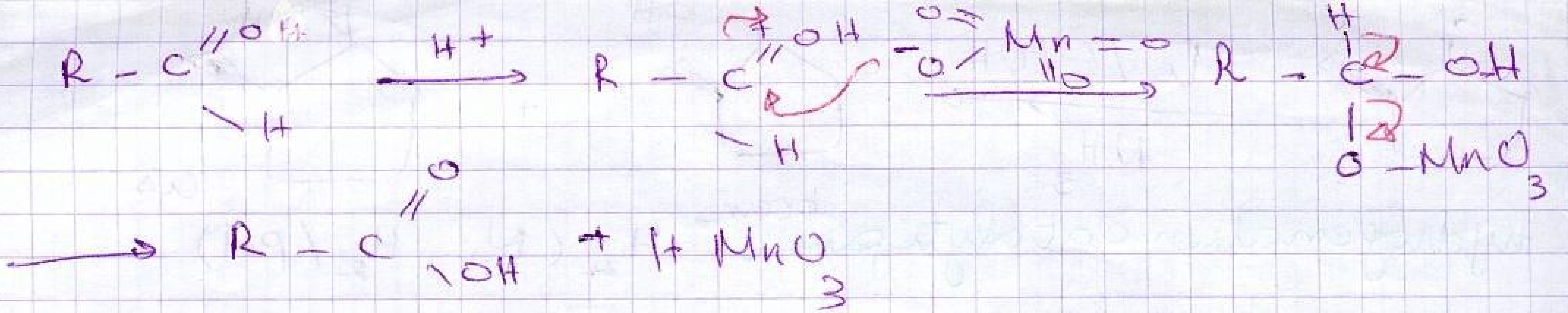
• avec K_2CrO_4 :





• avec $KMnO_4$:

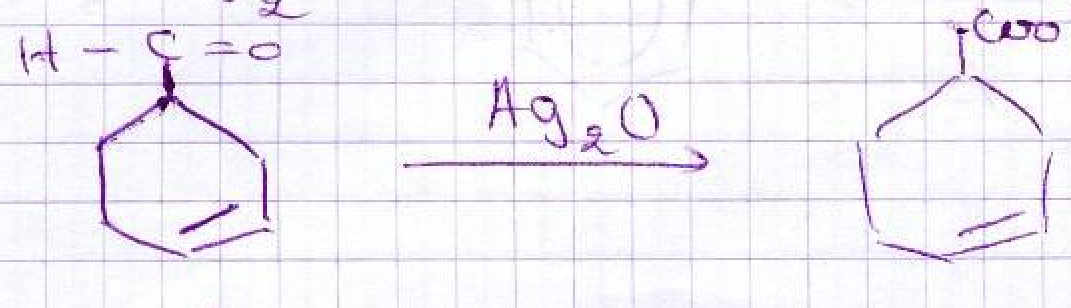




$$R-CHO \xrightarrow{H^+} R-\overset{+}{C}(OH)-H \quad {}^-O-MnO_3 \longrightarrow R-CH(OH)-O-MnO_3 \longrightarrow R-COOH + HMnO_3$$

autres reactifs : Ag_2O, CuO, MnO_2.

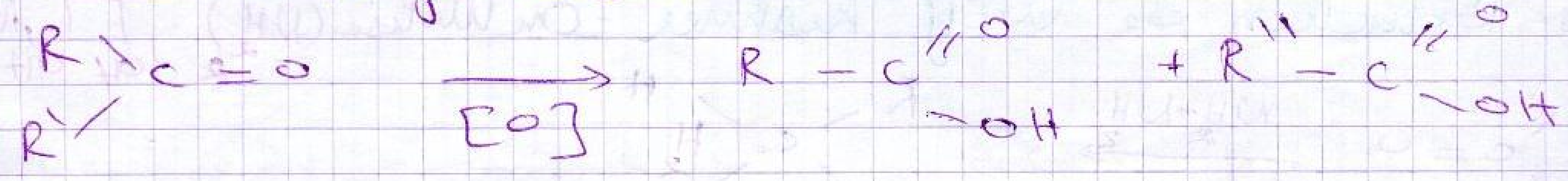
Ag_2O → oxydant selectif.



(Ag_2O n'a pas touché la =)

B/ Cétones :

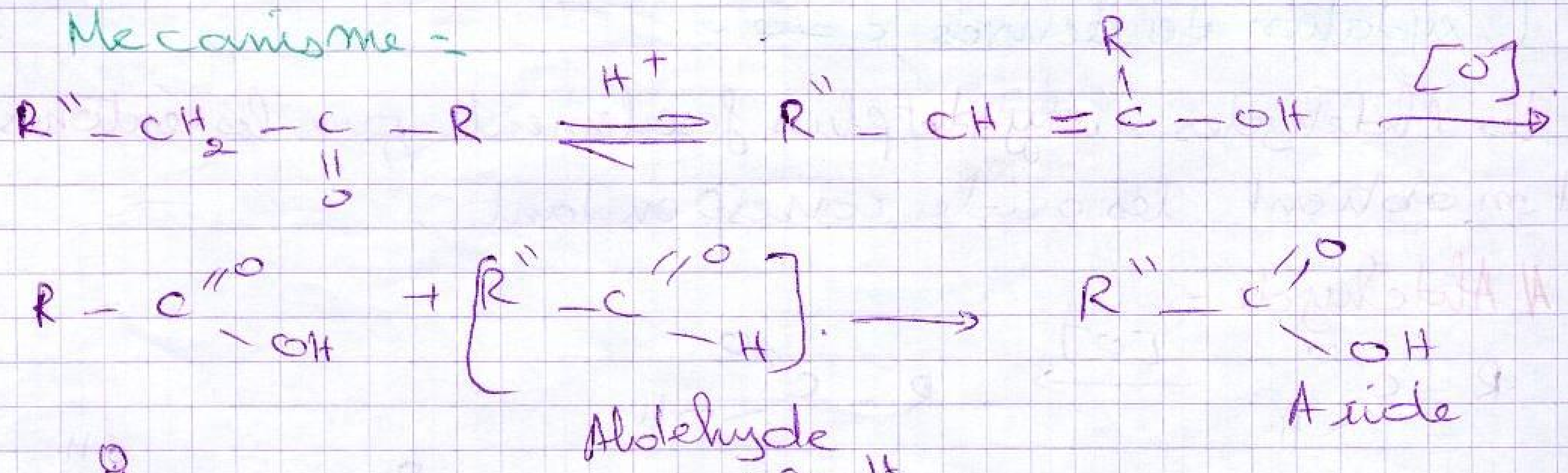
oxydation des Cetones par $KMnO_4$ ou K_2CrO_4 necessite des conditions vigoureuses.



$$\begin{matrix} R \\ R' \end{matrix}\!\!>C=O \xrightarrow[{[O]}]{} R-COOH + R''-COOH$$

$R' = R'' + CH_2$.

Mecanisme :

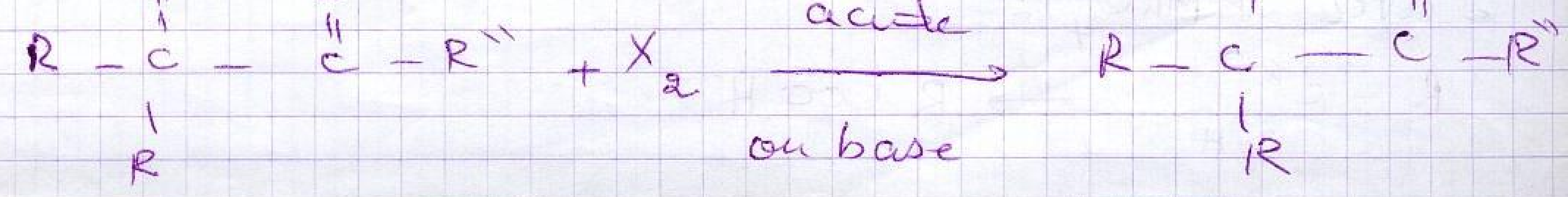


$$R''-CH_2-\underset{\overset{\|}{O}}{C}-R \underset{}{\overset{H^+}{\rightleftharpoons}} R''-CH=\overset{R}{\overset{|}{C}}-OH \xrightarrow{[O]}$$

$$R-COOH + \left[R''-CHO\right] \longrightarrow R''-COOH$$

Halogenation des derivés C=O

l'halogenation du C adjacent à une Cétone enolisable donne un produit de Monohalogenation.



$$R-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-R'' + X_2 \xrightarrow[\text{ou base}]{\text{acide}} R-\underset{R}{\overset{X}{C}}-\overset{O}{\overset{\|}{C}}-R''$$

on a remplacé un H par un X :

exp :