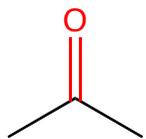
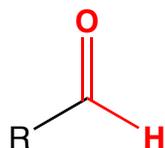


I FONCTION CARBONYLE

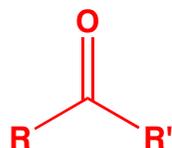
ALDEHYDES ET CETONES



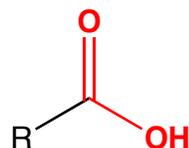
Carbonyle



Aldéhyde



Cétone



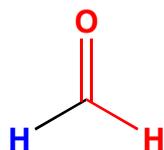
Acide

* Noms Systématiques:

Aldéhydes:

1) Nomenclature:

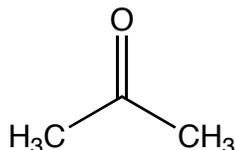
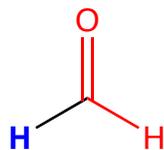
* Noms Courants:



Formaldéhyde

MéthanE (CH₄)

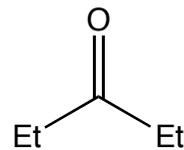
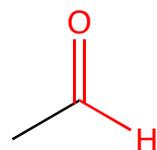
MéthanAL



Acétone

EthanE (C₂H₆)

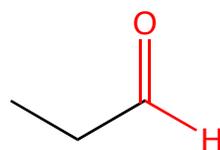
EthanAL



Diéthylcétone

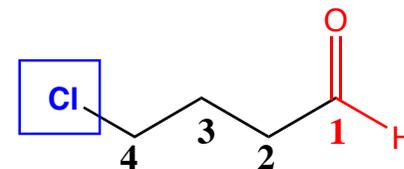
PropanE (C₃H₈)

PropanAL

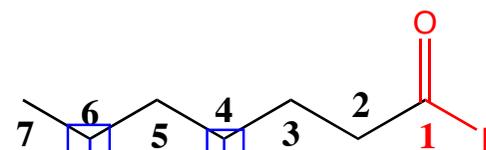


- 1) Considérer l'alcane correspondant
- 2) Remplacer terminaison E par AL
- 3) CO toujours en position 1

AlcanE → **AlcanAL**



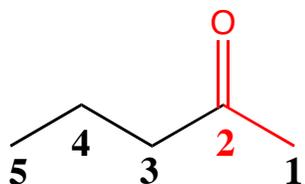
Chloro-4-butanal



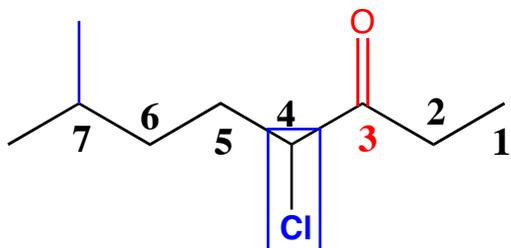
Diméthyl-4,6-heptanal

1) Nomenclature:

* Noms Systématiques:



Pentan-2-one



Chloro-4-méthyl-7-octan-3-one

Remarque:

Un aldéhyde (R-COH) ne peut faire partie d'un cycle.

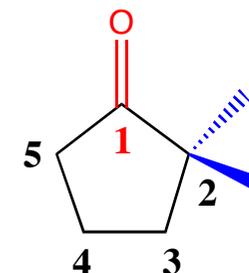
Une Cétone (R-CO-R') peut faire partie d'un cycle.

Cétones

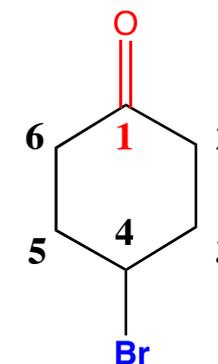
- 1) Considérer l'alcane correspondant
- 2) Remplacer terminaison E par ONE
- 3) Indiquer la Position* du CO

* Considérer la Chaîne la plus Longue
Si la plus petite

Alcan**E** → Alcan**ONE**



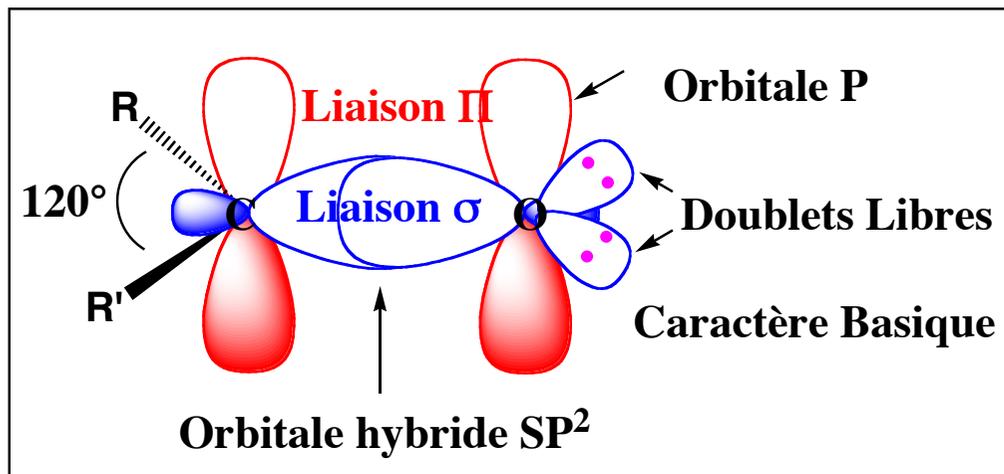
Diméthyl-2,2-cyclopentanone



Bromo-4-cyclohexanone

2) Propriétés Physiques:

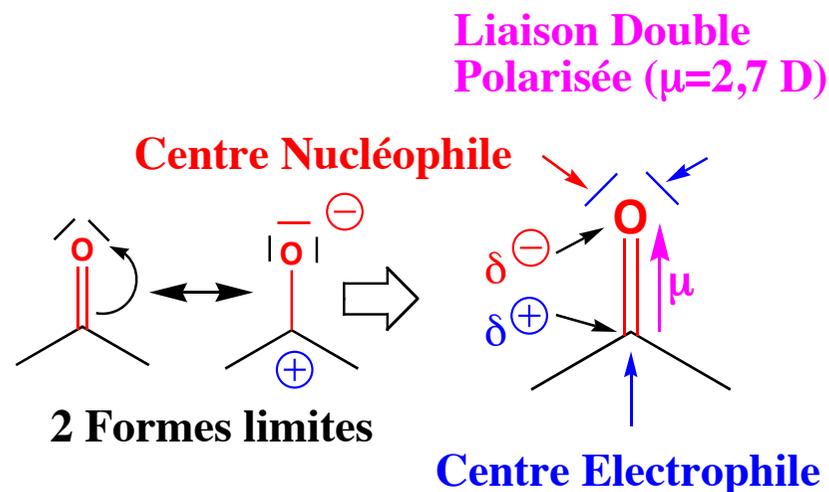
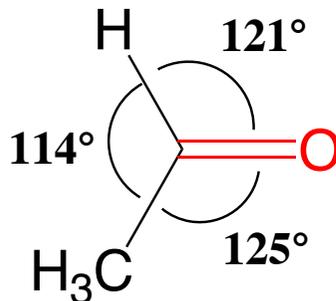
* Structure Electronique:



Conséquences: Analogie avec C=C
Fonction Carbonyle **PLANE**

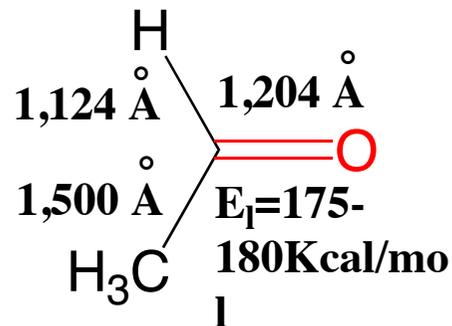
* Structure Spatiale:

Exemple typique:
l'Ethanal (CH₃-CHO)



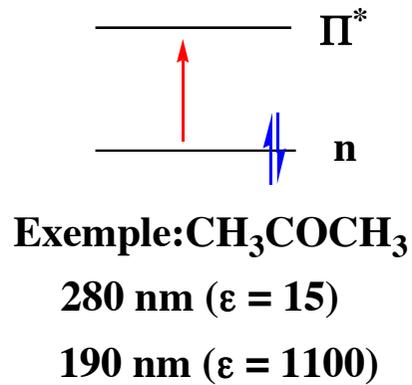
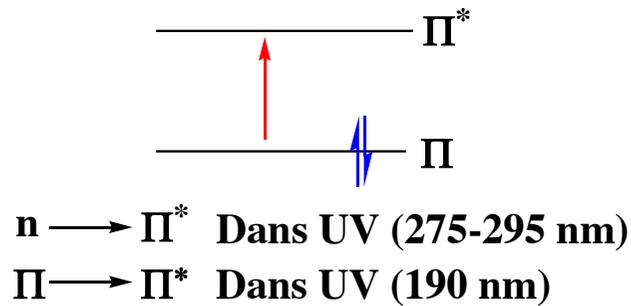
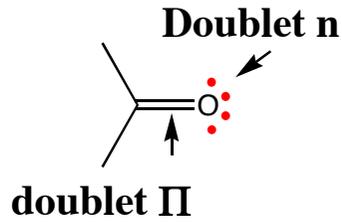
Conséquences:

- * Polarisation de C=O: Eb Elevées
- * Solubles dans H₂O (C₁-C₅)
- * C₁-C₁₂ Liquides; > C₁₃ Solides

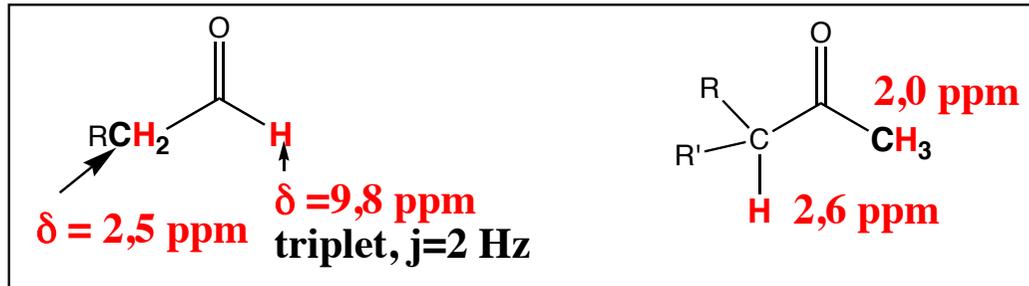


* Propriétés Spectroscopiques:

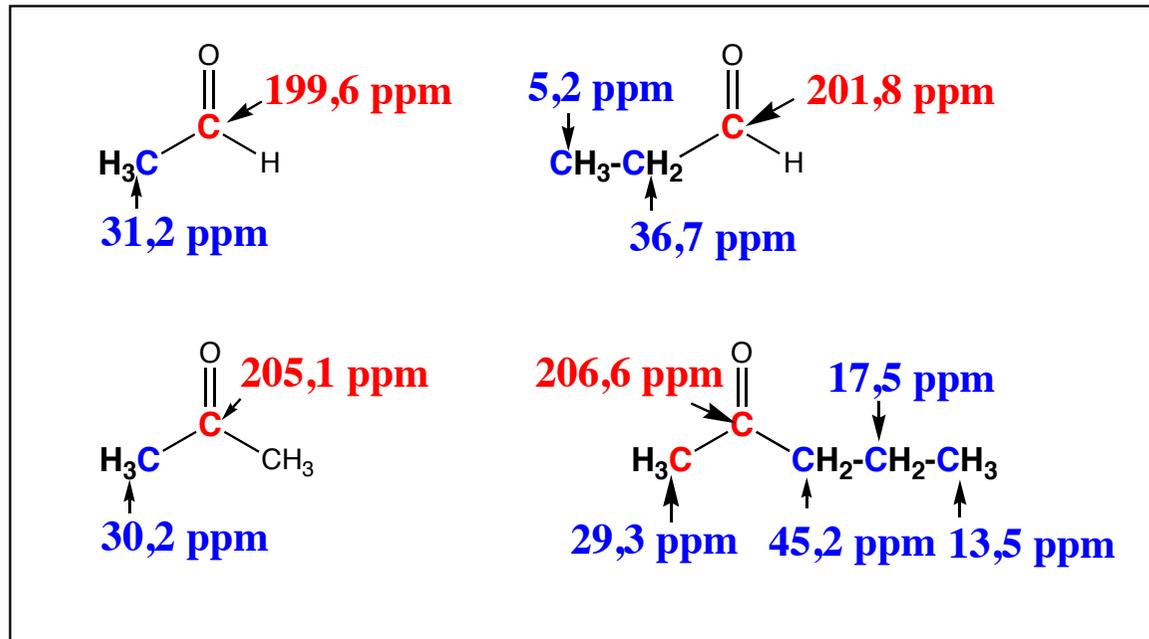
Spectroscopie Electronique



^1H RMN:

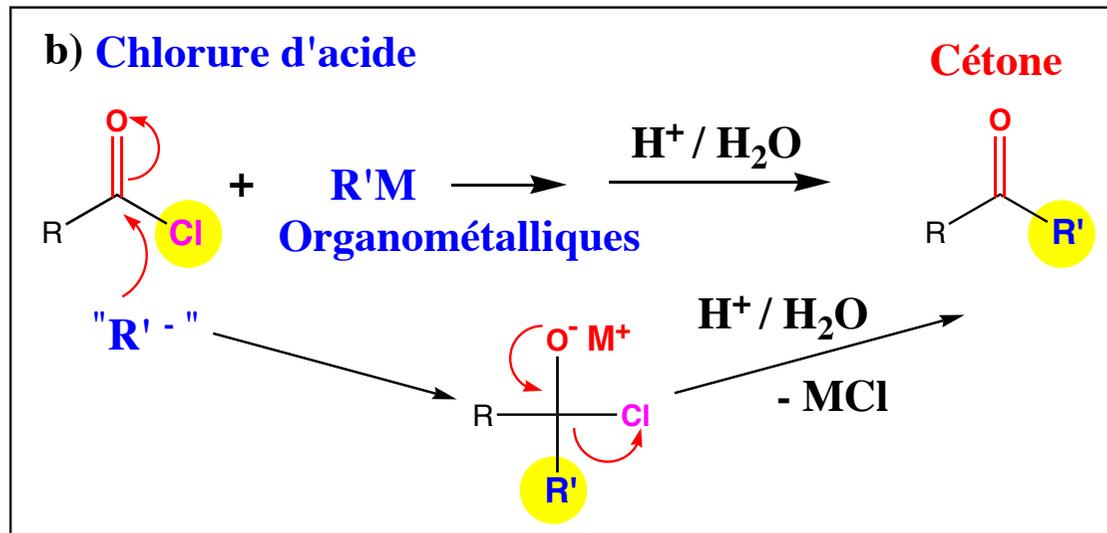
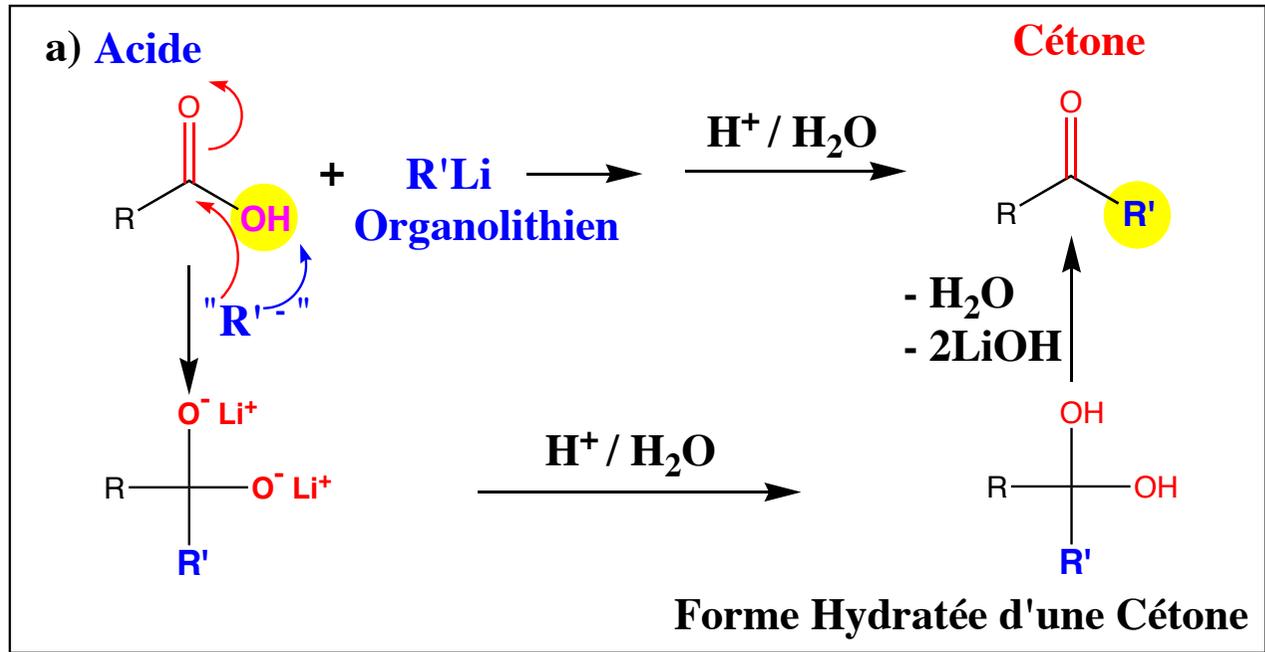


^{13}C RMN:



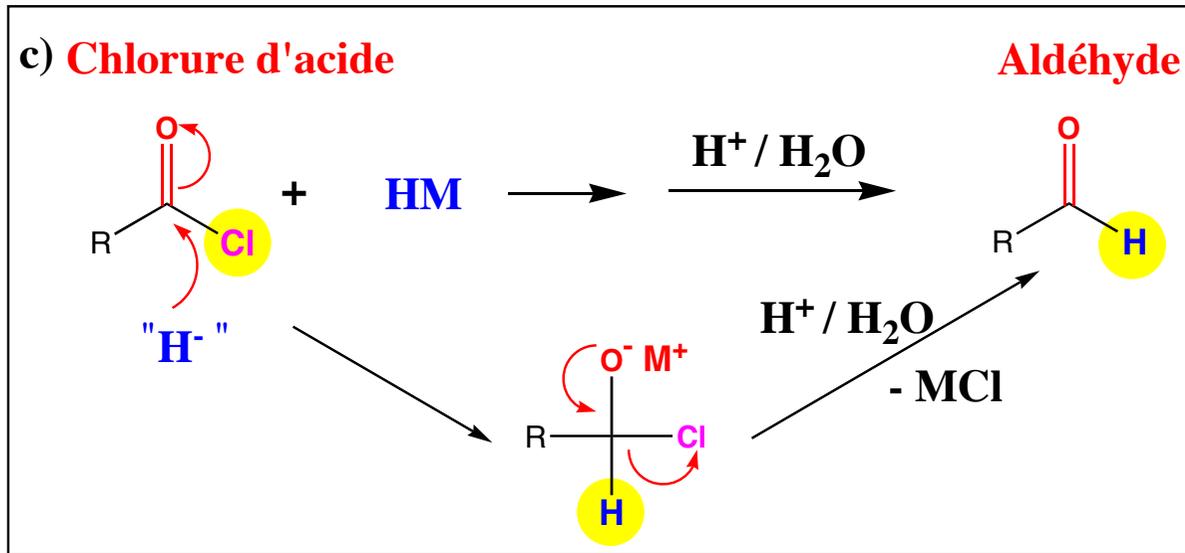
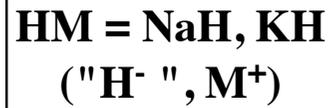
3) Méthodes de Préparation

Formellement
 $R'Li = "R' -" + Li^+$

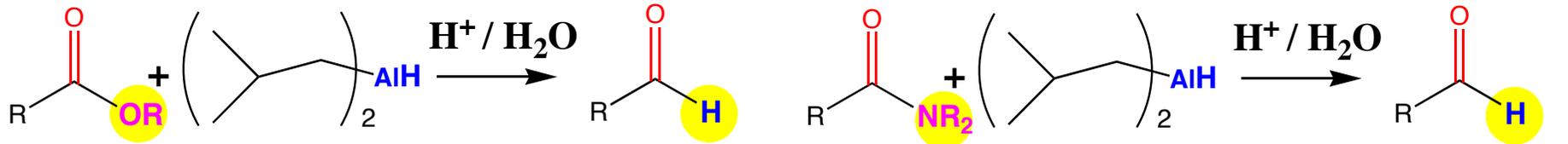


3) Méthodes de Préparation

Hydruure métalliques



d) Ester



***Di-isobutylAluminium Hydride**
Hydruure particulier
ne réduit pas l'ester

***Remarque:** On ne veut pas réduire l'ester en alcool (LiAlH₄), mais on veut remplacer OR par H

***Remarque:** On ne veut pas réduire l'amide en amine (B₂H₆), mais on veut remplacer NR₂ par H

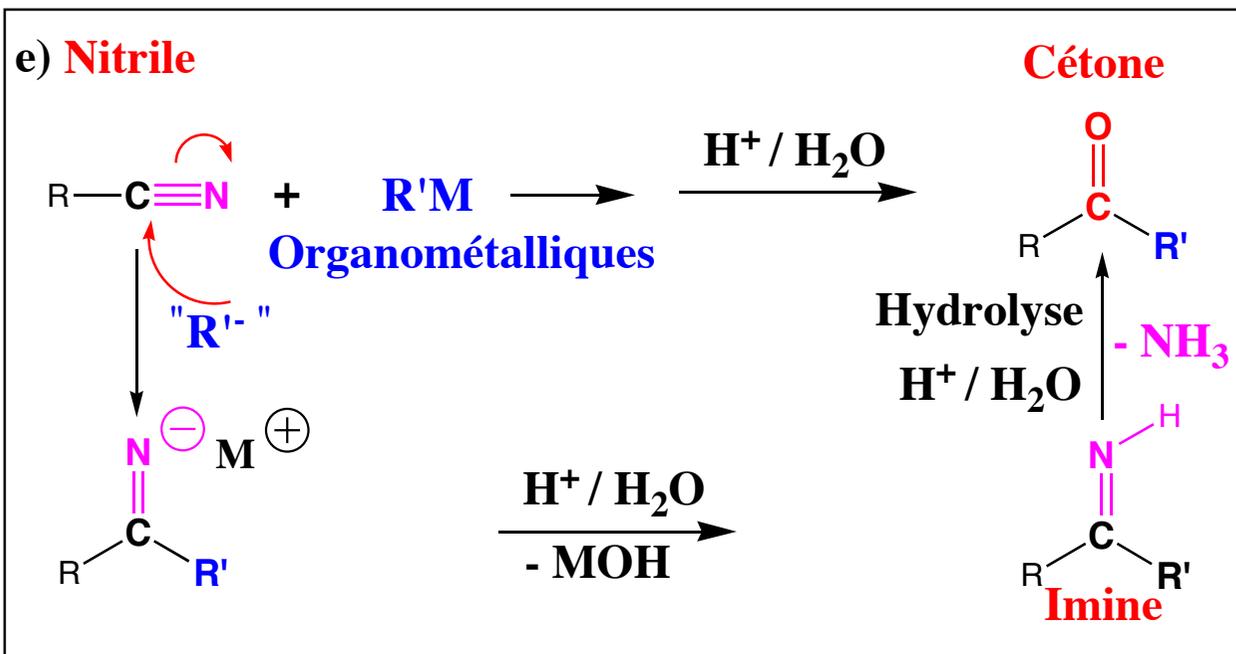
3) Méthodes de Préparation

Organométalliques

RMgX : Orgnomagnésien

R₂Cu,M : Cuprate

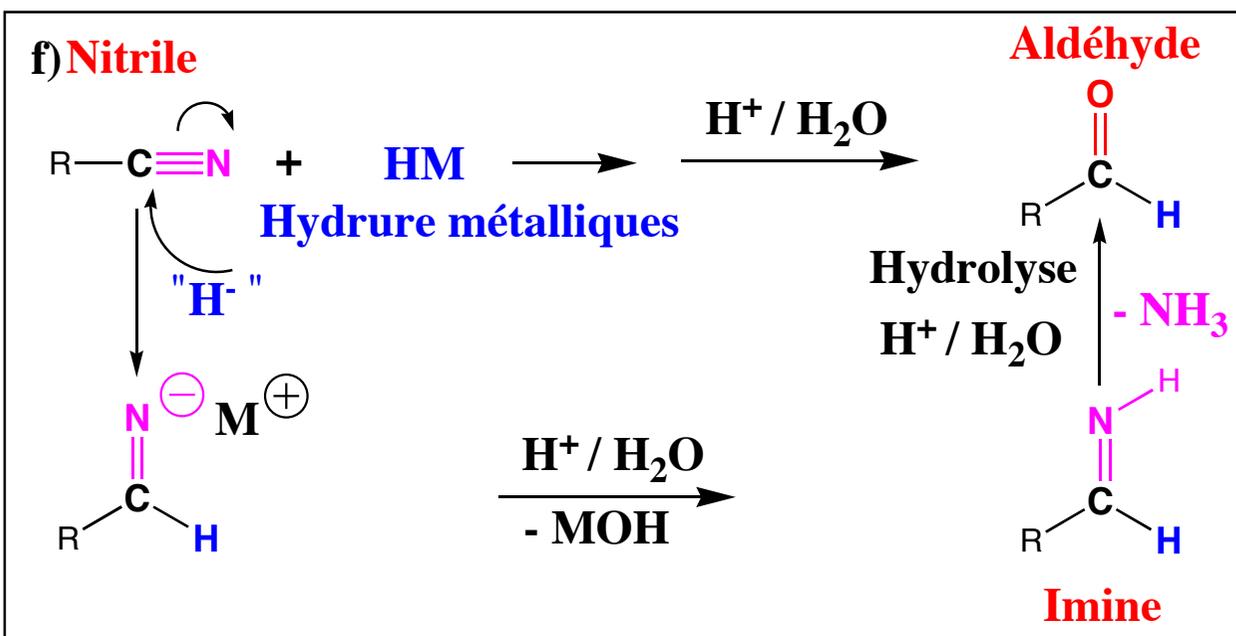
R₂Zn : Organozincique



Hydrure métalliques

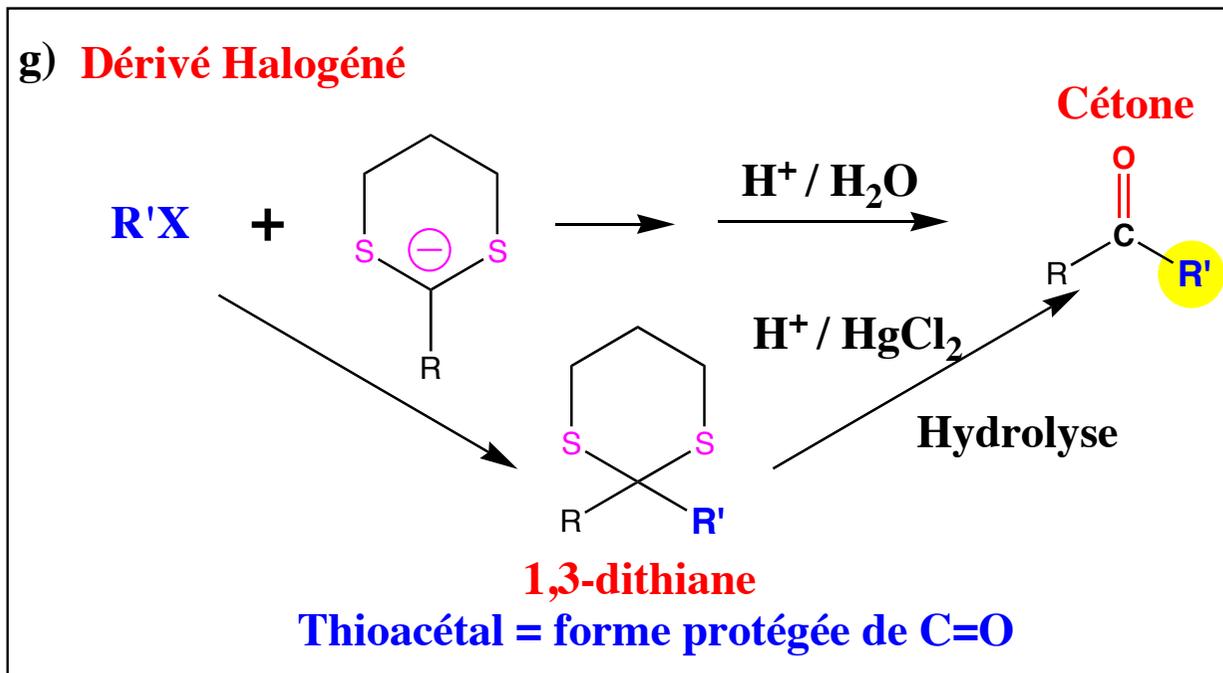
NaH

KH

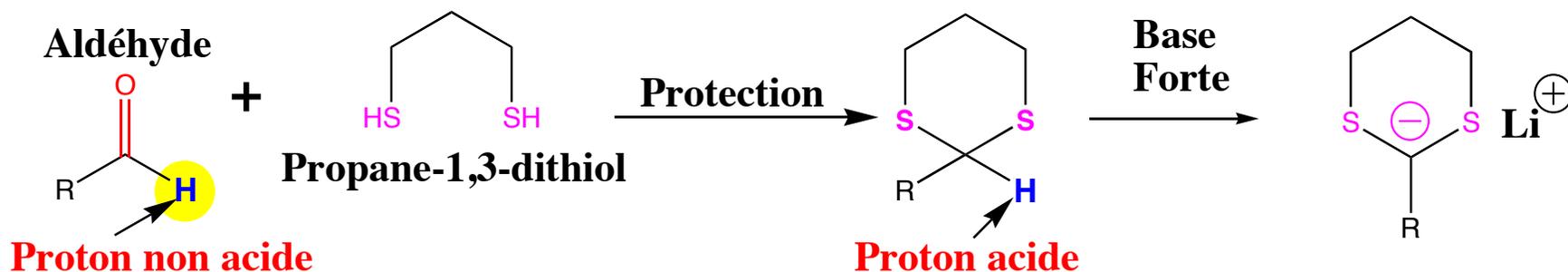


3) Méthodes de Préparation

Anion Stabilisé en α de Soufre



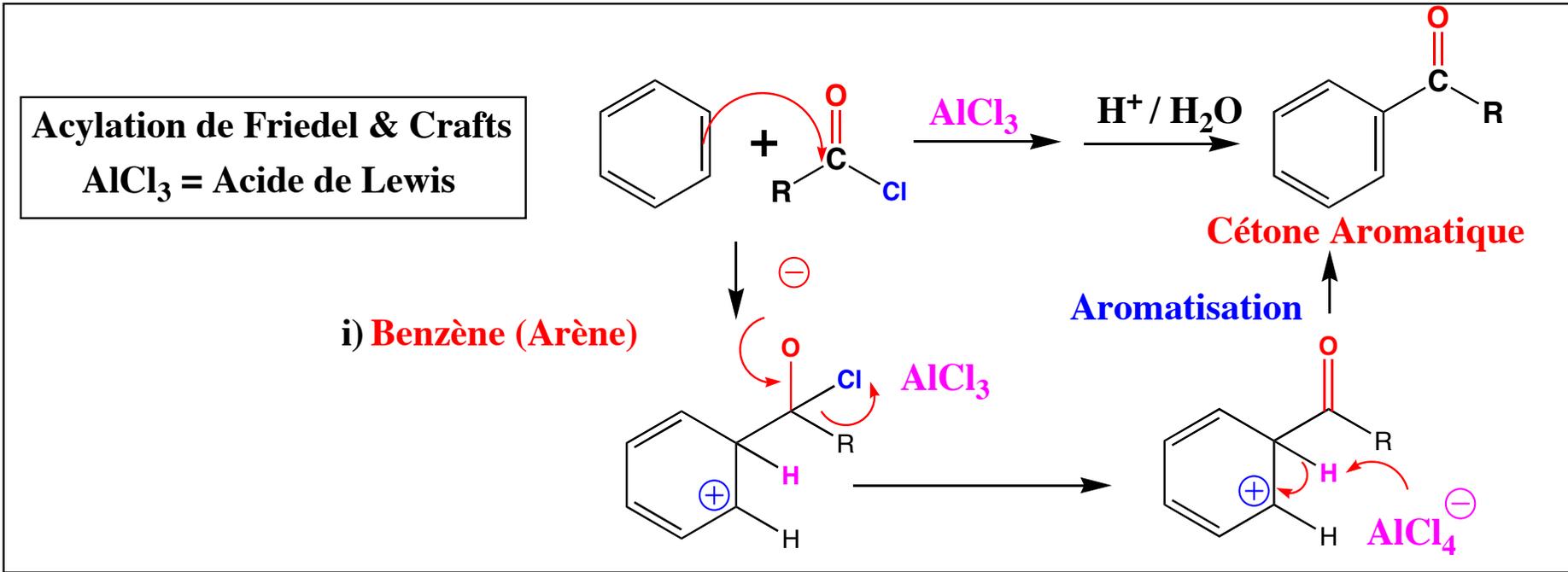
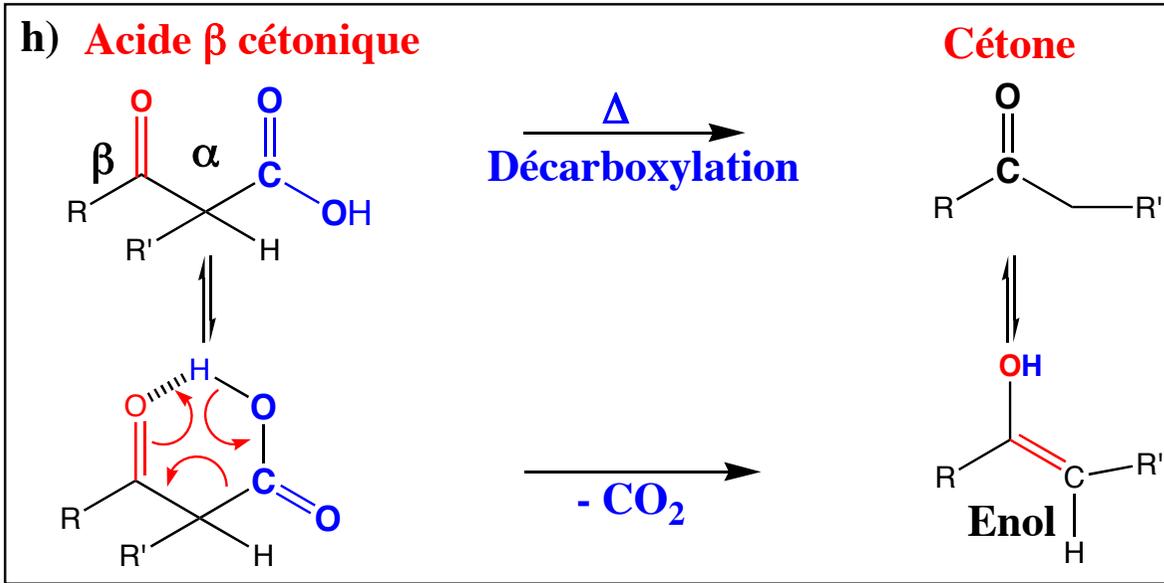
Remarque:



Inversion de Polarité = UMPOLUNG

Bilan : Transformation de R-COH (Aldéhyde) en R-CO-R' (Cétone)

3) Méthodes de Préparation



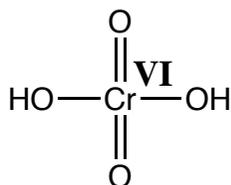
j) Oxydation des ALCOOLS

Obtention d'ALDEHYDES

Réactif de Jones:

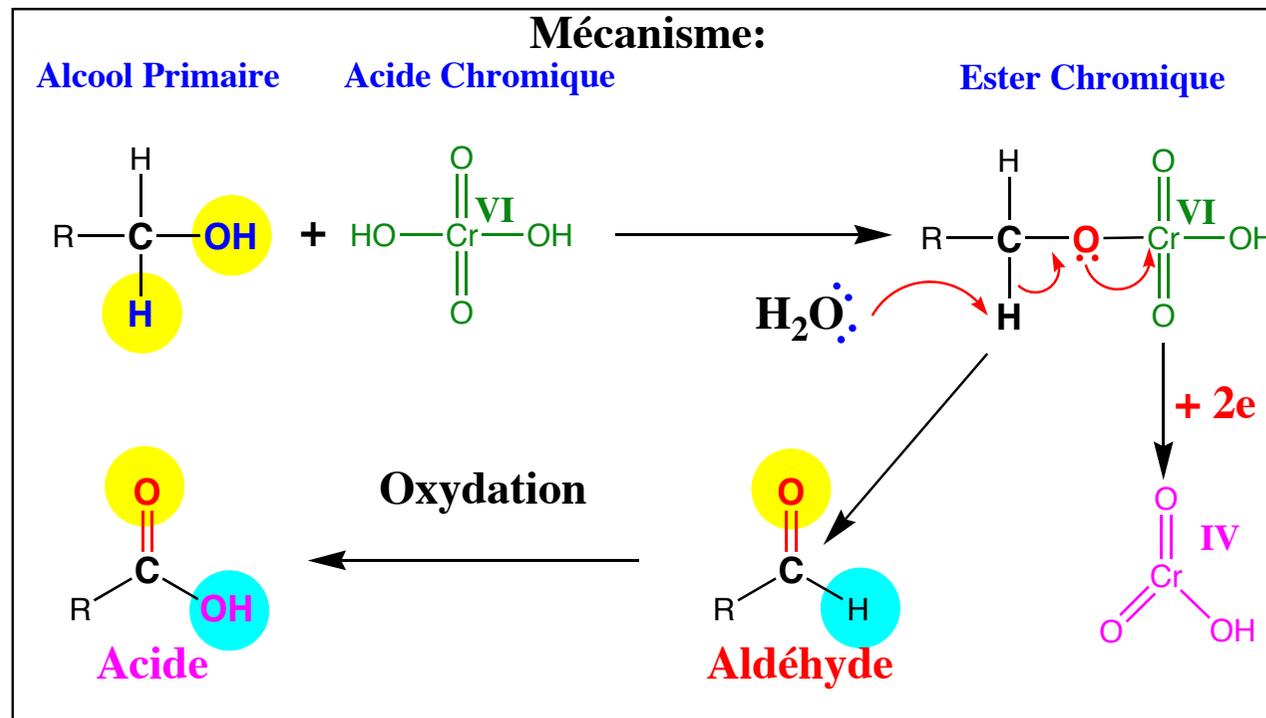
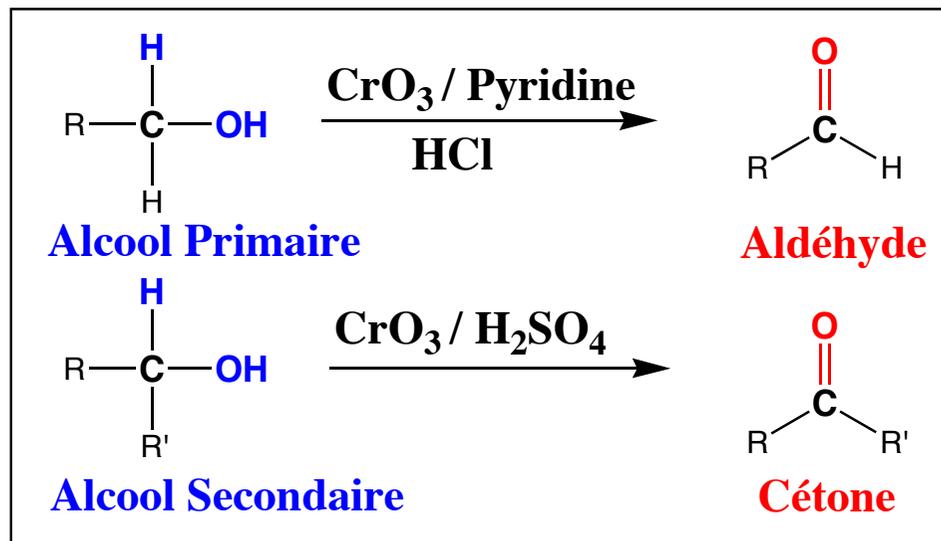


Hydratation du CrO_3 en milieu acide



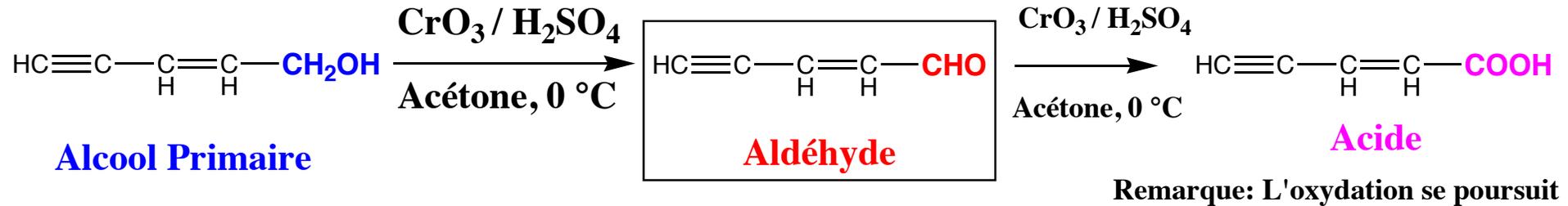
Acide Chromique

Remarque: Aldéhyde
Facilement Oxydable en Acide



3) Méthodes de Préparation

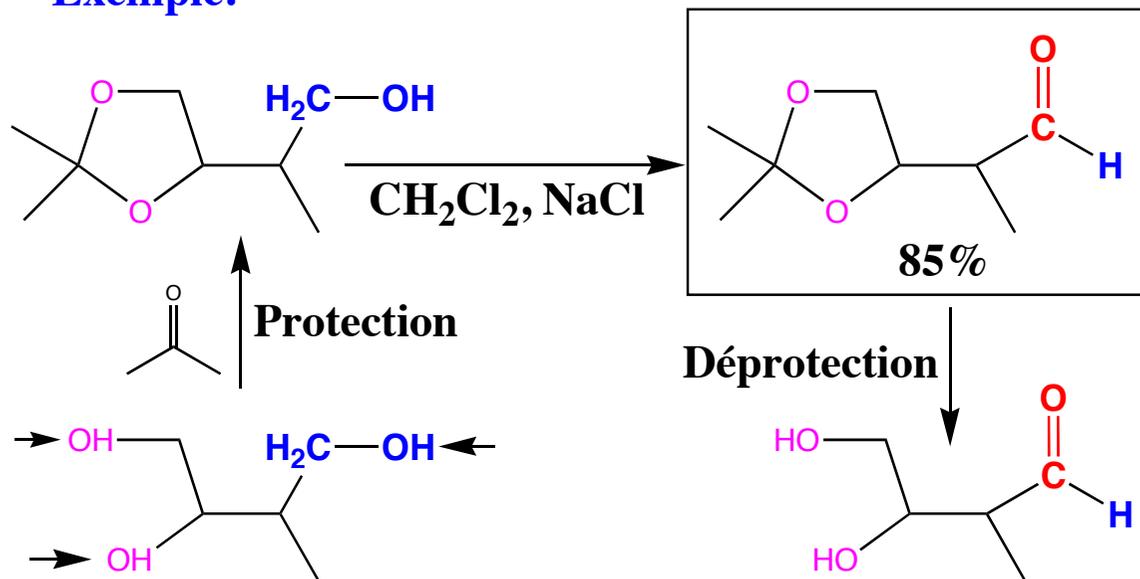
* Exemple:



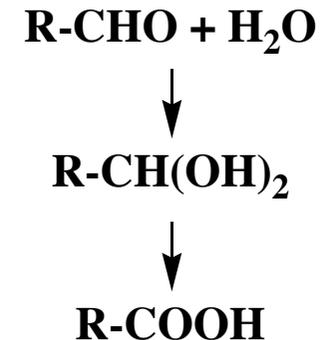
Pour Réaliser une Oxydation Ménagée On Désactive l'Oxydant en Utilisant de la Pyridine

Réactif de Corey: CrO₃ / Pyridine / HCl = PCC

* Exemple:

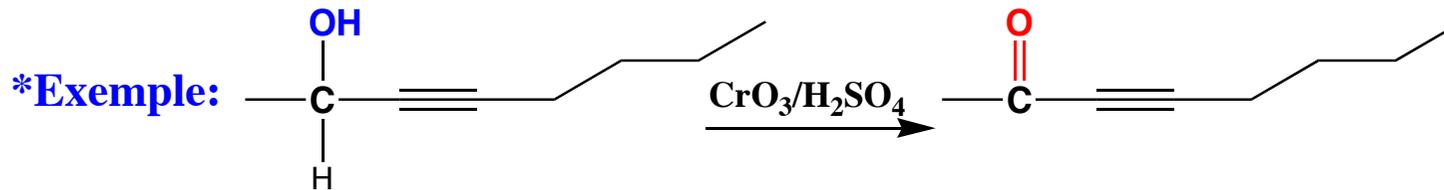
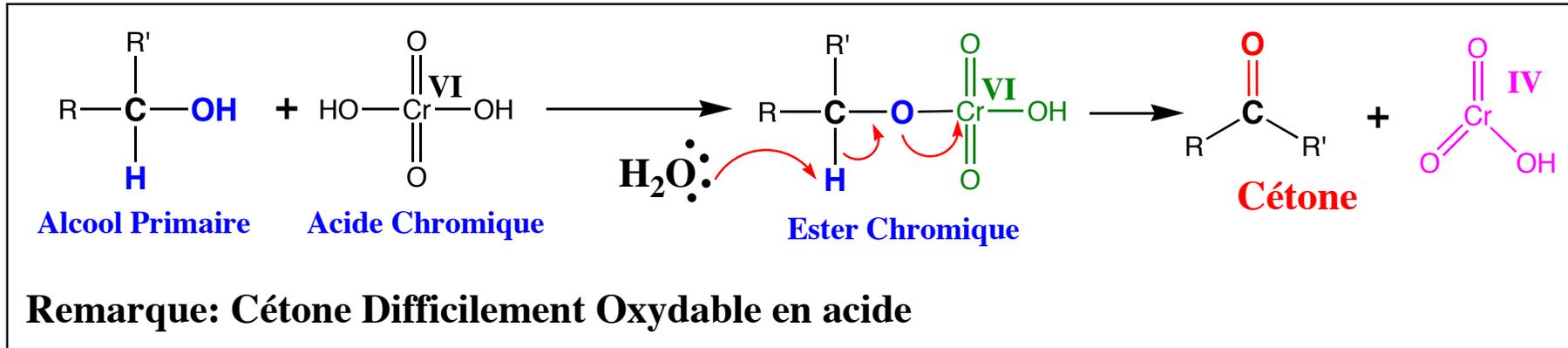


Remarque: Absence de H₂O
car suroxydation :

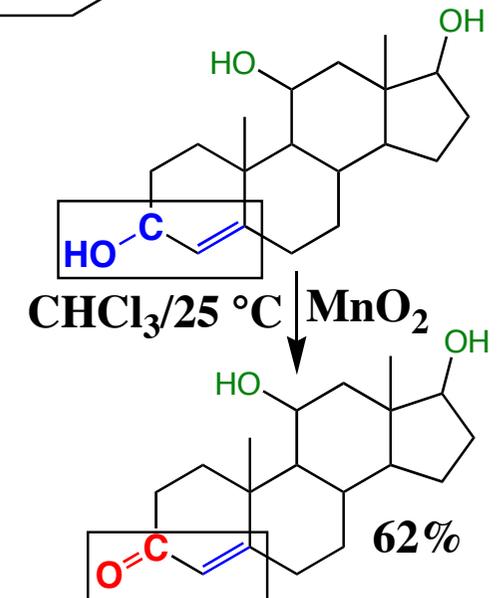
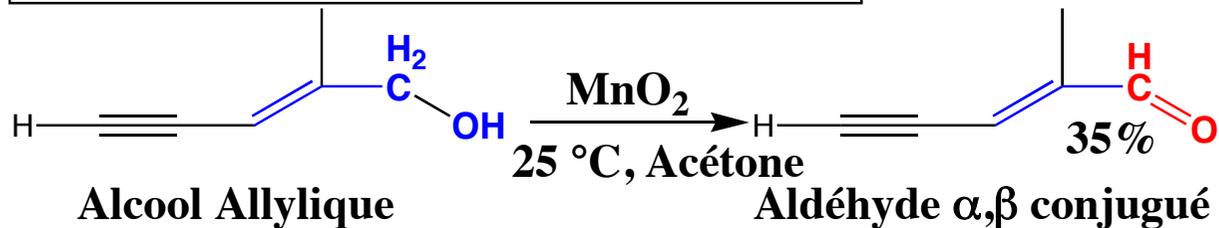


Obtention de CETONES

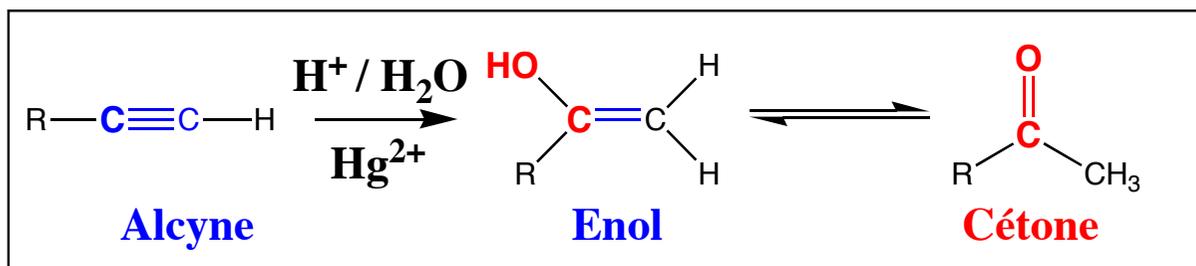
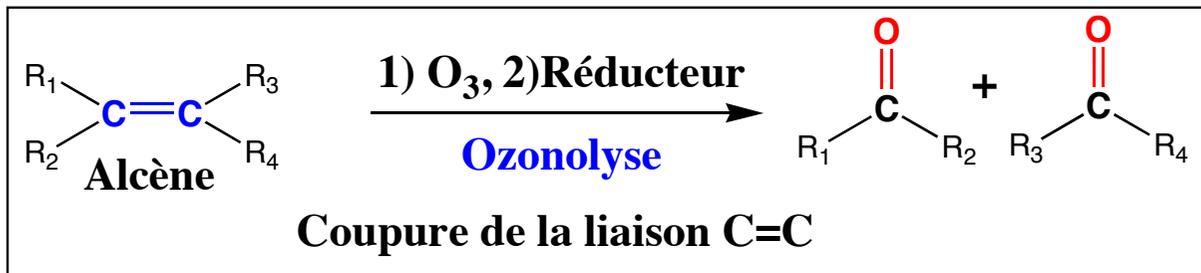
Mécanisme: Réactif de Jones: $\text{CrO}_3 + \text{H}_2\text{O}/\text{H}_2\text{SO}_4 \longrightarrow \text{HO}-\overset{\text{O}}{\parallel}{\text{Cr}}^{\text{VI}}-\text{OH}$ **Acide Chromique**
 Hydratation Du CrO_3 en milieu acide



Oxydation Par MnO_2 : Un Oxydant Doux

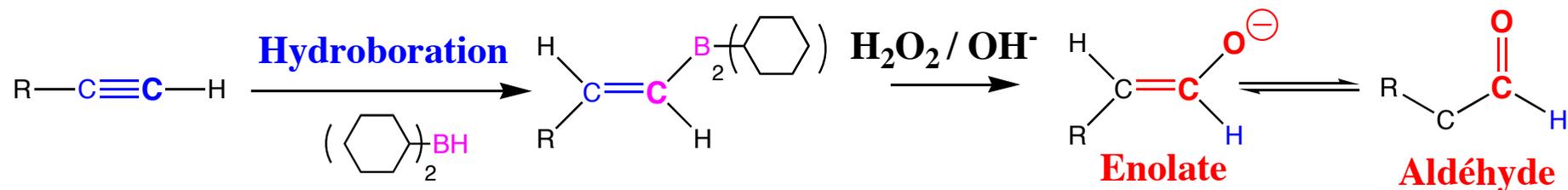


Formation de R-CHO et R-CO-R' par Clivage Oxydatif



*Addition MARKOWNICOV de H₂O

**Cis Addition de OH⁻ et H⁺



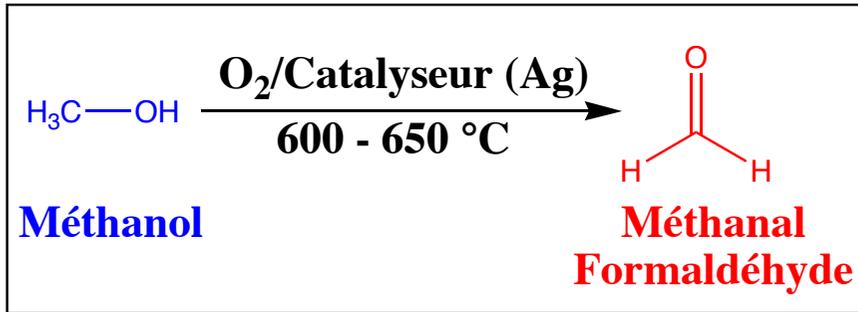
*Addition Anti-MARKOWNICOV de H₂O

3) Méthodes de Préparation

Préparation Industrielle



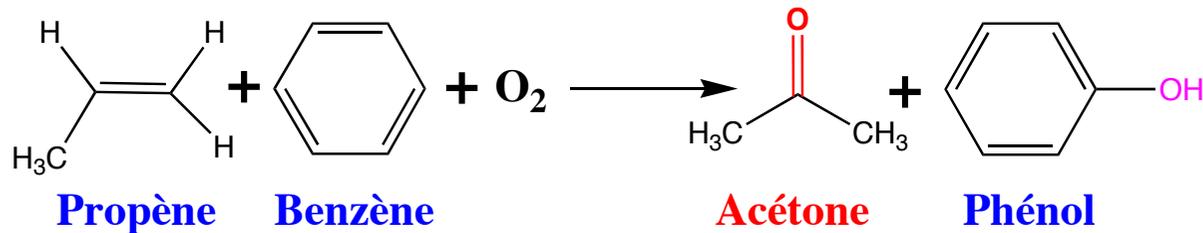
* Le méthanal est un produit très important.
Aux USA, 3 Millions de tonnes sont produites par an



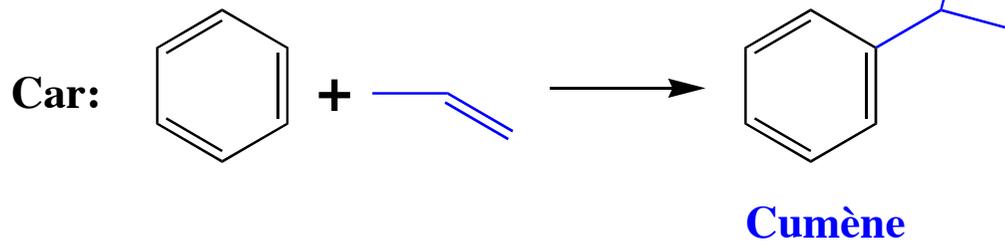
Utilisation du méthanal dans l'eau (le Formol):
Fongicide, Désinfectant, Germicide, Résines etc...



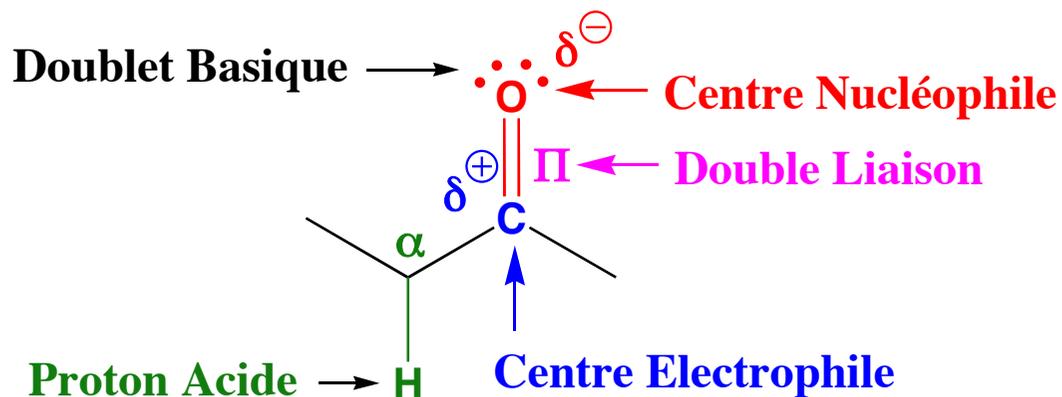
** L'acétone (Propanone) est utilisée comme solvant
Aux USA, 1 Million de tonnes sont produites par an



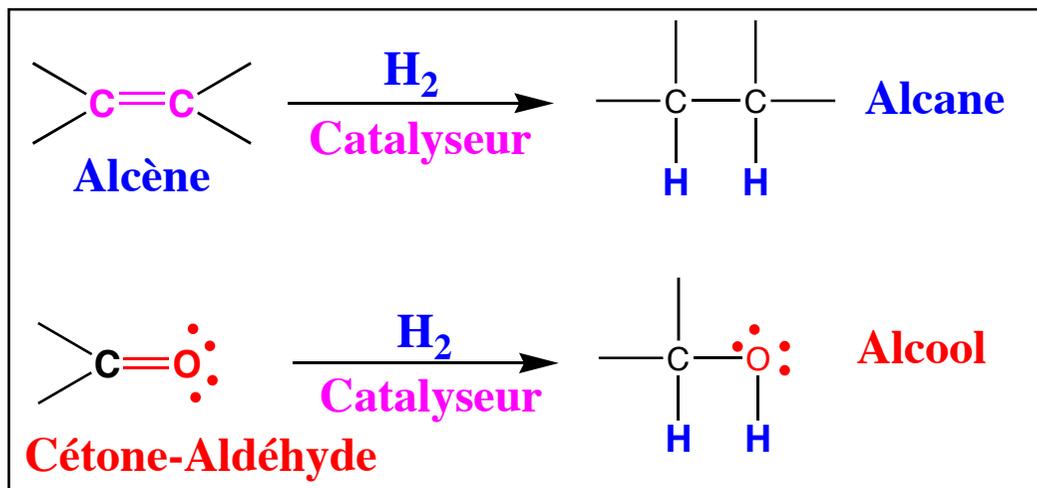
Procédé d'HYDROPEROXYDE
de CUMENE



4) Réactivité de la Fonction Carbonyle

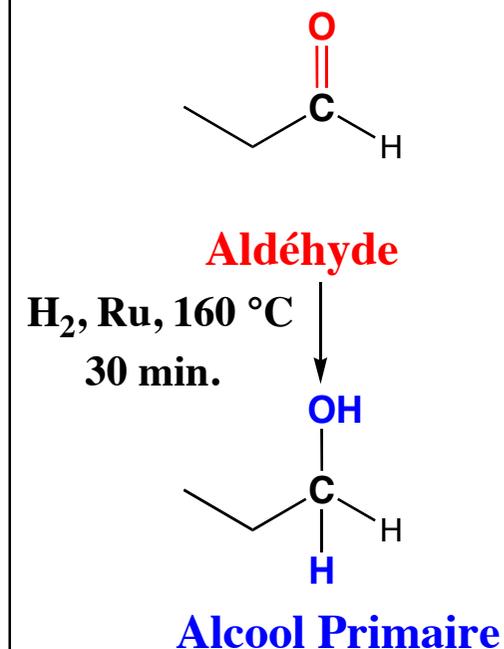


* HYDROGENATION

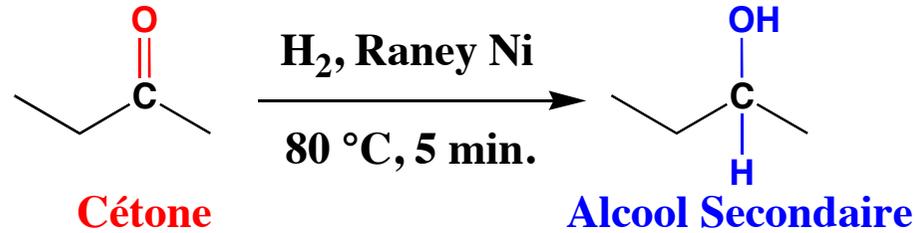


Remarque: $\text{C}=\text{O}$ réagit plus lentement que $\text{C}=\text{C}$.
Conséquence: Hydrogénation Sélective.

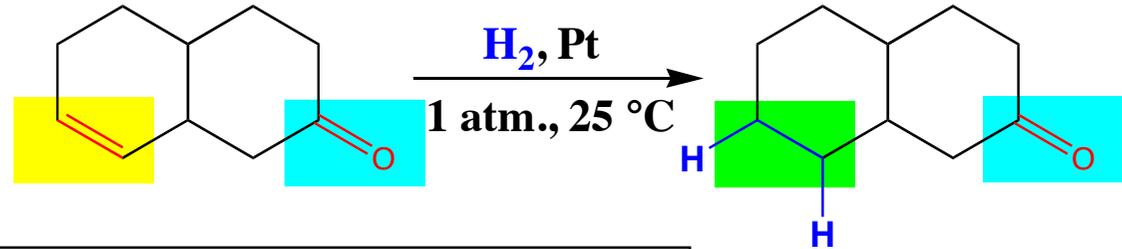
*Exemples:



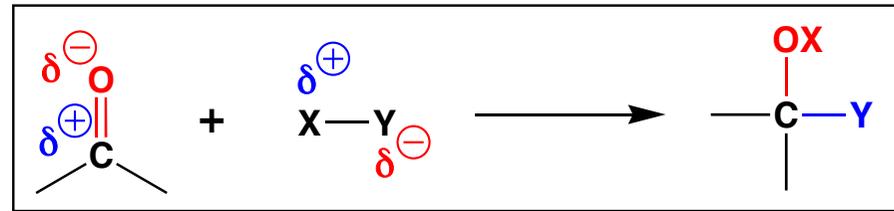
****Exemples:**



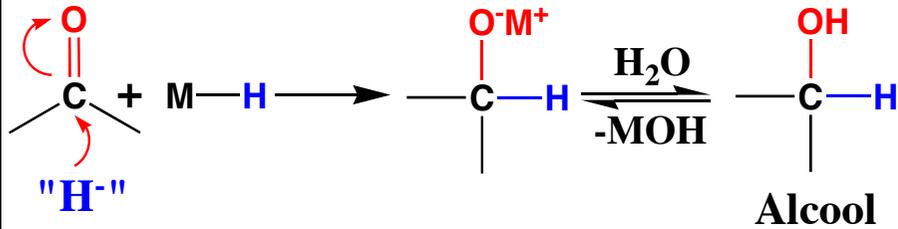
*****Exemple: Hydrogénation Sélective**



ADDITION IONIQUE

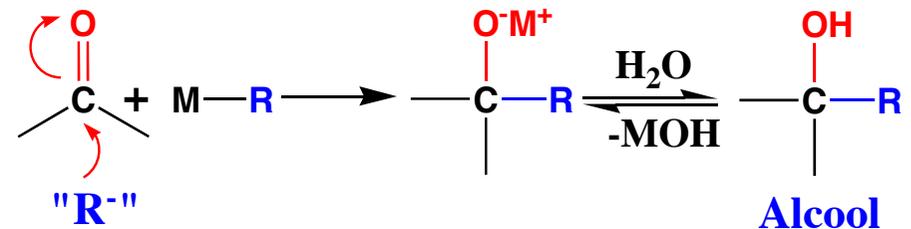


***Addition d'Hydruve Métallique MH:**



Remarque: Réaction NON REVERSIBLE

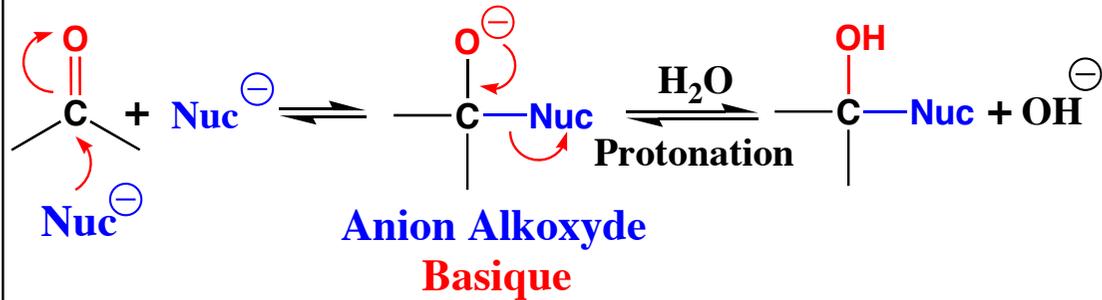
***Addition d'Organométallique RM:**



Remarque: Réaction NON REVERSIBLE

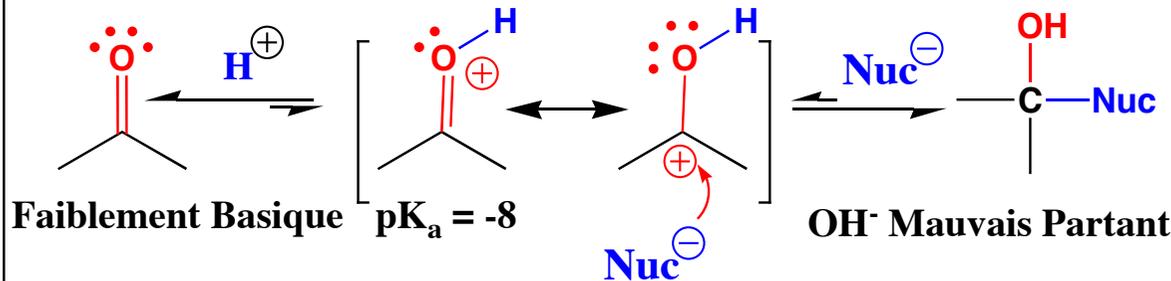
***Addition REVERSIBLE: Mécanisme**

En Milieu Basique:

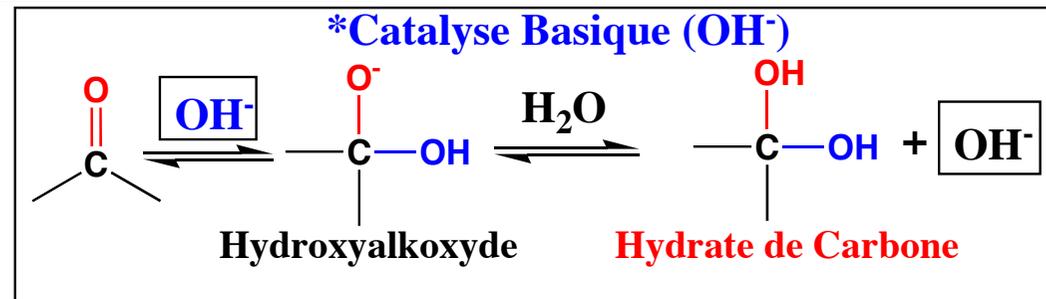
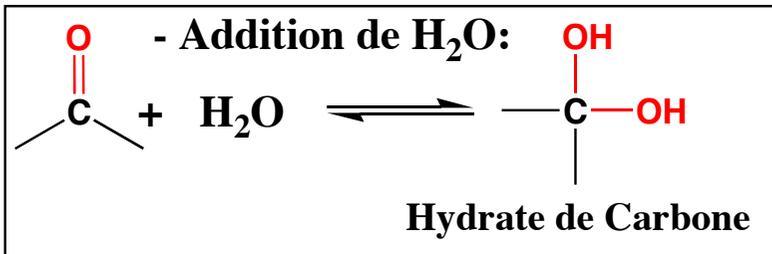


Remarque: Analogie avec une Réaction SN2
Pas de Départ d'un Groupe mais la Double Liaison
Bascule sur l'Oxygène

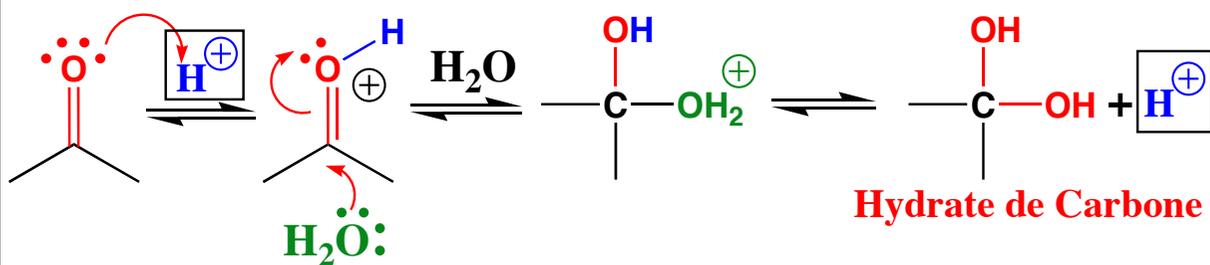
En Milieu Acide:



Remarque: C=O très faiblement Basique
Conséquence: C=OH⁺ très fortement Acide
Néanmoins: Faible Quantité de C=OH⁺



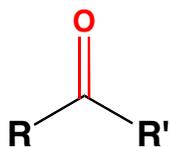
****Catalyse Acide (H⁺)**



Explication: Constante d'Equilibre K

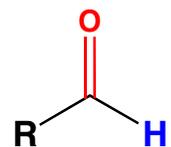


Remarque: L'Hydratation de C=O est REVERSIBLE
 Mais l'Equilibre Dépend de la Nature de C=O



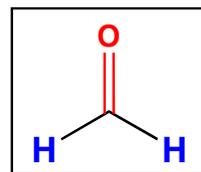
Cétone

Difficilement Hydratée



Aldéhyde

Moyennement Hydraté



Formaldéhyde

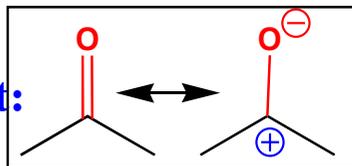
Facilement Hydraté

R ≠ R' ≠ H : Cétone
 R = H, R' = H : Aldéhyde
 R = R' = H : Formol

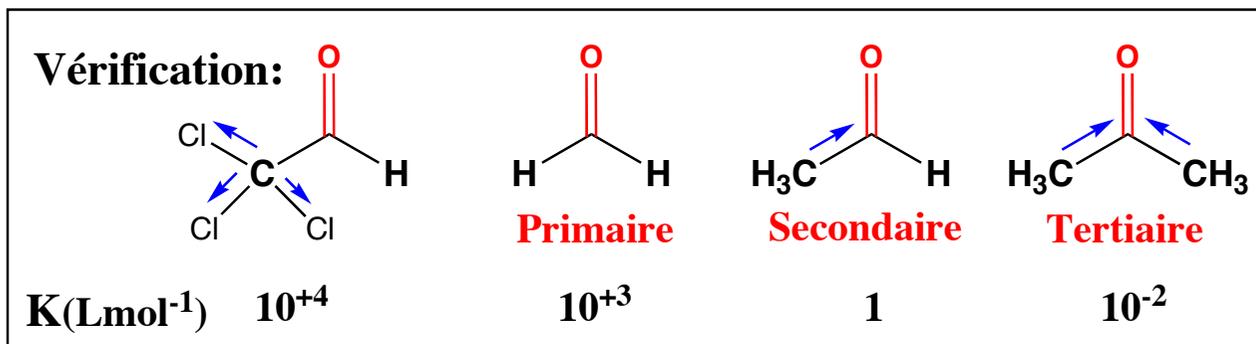
Avec:
$$K = \frac{[RR'C(OH)_2]}{[RR'C=O] \times [H_2O]}$$

R = R' = CH ₃ Acétone	R = H, R' = CH ₃ Ethanal	R = R' = H Formaldéhyde
K(L mol ⁻¹) = 10 ⁻²	1	10 ⁺³

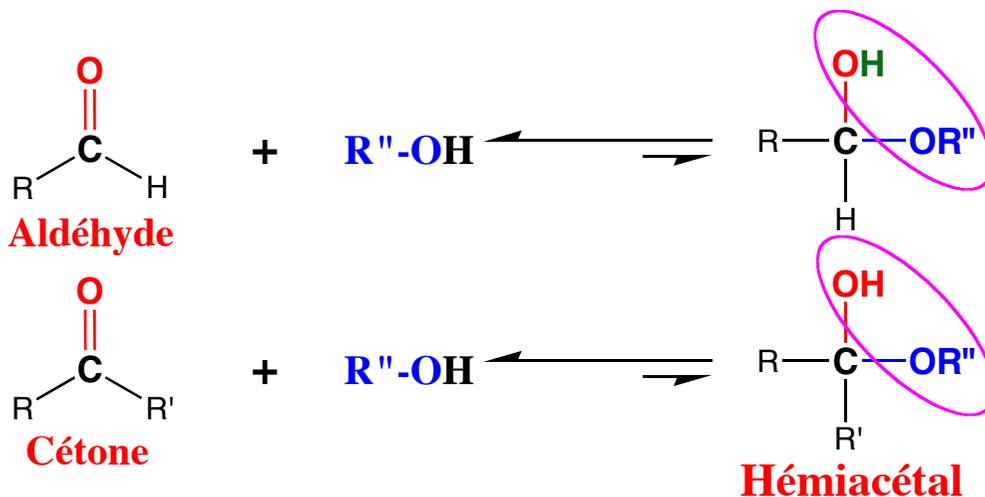
Raisonnement:



Toute Réaction d'Addition est d'autant plus Favorisée que le Carbone du C=O est Electrophile (déficient en Electron). En d'autres termes, la réaction se fait d'autant plus facilement que le "C⁺" est déstabilisé.

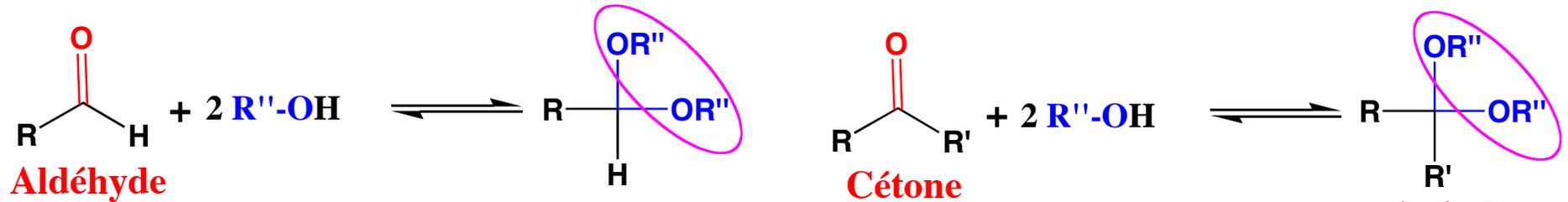


-Addition de R-OH: Formation d'**HEMIACETAL**



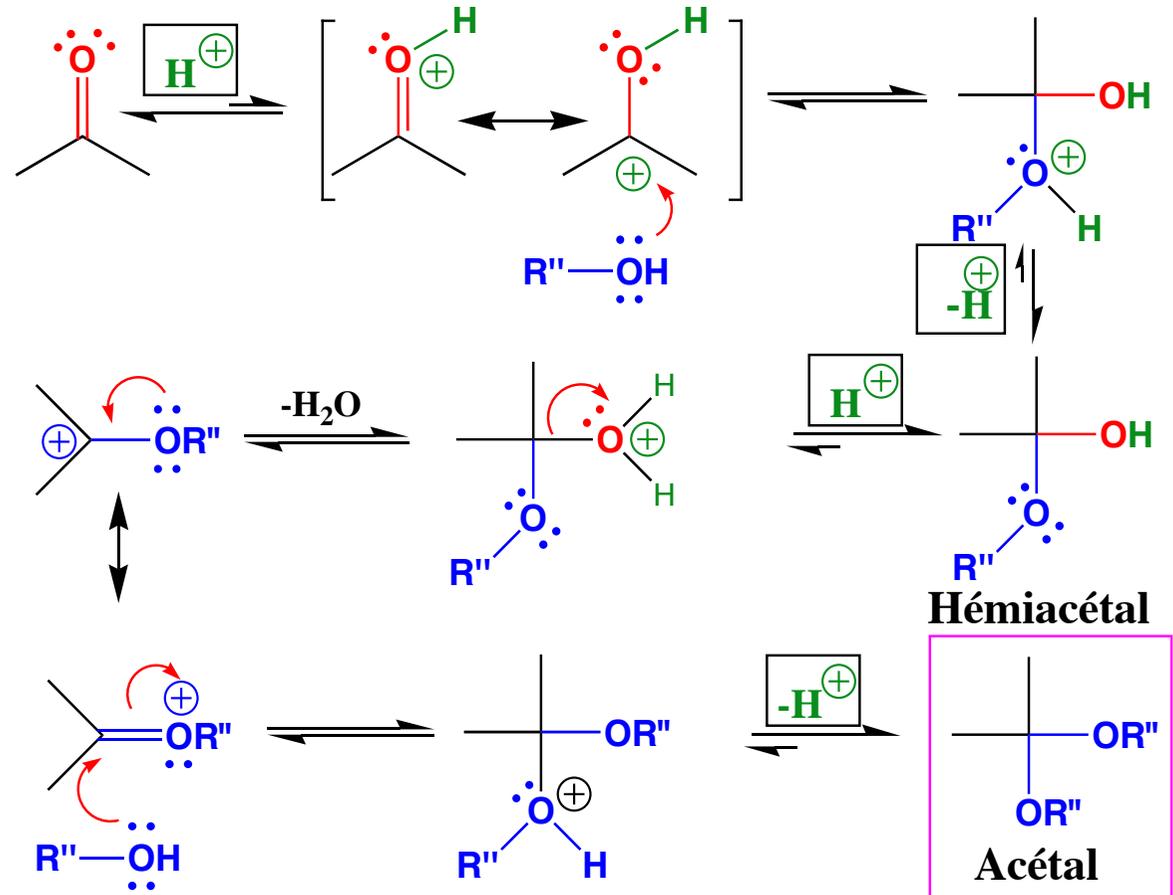
Remarque: Réaction Reversible, l'Equilibre est déplacé vers la Gauche (sauf Exception), les Hémiacétals ne sont pas Stables.

- Double Addition de R-OH: Formation d'**ACÉTAL**

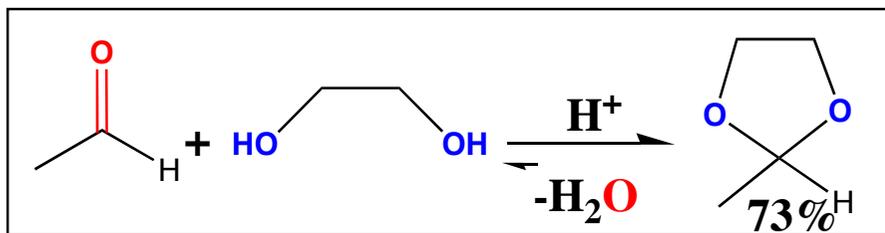


Remarque: Réaction Reversible, peut être déplacée vers l'Acétal (Stable) en milieu Acide en présence d'excès d'Alcool.

*Mécanisme de Formation:

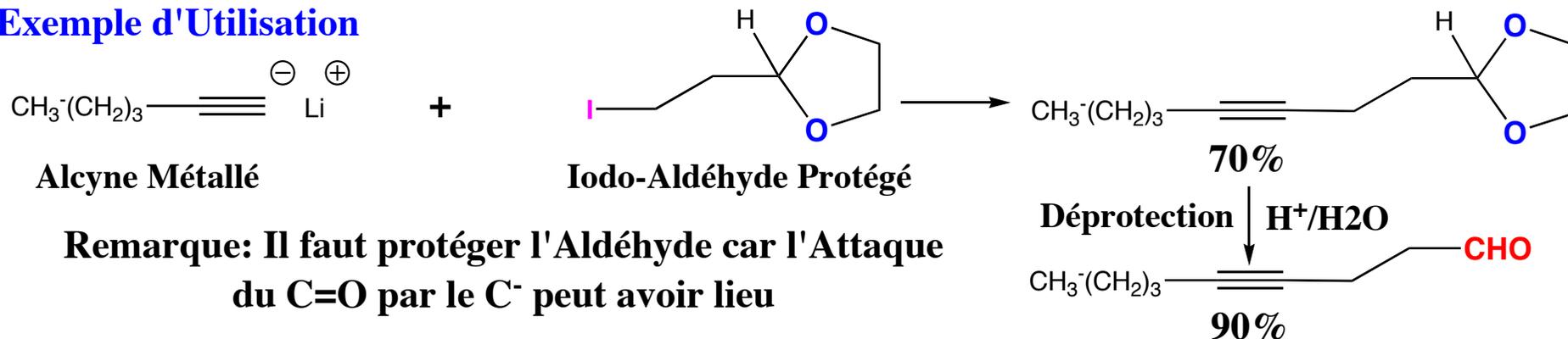


Acétals Cycliques = Groupes Protecteurs

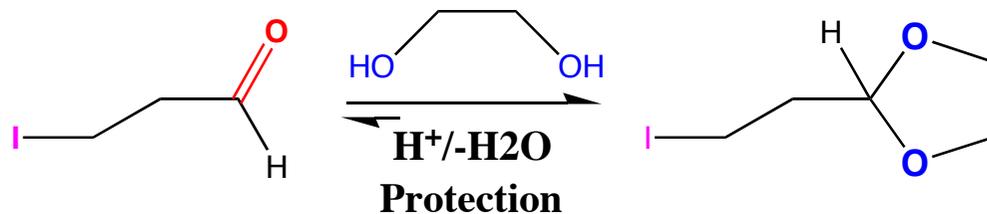


- *Les Acétals Cycliques Sont Stables.
- **Leur Formation est Réversible.
- ***Leur Hydrolyse Produit le C=O de Départ.

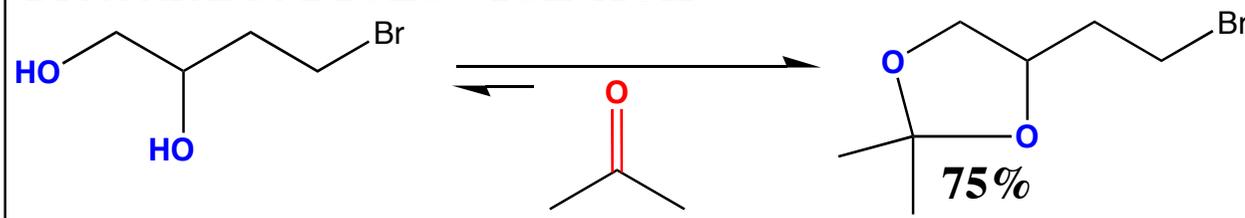
Exemple d'Utilisation



Remarque: Il faut protéger l'Aldéhyde car l'Attaque du C=O par le C⁻ peut avoir lieu

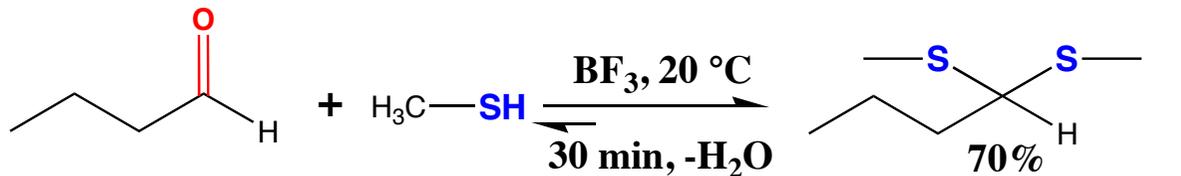


Protection de DIOLS VICINAUX

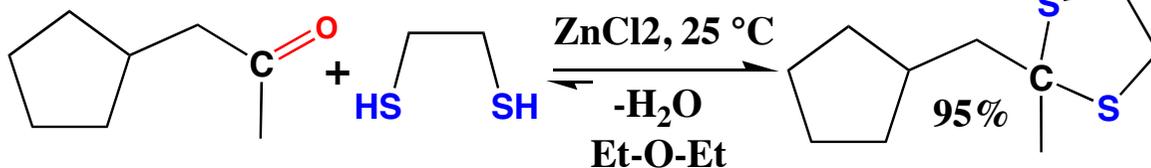


Les Thioacétals

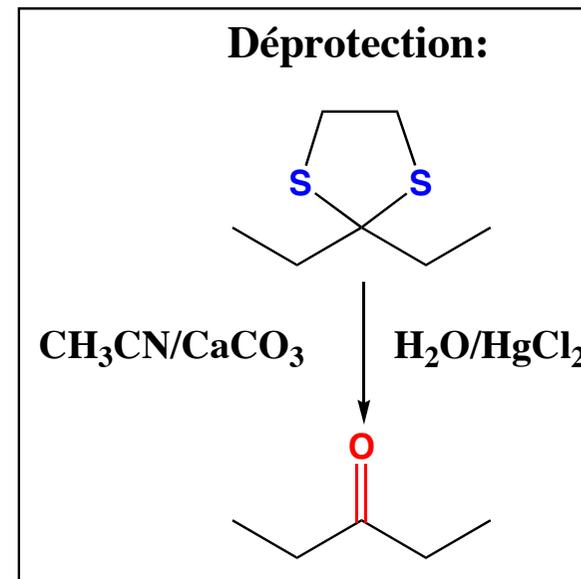
R-OH est remplacé par R-SH.
Le Catalyseur H^+ est remplacé par BF_3 , $ZnCl_2$...
Les Thioacétals sont plus Stables que les Acétals.



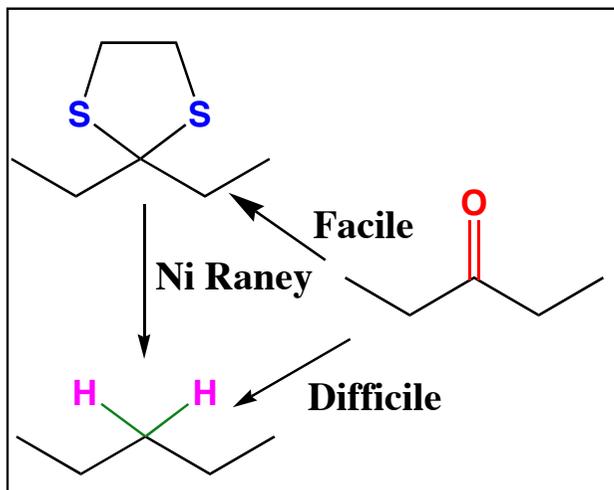
Thioacétal



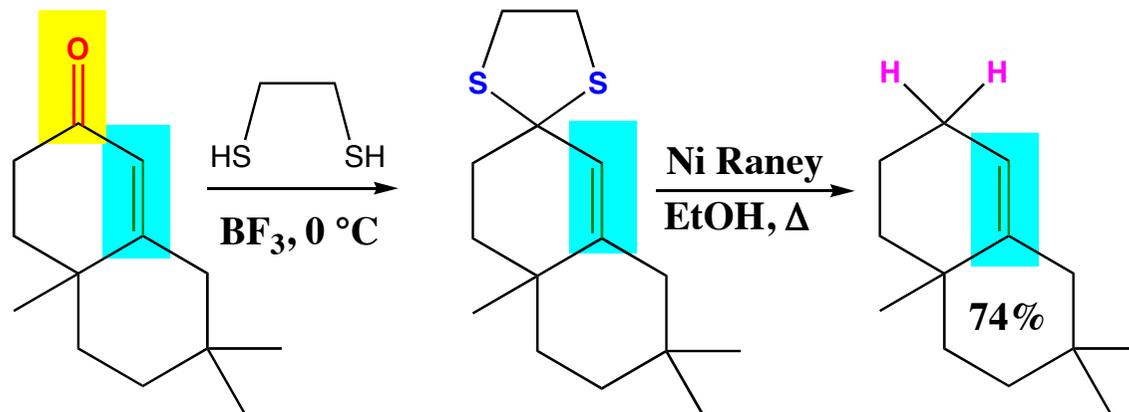
Thioacétal Cyclique



Remarque: Réduction des Thioacétals



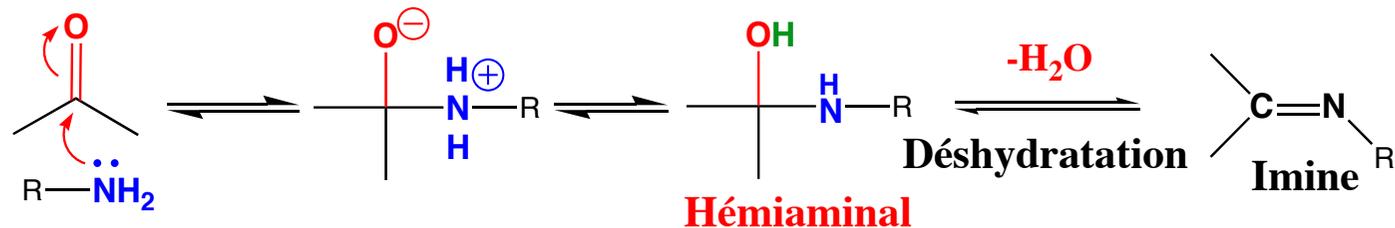
Application: Réduire $C=O$ SANS Réduire $C=C$



-Addition d'AMINE

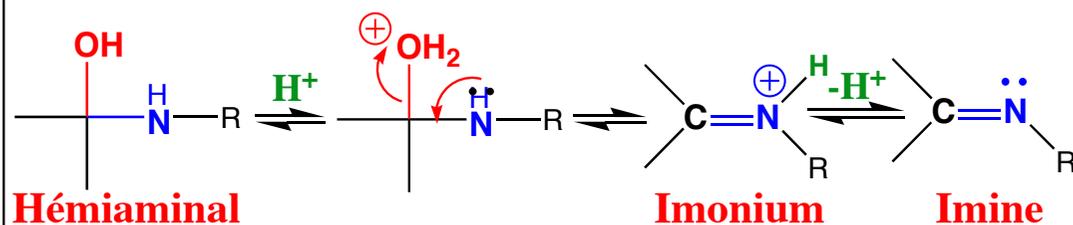
Analogie formelle entre H-OH, R-OH et R₃-N.
Cependant R₃-N est plus Nucléophile que R-OH.

*Amines Primaires:



Remarque: **Hémiaminal** = Equivalent Azoté d'**Hémiacétal**

Mécanisme de Formation d'Imine:

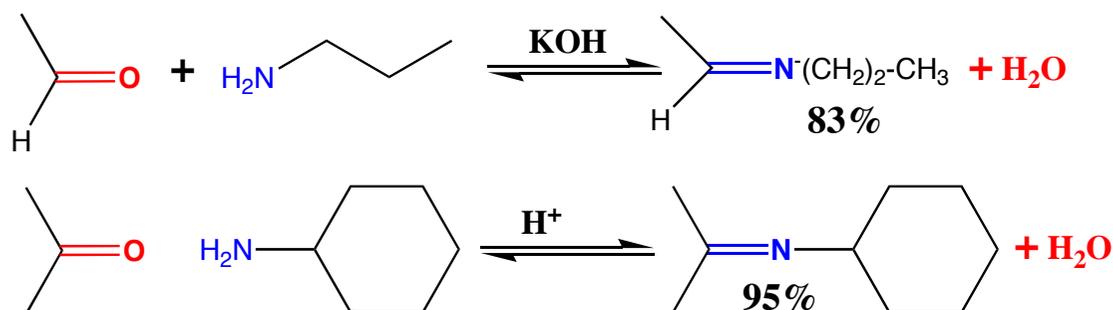


Remarque 1: R-N est plus Basique que R-OH. Néanmoins, le PEU de R-OH₂⁺ (bon partant) qui se forme réagit pour donner l'Imine.

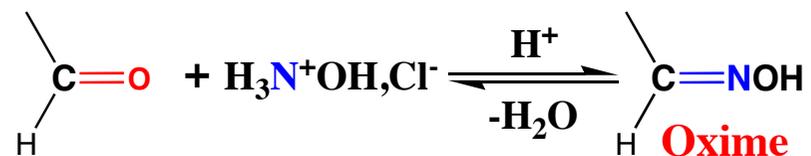
Remarque 2: Imine (C=N) = Analogue Azoté de Carbonyl (C=O).

Remarque 3: 2 Isomères possibles pour les Imines ou Base de Schiff.

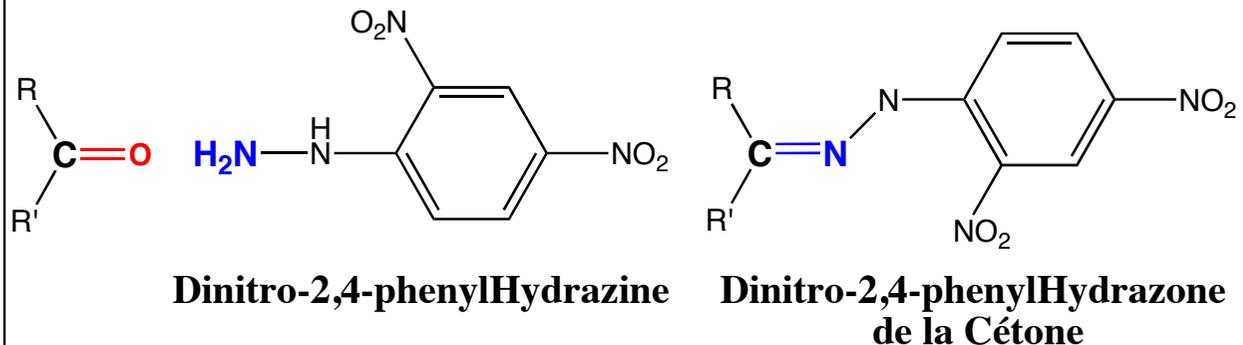
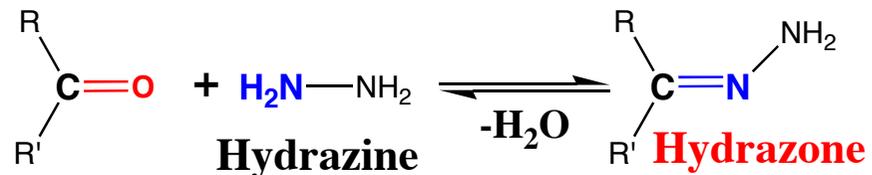
Exemples:



***Synthèse d'OXIME:**



****Synthèse d'HYDRAZONE:**

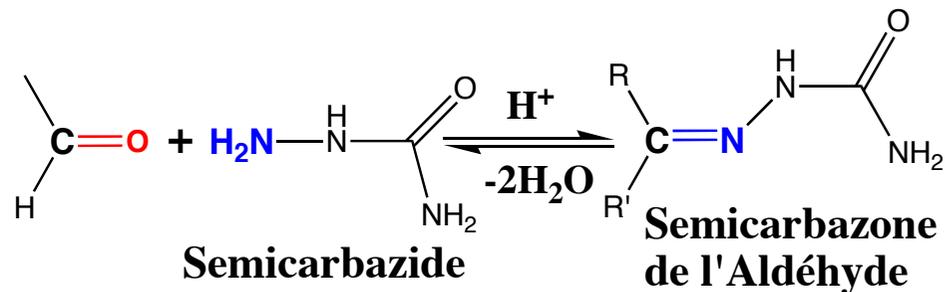


Remarque: Formation de Dérivés Cristallisés pour Identification de Cétones Liquides

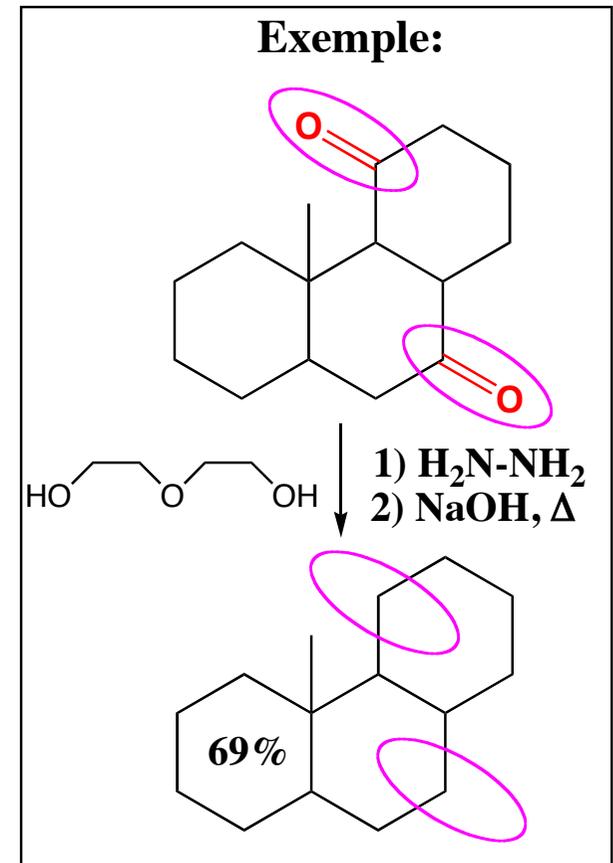
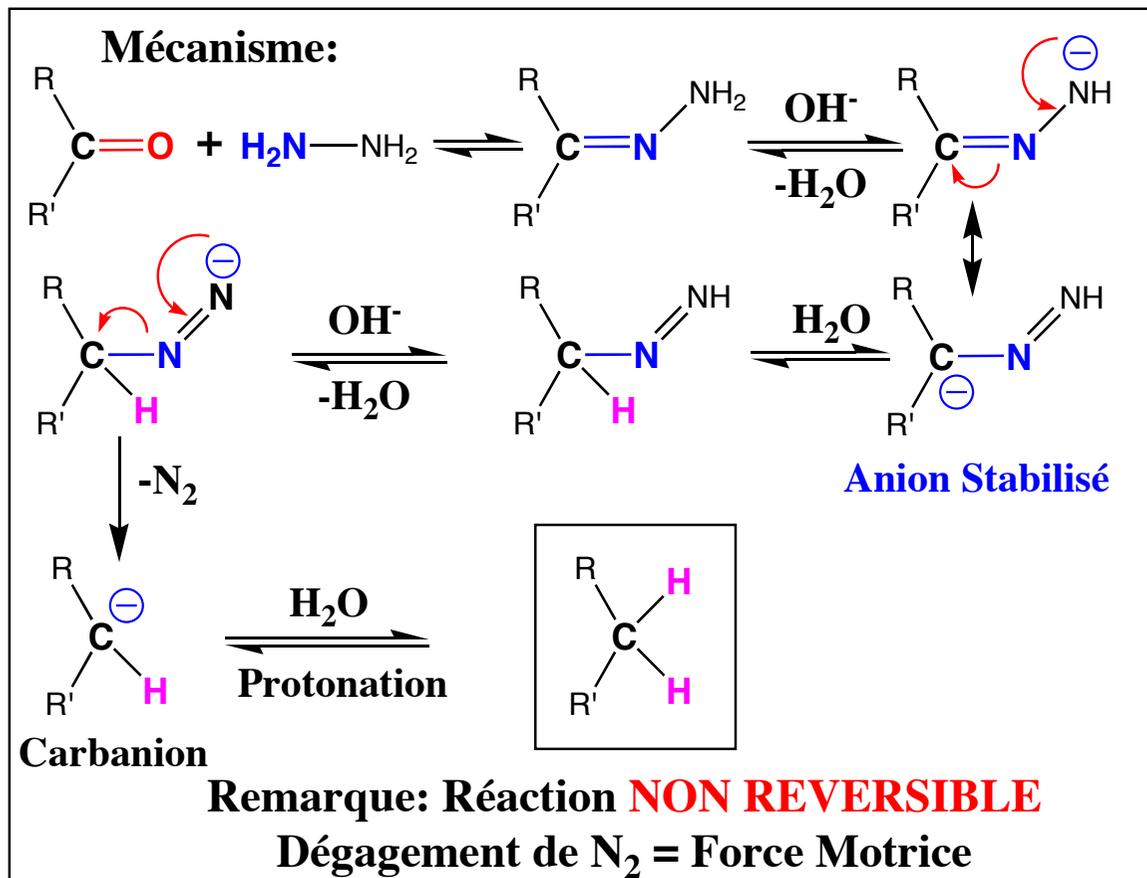
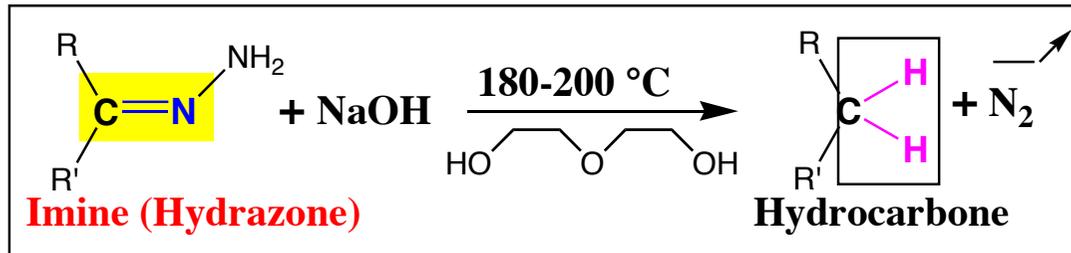
*****Synthèse d'AZINE:**



******Synthèse de SEMICARBAZONE:**

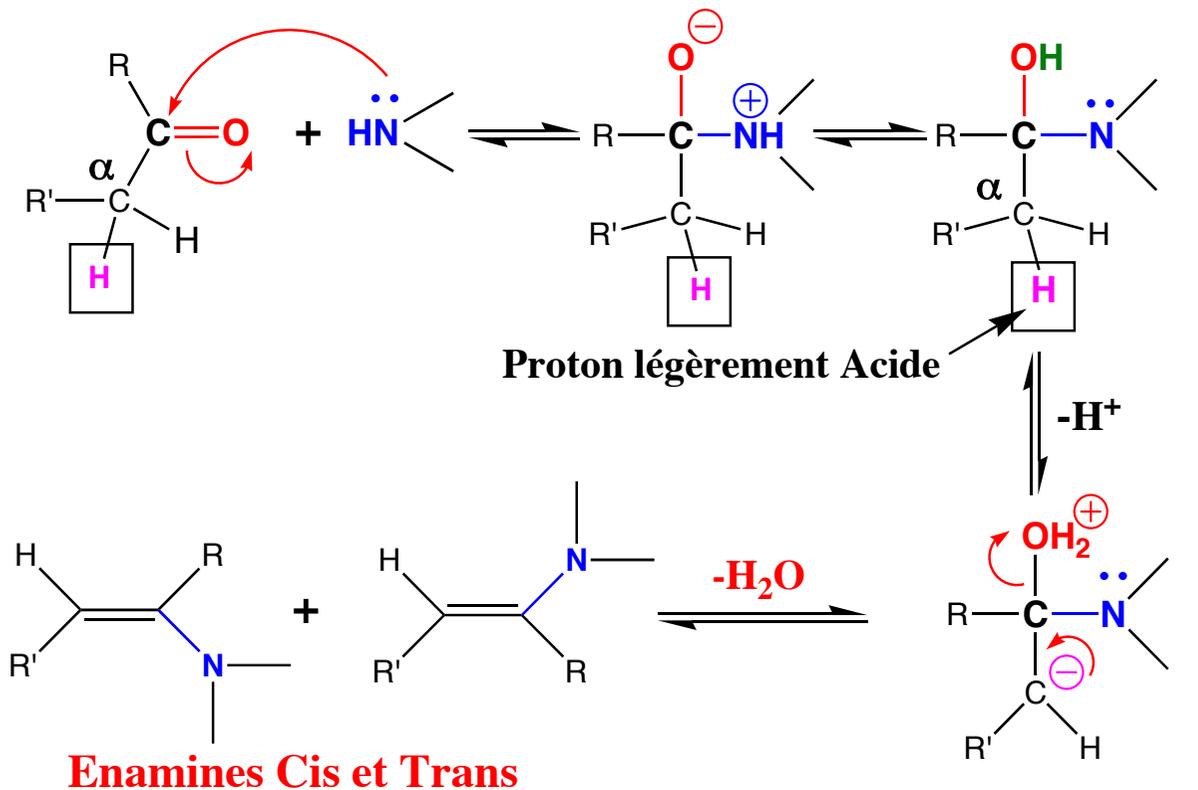


Application: Désoxygénation de C=O Via Imine La Réduction de Wolff-Kishner



**Amine Secondaire: Formation d'ENAMINE

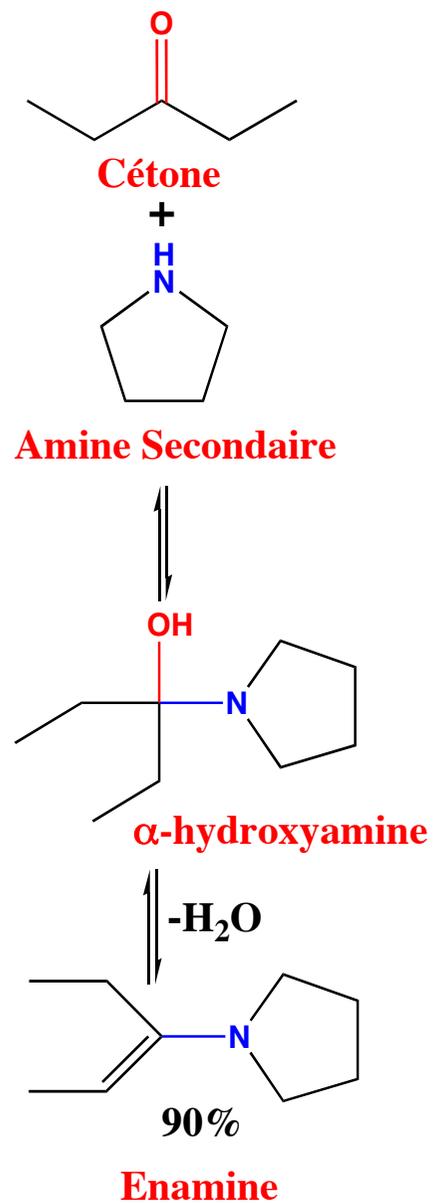
Mécanisme de Formation



Remarque 1: 2 Isomères Possibles

Remarque 2: Réaction REVERSIBLE, Hydrolyse d'ENAMINE se fait Facilement en milieu Acide

*Exemple

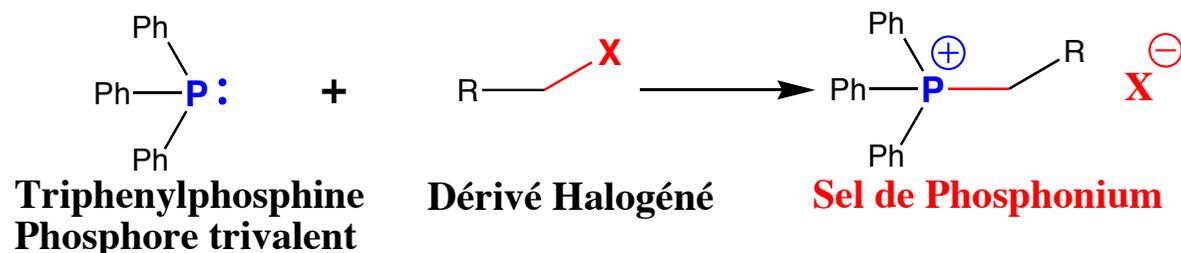


-Addition de Nucléophiles Carbonés:

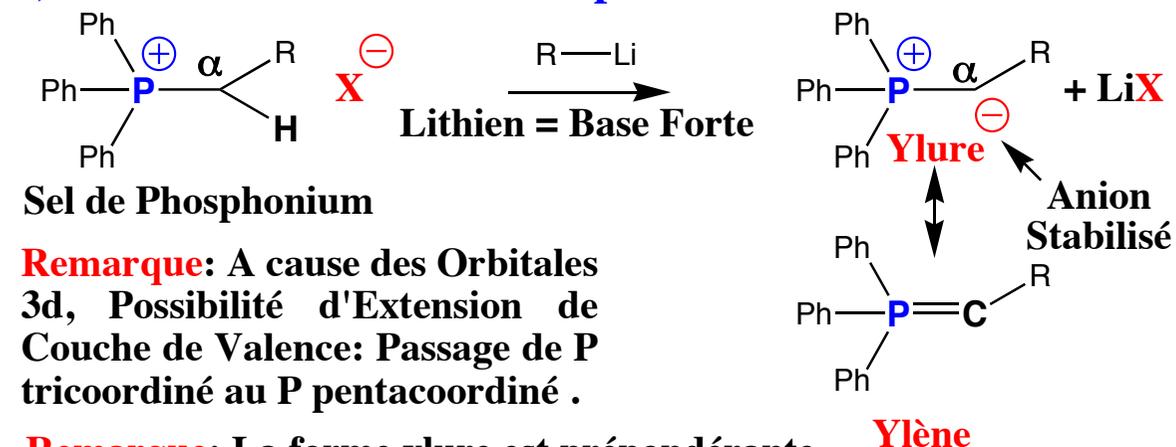
Remarque: Réaction très Importante car elle permet de Former des Liaisons C-C.

* Addition d'YLURES de Phosphore: La Réaction de Wittig Wittig (1897-1987), Heidelberg, Nobel en 1979.

1) Formation de Sel de Phosphonium:



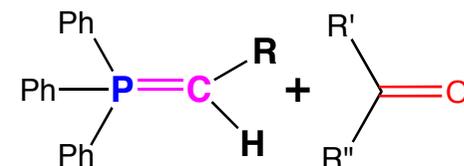
2) Formation d'Ylure de Phosphore:



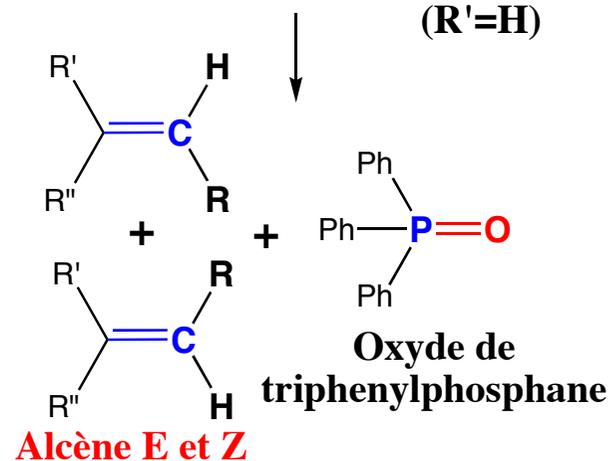
Remarque: A cause des Orbitales 3d, Possibilité d'Extension de Couche de Valence: Passage de P tricoordiné au P pentacoordiné .

Remarque: La forme ylure est prépondérante par rapport à la forme ylène

3) Réaction de Wittig:

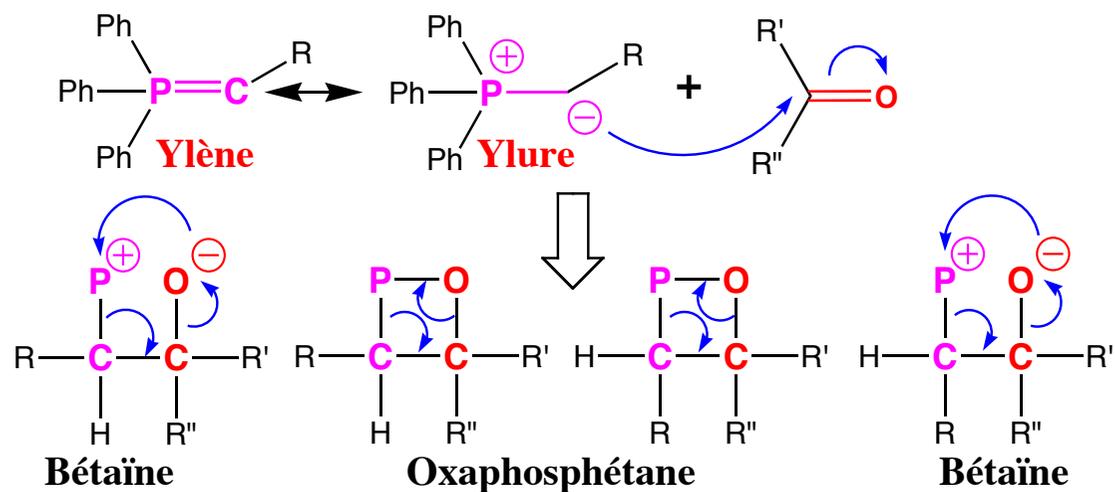


Ylure de Phosphore Cétone
Aldéhyde
(R'=H)



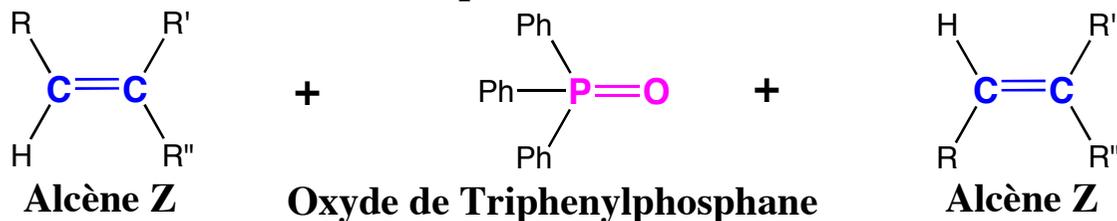
Remarque: La **STEREOSELECTIVE** dépend du type d'ylure (stabilisé, semi stabilisé ou non stabilisé) utilisé, de la nature du cation de la base utilisée (Na⁺, Li⁺) et des conditions opératoire (température, sel auxiliaire)

Mécanisme de la Réaction de Wittig:



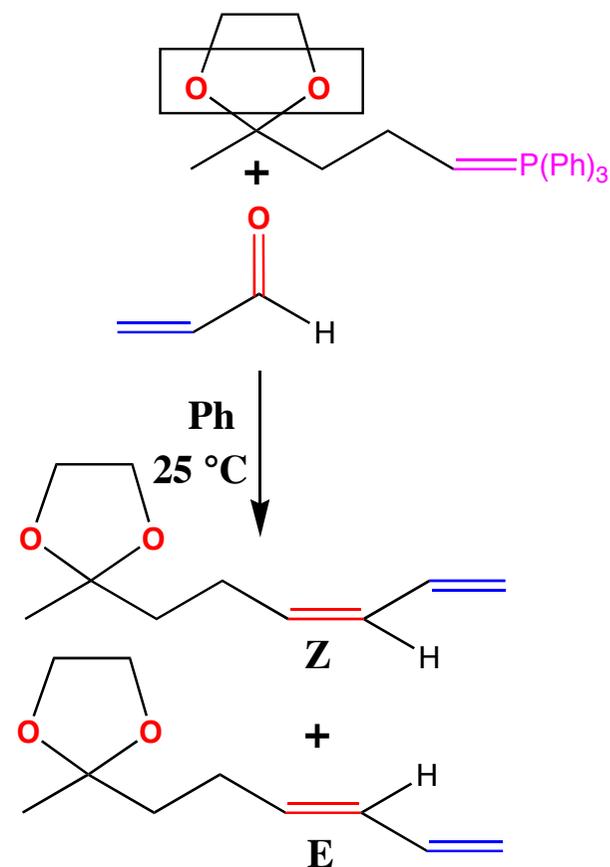
Remarque: Bétaïne et oxaphosphétane sont des intermédiaires. L'oxaphosphétane est plus stable

Remarque: A cause des Orbitales 3d, Possibilité d'Extension de Couche de Valence: Passage de P tricoordiné au P pentacoordiné.



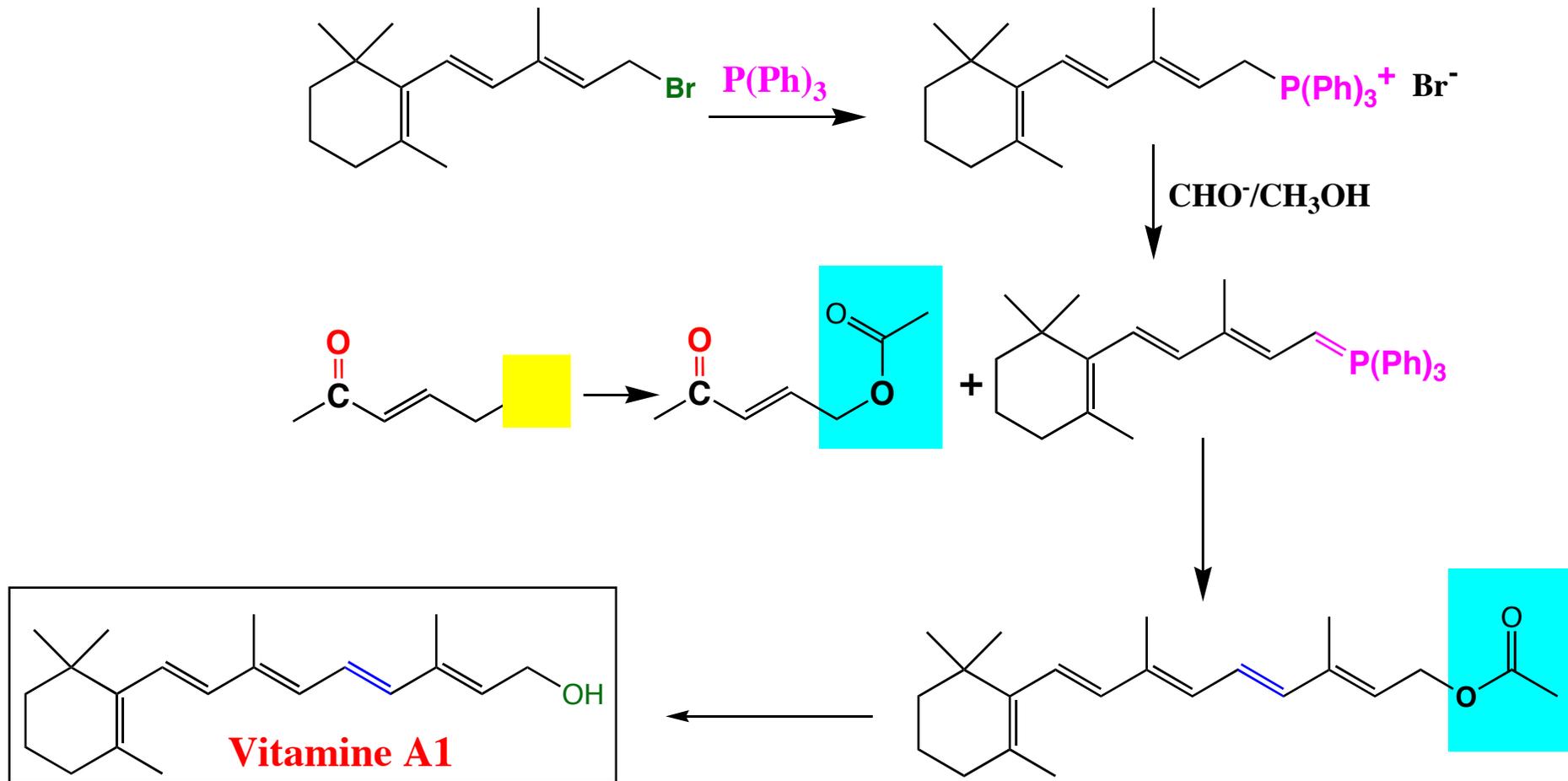
Remarque: La Stéréosélectivité dépend du type d'ylure (stabilisé, semi stabilisé ou non stabilisé) utilisé, de la nature du cation de la base utilisée (Na^+ , Li^+) et des conditions opératoire (température, sel auxiliaire)

Exemple:



Remarque: Il faut protéger le $\text{C}=\text{O}$ au niveau de l'Ylure. La Réaction ne Touche pas au $\text{C}-\text{O}-\text{C}$ et au $\text{C}=\text{C}$.

Application: Synthèse de la Vitamine A1 par BASF

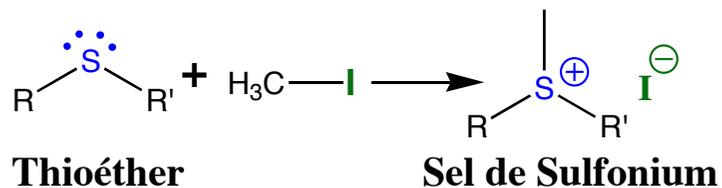


Remarque 1: La protection de l'Alcool est Indispensable pour Eviter la formation d'Hémiacétal Cyclique.

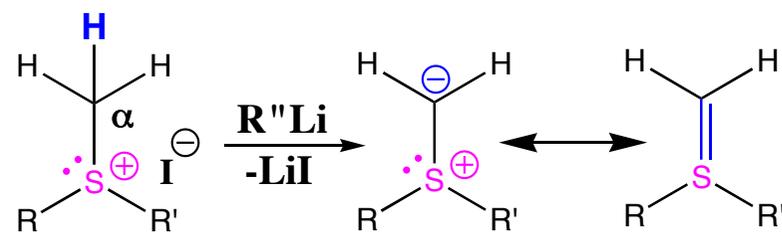
Remarque 2: Dans la Vitamine A1 toutes les $C=C$ sont Tans.

*Addition d'Ylure de Soufre:

Formation de Sel de Sulfonium:



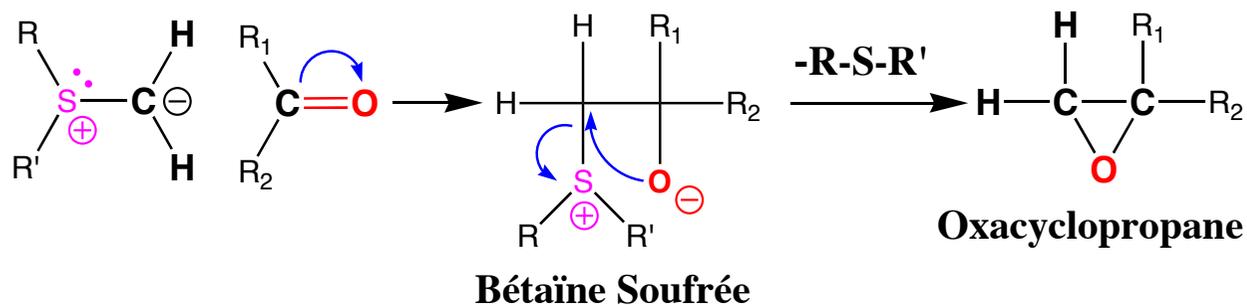
Formation d'Ylure de Soufre:



Sel de Sulfonium Anion Stabilisé Ylure de Soufre

Remarque: Pour arracher le Proton en α du soufre il faut une base forte (Alkyl Lithien)

Réaction avec la Fonction Carbonyle:

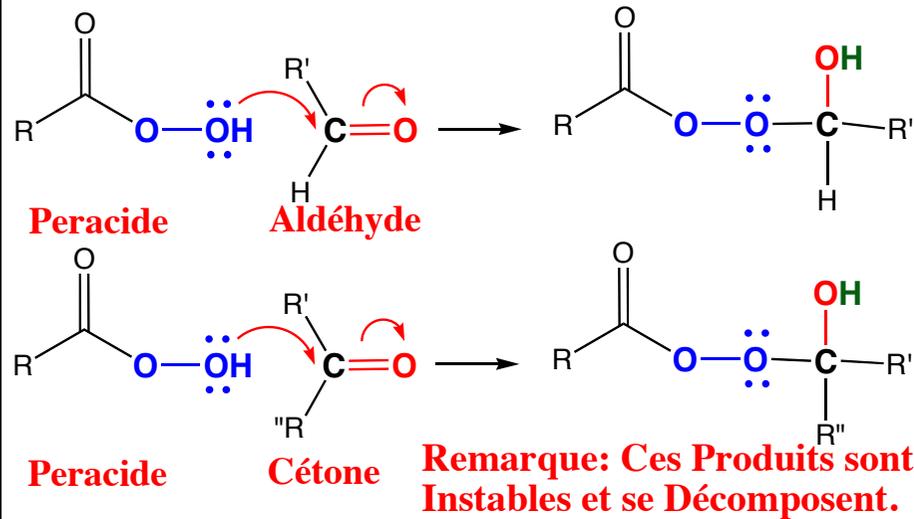


Bilan: Insertion de CH_2 dans la Liaison $\text{C}=\text{O}$

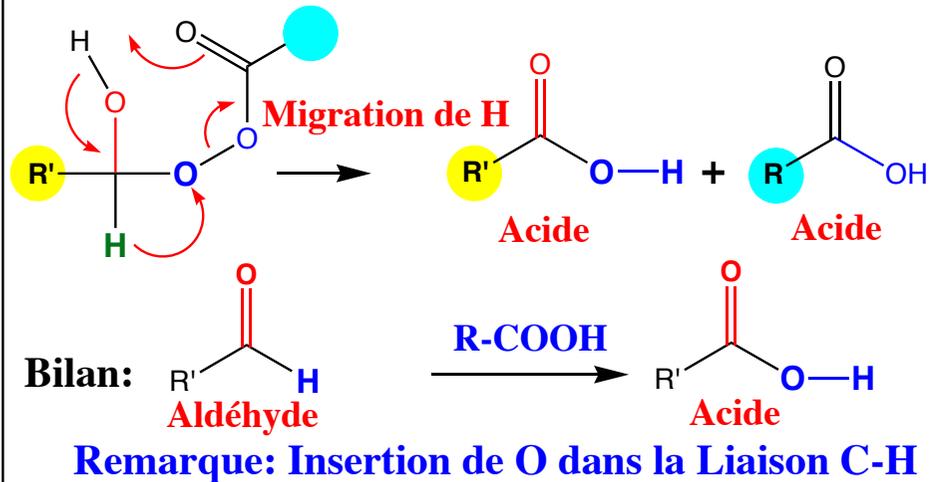
Remarque: Contrairement au Ylures du P, au niveau de la Bétaine Soufrée il n'y pas d'Extension de Valence mais il y a l'Élimination du thioéther.

5) OXYDATION et REDUCTION

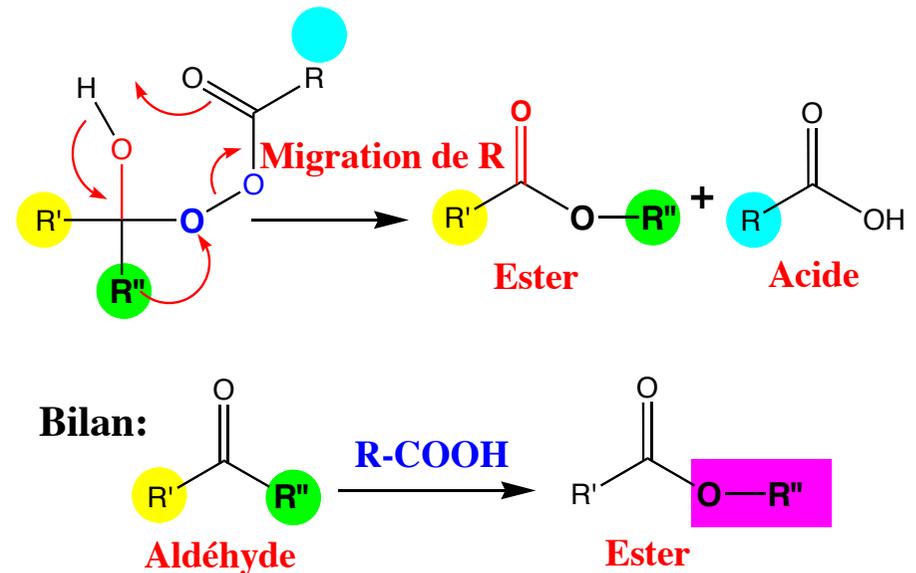
***Oxydation par les Acides Peroxycarboxyliques:**



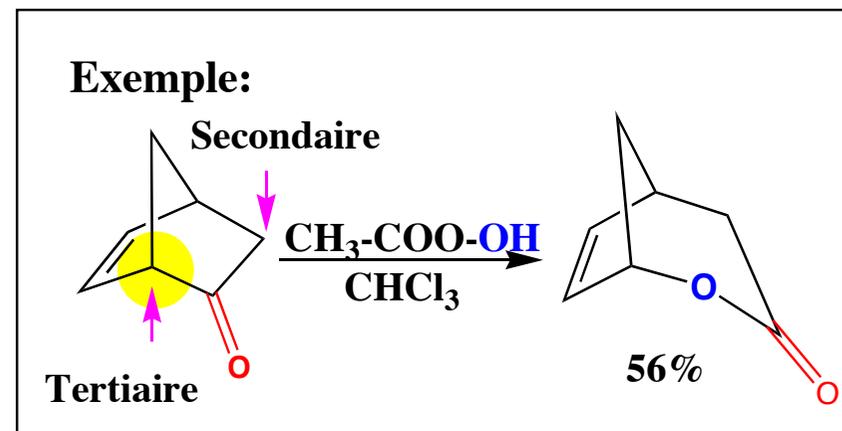
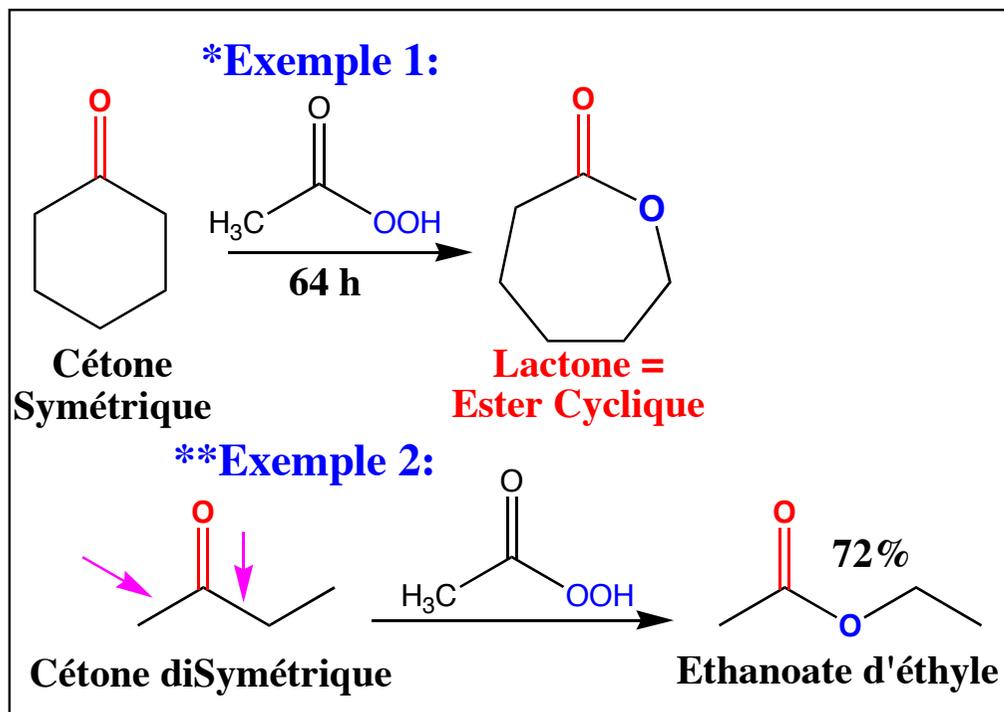
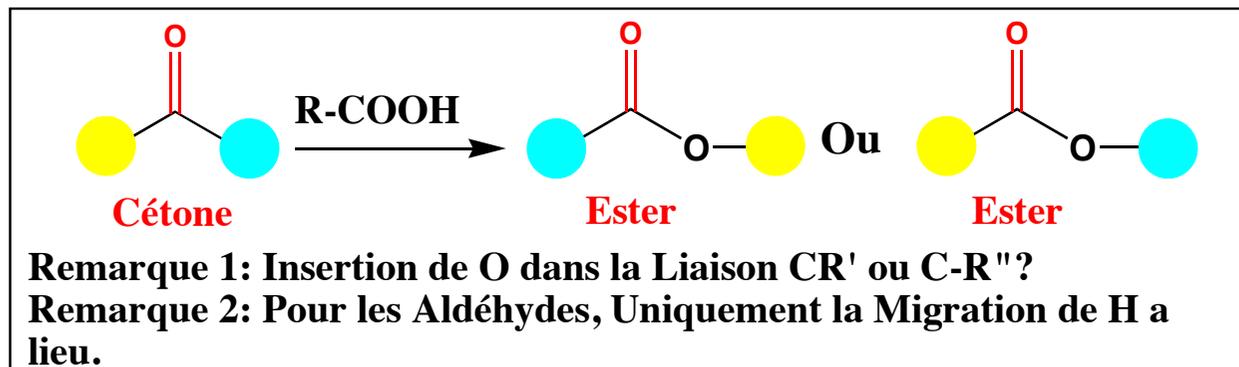
Le Cas des Aldéhydes: Migration de H



**Le Cas des Cétones: Migration de R
(Oxydation de Bayer-Villiger)**



Remarque: Insertion de O dans la Liaison C-R''



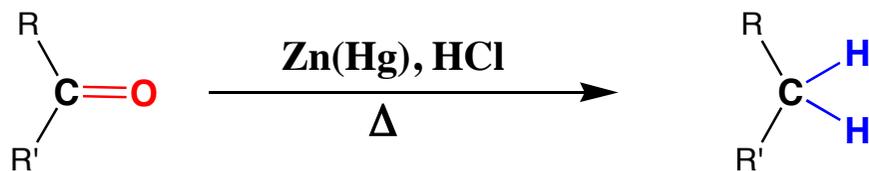
Remarque: L'Oxydation de Bayer-Villiger ne Touche pas au C=C.

Aptitude Migratoire: Tout se passe comme si on passait par un C⁺.

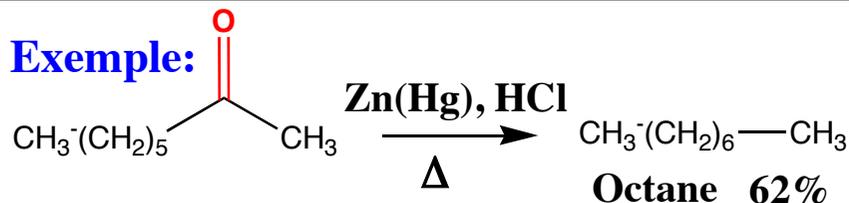
H > Tertiaire > Cyclohexyle > Secondaire - Phényle > Primaire > CH₃ (Nullaire)

REDUCTION

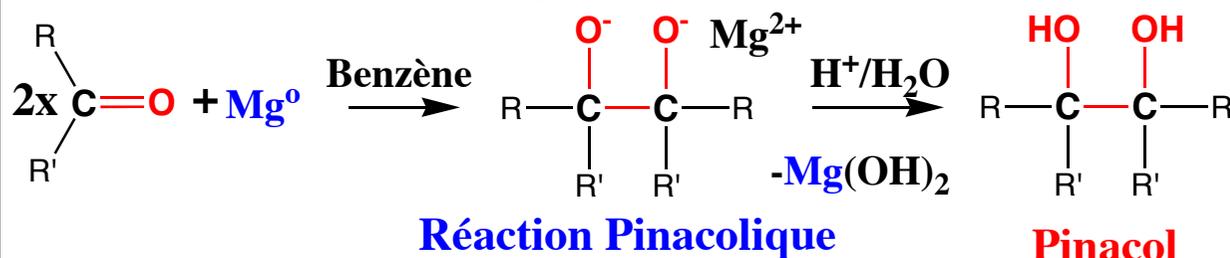
*Réduction de Clemmensen:



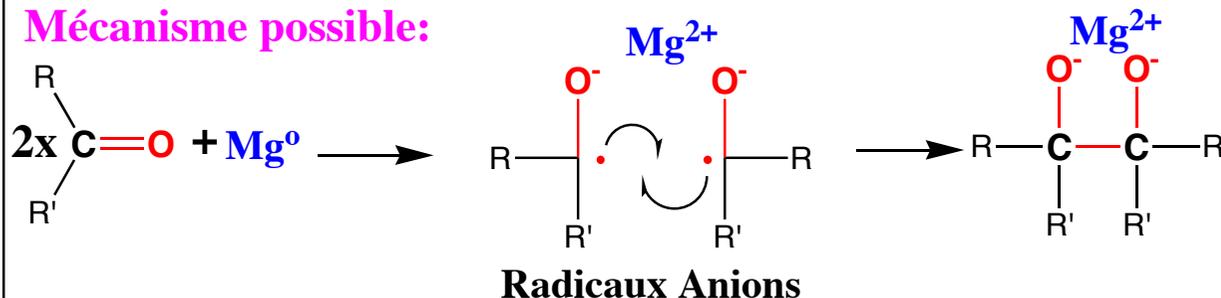
Exemple:



**Réduction Avec Couplage: Transfert MonoElectronique



Mécanisme possible:

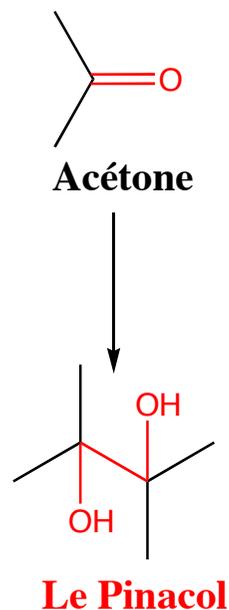


Remarque 1:* Mécanisme non Connue, il y un transfert d'Electron des Métaux sur le C=O.

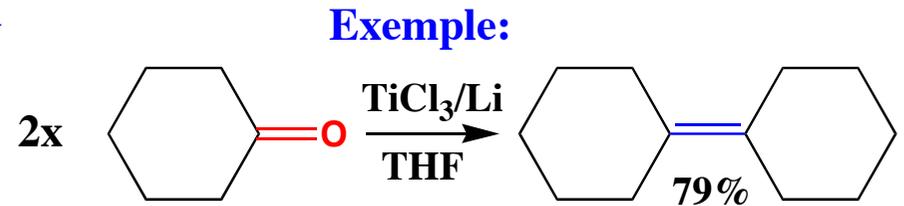
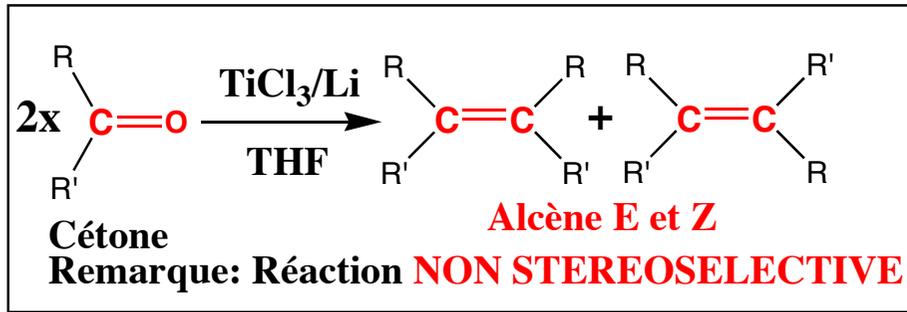
** Conditions très Dures.

Remarque 2: La même Réaction se fait dans des conditions douces en passant par un Thioacétal Cyclique puis Réduction (Ni Raney).

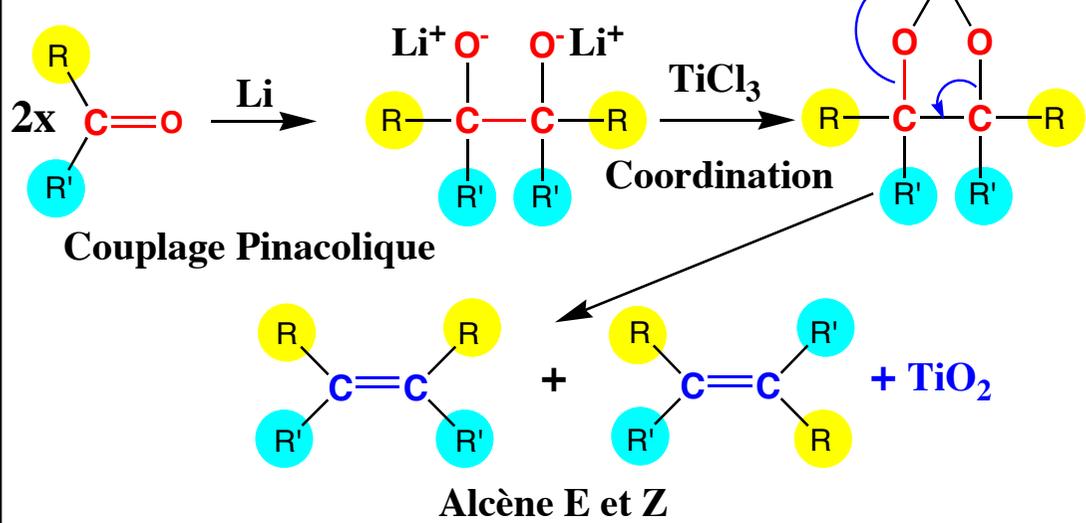
Exemple:



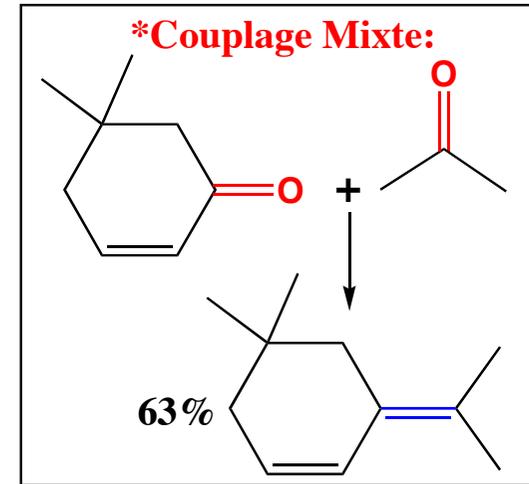
Couplage Sur le Titane: Réaction de Mc Murry



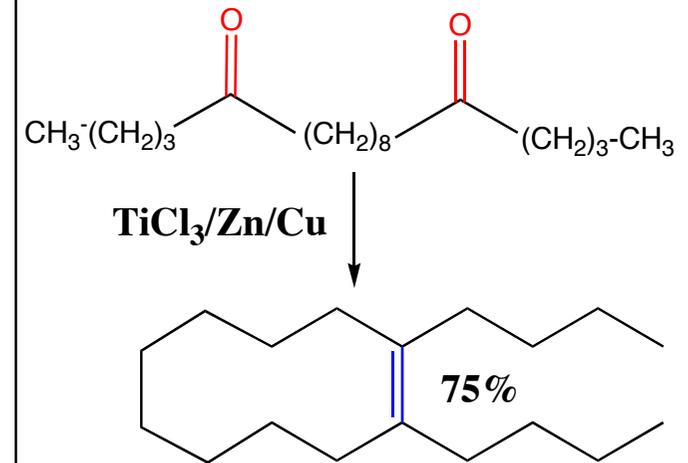
Mécanisme Possible:



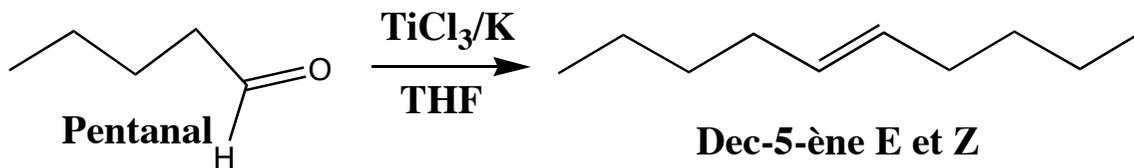
*Couplage Mixte:



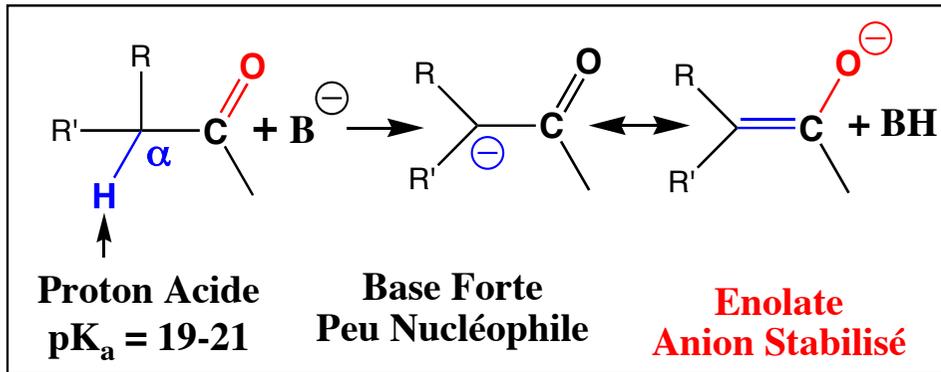
**Couplage Intramoléculaire:



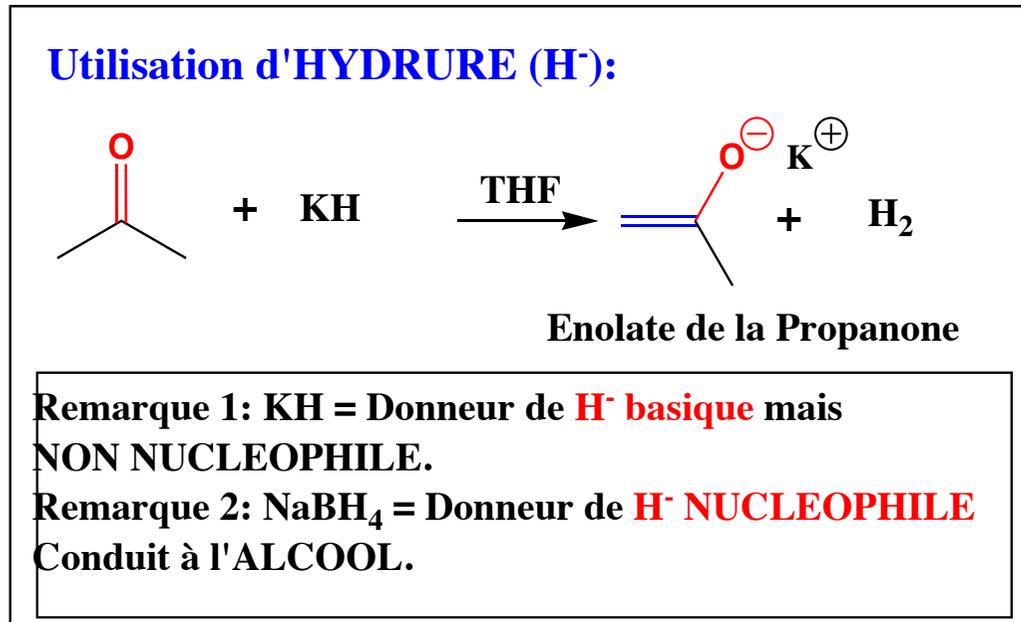
Exemple:



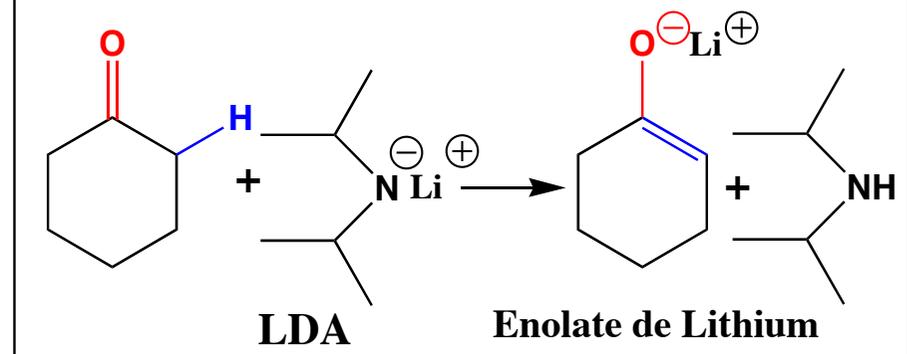
ENOLS et ENONES



*Préparation:

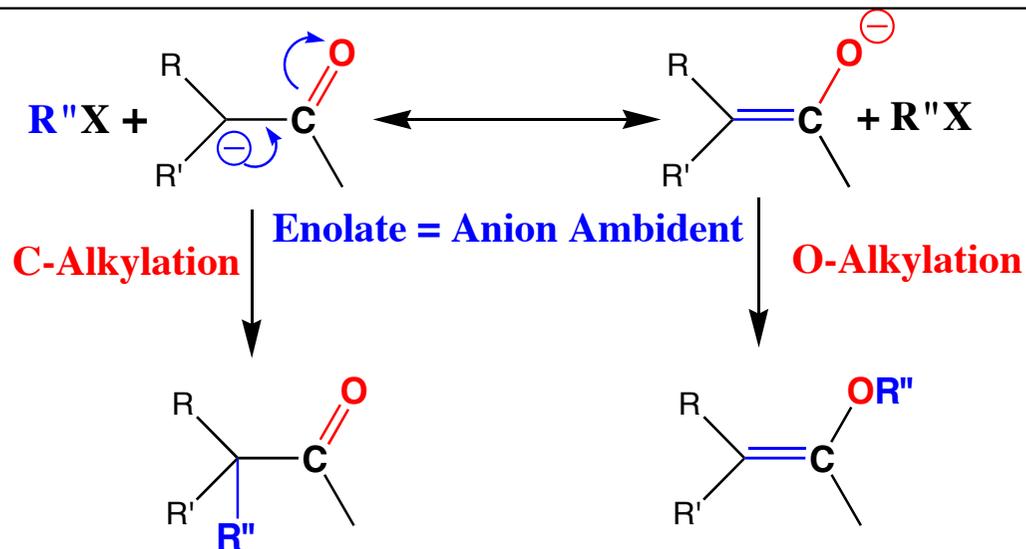


Utilisation d'AMIDURE (N^-):



Remarque: LDA = Lithium DiisopropylAmidure, C'est une base forte ($\text{pK}_a = 35$) et Encombrée donc **PEU NUCLEOPHILE**

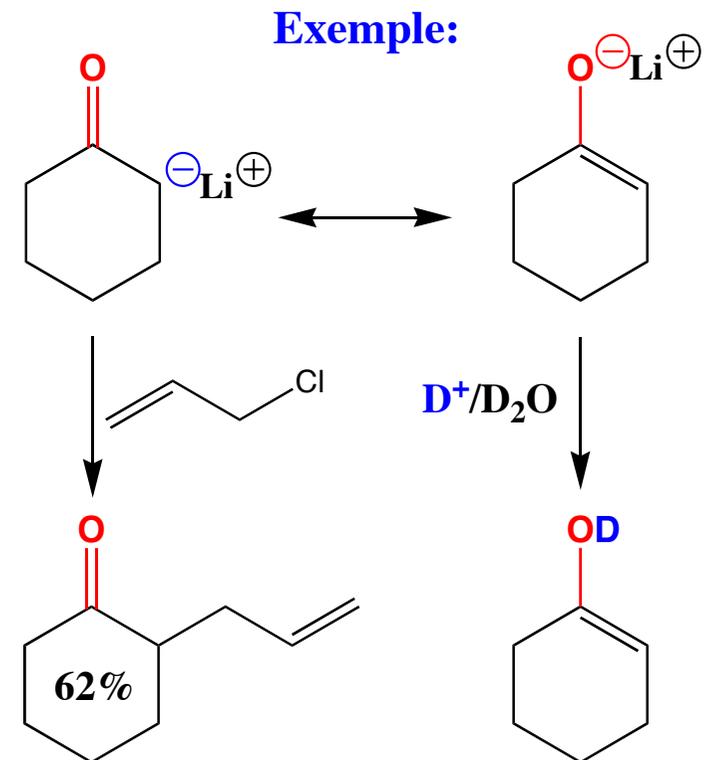
**Réactivité:



Remarque 1: 2 Possibilités d'Alkylation la C- et la O-Alkylation.

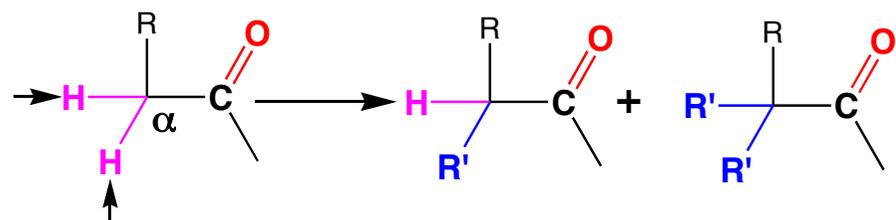
Remarque 2: Souvent l'Attaque Electrophile se fait sur le C⁻.

Remarque 3 : La C-Alkylation Permet d'Introduire un groupe R en α du C=O.



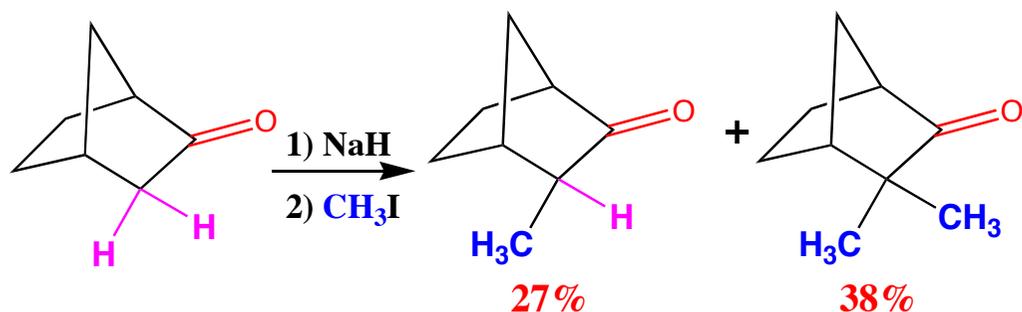
Complications:

*Double Alkylation:

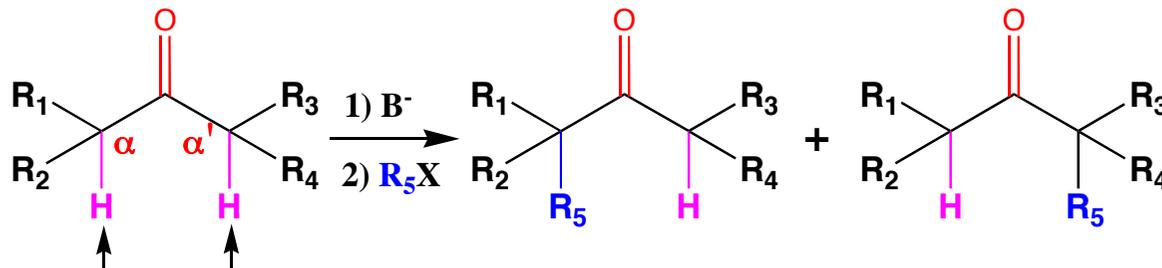


Remarque: Si 2H Acide en α : Double Alkylation

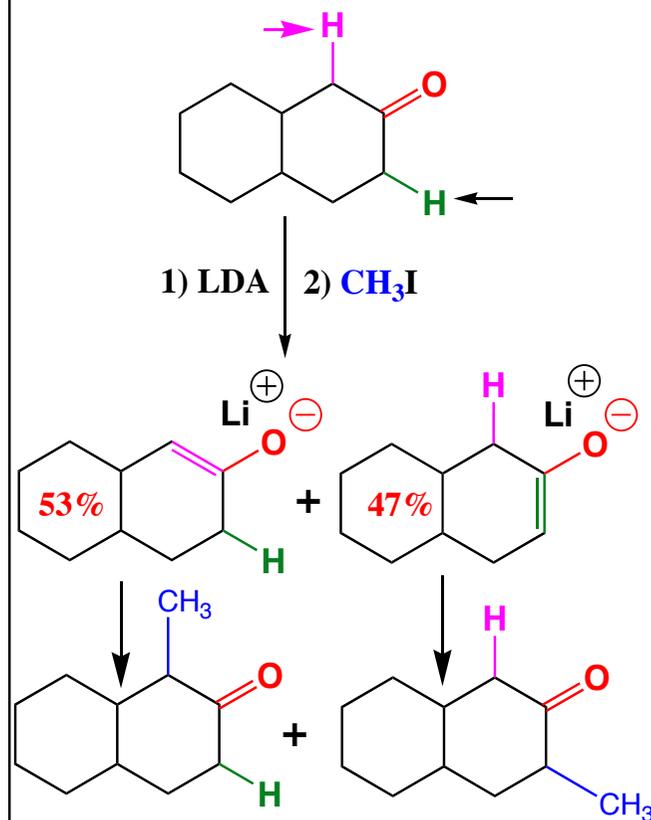
Exemple:



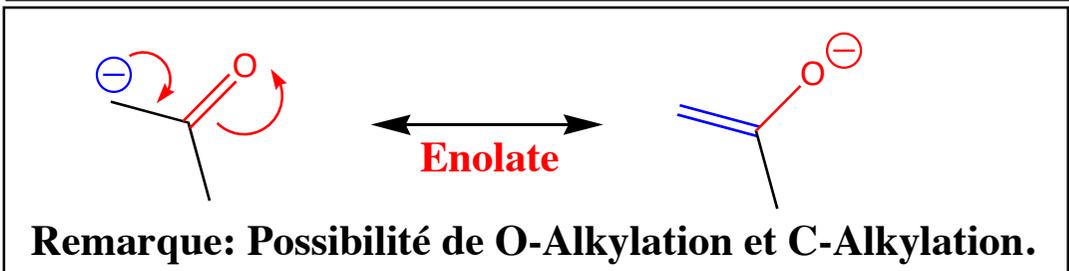
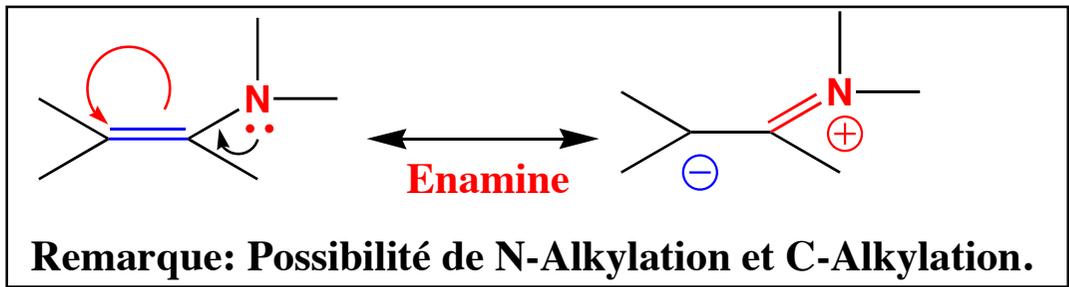
**Régiosélectivité d'Alkylation:



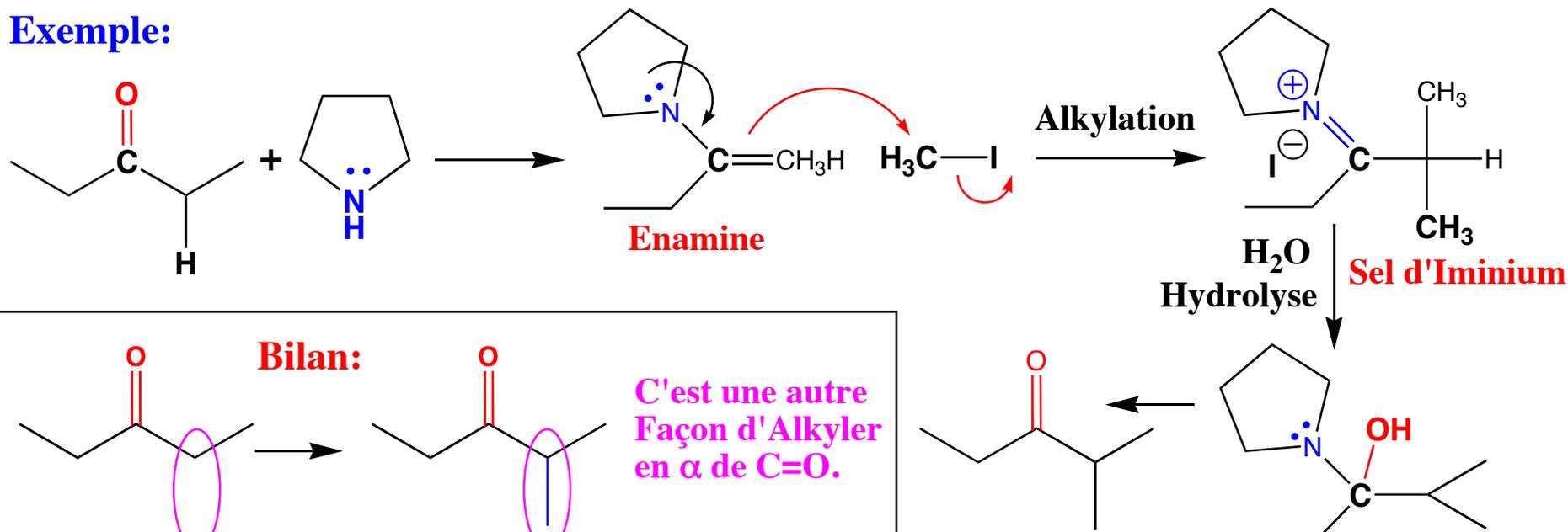
Exemple:



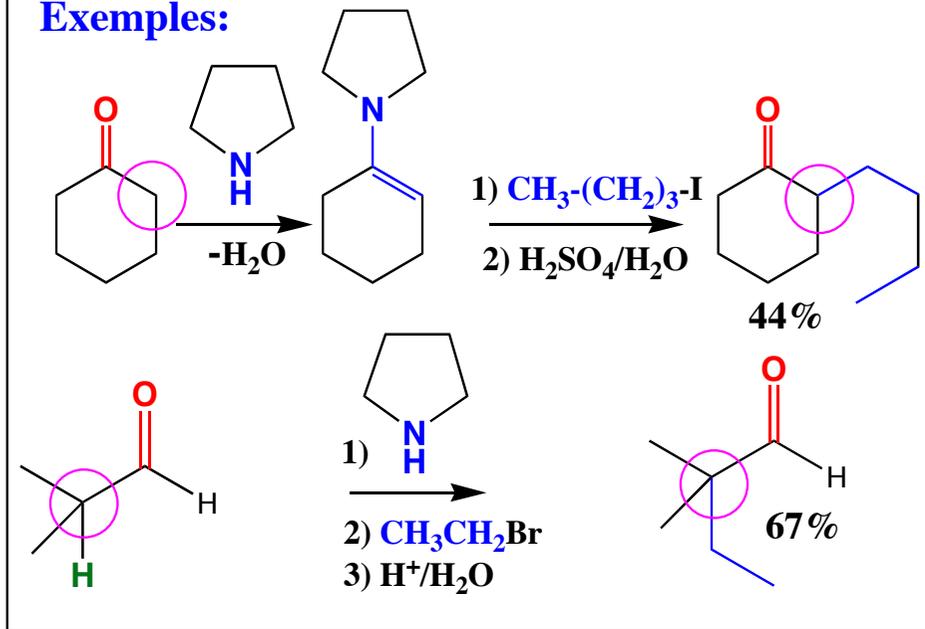
Analogie entre ENOLATES et ENAMINES



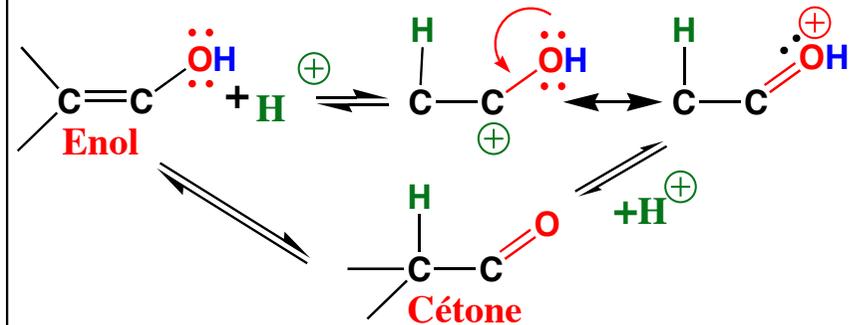
Exemple:



Exemples:

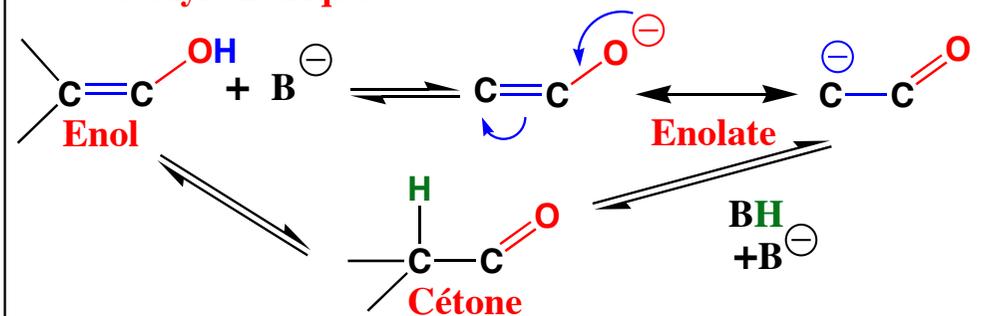


**Catalyse Acide:

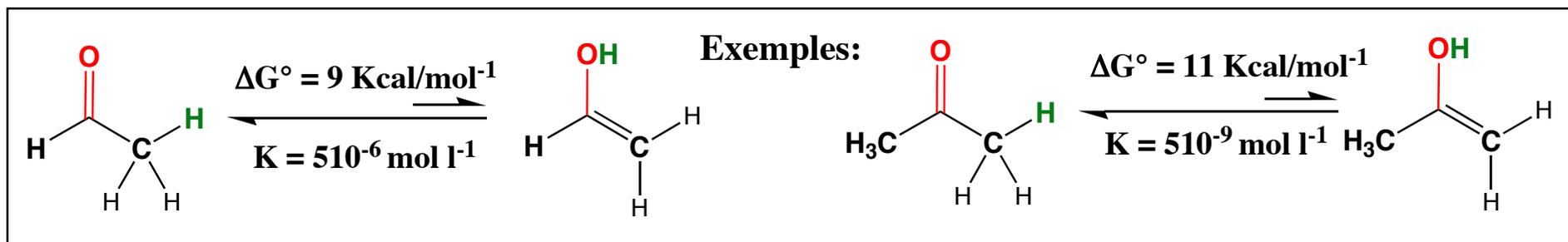
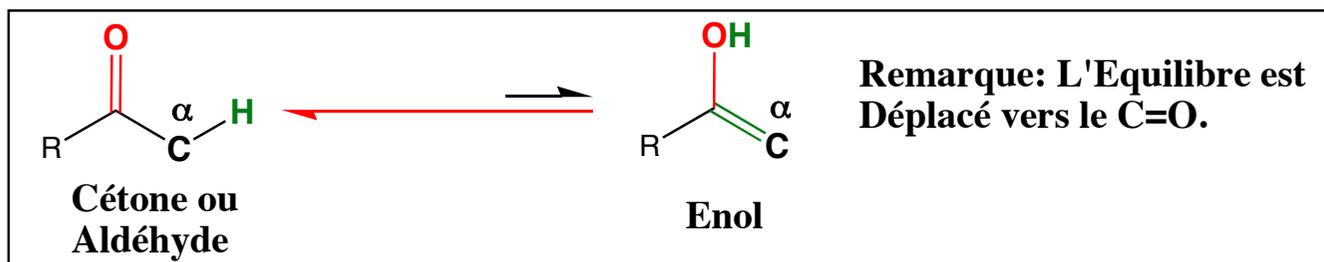


TAUTOMERIE CETO-ENOLIQUE

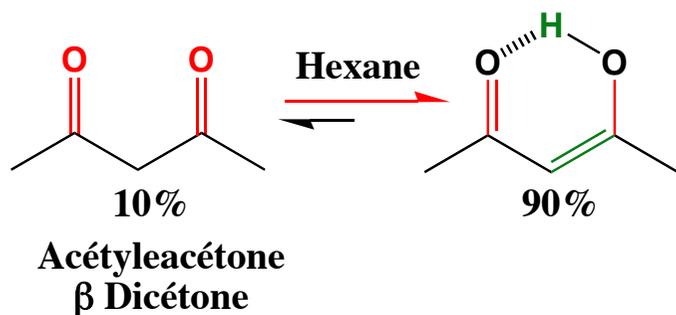
*Catalyse Basique:



Facteurs Modifiant l'EQUILIBRE:

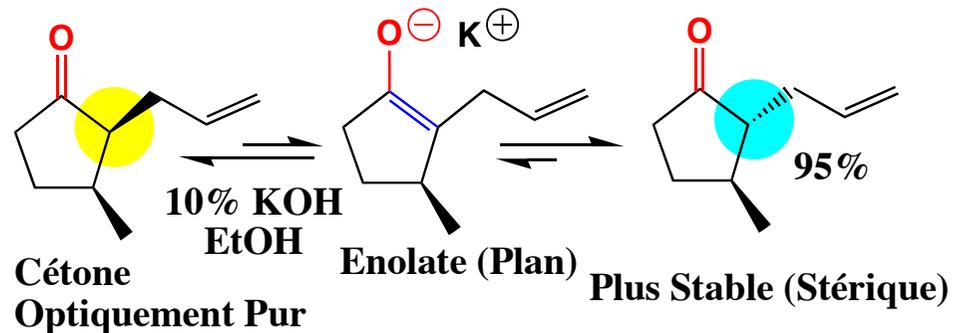


Cas Particuliers: Formation de Liaison H

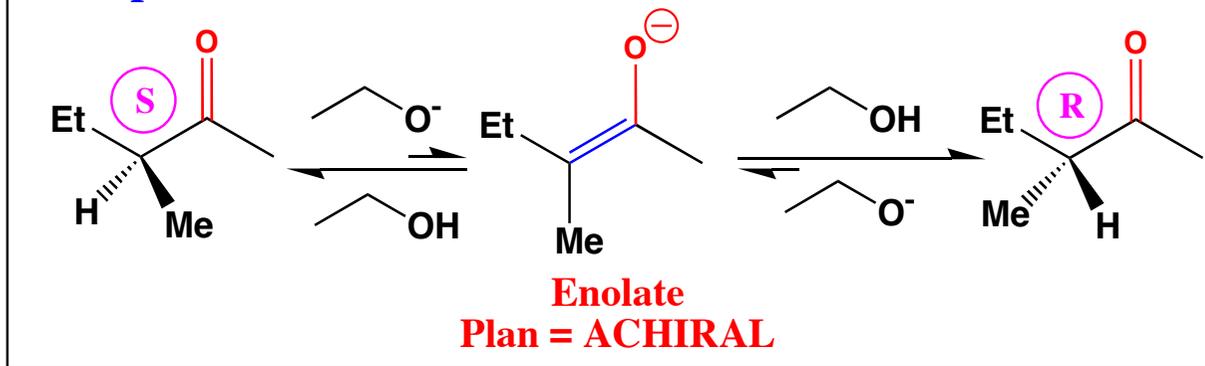


Remarque: Stabilisation de la Forme
Enol par Liaison H Intramoléculaire

Conséquence de la Tautomérie: Perte de la Stéréochimie



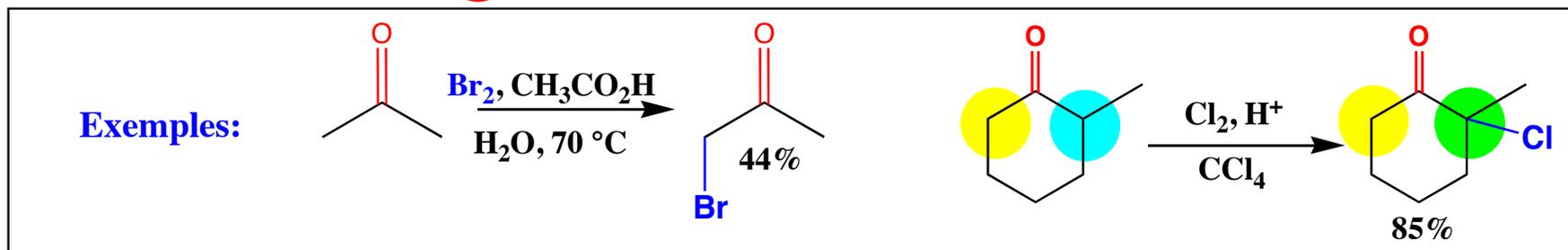
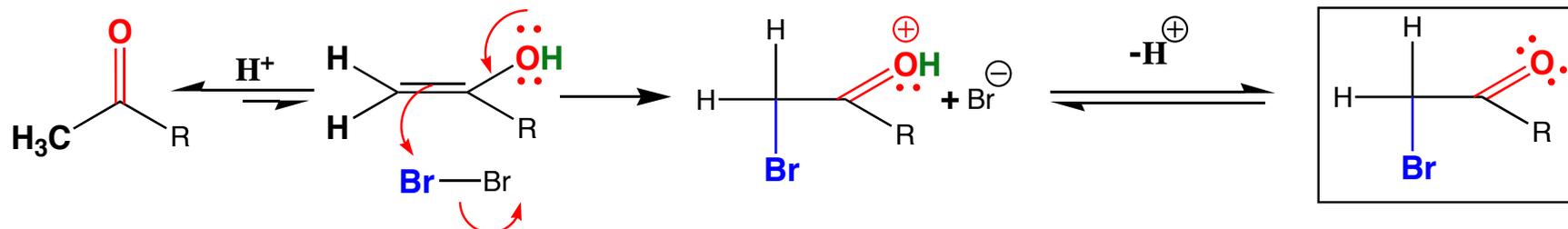
Exemple: Racémisation



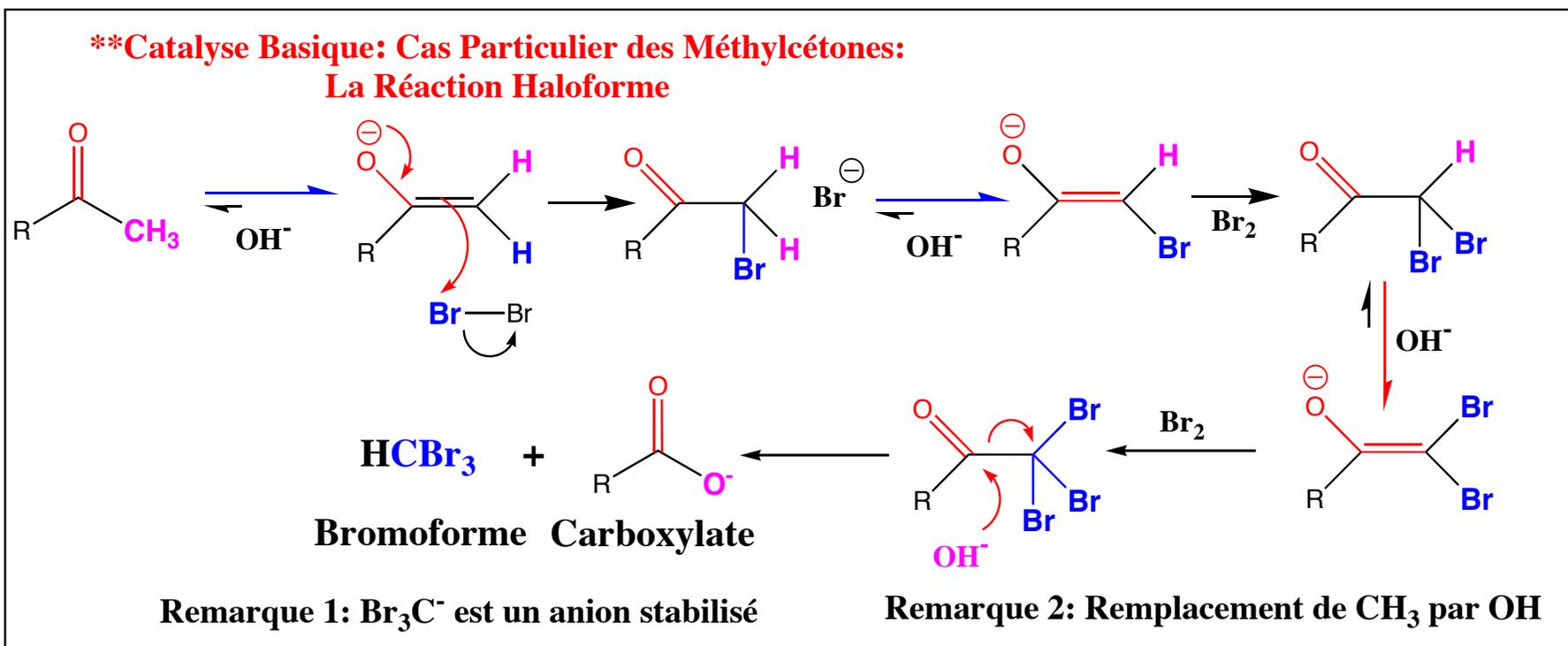
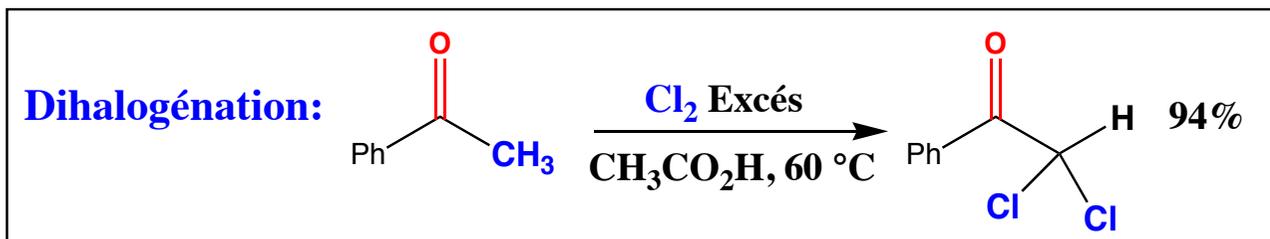
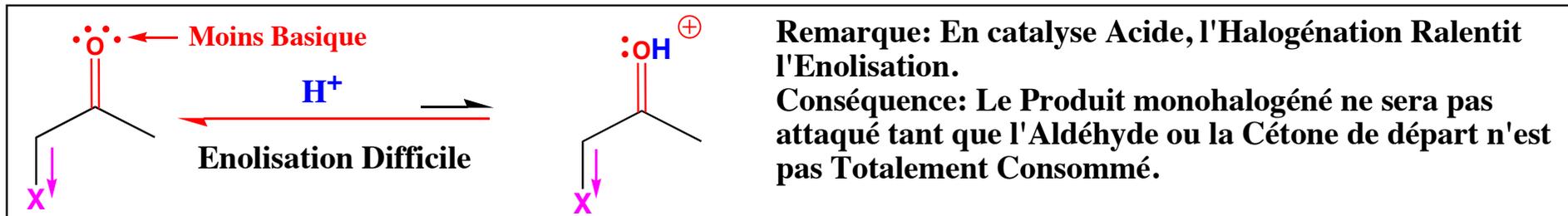
Remarque 1: Passage par un Enolate Plan donc Perte de la Stéréochimie.
Remarque 2: Racémisation en Quelques Minutes.
Remarque 3: Difficile de Conserver l'Activité Optique en α de $\text{C}=\text{O}$.

Halogénéation des Aldéhydes et Cétones:

***Catalyse Acide: Mécanisme**

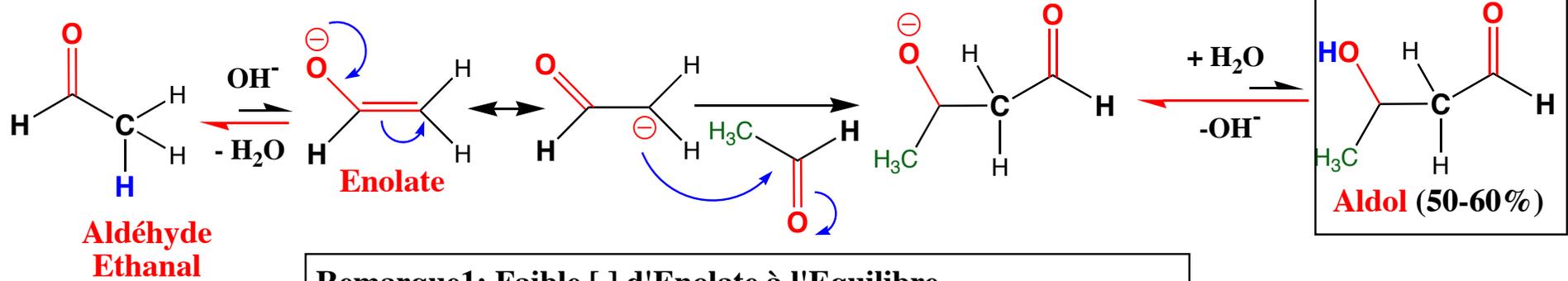


Remarque: Régiosélectivité de la Formation de l'Enol
L'ENOL le plus Stable est l'ENOL le plus Substitué (Analogie avec les ALCENES).



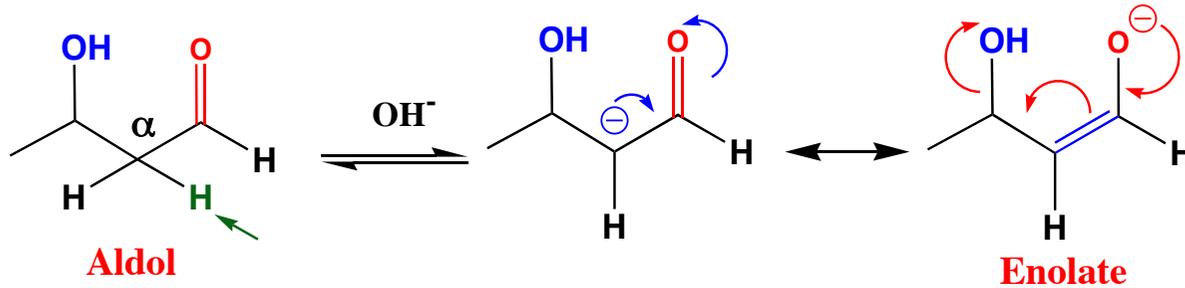
ALDOLISATION:

*Aldéhydes: Mécanisme de la Condensation Aldolique

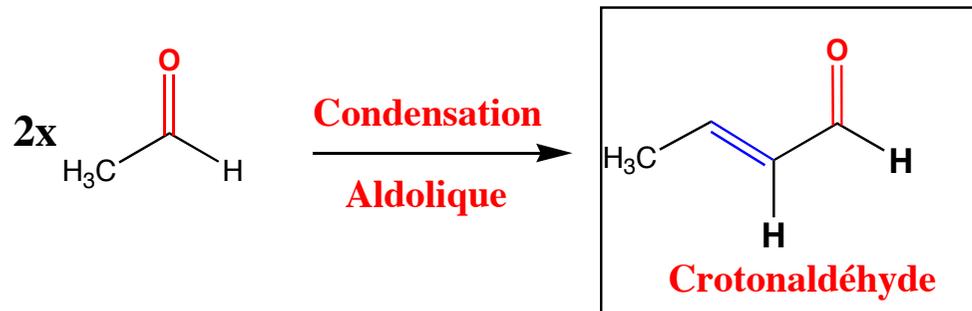


Remarque1: Faible [] d'Enolate à l'Equilibre.
Remarque2: Aldol Relativement Stable à Basse Température.
Remarque3: A Haute Température l'Aldol est Deshydraté.

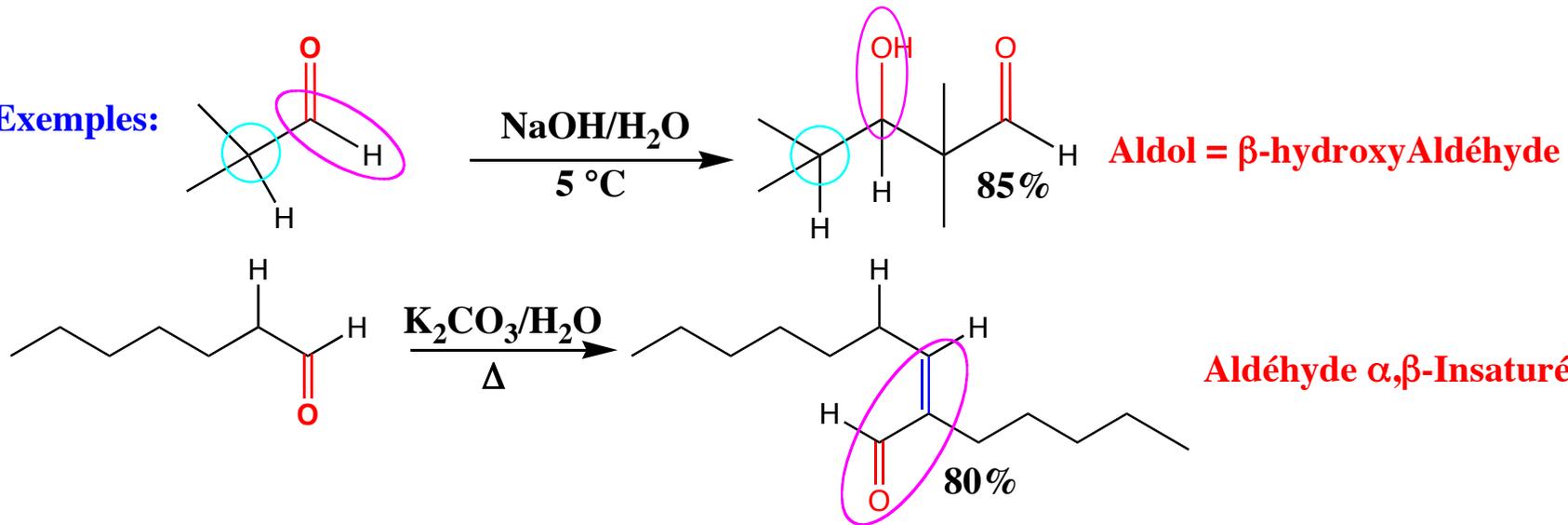
Mécanisme:



Bilan:

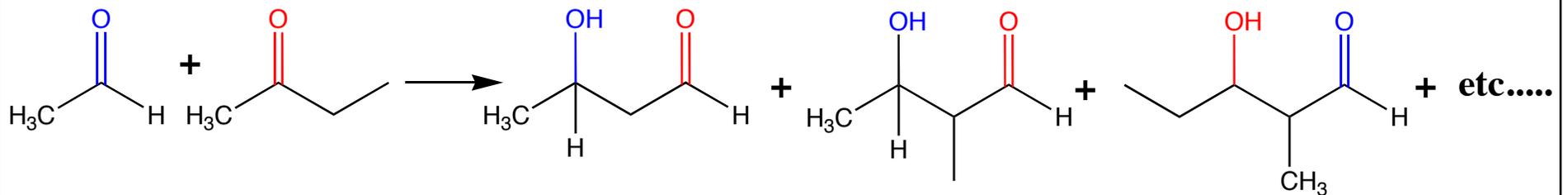


Exemples:



**Remarque: Réaction intéressante car elle donne:
Des Composés Carbonylés β -Hydroxylés et des α,β -Insaturés**

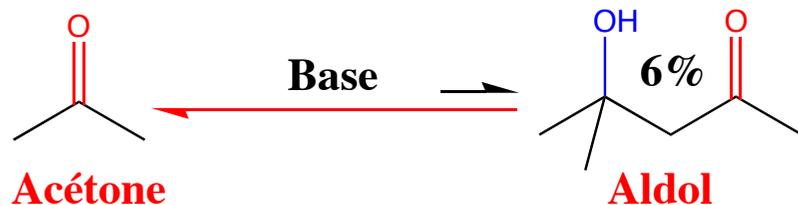
Aldolisation Croisée:



Remarque 1: Réaction **NON Spécifique (Mélange)**

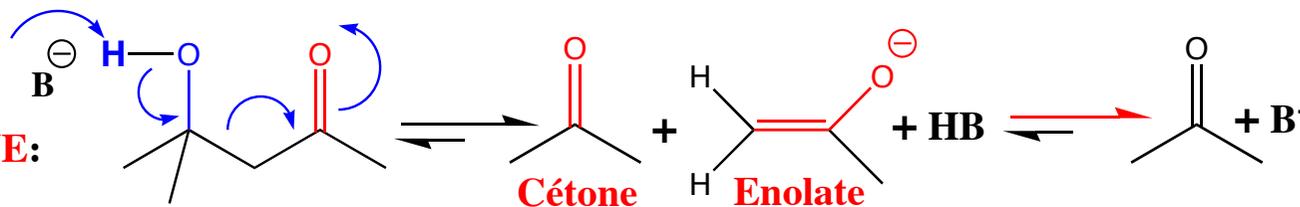
Remarque 2: Réaction Intéressante si l'un des composés ne possède pas de H en α .

****Cétones**



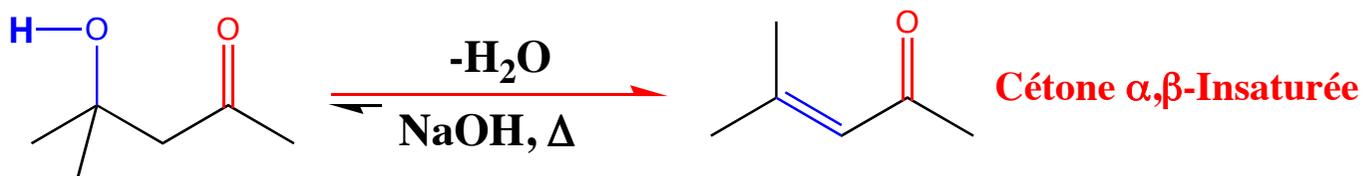
Remarque: Equilibre Largement Déplacé vers la Cétone.

Réaction RETROALDOLIQUE:

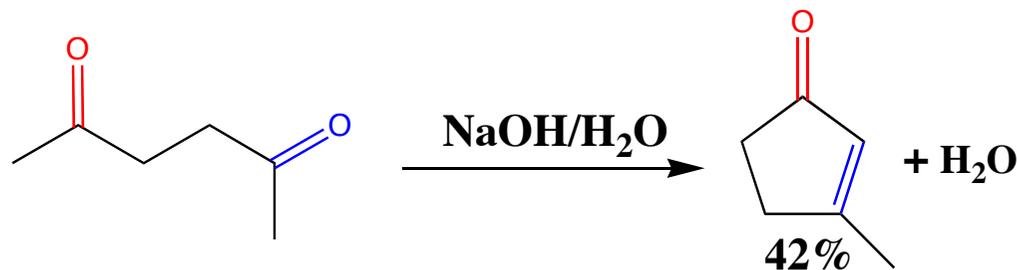


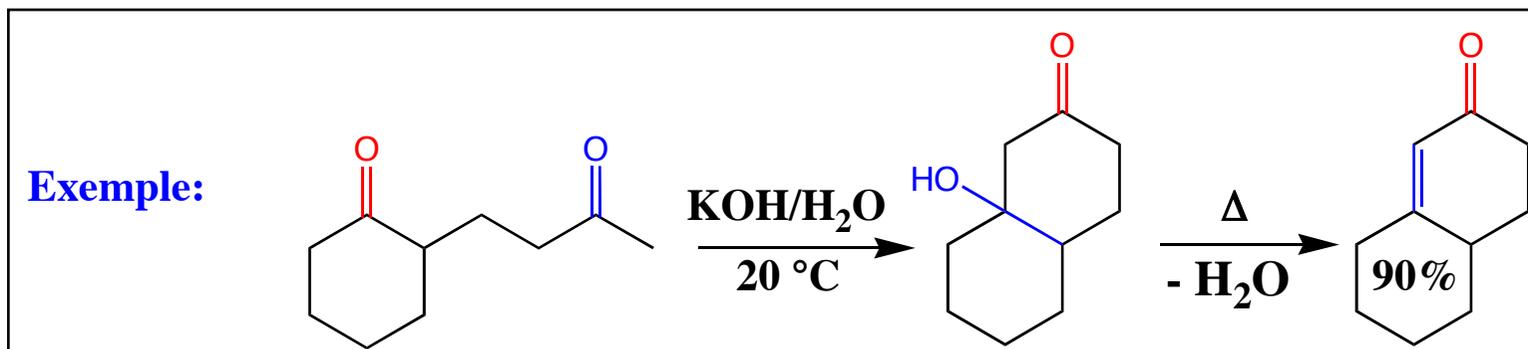
Remarque: La Réaction avec les Aldéhydes est EXOTHERMIQUE alors que la Réaction avec les Cétones est Légèrement ENDOTHERMIQUE.

Remarque: L'Equilibre peut être Déplacé si l'on Elimine H₂O.

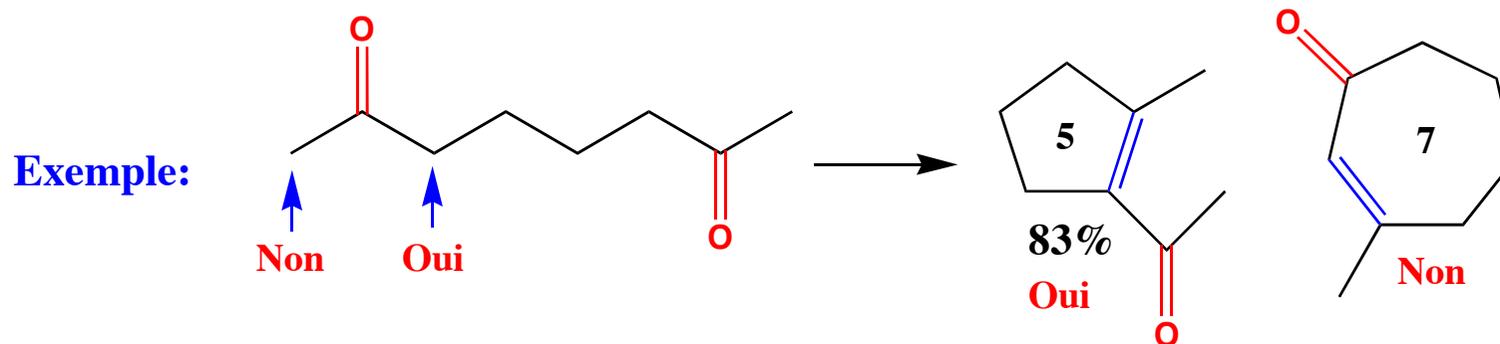
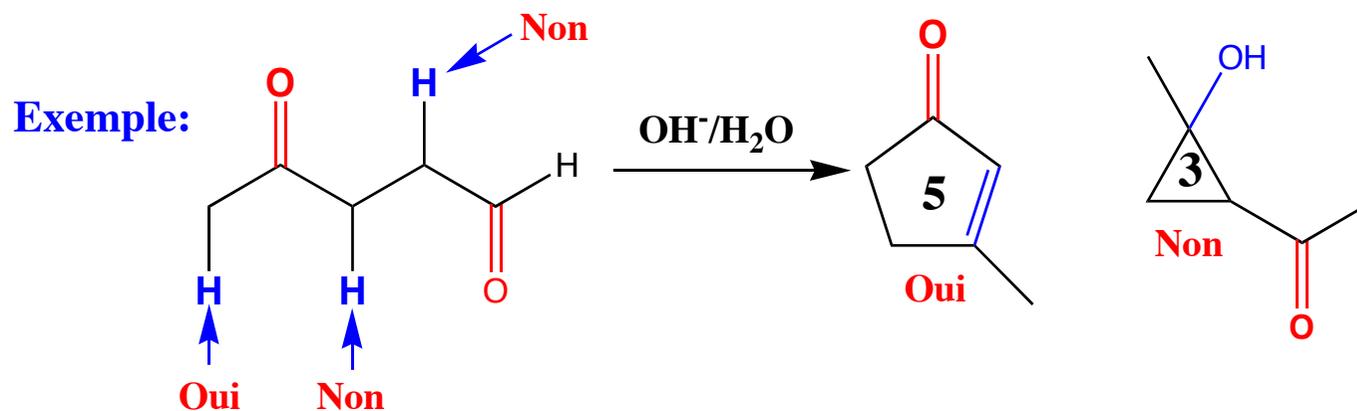


Remarque: Réaction Intramoléculaire Déplace L'Equilibre



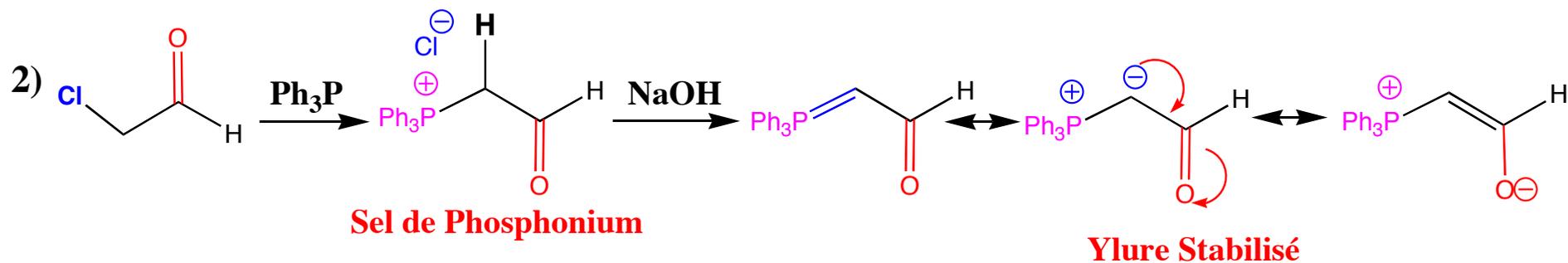
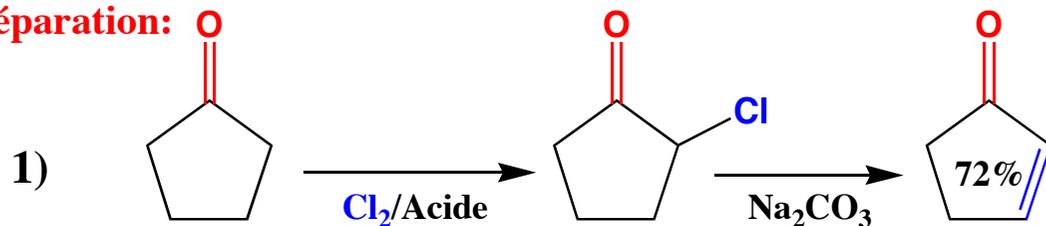


Remarque: La Condensation Aldolique Intramoléculaire Conduit à la Formation du Cycle (5,6) le Moins Tendu.



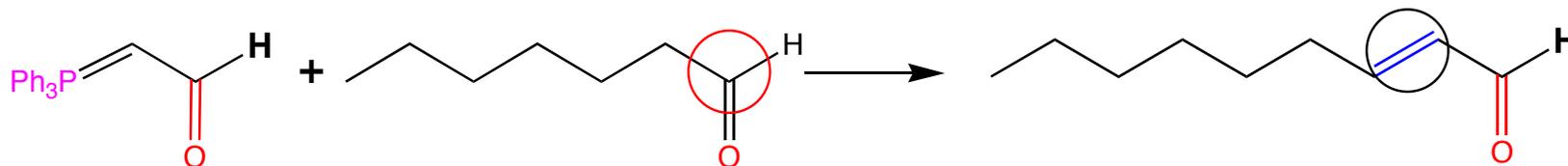
La Préparation et la Chimie des Aldéhydes et Cétones α,β -Insaturés

***Préparation:**

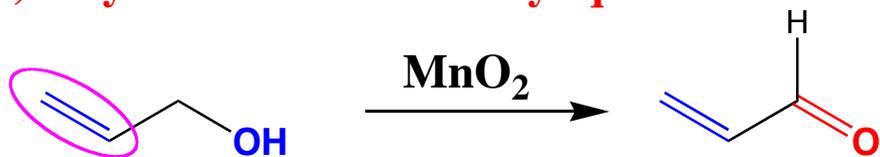


Remarque: ylure de phosphore stabilisé est peu réactif, Il ne réagit pas bien avec les Cétones mais avec les Aldéhydes, intrinsequement plus réactifs, il effectue une réaction de Wittig.

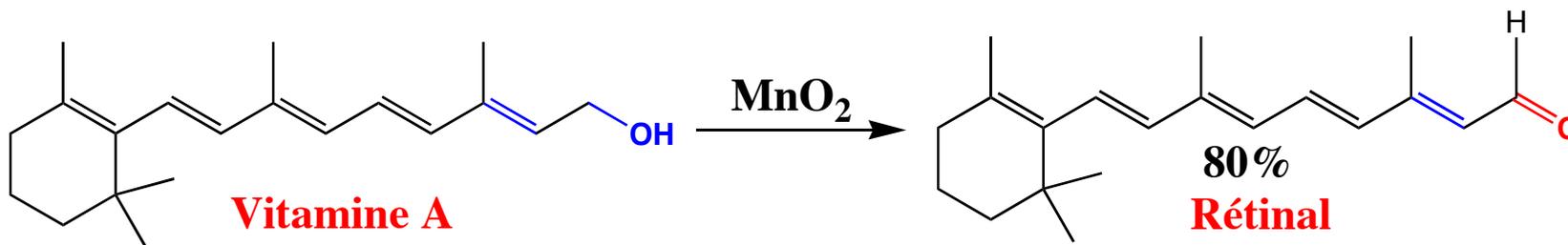
Exemple:



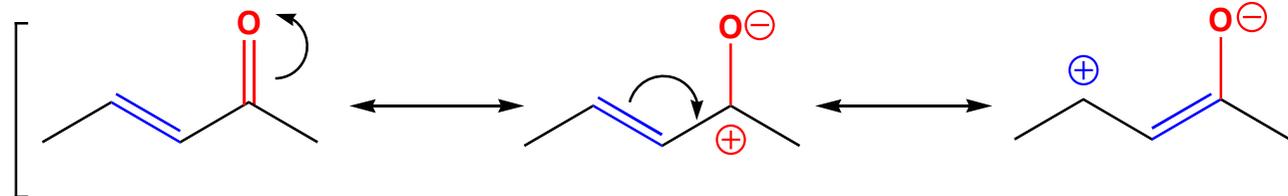
3) Oxydation d'Alcools Allyliques



Exemple:



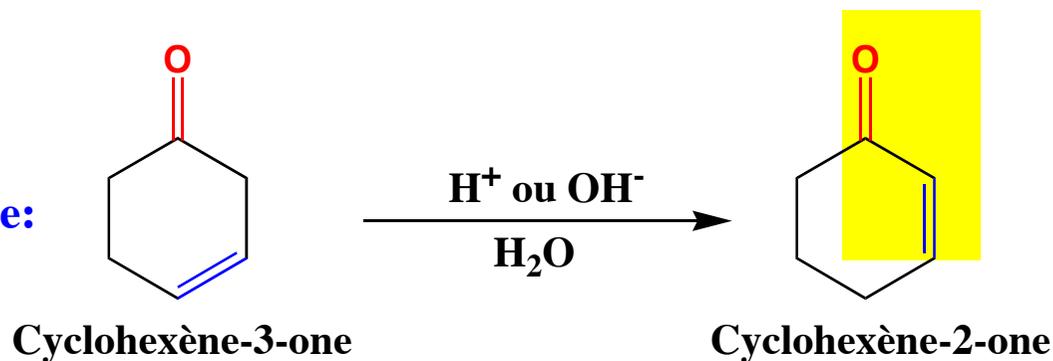
4) Isomérisation:



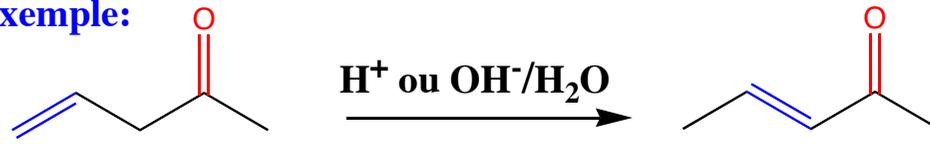
Remarque: Stabilisation par Résonance des Aldéhydes et Cétones α,β -Insaturés.

Conséquence: Les Composés NON Conjugués se Réarrangent pour Donner des Dérivés α,β -Insaturés.

Exemple:



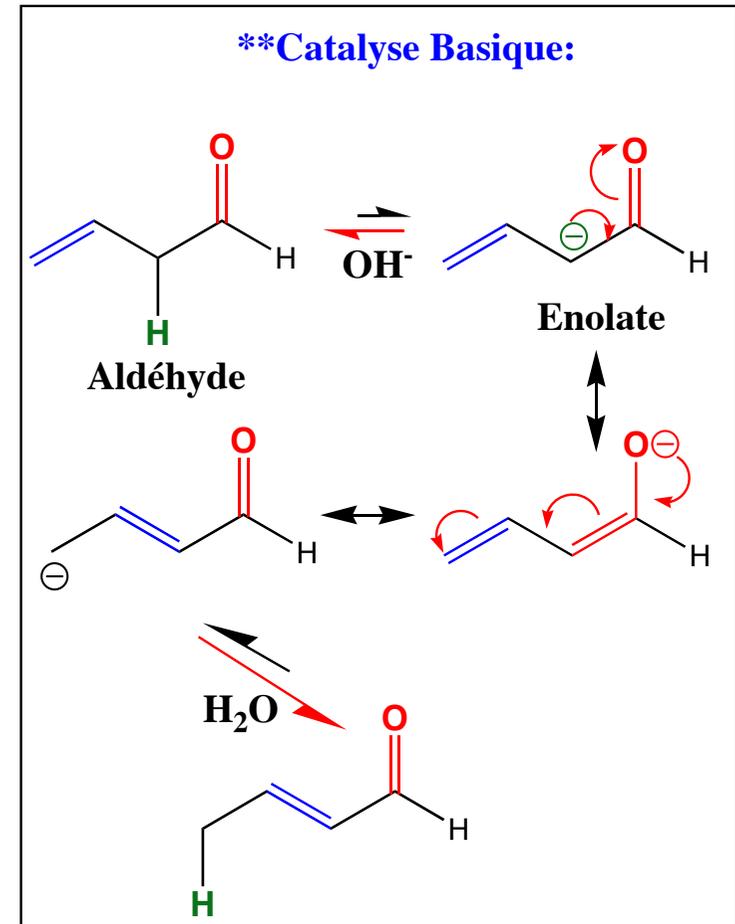
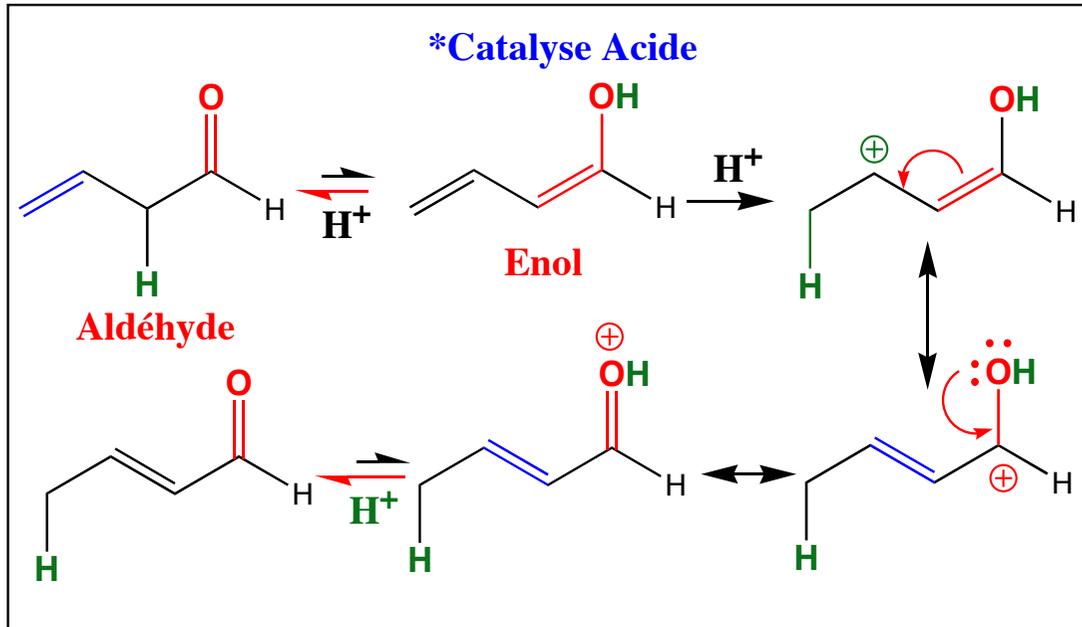
Exemple:

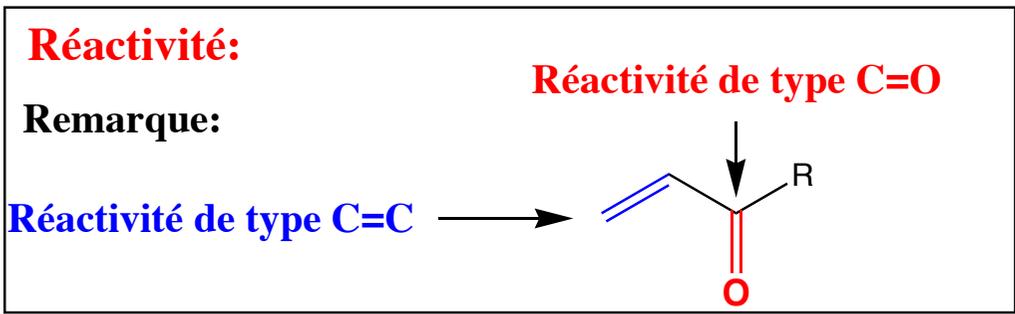


Non Conjuguée

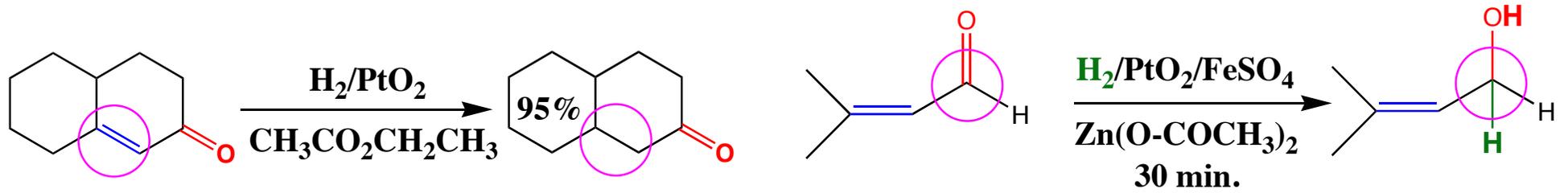
Conjuguée

Mécanisme:

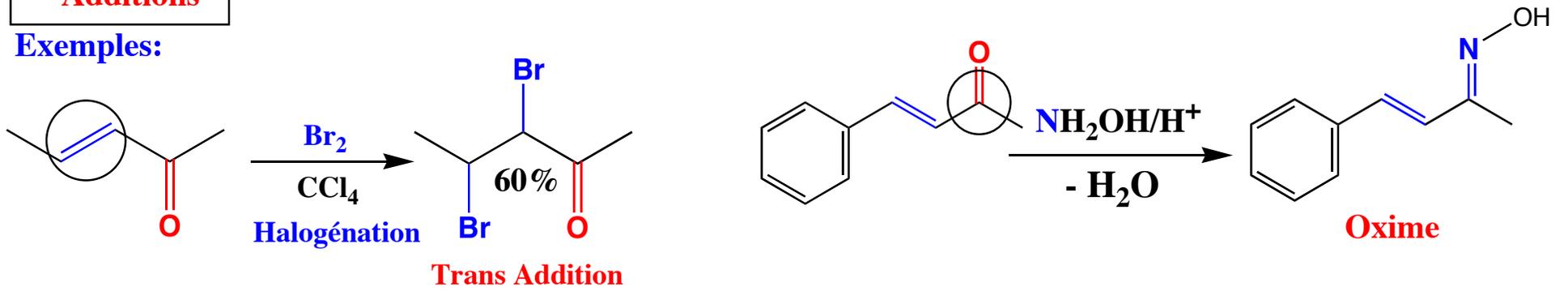




***Réduction**
Exemples:

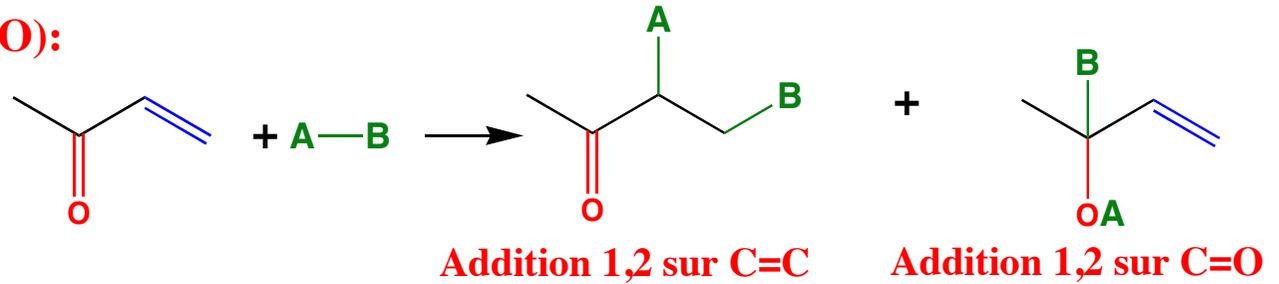


****Additions**
Exemples:

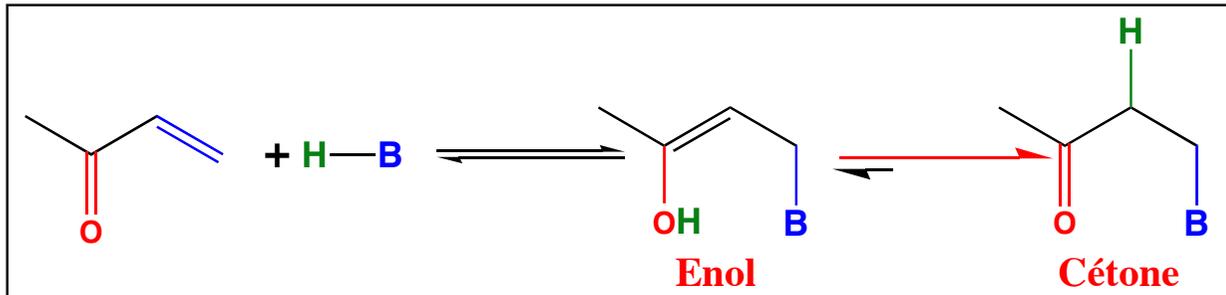
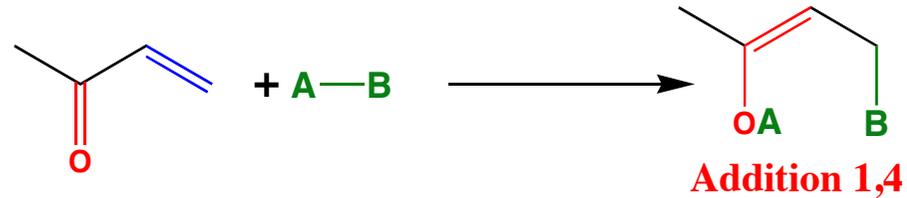


ADDITION 1,4: (C=C et C=O):

Remarque: Addition 1,2:

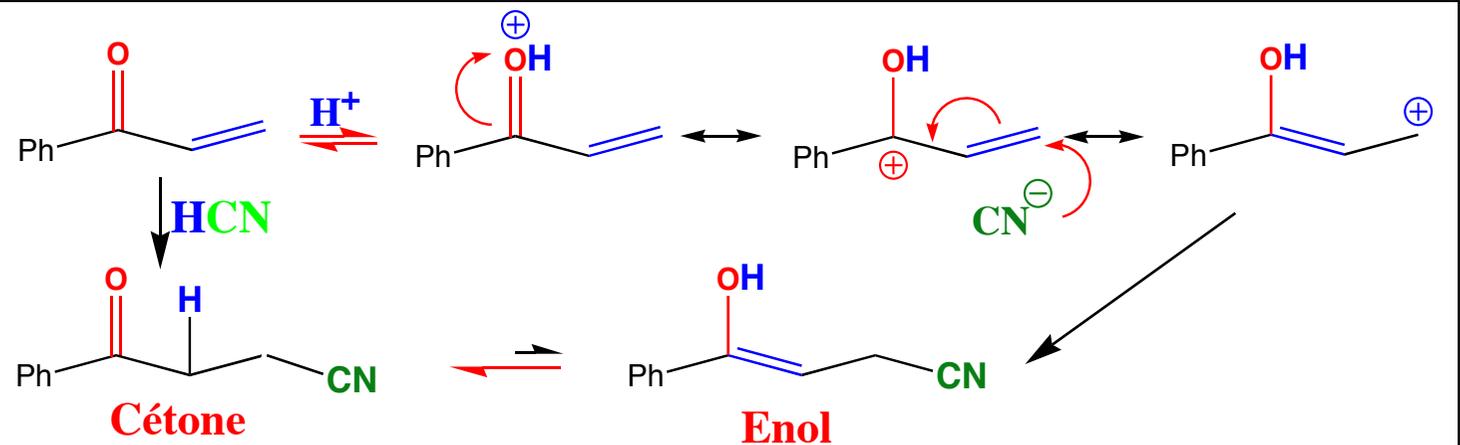


Remarque: Addition 1,4:

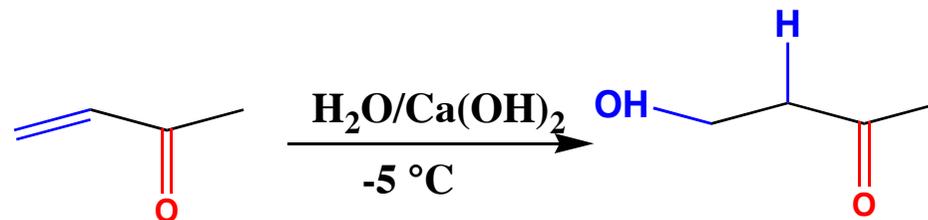


Remarque Si $A = H$, Il y a une Addition 1,4 mais le Résultat apparaît comme une Addition 1,2.

*Addition de HCN:

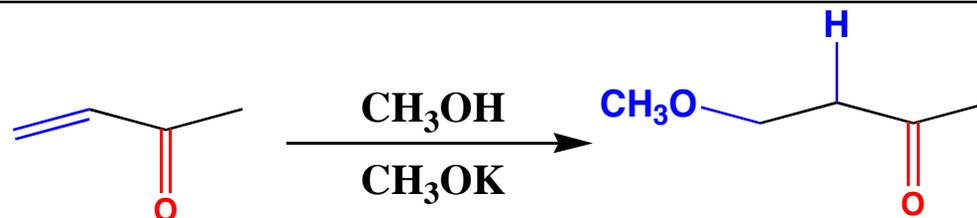


****Addition de H₂O:**

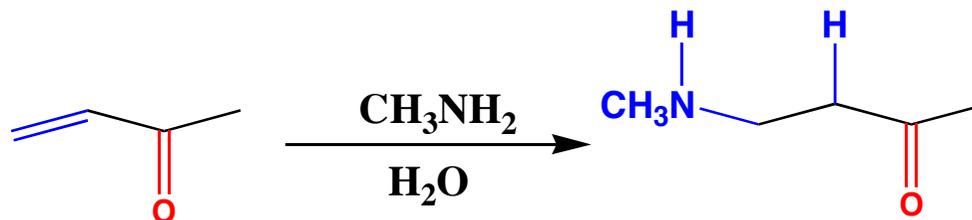


Anti Markownikov

*****Addition de ROH:**

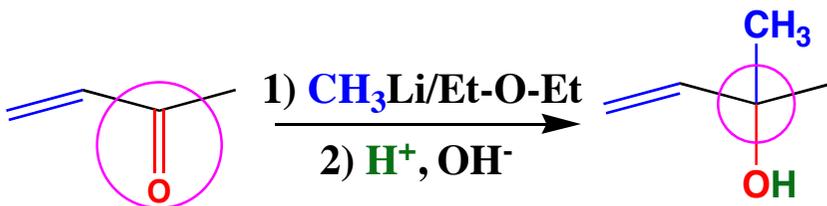


******Addition d'Amine:**



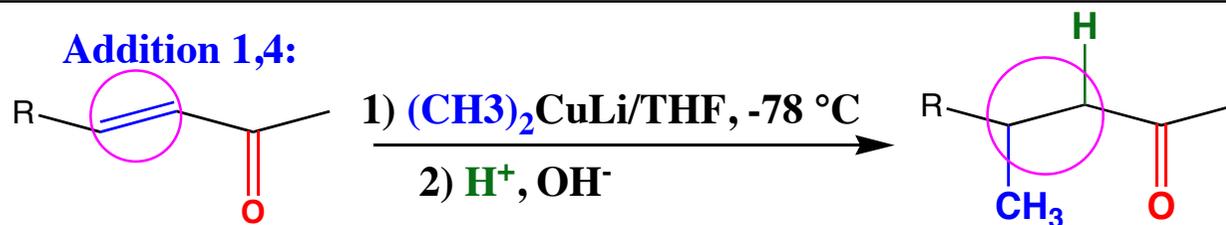
*******Addition d'Organométallique:**

Addition 1,2:

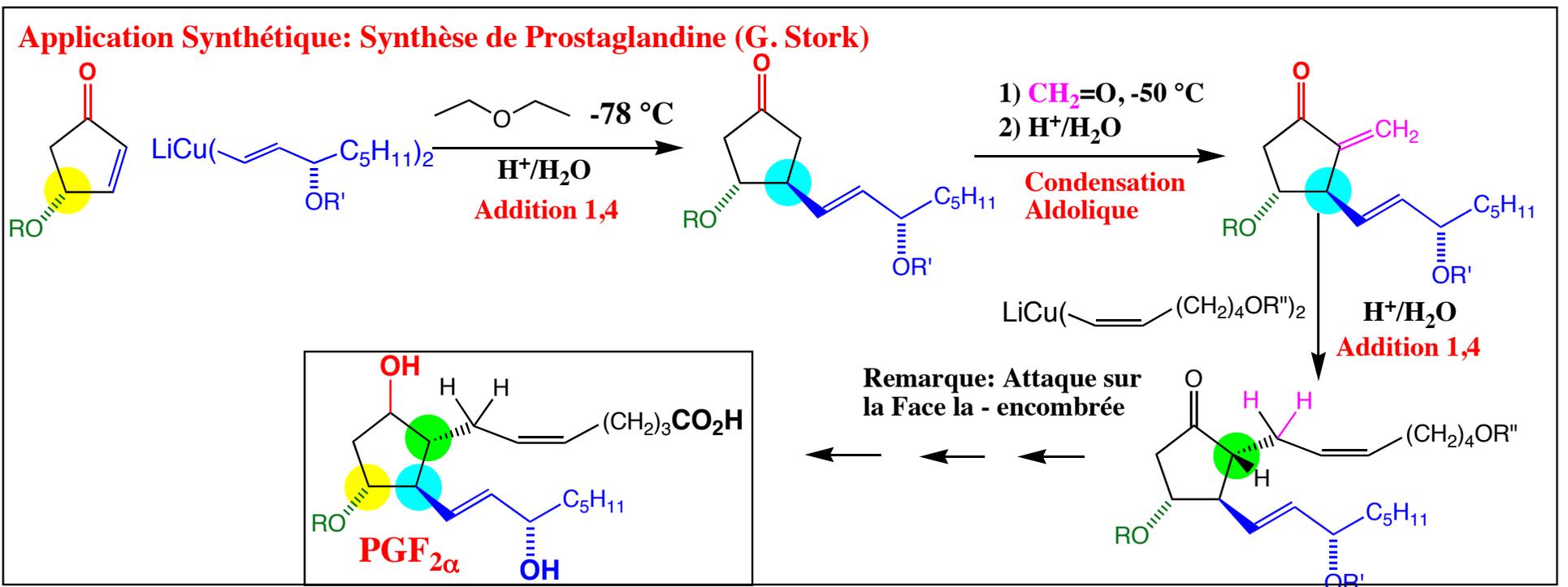
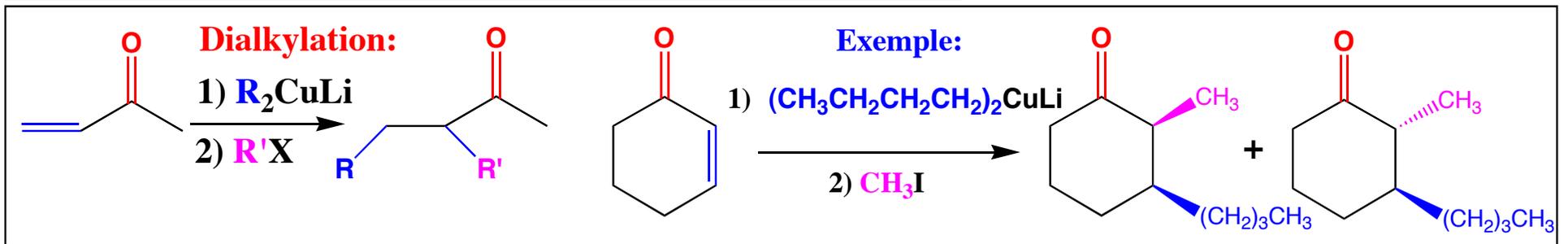
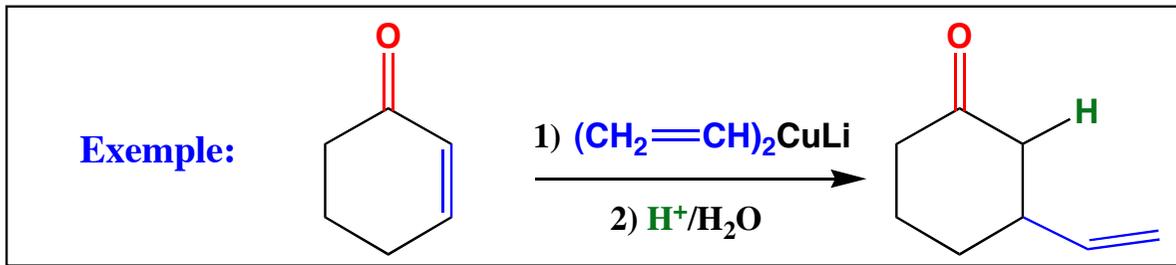


**Remarque: Les Lithiens
Donnent une Addition 1,2
par l'Attaque nucléophile
directe sur le C=O.**

Addition 1,4:

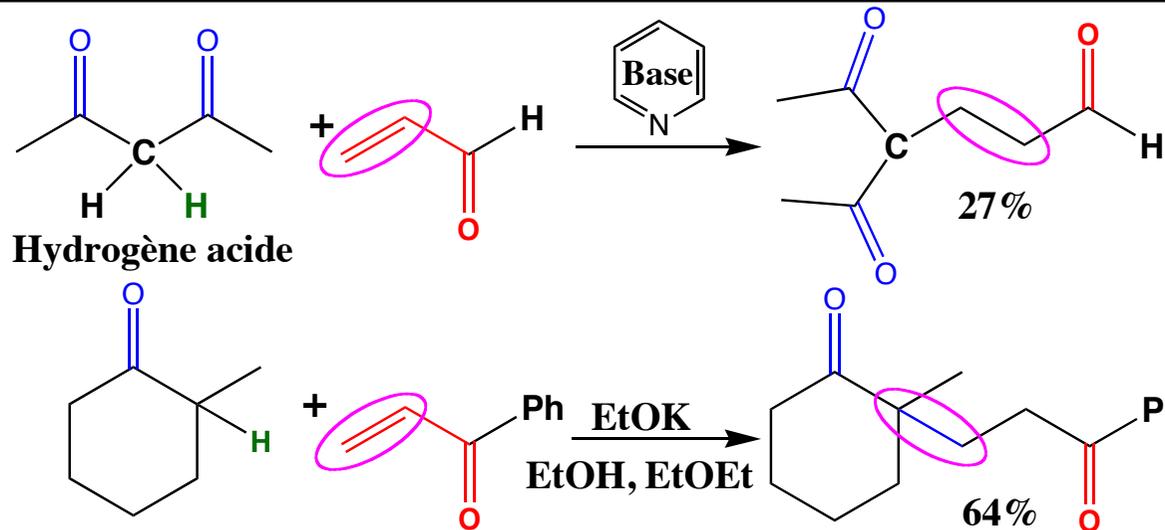


**Remarque: Les Cuprates
Donnent une Addition 1,4
sur le C=O. Le Mécanisme
est peu Connue et Compliqué.**

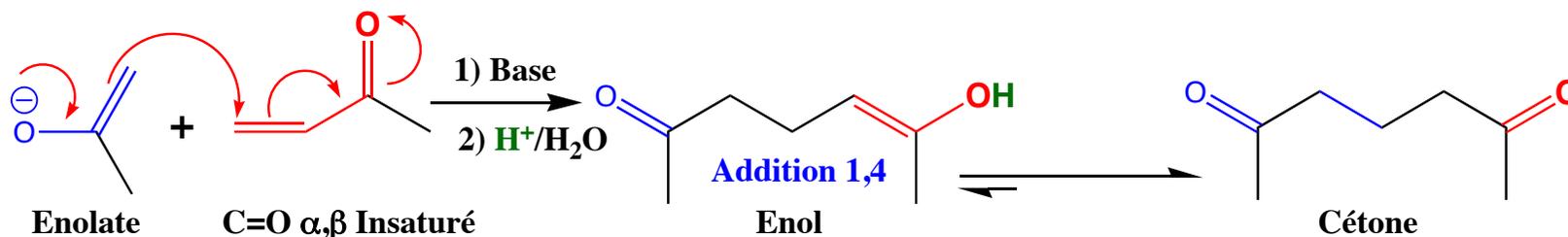


Réaction de Michael:

Exemples:

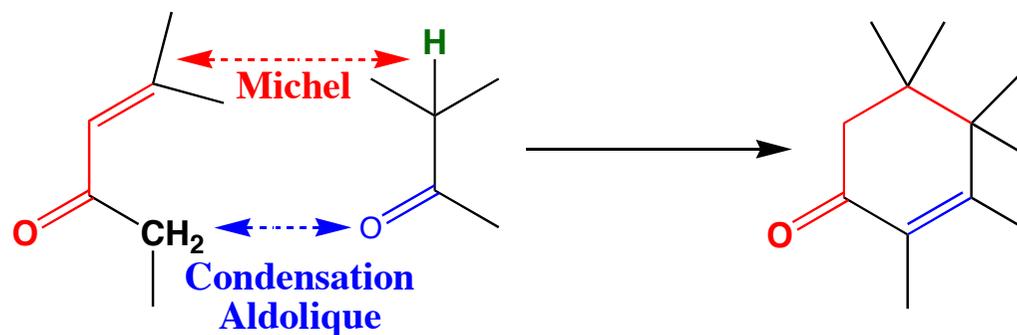


Mécanisme:

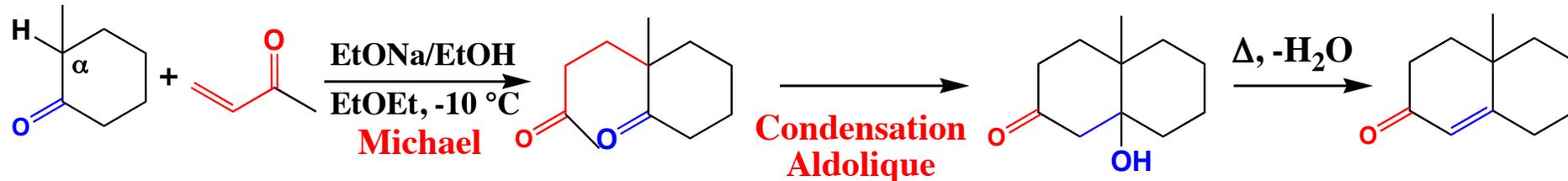


Annélation de Robinson:

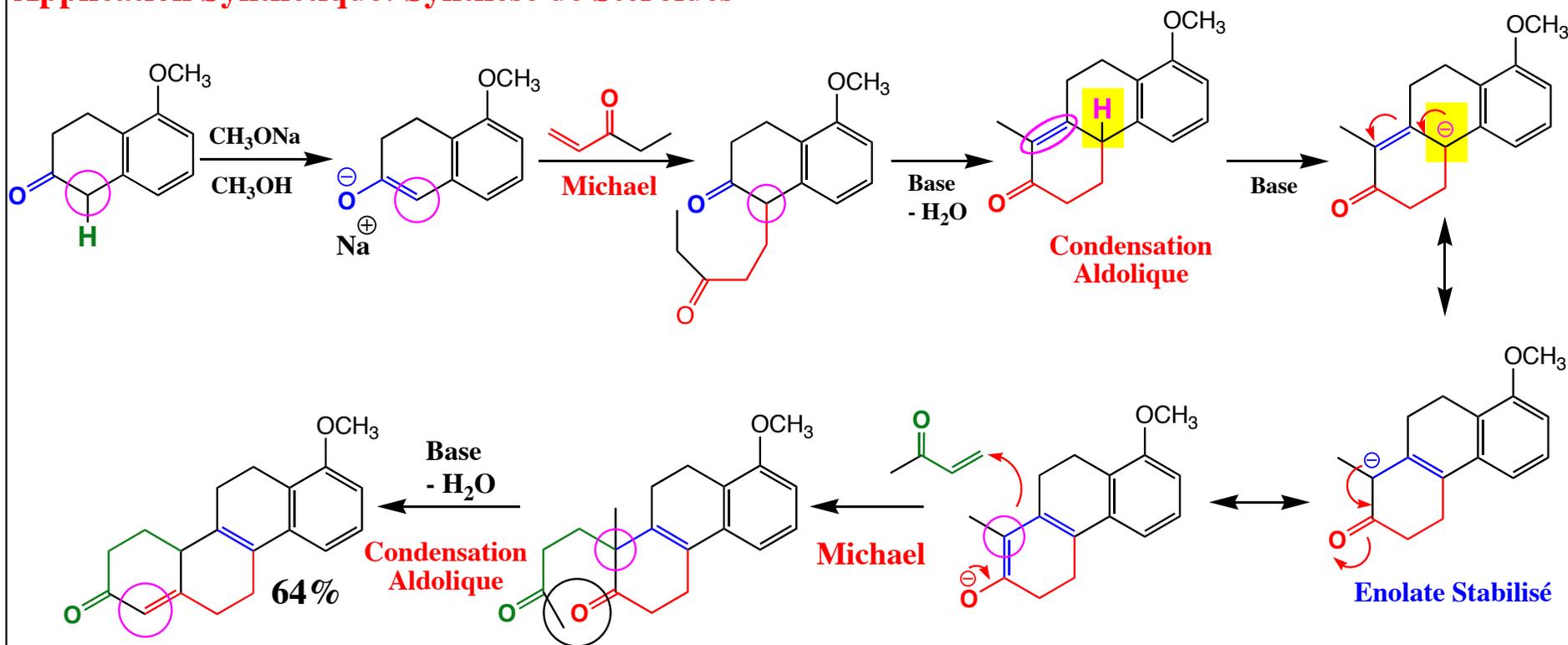
C'est une séquence: Addition de Michael-Condensation Aldolique



Exemple:

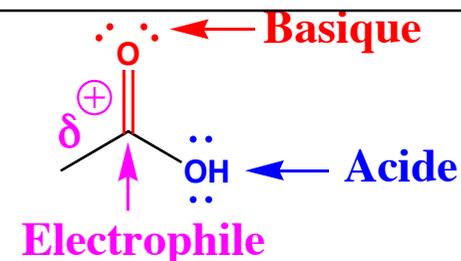


Application Synthétique: Synthèse de Stéroïdes

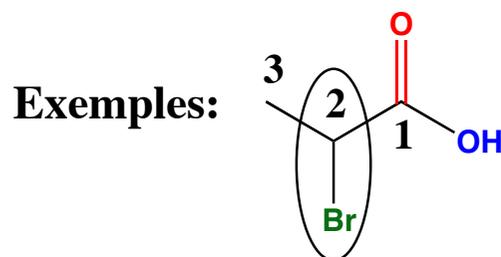


Acides Carboxylique

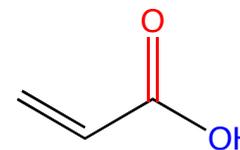
Remarques: Trois types de Réactivité
 1) Réactivité de type Alcool (OH)
 2) Réactivité de type Carbonyle (C=O)
 3) Réactivité de Type Acide (COOH)



- 1) Nomenclature: a) On remplace le E d'AlcanE par OÏQUE le carbone de l'Acide est numéroté en 1.
 b) Si il y a d'autres fonctions, on considère la chaîne la plus longue et on intercale le nom de la fonction entre Acide et **ALCANOÏQUE**.



Acide bromo-2-propanoïque

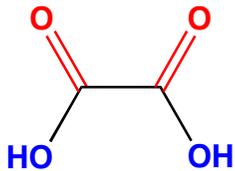


Acide propénoïque
(Acide Acrylique)

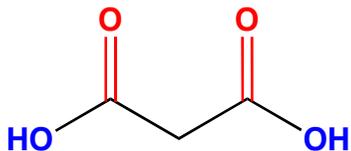
Noms Usuels:

Structure	Nom IUPAC	Nom Courant
HCOOH	Acide Méthanoïque	Acide Formique
CH ₃ COOH	Acide Ethanoïque	Acide Acétique
CH ₃ CH ₂ COOH	Acide Propanoïque	Acide Propionique
CH ₃ -(CH ₂) ₂ -COOH	Acide Butanoïque	Acide Butyrique
CH ₃ -(CH ₂) ₃ -COOH	Acide Pentanoïque	Acide Valérique
CH ₃ -(CH ₂) ₄ -COOH	Acide Hexanoïque	Acide Caproïque

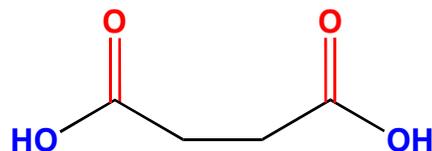
Les **Diacides**: ACIDE ALCANE DIOÏQUE



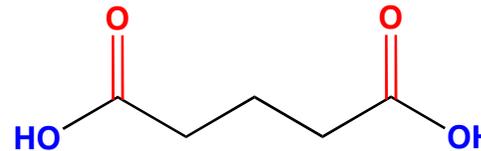
Acide éthanedioïque
Acide Oxalique



Acide propanedioïque
Acide Malonique



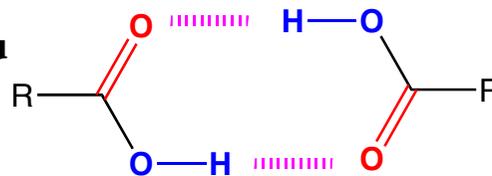
Acide butanedioïque
Acide Succinique



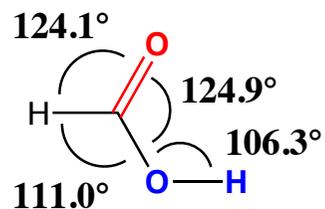
Acide pentanedioïque
Acide Glutarique

2) **Propriétés Physiques**: Possibilité de Formation de Liaison H: Formation de Dimère

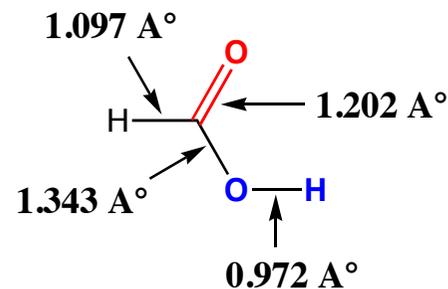
Poids moléculaires faibles: Soluble dans l'Eau
Points d'Ebullition et de Fusion Elevés

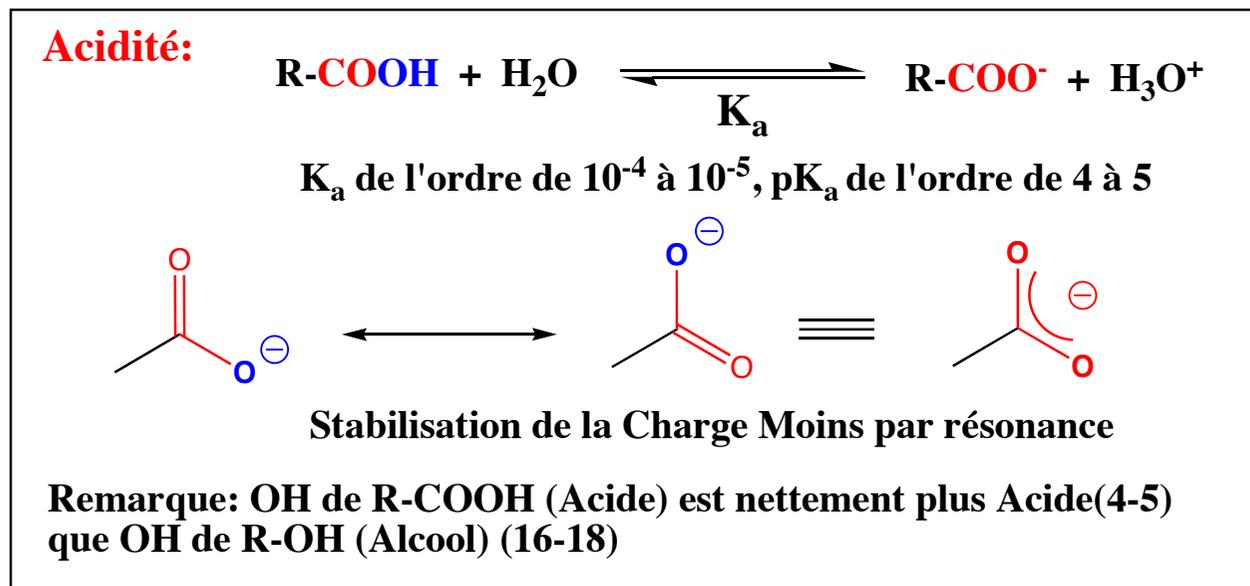
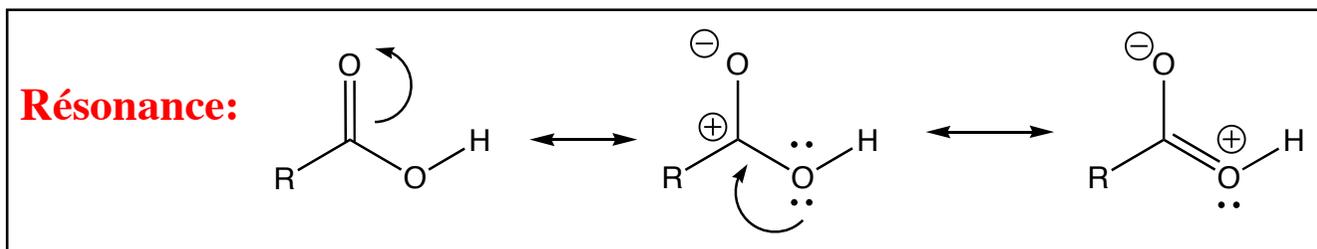
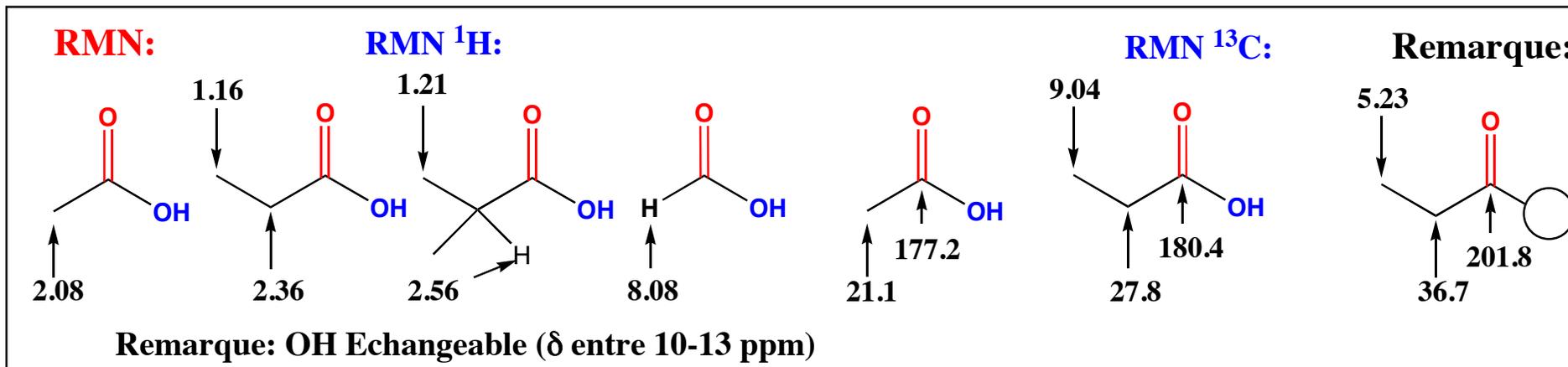


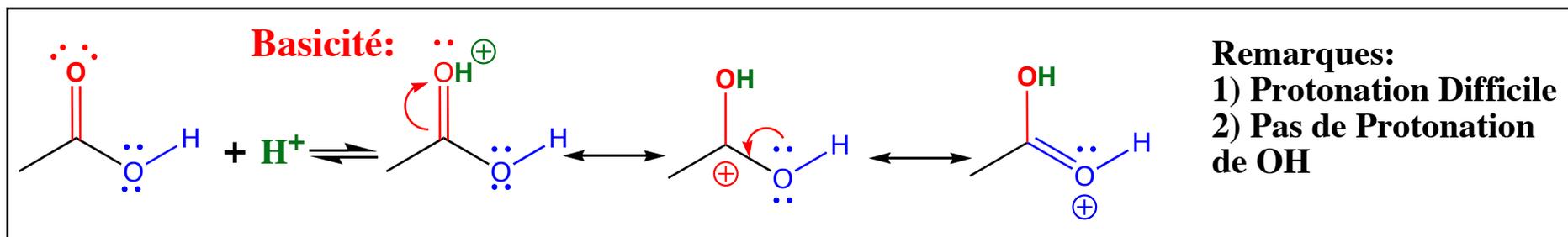
Structure:



Acide Méthanoïque

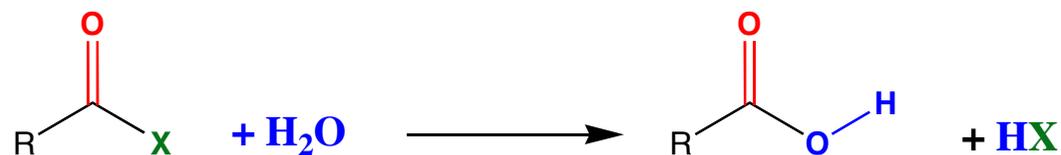




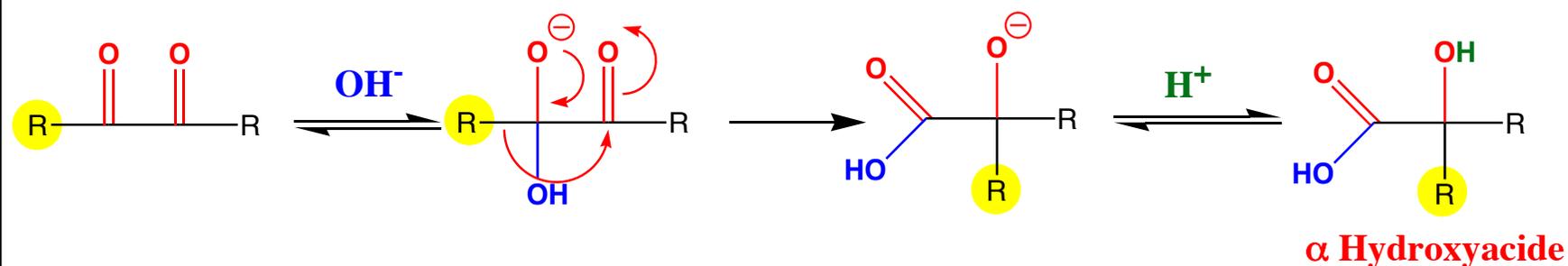


3) Méthodes de Préparation:

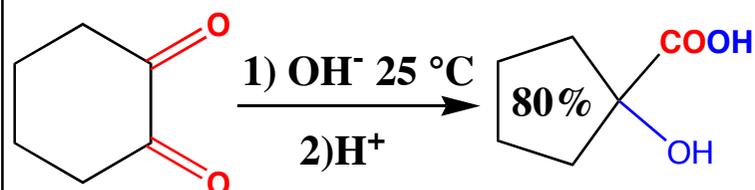
A) Hydrolyse de Chlorure d'Acide:



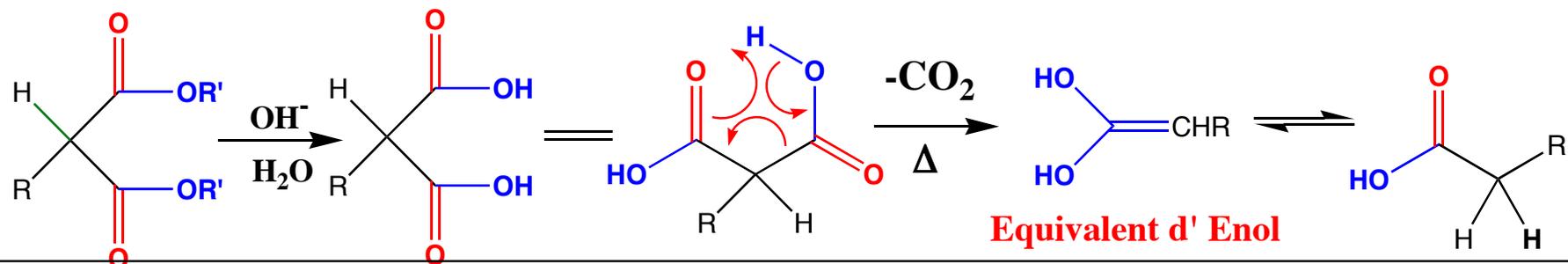
B) Réarrangement Benzilyque:



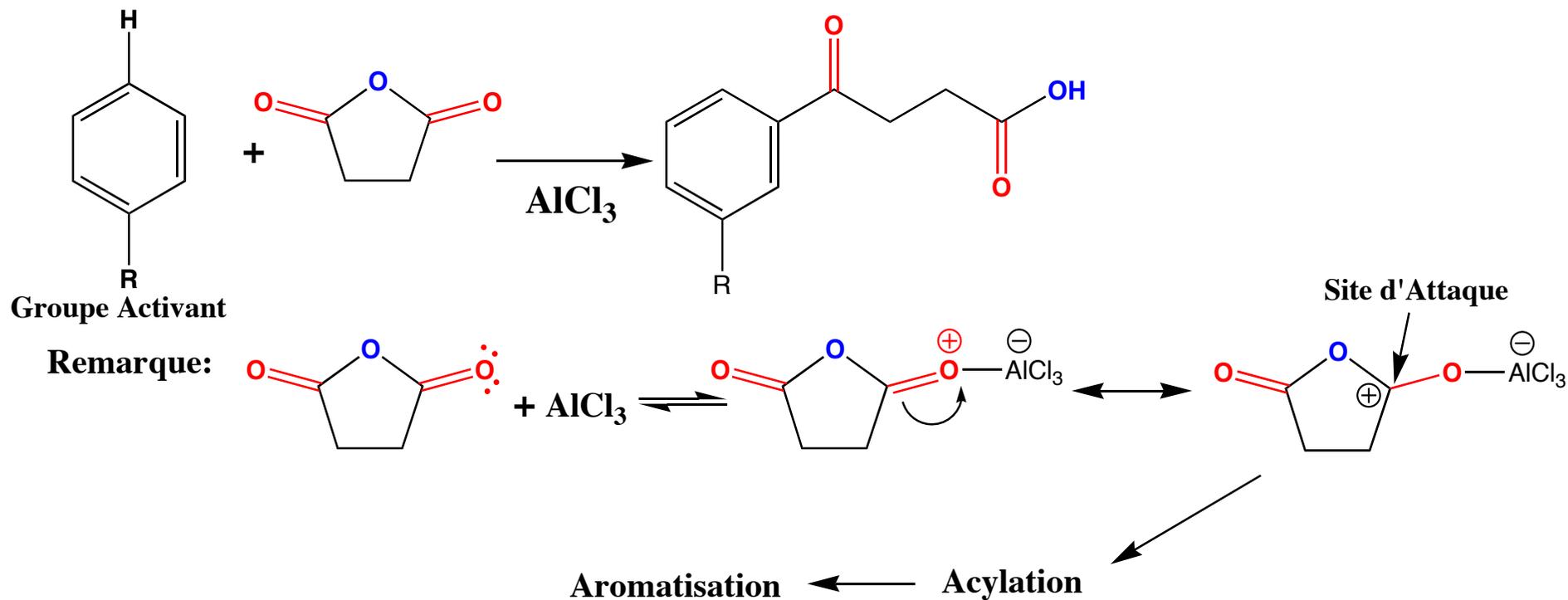
Exemple:

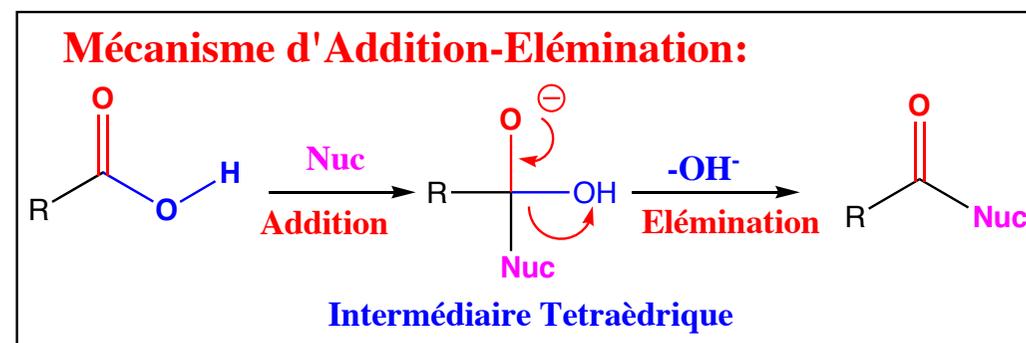
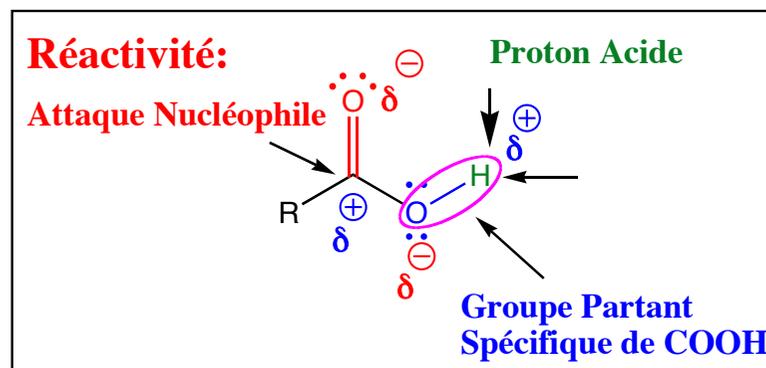
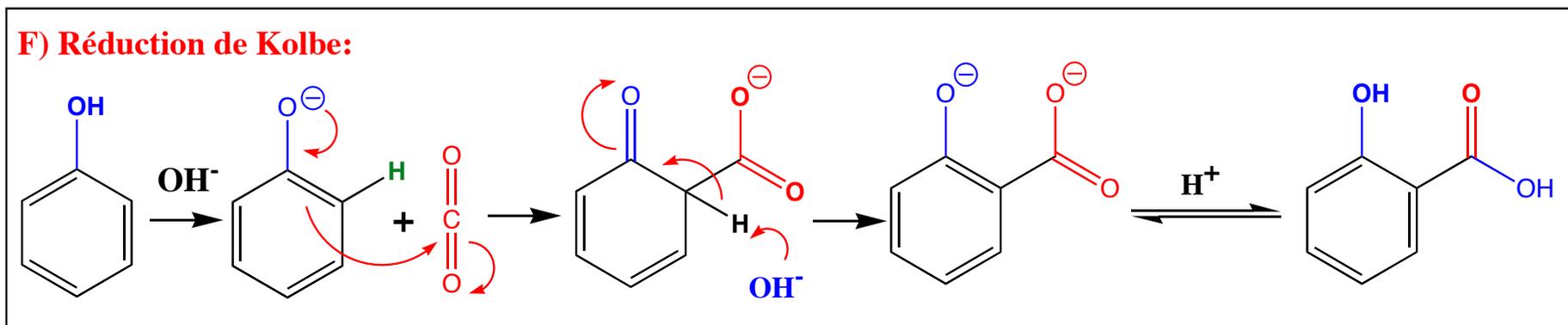
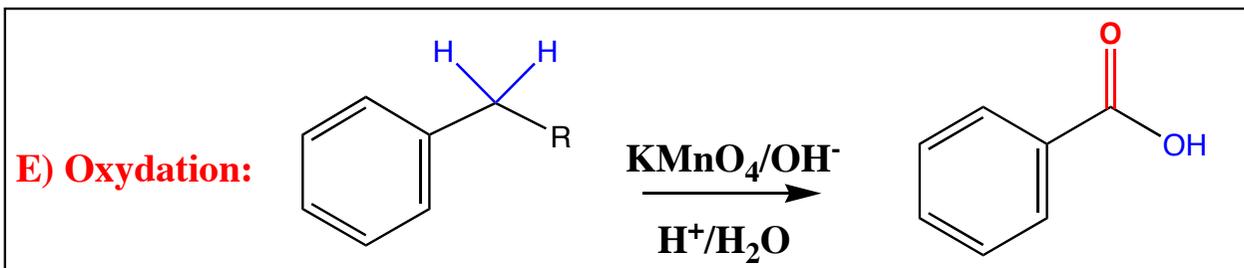


C) Synthèse Malonique:



D) Alcanoylation de Friedel et Crafts

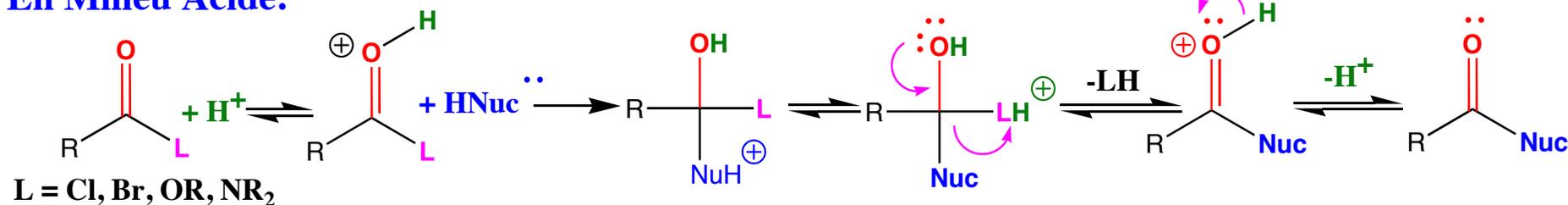




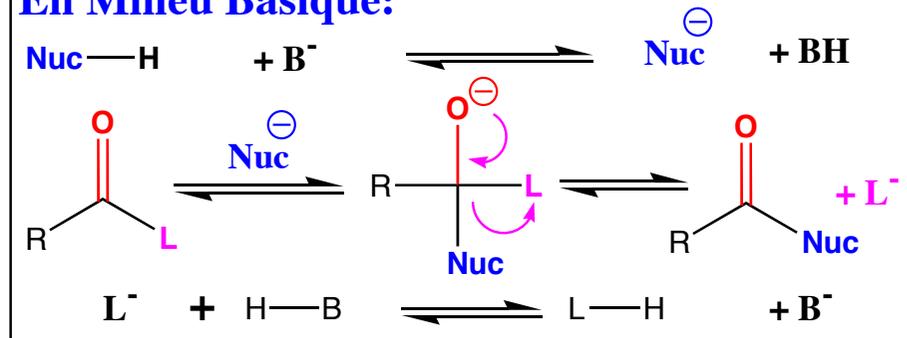
Remarque: Nu est en même temps une base. Par conséquent il y a une compétition entre l'attaque du C=O et la déprotonation. Si on utilise un excès de Nu, il y aura d'abord la déprotonation de COOH puis l'attaque de COO⁻ qui sera difficile car centre chargé -.

Pour contourner cette complication, on utilise souvent des dérivés (RCOL) qui eux subissent facilement des réactions de type S_N

En Milieu Acide:

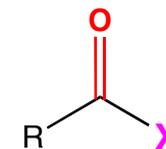


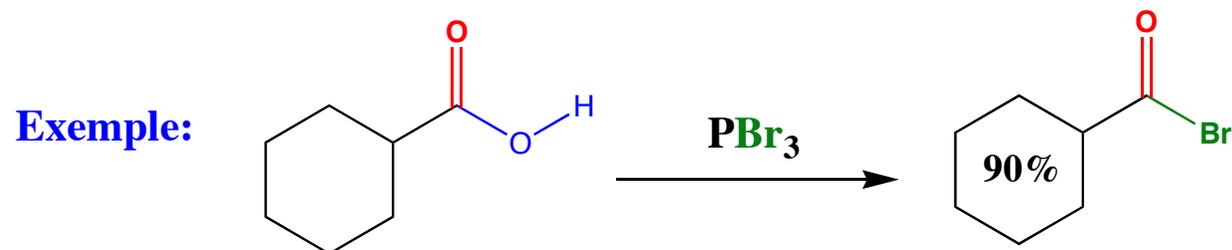
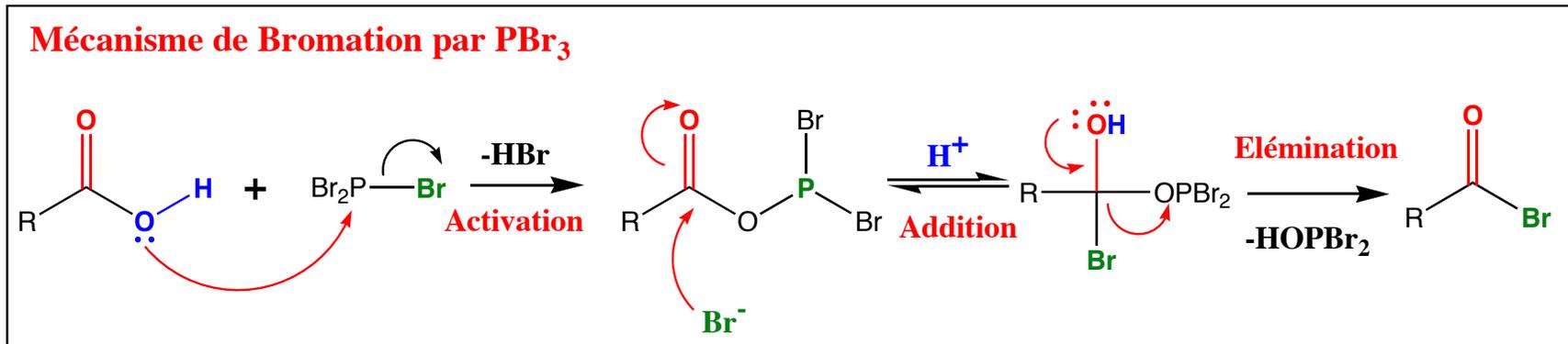
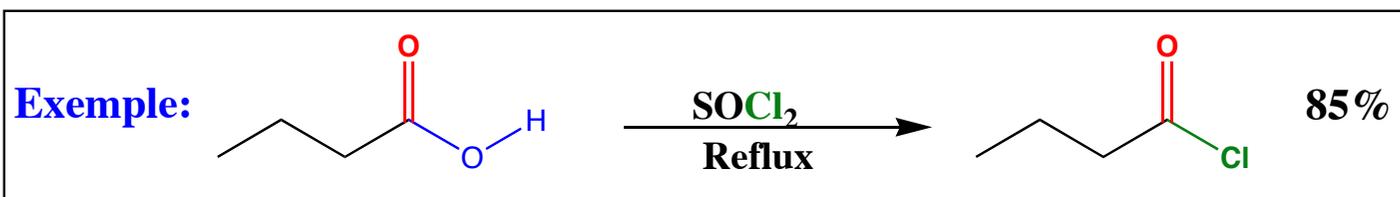
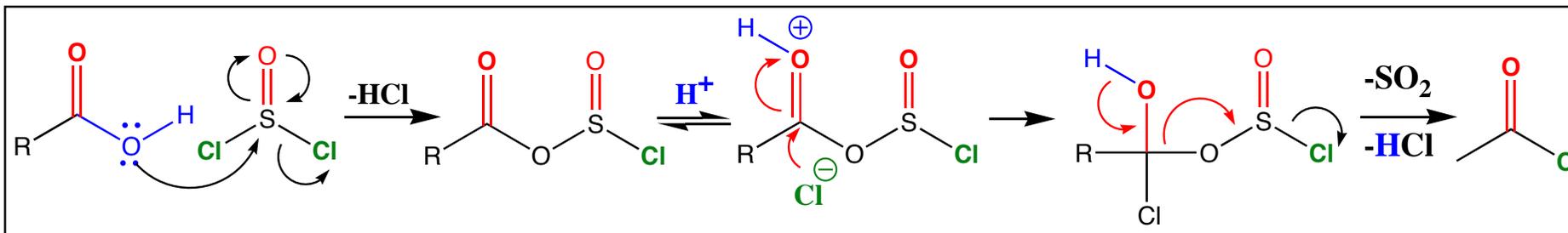
En Milieu Basique:



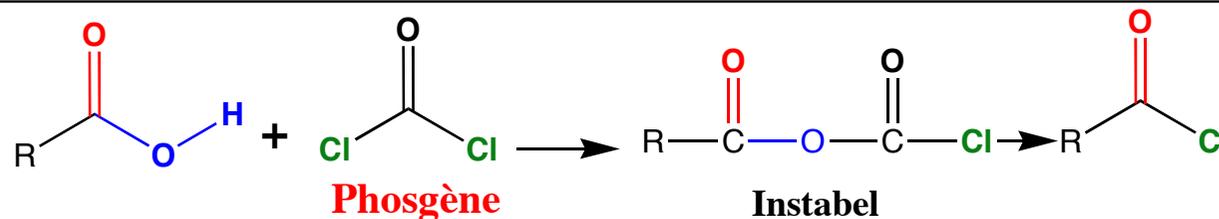
Obtention de Dérivés (Halogénure d'Acyle et Anhydride):

Halogénure d'Acyle: R-COX, X=Cl, Br



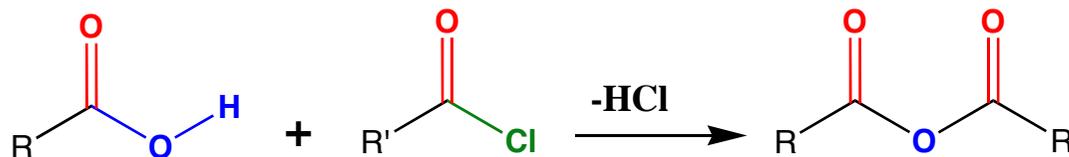


Remarque: Une autre façon



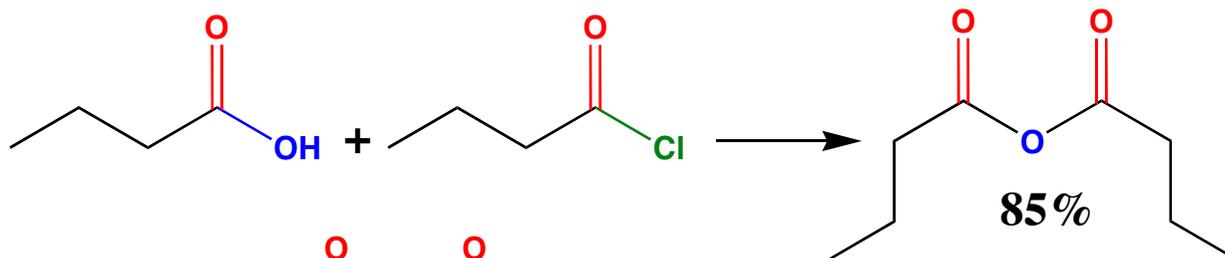
Anhydride d'Acide:

Formation:

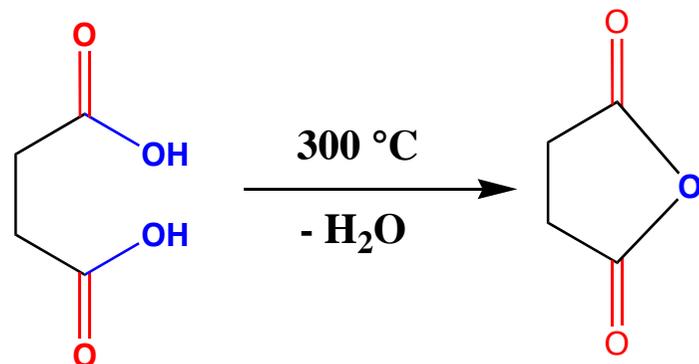
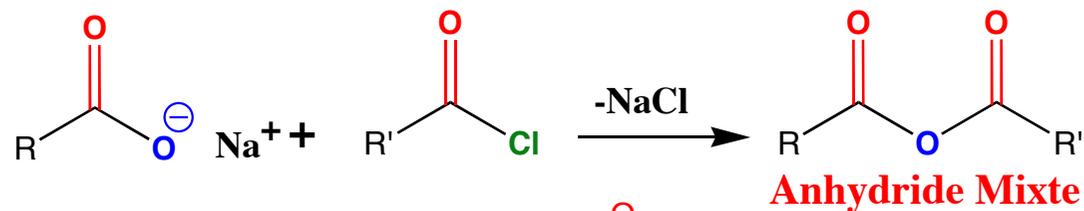


Anhydride

Exemple:



Autre Possibilité:

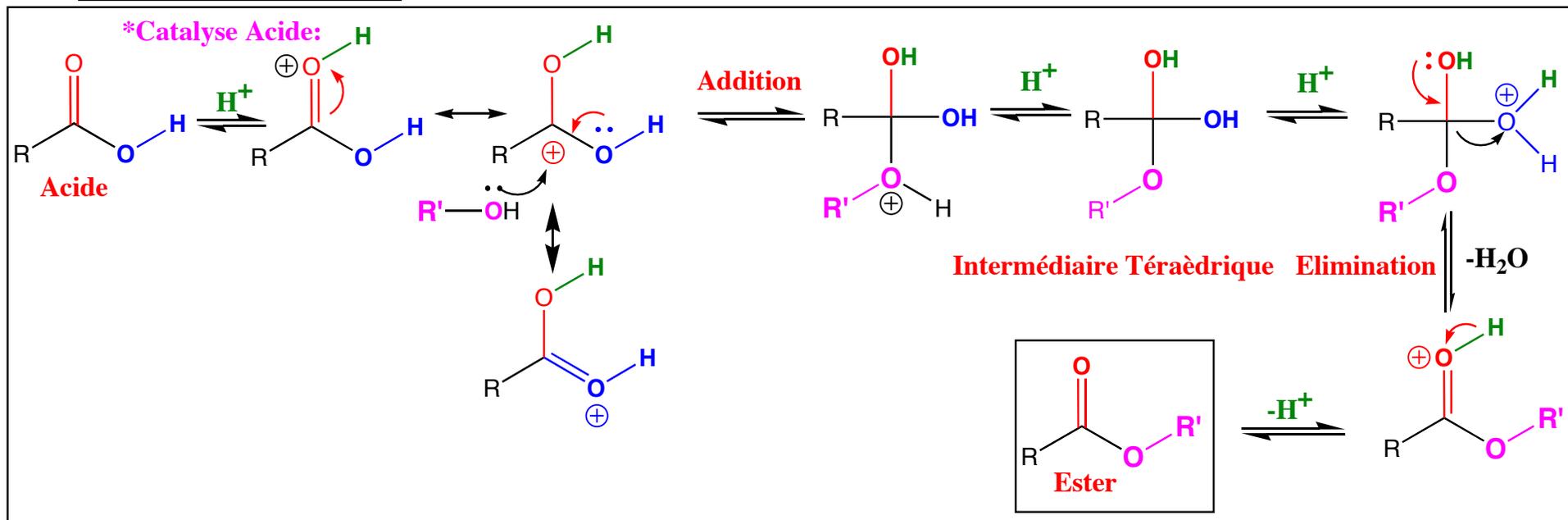


Remarque: Formation de Cycle à 5 et à 6 atomes

Anhydride Cyclique (**succinique**)

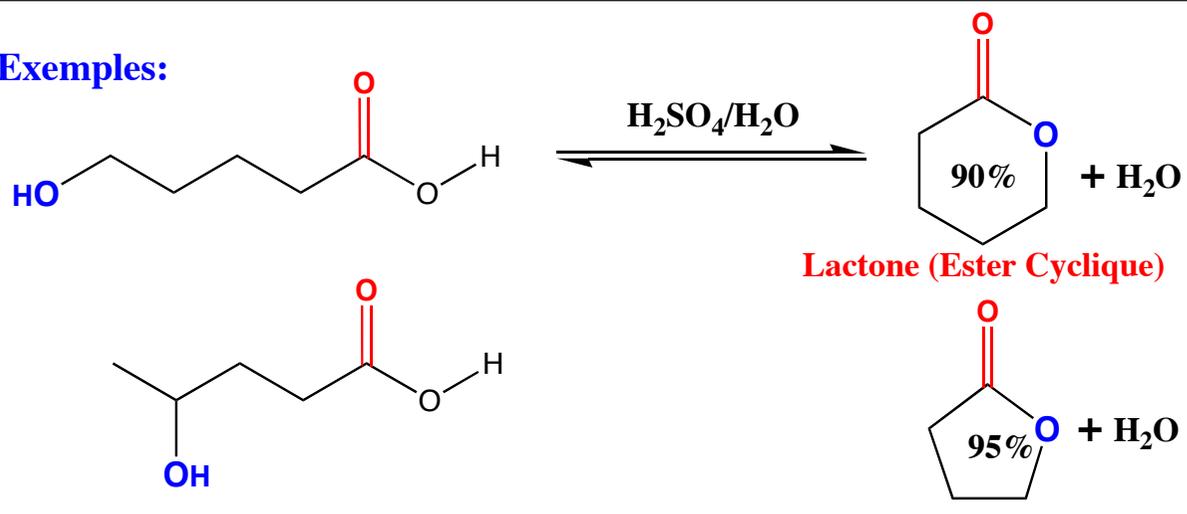
Obtention d'Esters

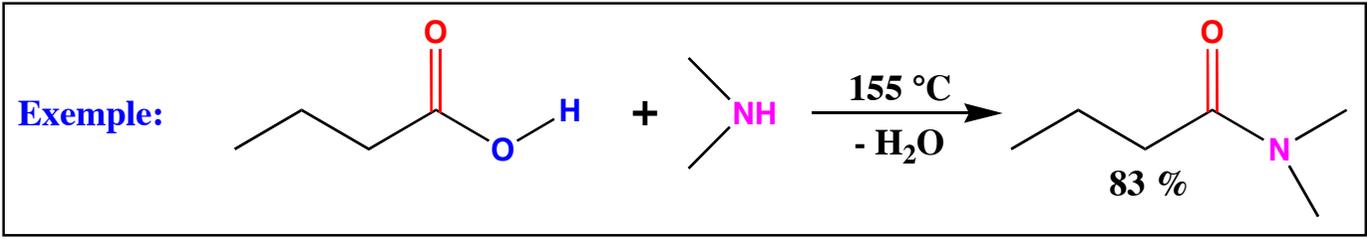
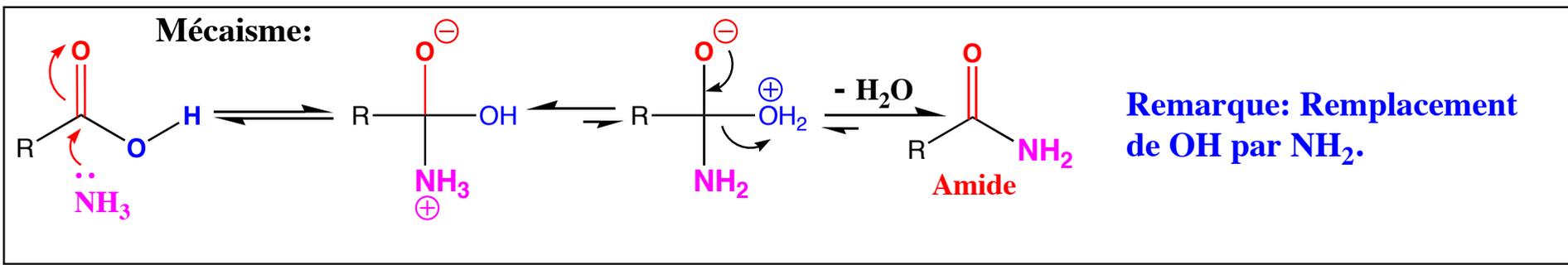
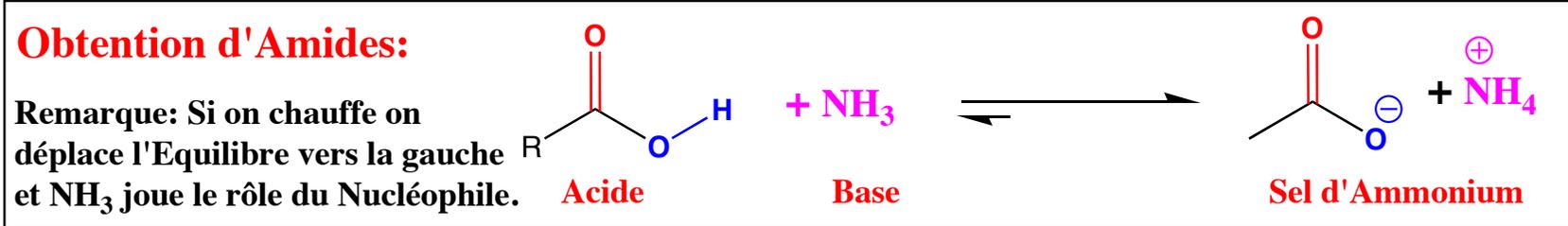
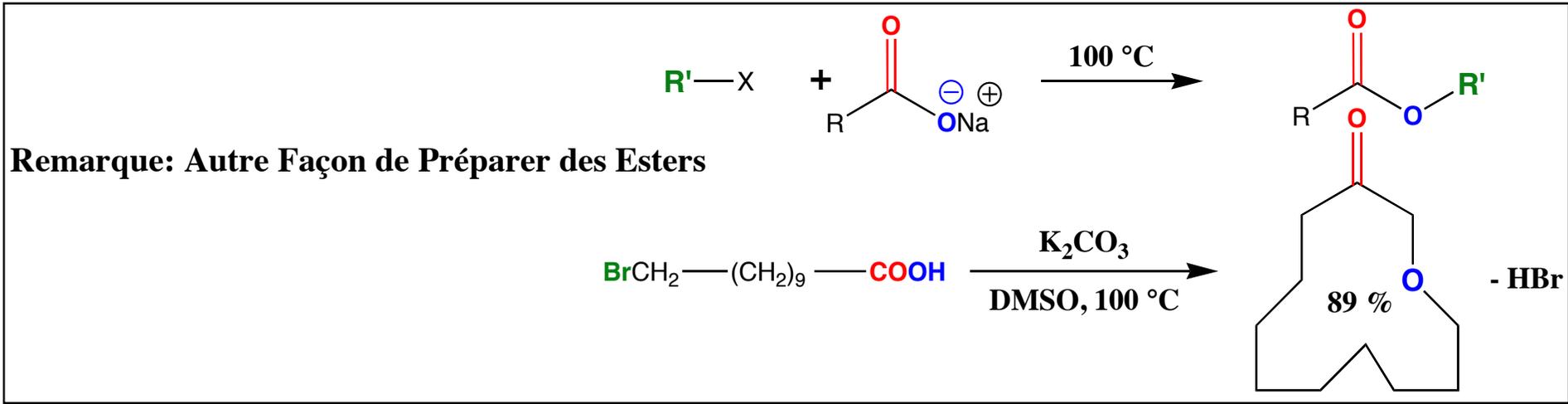
Réaction avec les Alccols: Mécanisme:

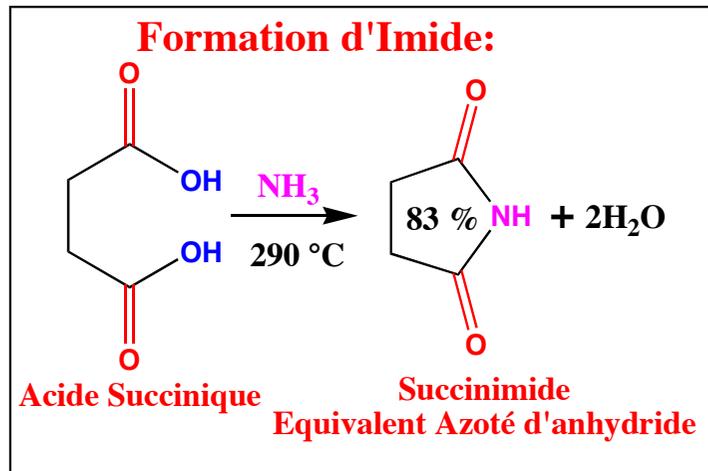


Remarque: Formation de Lactone ou Esterification Intramoléculaire.

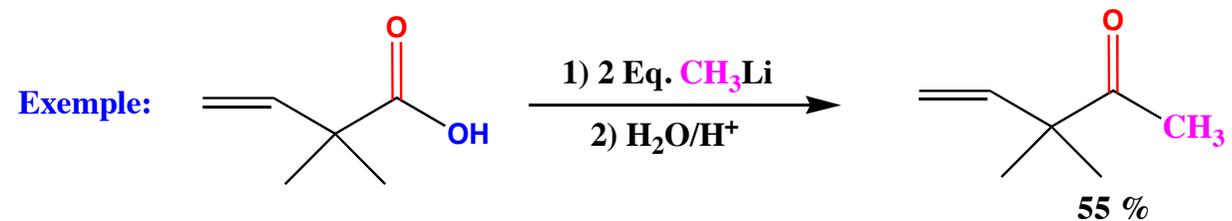
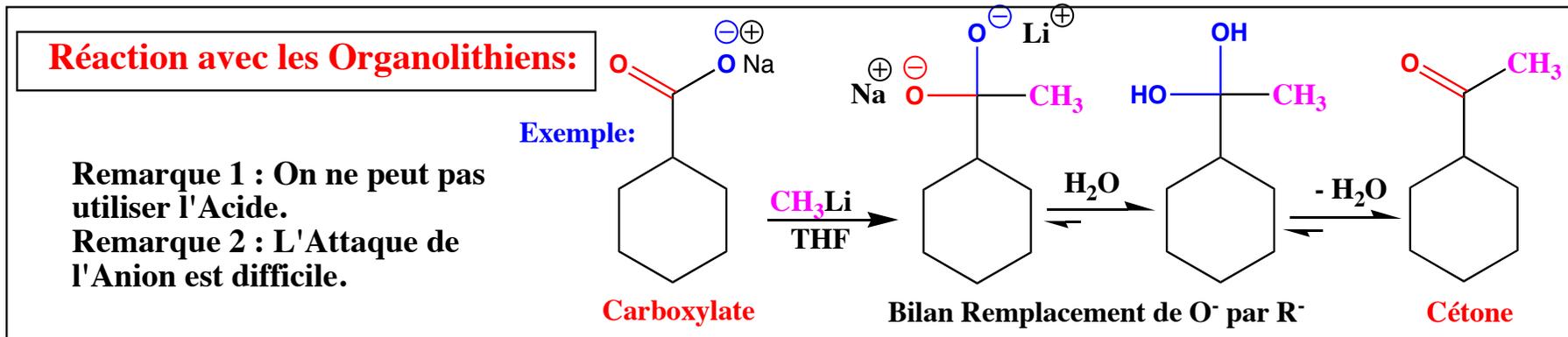
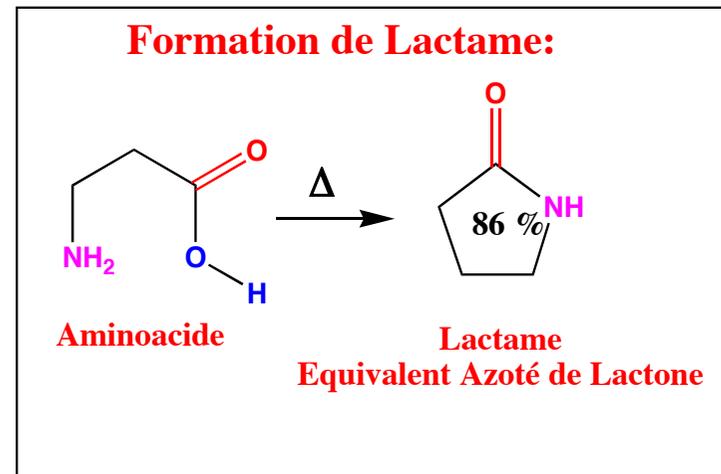
Exemples:



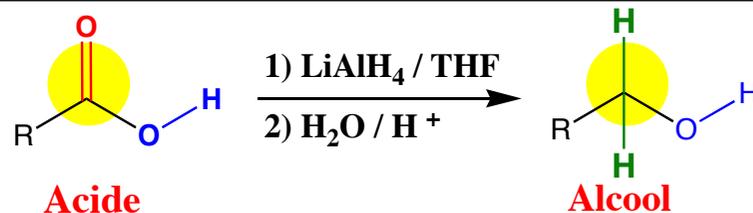




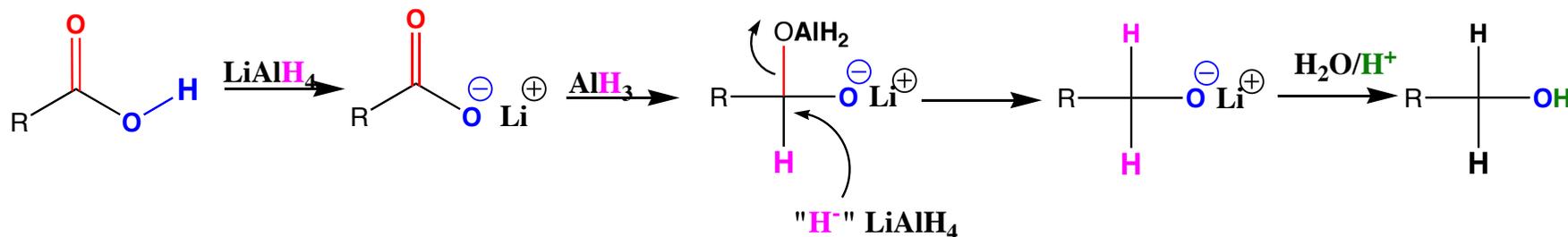
Exemples:



Réaction avec LiAlH_4 :

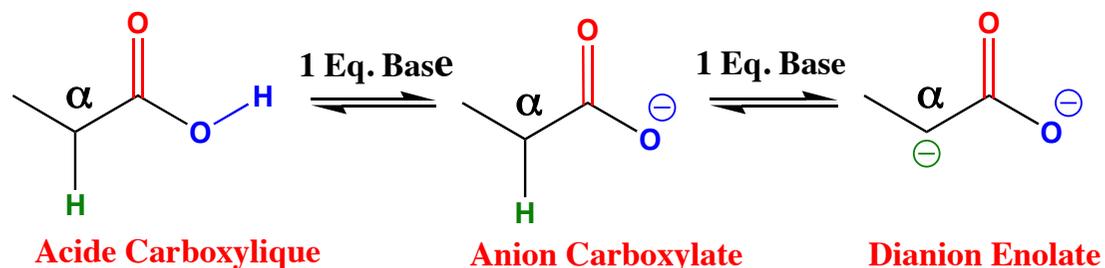


Mécanisme Possible:

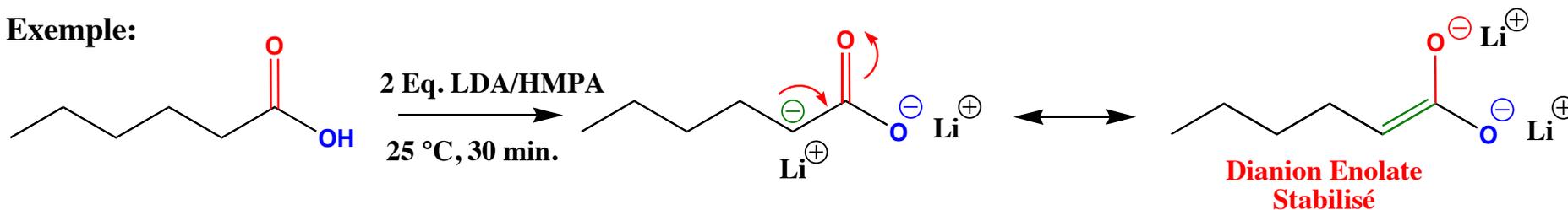


Réactivité du Carbone en α de COOH :

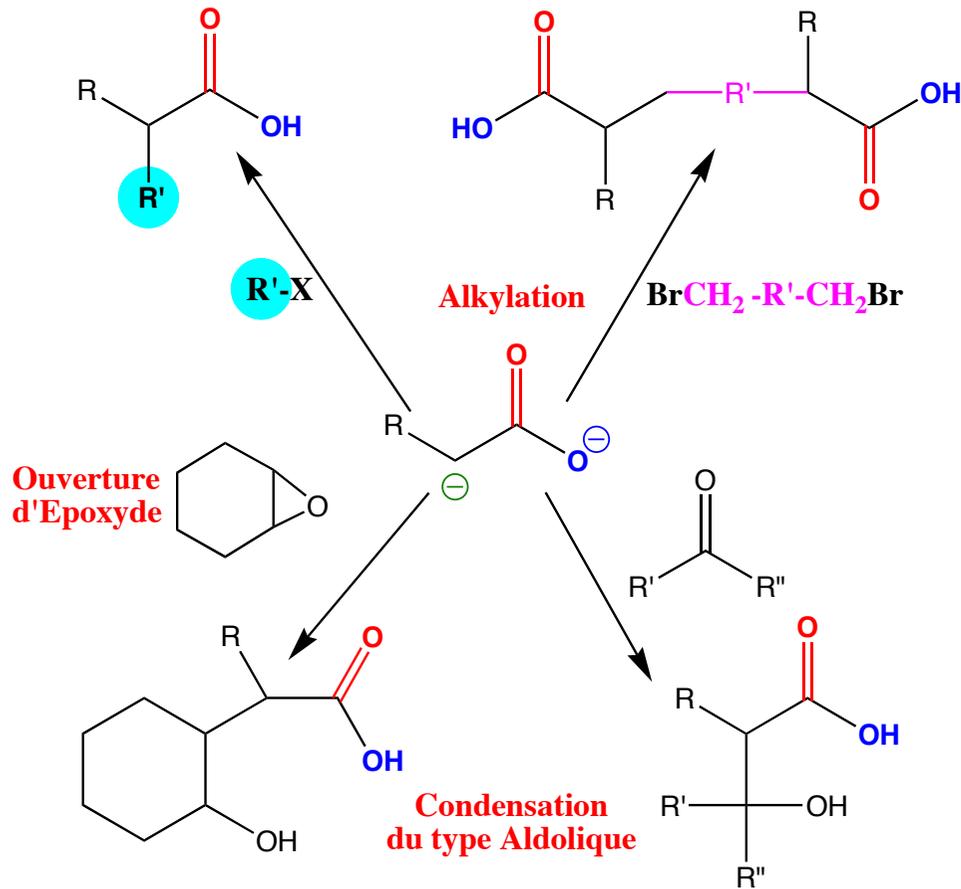
Remarque 1 : Comme tout composé dutype $\text{C}=\text{O}$, le proton en α est acide.
Remarque 2 : L'Enolate se forme dans un solvant APROTIQUE polaire (exemple : HMPA) en présence d'une base forte (exemple: LDA).



Exemple:



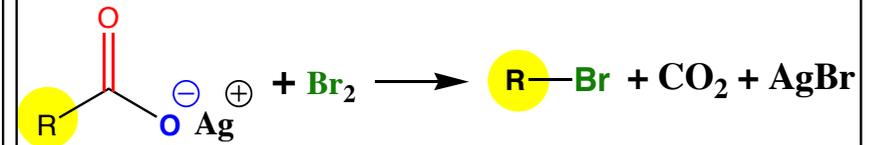
Réactivité du Dianion Enolate:



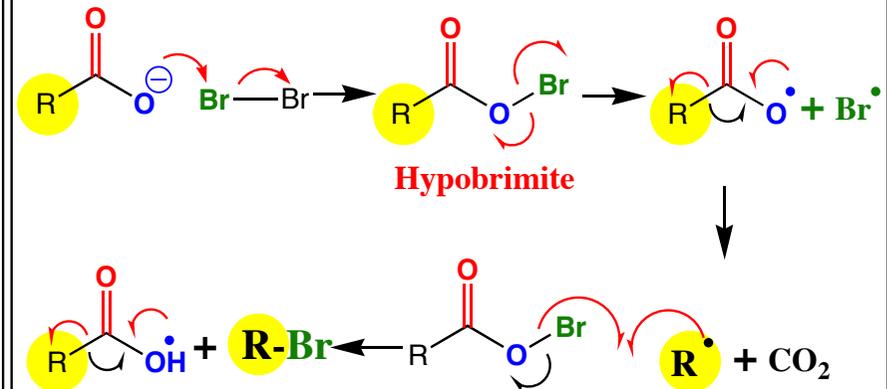
Remarque: L'Enolate est fortement Basique, Seul dans le cas des R-X primaires l'alkylation se fait. Dans les autres cas il y a Elimination.

Bromation des Acides Carboxyliques:

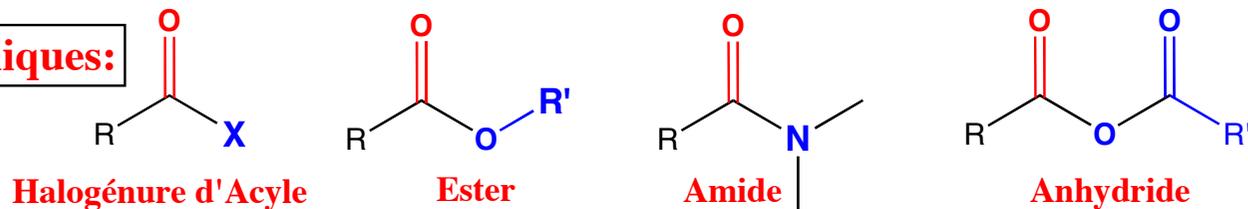
La Réaction de HUNSDIECKER:



Mécanisme:



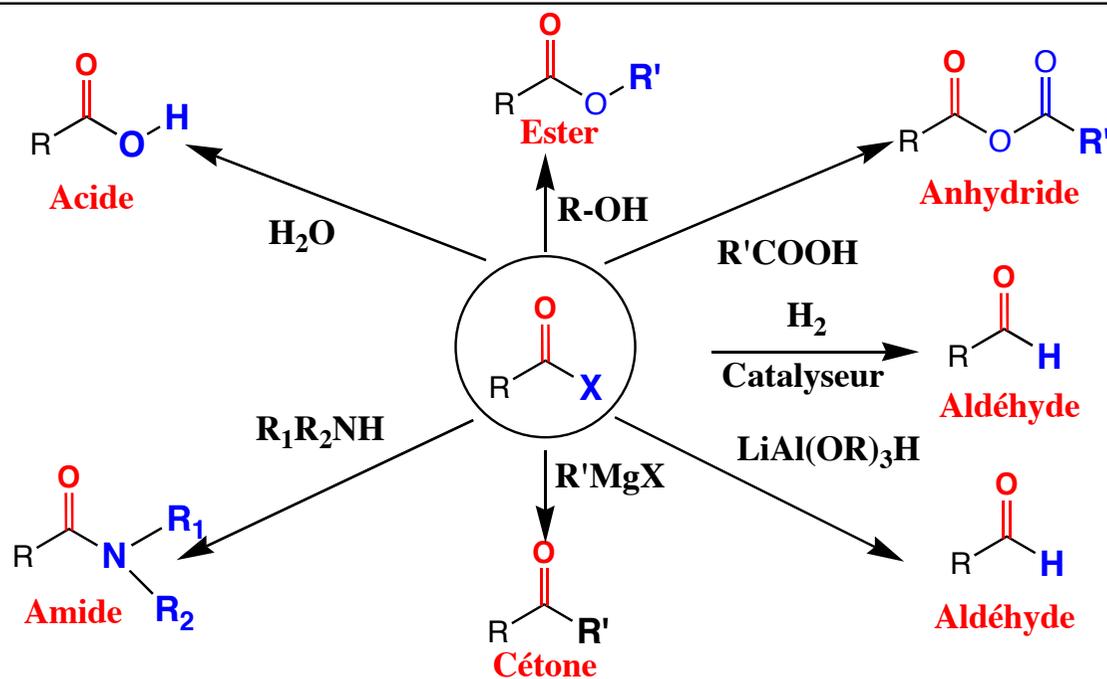
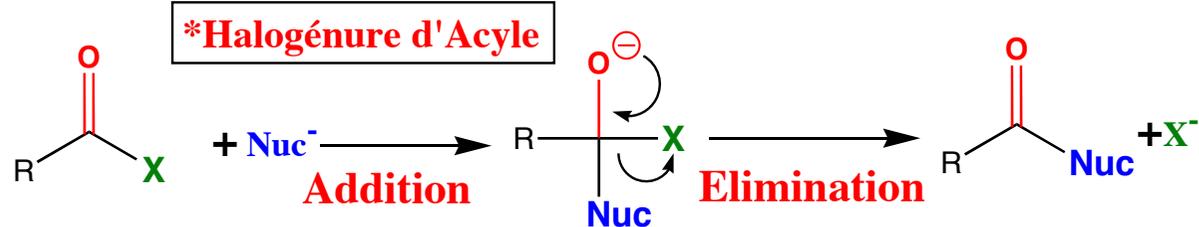
Les Dérivés d'Acides Carboxyliques:



Réaction avec les Nucléophiles

Mécanisme d'Addition - Elimination

Bilan: Remplacement de X^- par Nu^- .

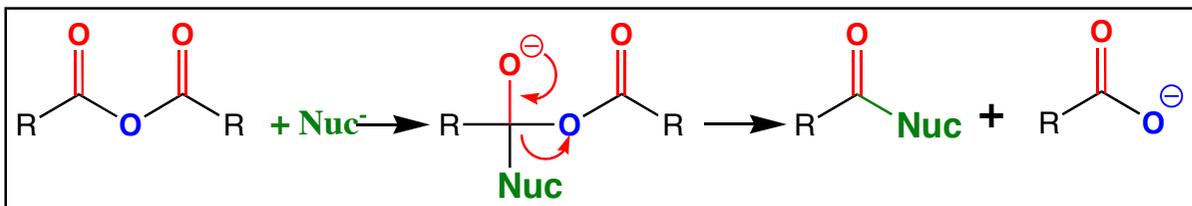


Remarque: En présence de LiAlH_4 , la fonction $\text{C}=\text{O}$ est réduite en Alcool ($\text{R}-\text{COX} + \text{LiAlH}_4$ donne $\text{R}-\text{CH}_2\text{OH}$).

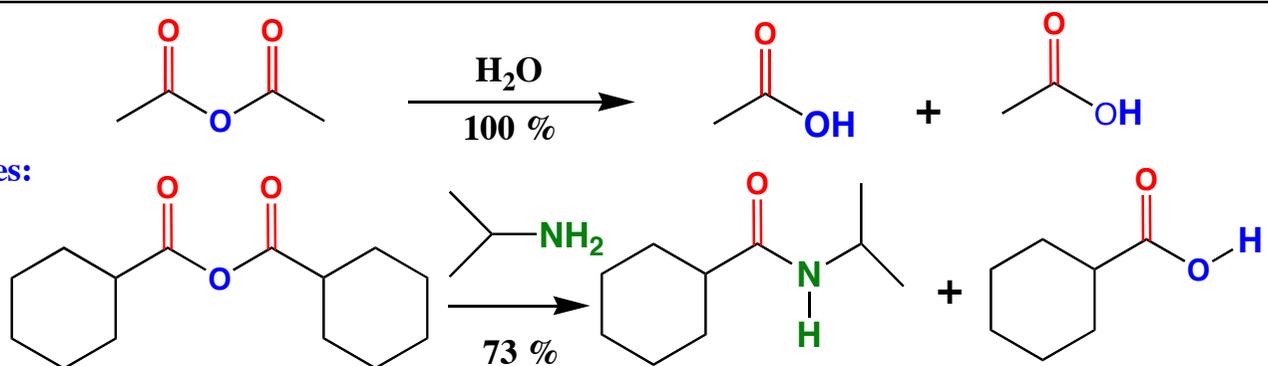
Les Anhydrides

Réaction avec les Nucléophiles

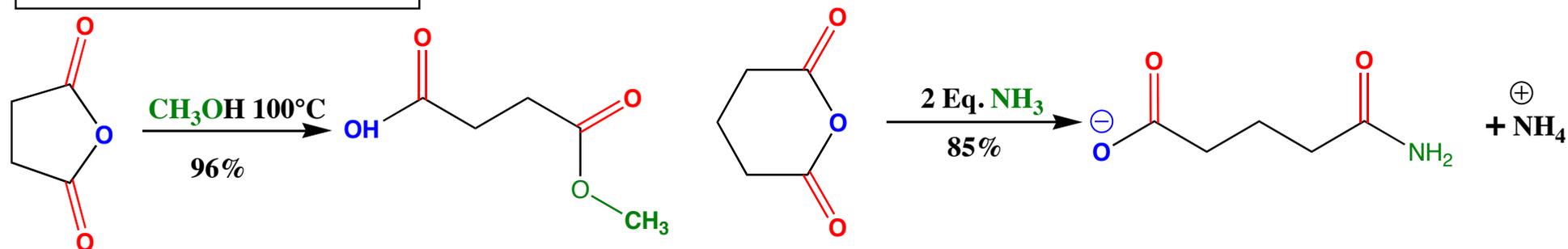
Mécanisme:



Exemples:

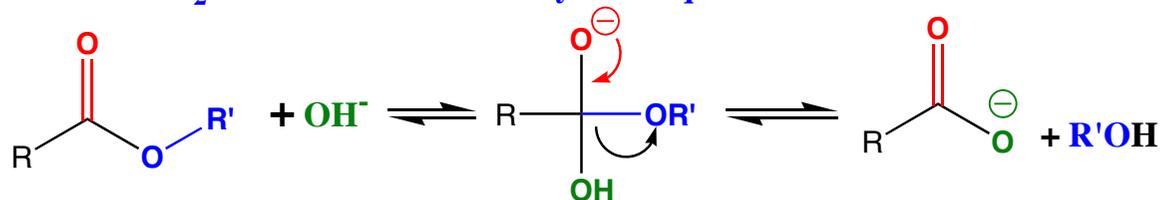


Les Anhydrides Cycliques:

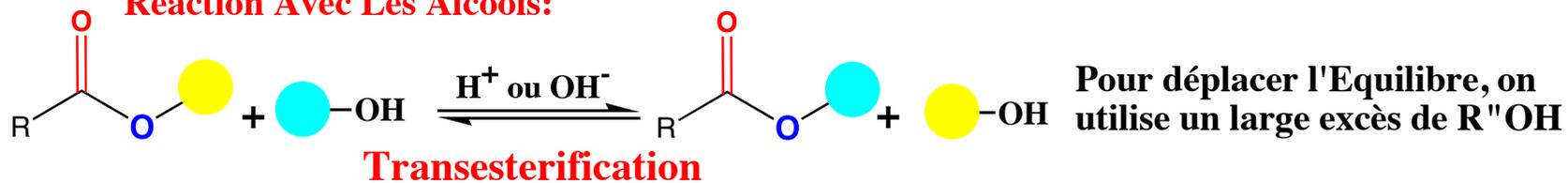


Réaction avec H_2O : Mécanisme en Catalyse Basique

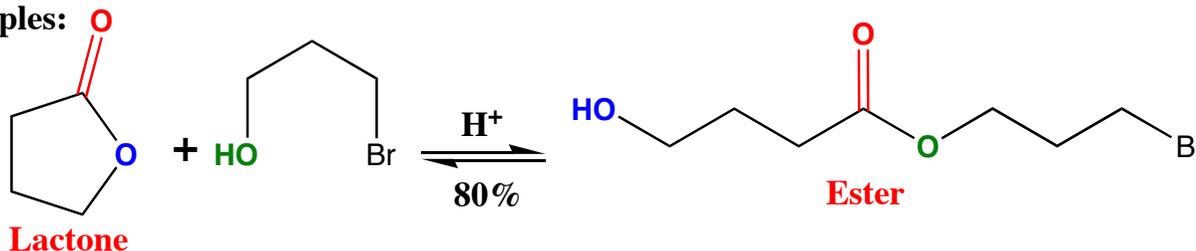
Les Esters:



Réaction Avec Les Alcools:

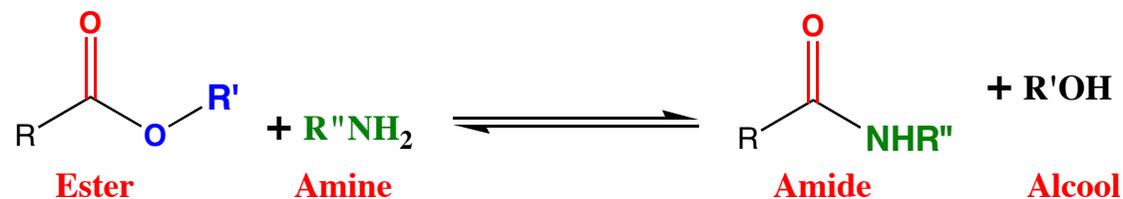


Exemples:

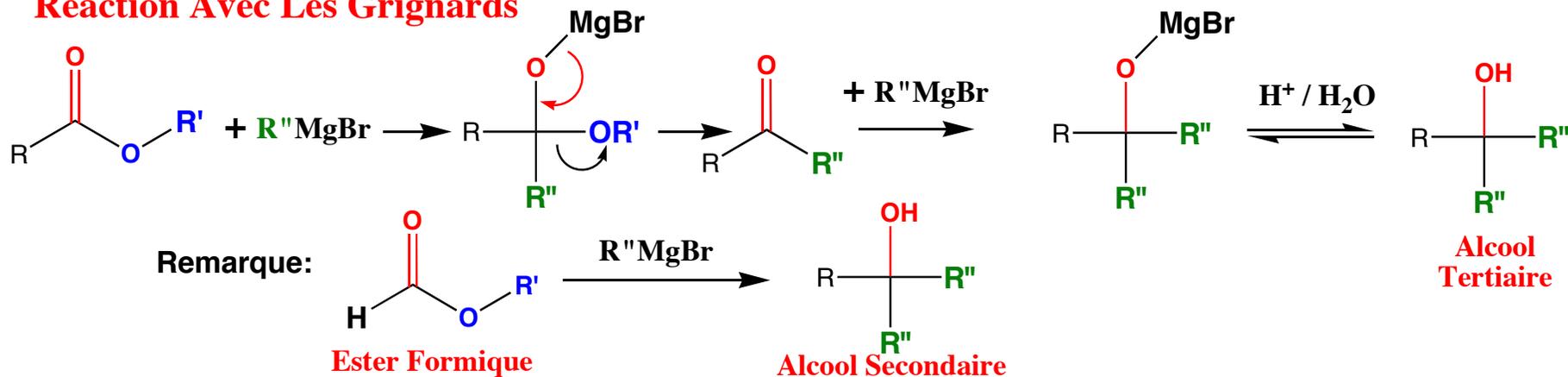


Remarque: la Réaction avec les Lactone (Ester Cyclique) Conduit à l'Ouverture du Cycle.

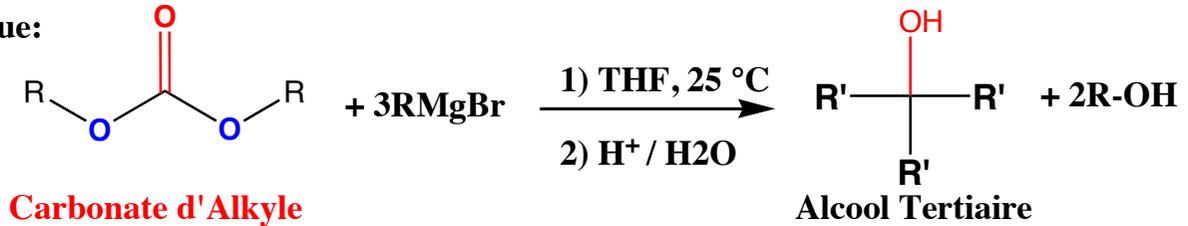
Réaction Avec Les Amines



Réaction Avec Les Grignards

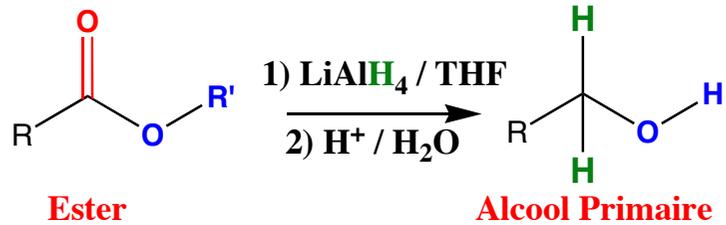


Remarque:

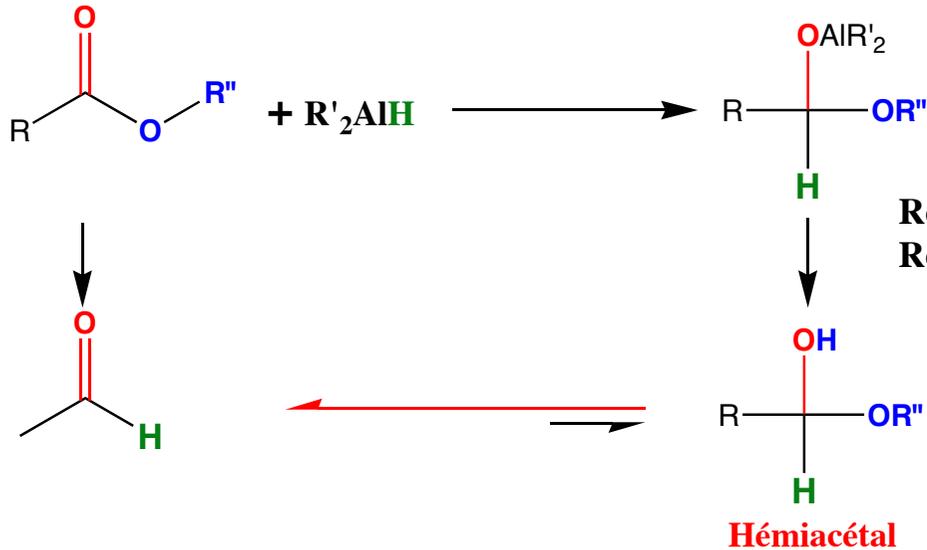
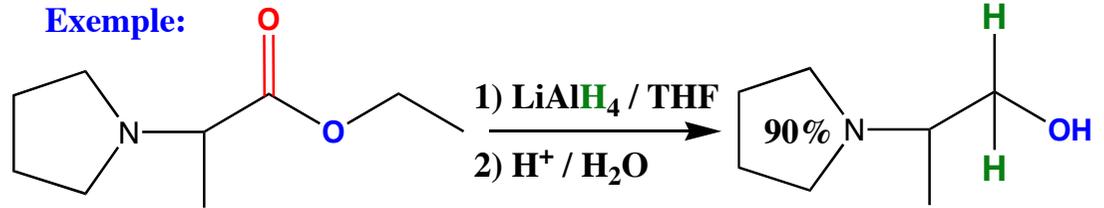


Une Bonne Méthode de Préparation d'Alcool Tertiaire.

Réduction des Esters:

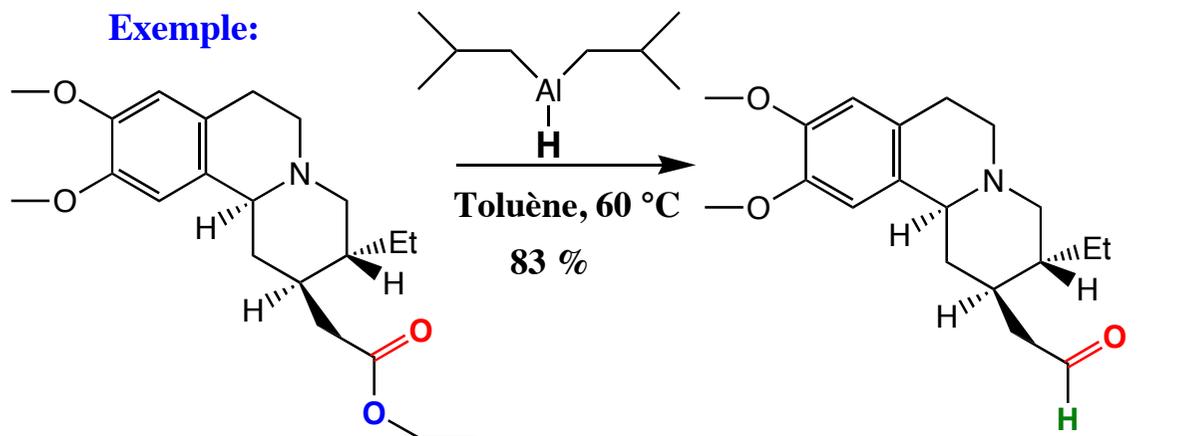


Exemple:

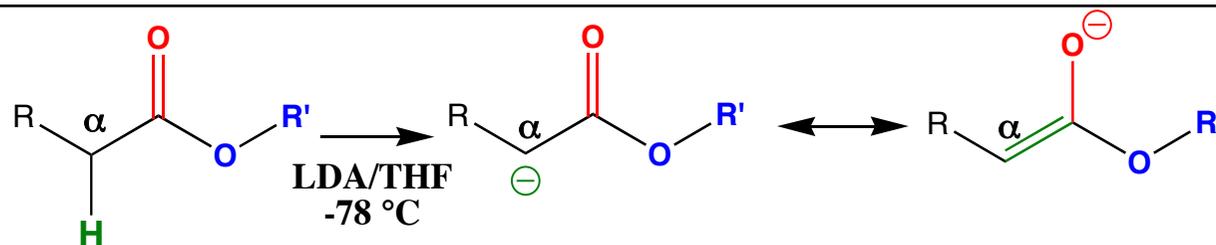


Remarque: Si l'on veut s'arrêter à l'Aldéhyde, on désactive le Réducteur ($\text{R}'_2\text{AlH}$).

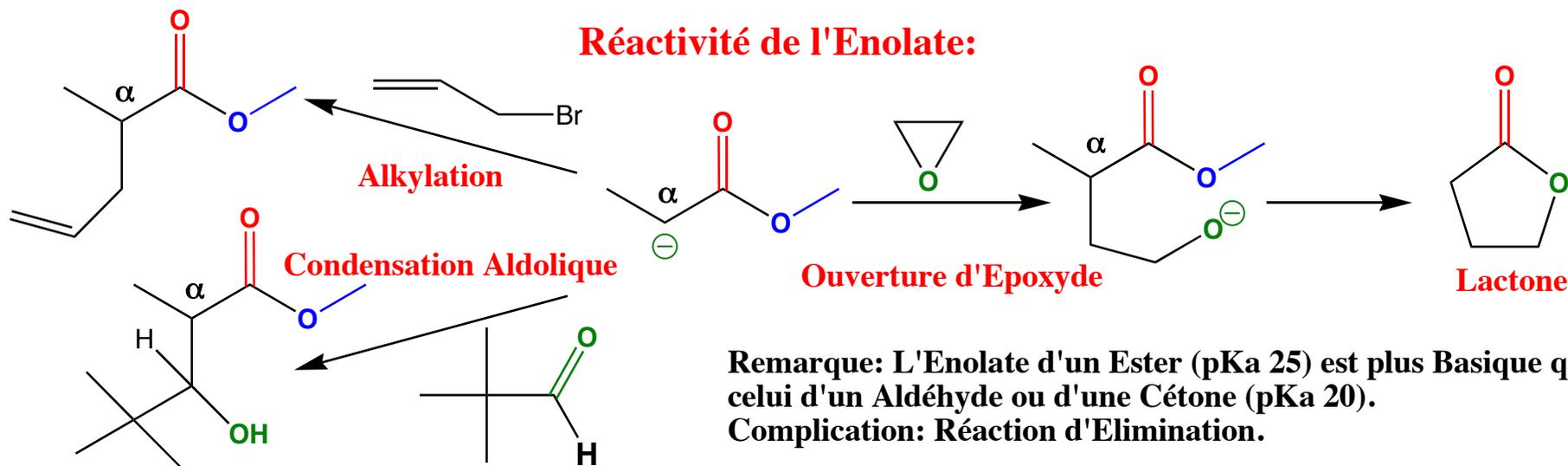
Exemple:



Formation d'Enolate:



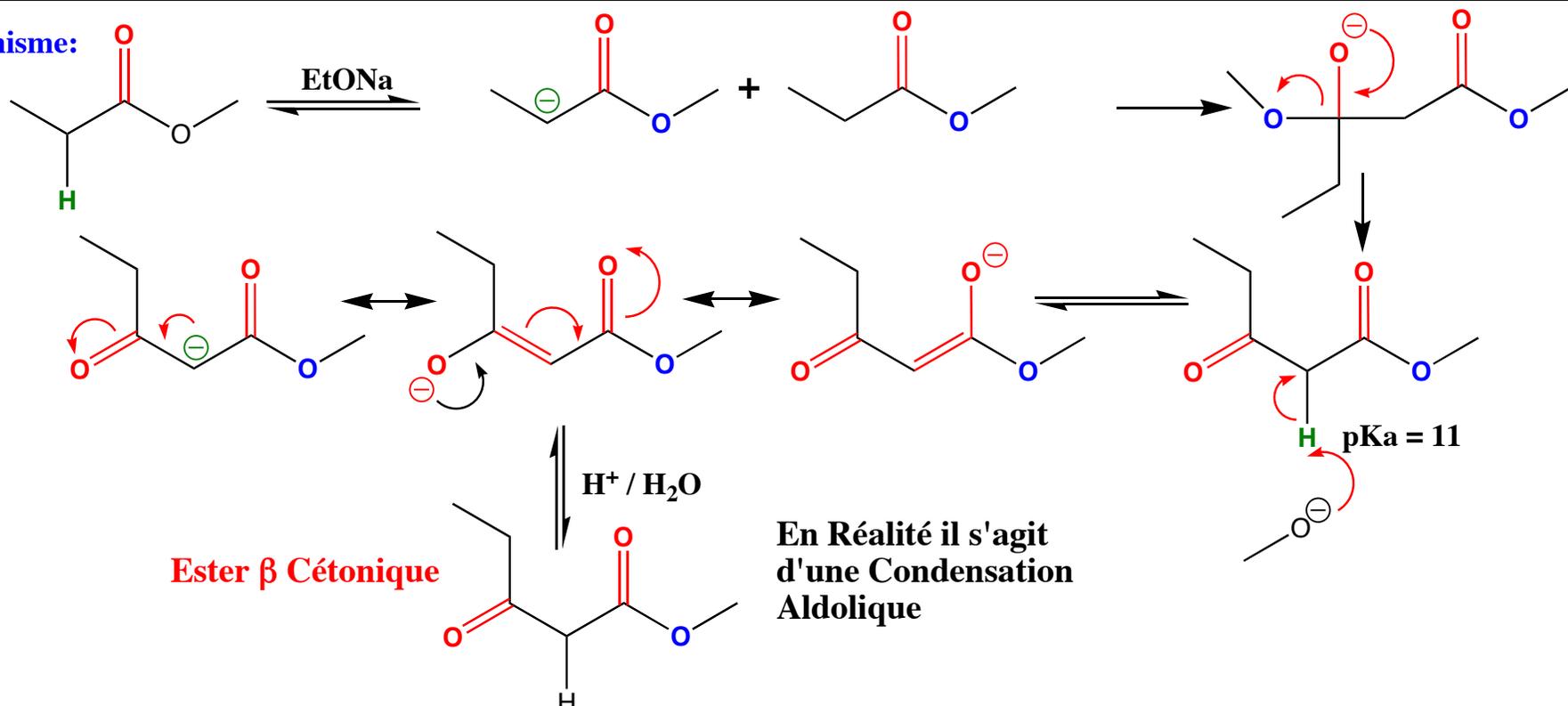
Réactivité de l'Enolate:



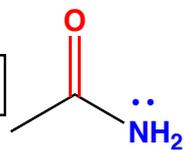
Remarque: L'Enolate d'un Ester (pKa 25) est plus Basique que celui d'un Aldéhyde ou d'une Cétone (pKa 20).
Complication: Réaction d'Elimination.

Condensation de Claisen:

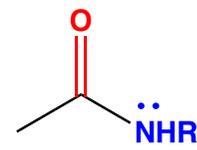
Mécanisme:



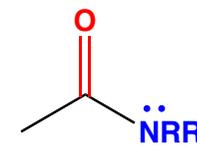
Les Amides:



Primaire

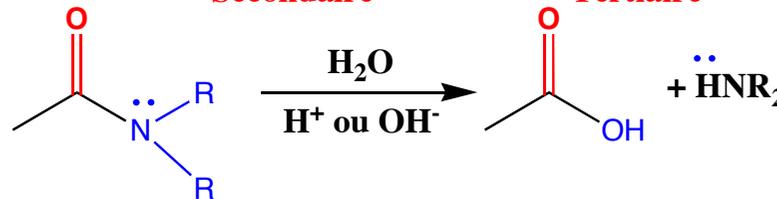


Secondaire

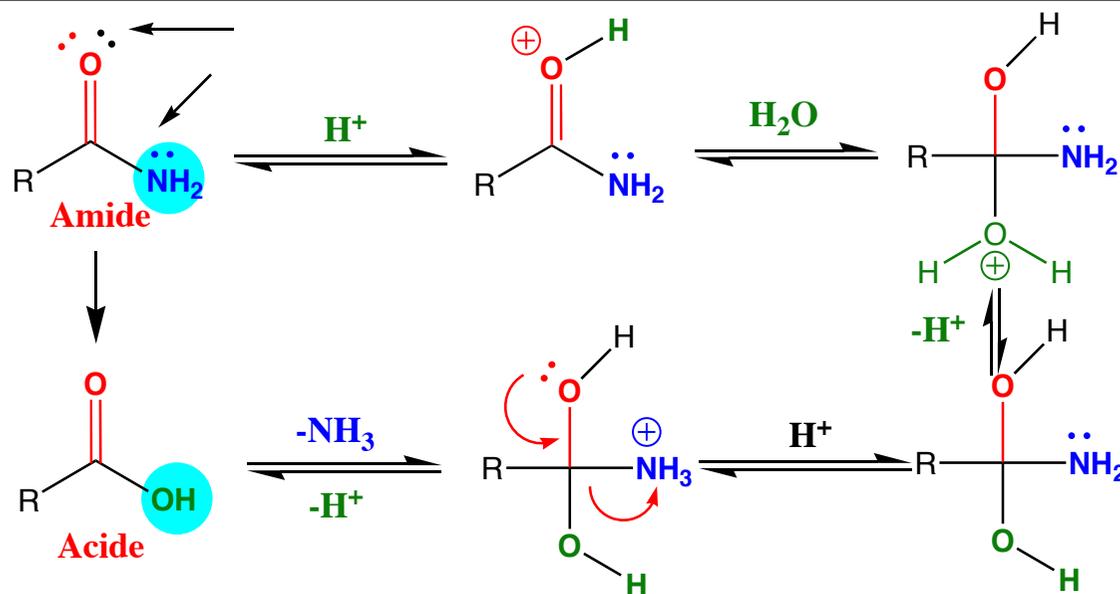


Tertiaire

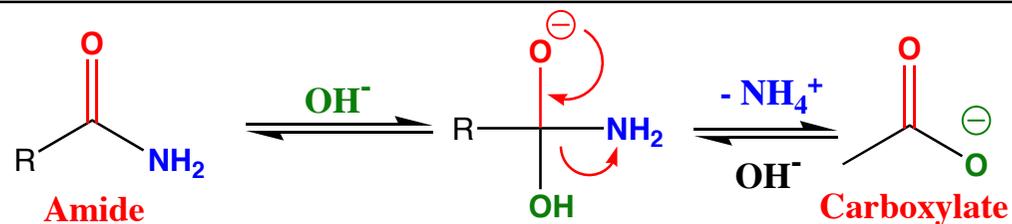
Réaction Avec H_2O :



Catalyse Acide:

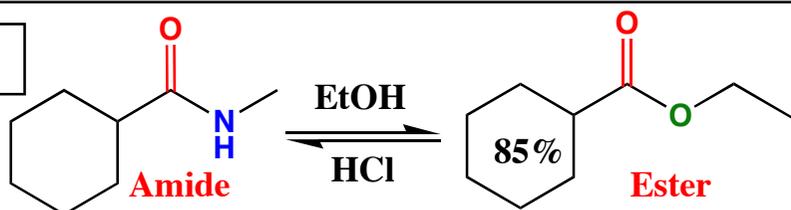


Catalyse Basique:



Réaction Avec les Alcools:

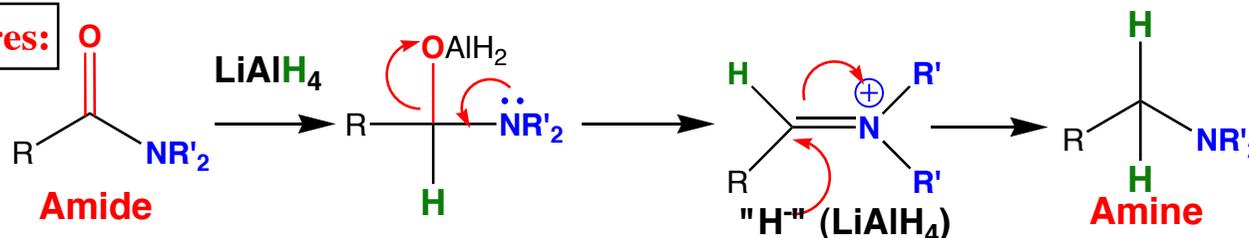
Exemple:

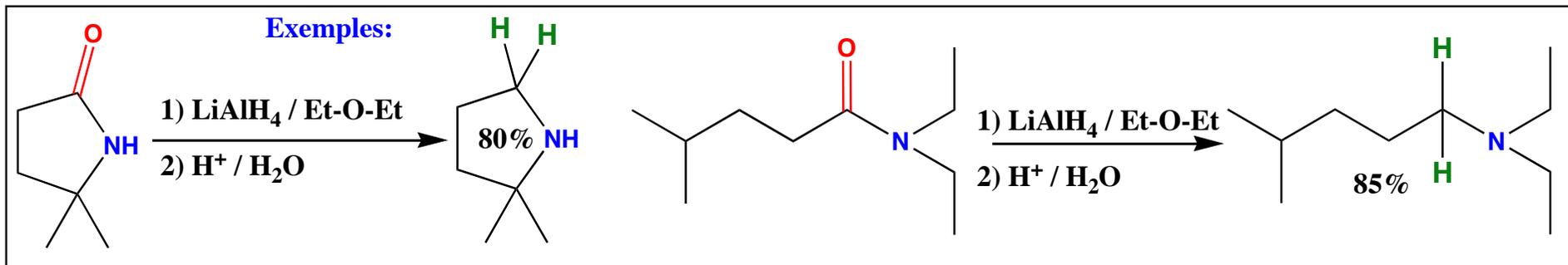


Remarque: Même Mécanisme que pour H₂O, On remplace H-O-H par R-O-H.

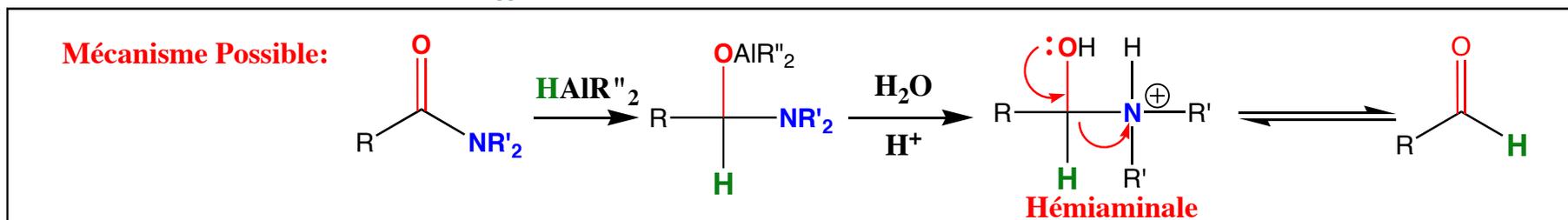
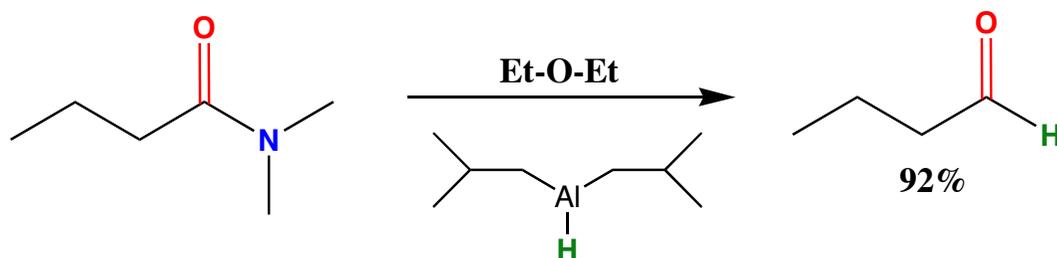
Réaction Avec les Hydrures:

Mécanisme Possible:

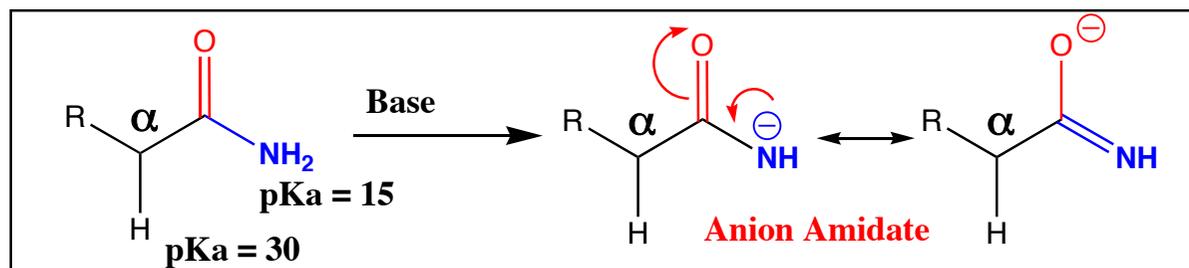




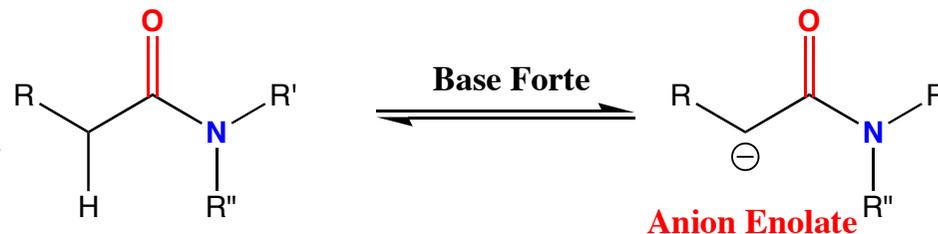
Remarque: Avec des Hydrures Particuliers, On Peut Transformer un Amide en ALDEHYDE.



Formation d'Enolate:

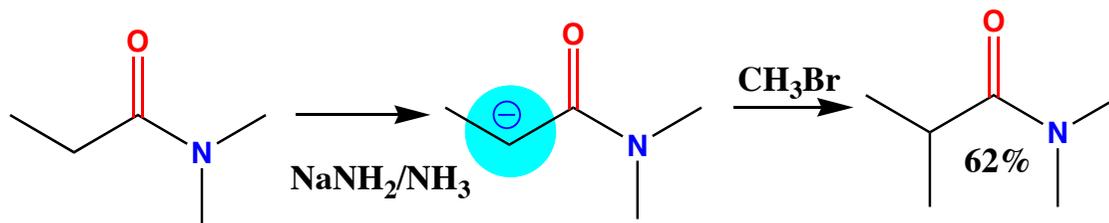
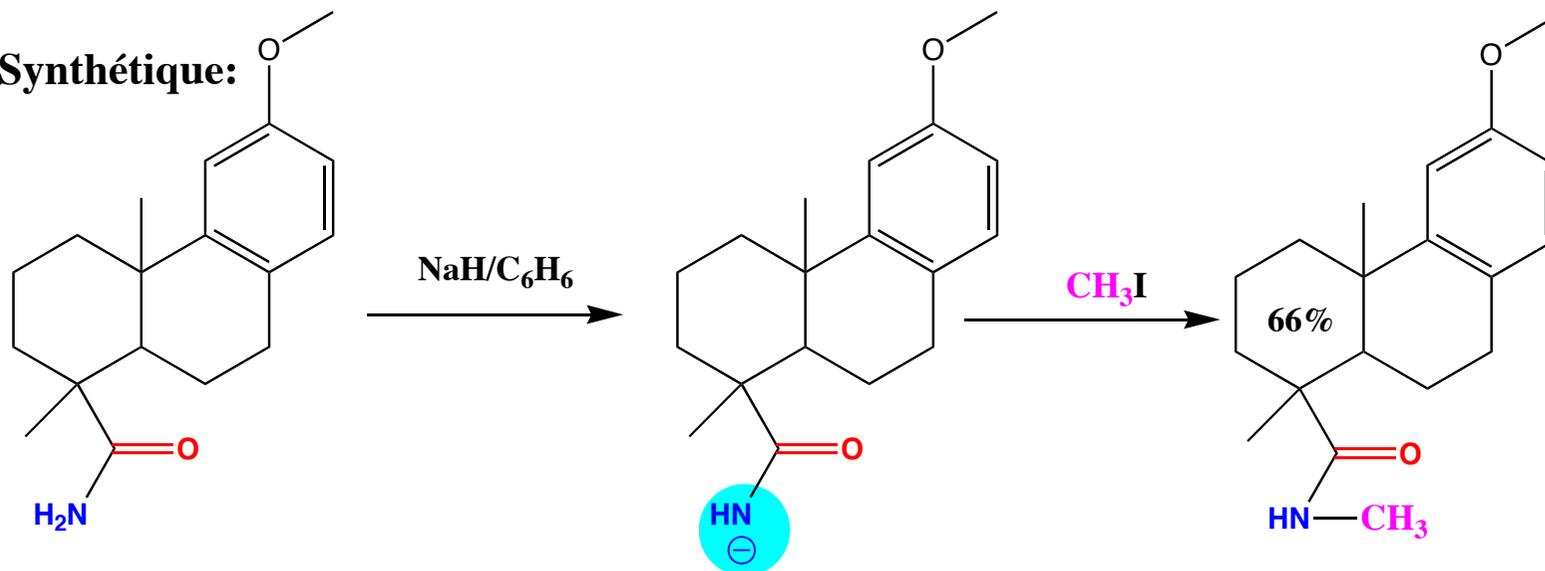


Remarque: NH plus Acide que CH en a du C=O, par conséquent il se forme l'Anion AMIDATE. Par contre, dans le cas d'Amide Tertiaire on peut former l'Anion Enolate.

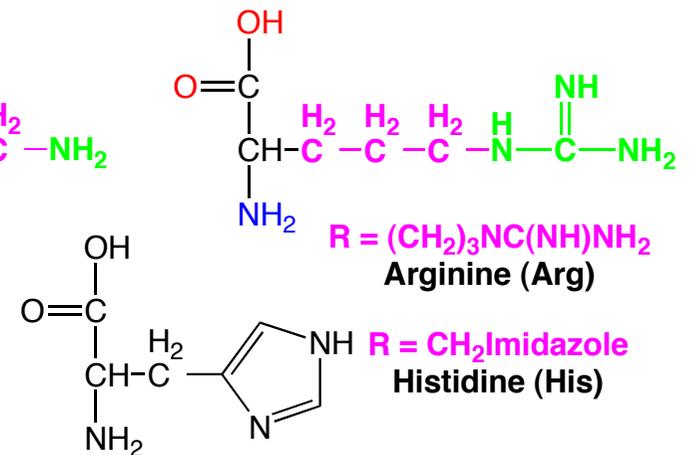
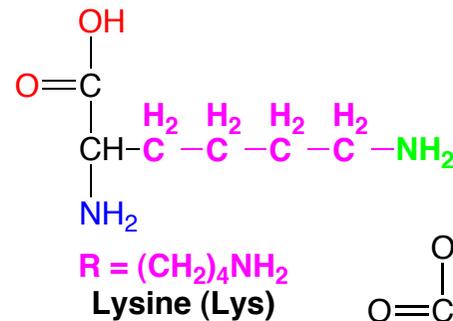
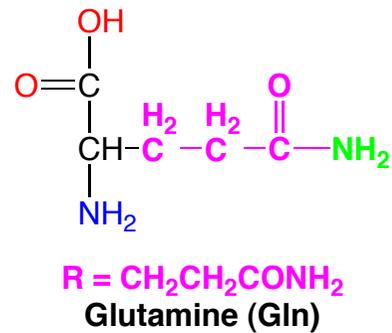
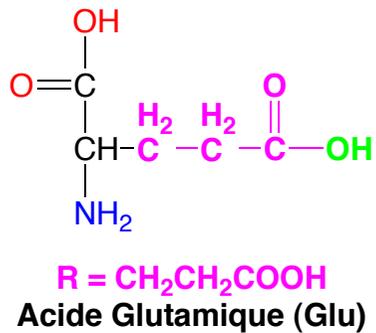
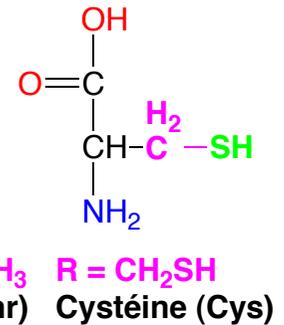
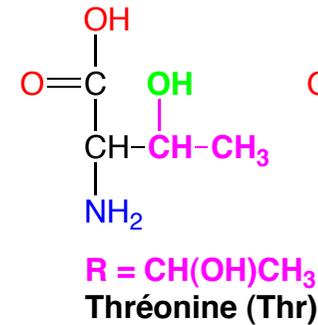
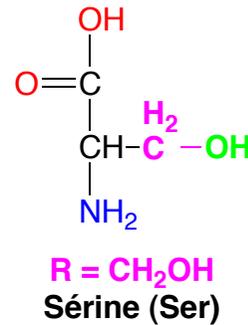
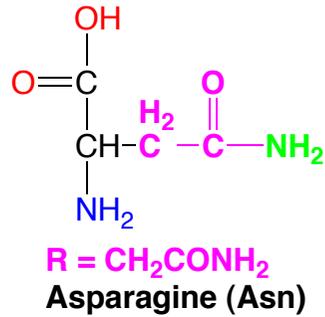
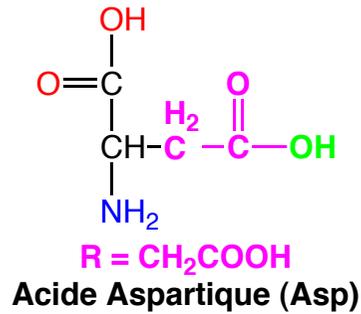
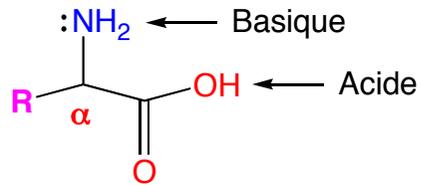


L'Anion Enolate et l'Anion Amidate sont Nucléophile.

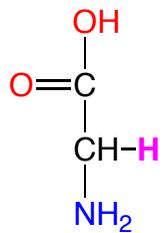
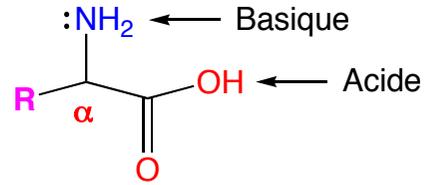
Application Synthétique:



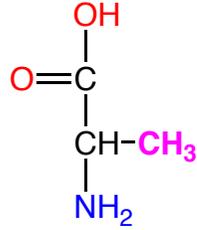
Aminoacides



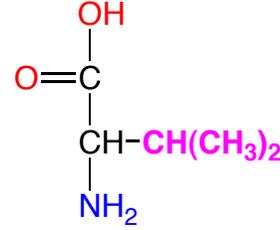
Aminoacides



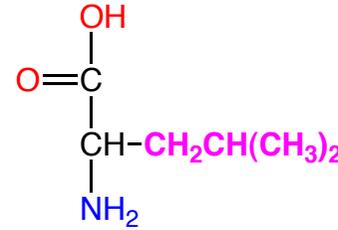
R = H
Glycine (Gly)



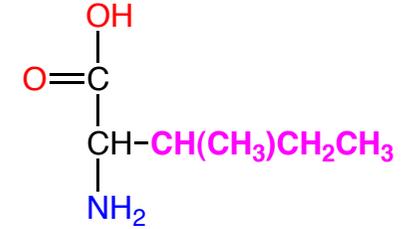
R = CH₃
Alanine (Ala)



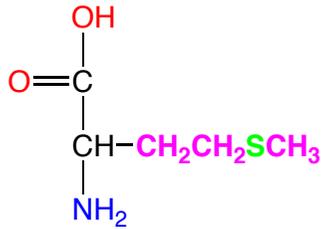
R = CH(CH₃)₂
Valine (Val)



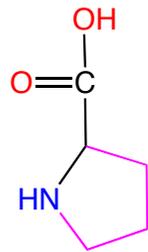
R = CH₂CH(CH₃)₂
Leucine (Leu)



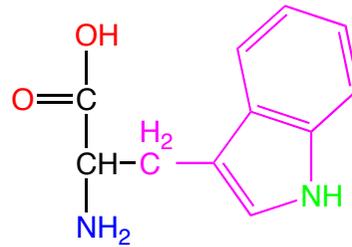
R = CH(CH₃)CH₂CH₃
IsoLeucine (Ile)



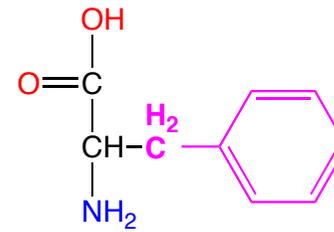
R = CH₂CH₂SCH₃
Méthionine (Met)



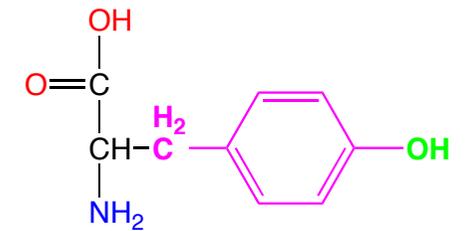
Proline (Pro)



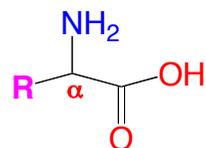
R = CH₂Indole
Tryptophane (Trp)



R = CH₂Ph
Phénylalanine (Phe)



R = CH₂PhOH
Tyrosine (Tyr)



	R apolaire	R ionisé	R polaire non chargé
C2	R = H Glycine (Gly)		
C3	R = CH ₃ Alanine (Ala)		R = CH ₂ OH Sérine (Ser) R = CH ₂ SH Cystéine (Cys)
C4		R = CH ₂ COOH Acide Aspartique (Asp)	R = CH ₂ CONH ₂ Asparagine (Asn) R = CH(OH)CH ₃ Thréonine (Thr)
C5	R = CH(CH ₃) ₂ Valine (Val) R = CH ₂ CH ₂ SCH ₃ Méthionine (Met) Proline (Pro)	R = CH ₂ CH ₂ COOH Acide Glutamique (Glu)	R = CH ₂ CH ₂ CONH ₂ Glutamine (Gln)
C6	R = CH ₂ CH(CH ₃) ₂ Leucine (Leu) R = CH(CH ₃)CH ₂ CH ₃ IsoLeucine (Ile)	R = (CH ₂) ₄ NH ₂ Lysine (Lys)	R = (CH ₂) ₃ NC(NH)NH ₂ Arginine (Arg)
> = 6	R = CH ₂ Ph Phénylalanine (Phe) R = CH ₂ PhOH Tyrosine (Tyr) R = CH ₂ Indole Tryptophane (Trp)	R = CH ₂ Imidazole Histidine (His)	

