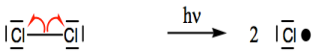
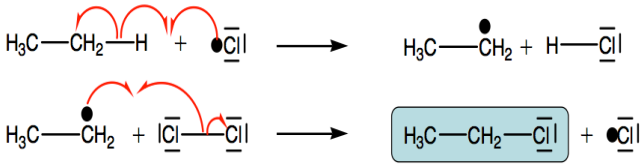
REACTIONS DE CHIMIE ORGANIQUE

Halogénation d'alcane

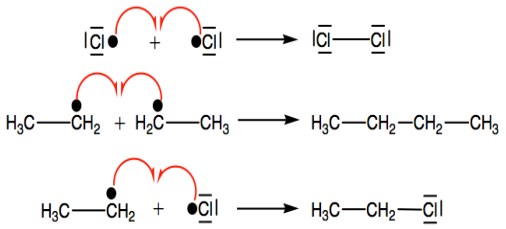
✓ **phase d'initiation** : formation des radicaux X• (Cl•) par **photochimie (hν)**



✓ **phase de propagation** : formation des produits

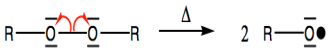


phase de terminaison (de rupture) : n'importe quel radical présent réagit avec n'importe quel autre pour fournir une espèce non réactive, puis la réaction en chaine s'arrête.

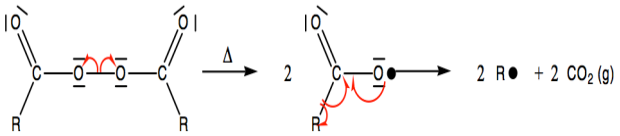


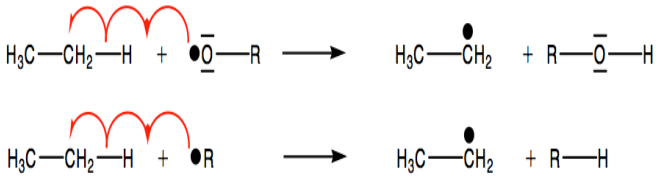
A) L'initiation peut être réalisée par chauffage d'espèces instables (peroxydes ou peracides) **Puis 2ème étape** où le radical In• fournit avec une molécule d'alcane un **carboradical**.

Peroxydes :



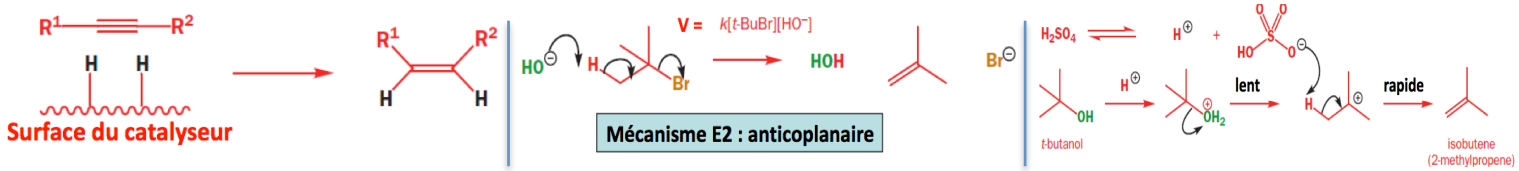
Peracides :



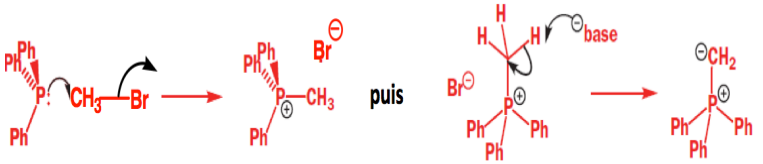


Formation d'alcène

Réduction Z Alcyne / catalyseur Lindlar *Déshydrohalogénation* *Déshydratation*

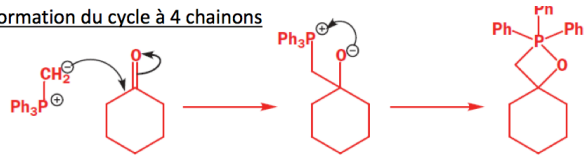


Reaction de wittig



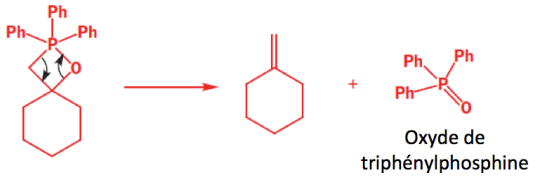
NB : Ylure stabilisé -> E / non stabilisé -> Z

1) Formation du cycle à 4 chainons



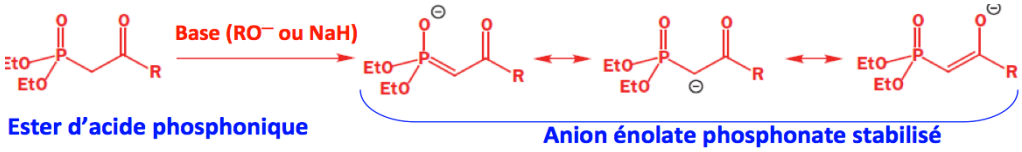
Oxaphosphétane (instable)

2) Décomposition du cycle à 4 chainons

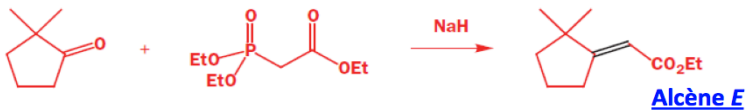


Oxyde de triphénylphosphine

Reaction de wittig-honer



Réaction HWE :

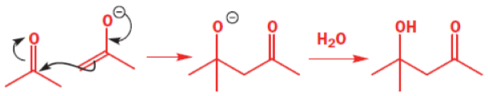


Réaction d'Horner–Wadsworth–Emmons (HWE)
(ou Horner–Emmons, Wadsworth–Emmons, ou encore Horner–Wittig)

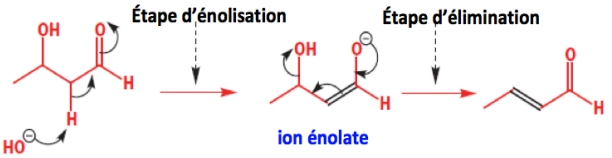
Aldolisation *Crotinisation*

1) Formation énolate :

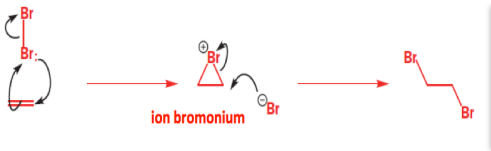
2) Aldolisation (C-C) :



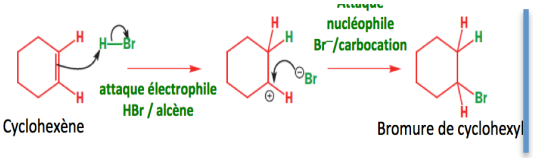
Elimination H_2O en milieu basique !!!! Par mécanisme E1cB (2 étapes) :



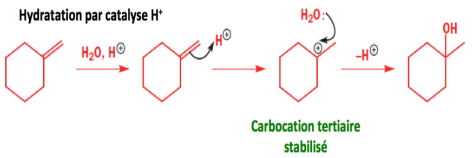
Dihalogénation



Hydrohalogénation

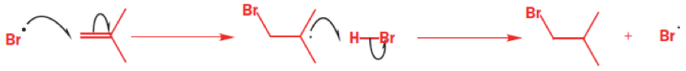


Hydratation

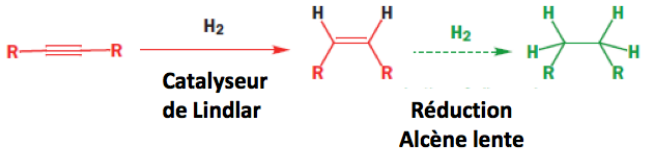


Hydrohalogénation par reaction radicalaire, Karash

Initiation peroxyde



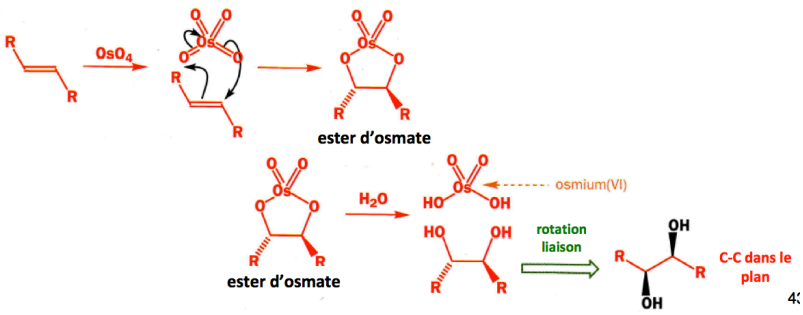
Reaction de reduction, *hydrogénation*

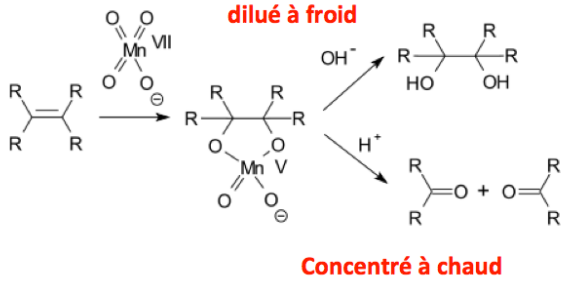


Reaction d'oxydation : *1) Epoxydation*

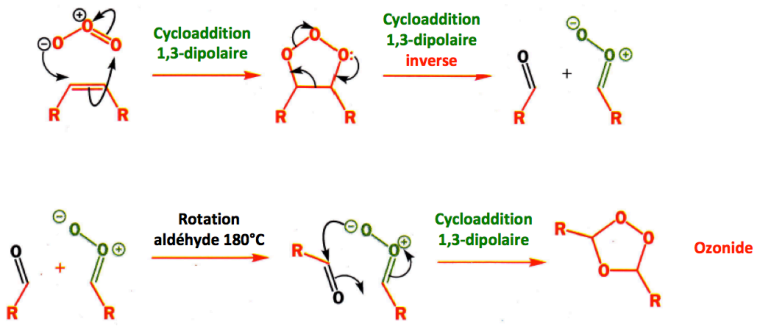
Epoxydation est stéréospécifique : *cis*-alcènes→ *cis*-époxyde et *trans*-alcènes → *trans*-époxyde.

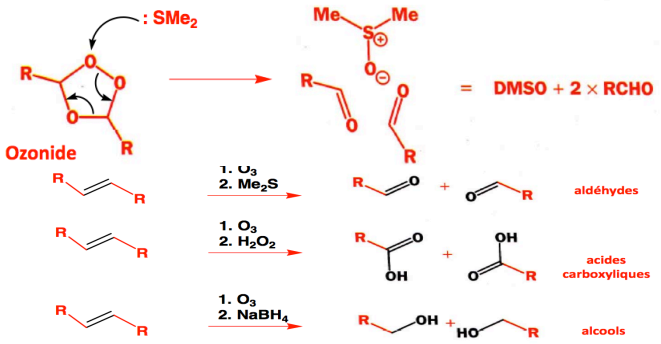
2) dihydroxylation





3) Ozonolyse, cycloaddition

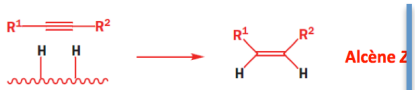




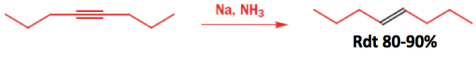
Alcyne

Réduction

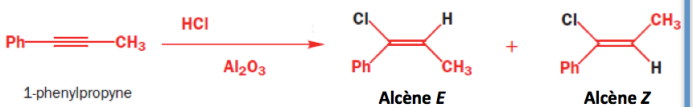
A : **Catalyseur de Lindlar** = $Pd/CaCO_3$, $Pb(OAc)_2$



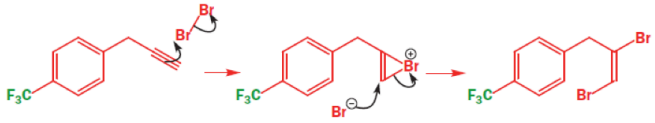
B : **Réduction de Birch**



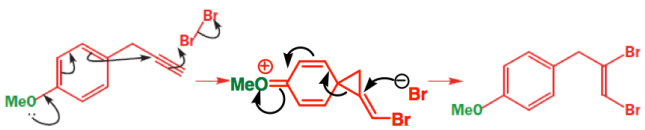
Hydrohalogénation



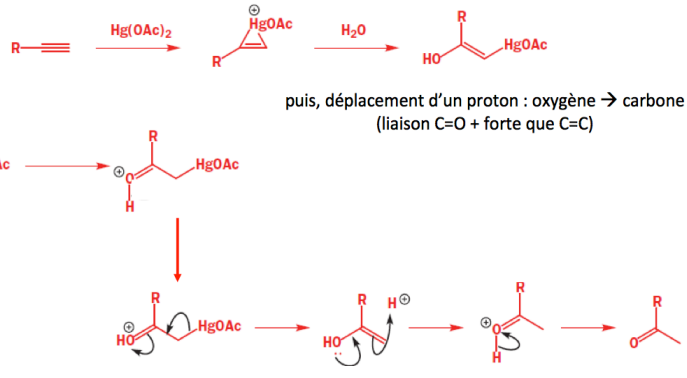
Halogénation



addition anti

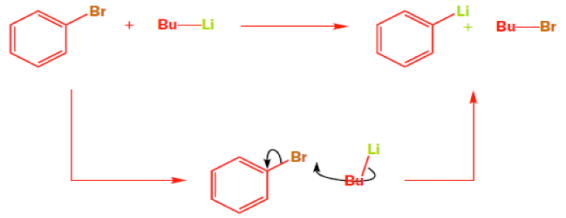


Hydratation

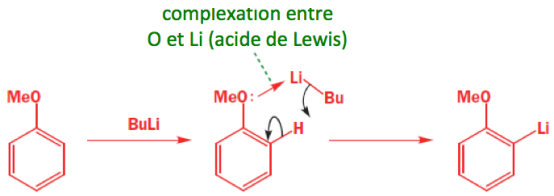


Dérivé halogéné et organométallique

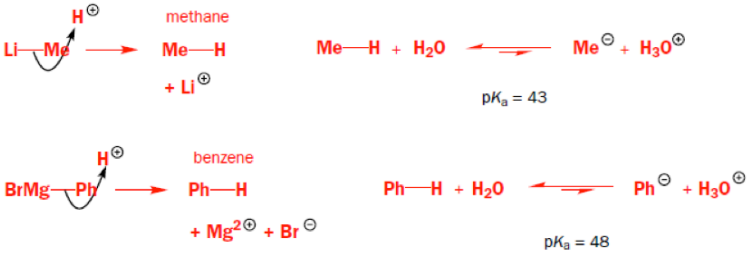
Echange Halogène/Métal



Ortholithation

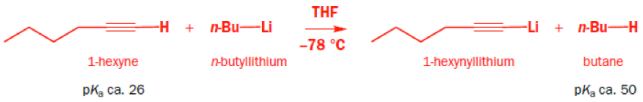


***Reactivité des orgonométallique** : 1) comme base*

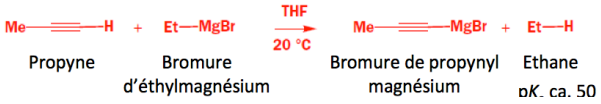


2) Avec Alcynes

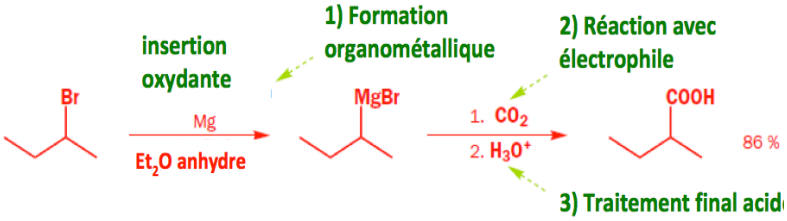
*** Formation alcynure de lithium :**



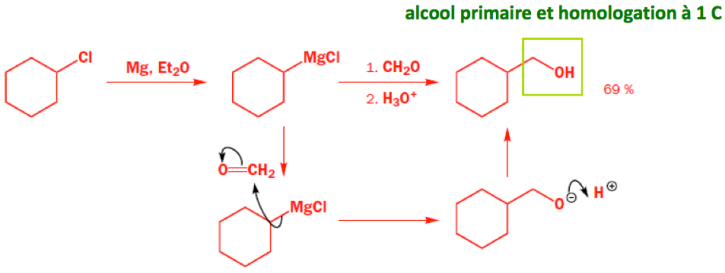
*** Formation Bromure d'alcynyl magnésium :**



3) Obtention d'acide

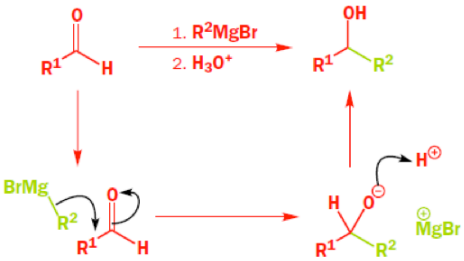


3) Obtention d'alcool primaire

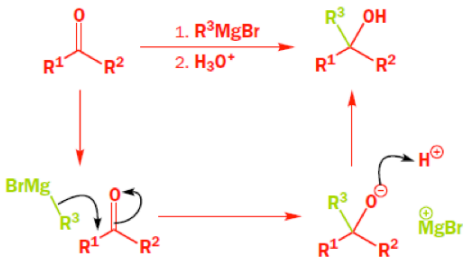


3) Obtention d'alcool secondaire et tertiaire

aldéhydes

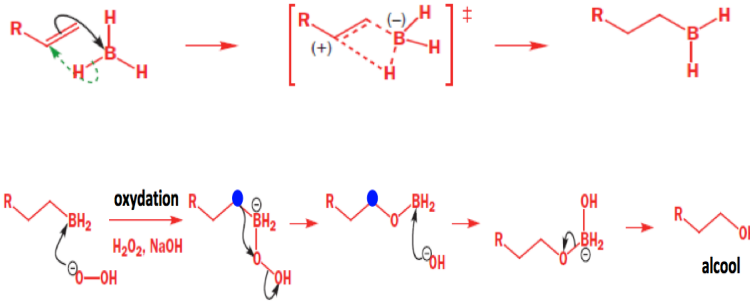


cétones

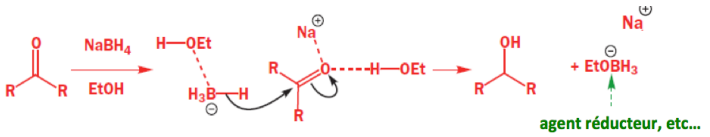


Carboxyliques, Esters, Amides

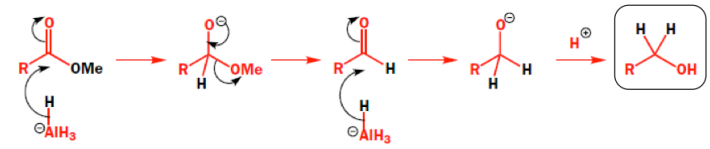
***Obtention d'alcool** : 1) Hydroboraton et oxydation*



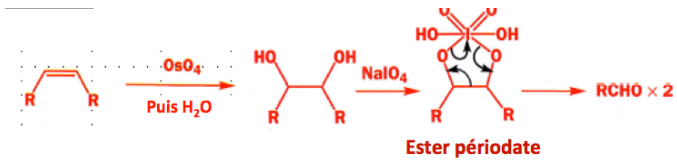
Reduction de fonctions carbonyle



Reduction de fonctions carboxyle

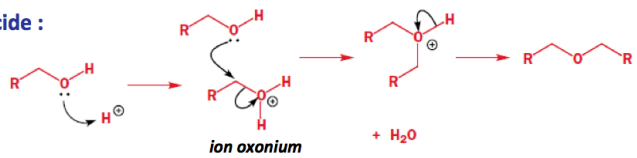


***Réactivité d'alcool** : 1) Coupure 1,2 diols*



Formation d'ether

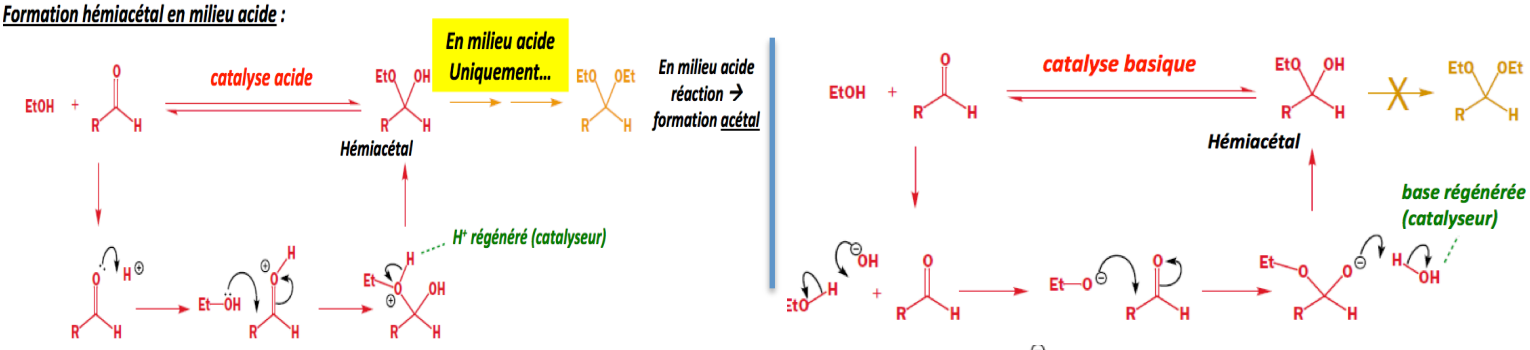
Milieu acide :



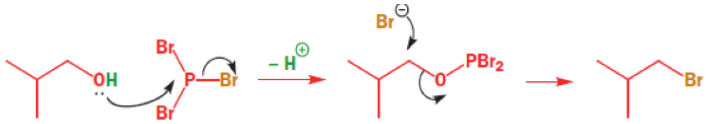
Milieu basique :

Formation hémiacétal et hémicétal

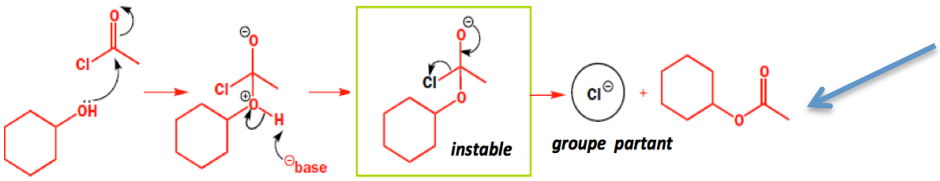
Formation hémiacétal en milieu acide :



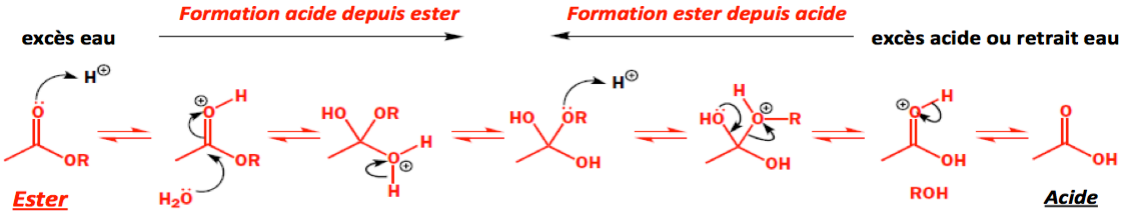
Formation composé halogéné



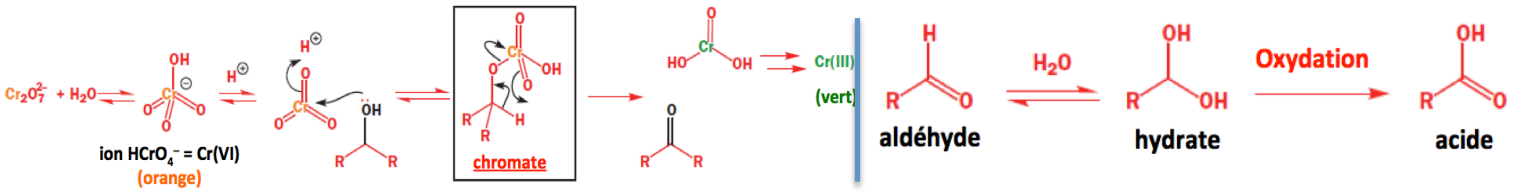
Formation d'esters



Peut se faire à partir d'anhydride



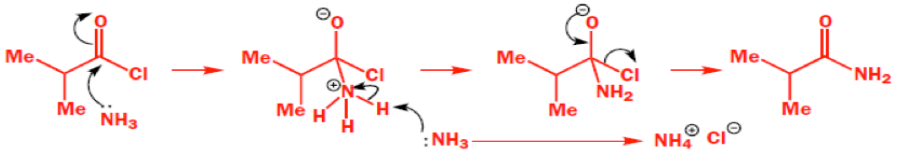
Oxydation des alcools



Avec alcool primaire -> Aldéhydes

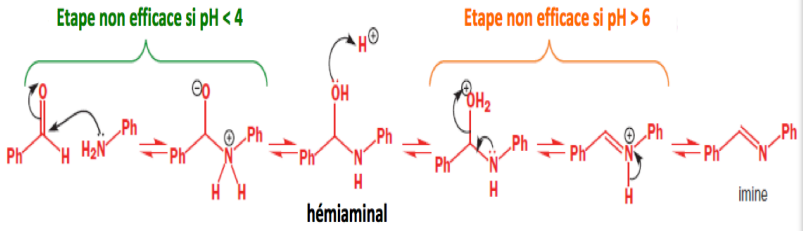
Suite de la réaction

Réactivité des amines *: 1) Formation amide*

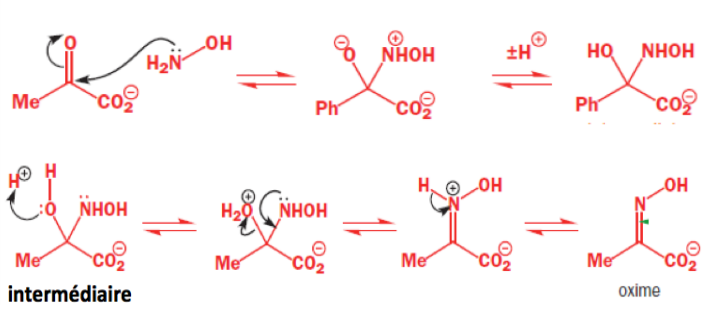


Peut se faire également à parti d'un ester

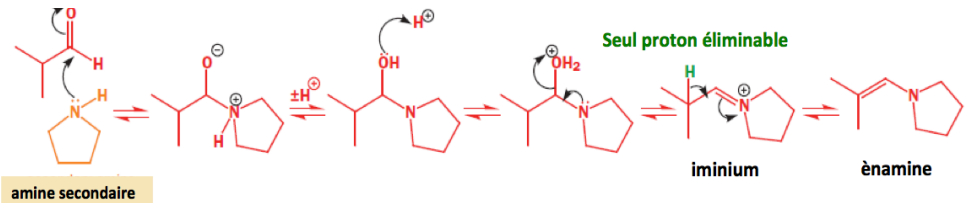
2) Formation d'imines



3) Formation d'oximes



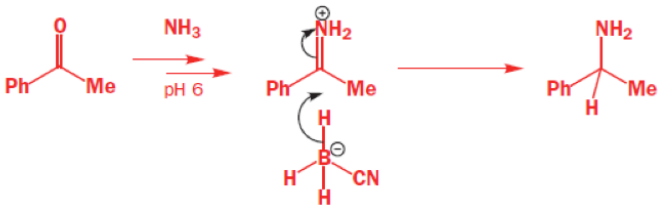
4) Formation énamine



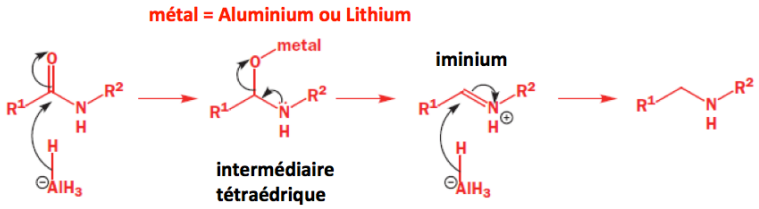
Imines et Enamines

- Imines formées à partir d'aldéhydes/cétone + amines primaires
- Enamines formées à partir d'aldéhydes/cétone + amines secondaires
- Pour les deux : catalyse acide et retrait eau

4) Amination réductrice

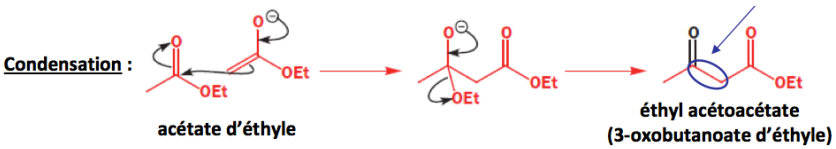


5) Réduction des amides par LiAlh4

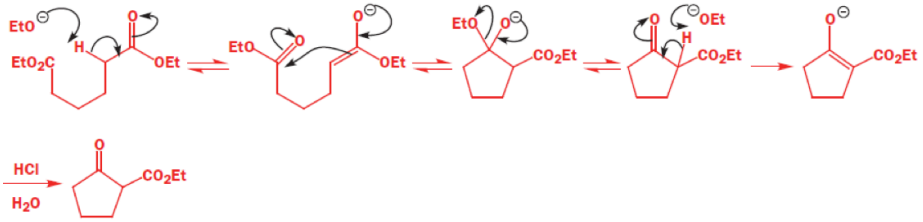


Notions complémentaires :

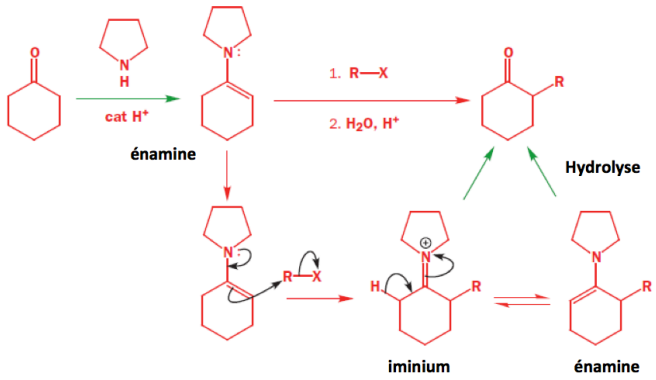
- Hydrolyse d'ester : Reaction inverse impossible en milieu basique à cause de la déprotonation de l'acide carboxylique.
- Un acide carboxylique réagissant avec du chlorure de thionyle (SOcl2) donne un chlorure d'acyle.
- Idem avec tétrachlorure de phosphore (PCl5)
- Hydrolyse Amide en milieu acide : 3H, 100°c, eau, rdt 70%
- Condensation de claysen :



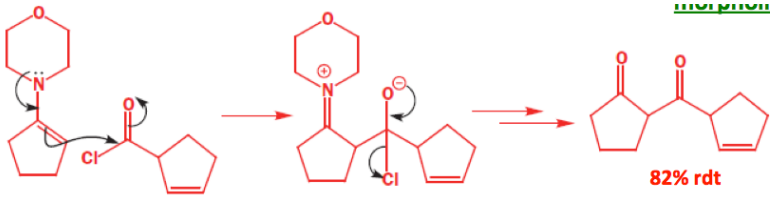
- Reaction de Dieckman = Claysen en intremoleculaire, parfois différent produits possible



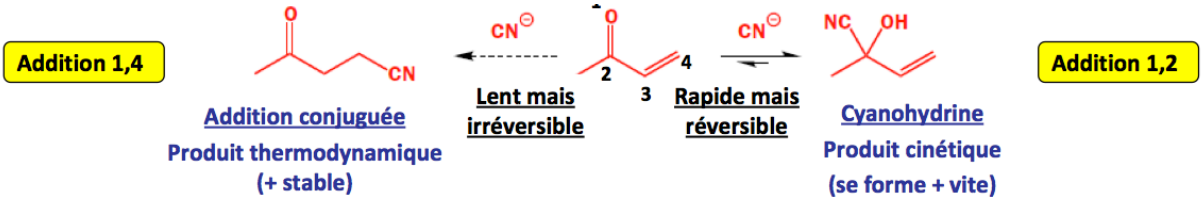
Alkylation d'énamine, N-alkylation possible pour halogéno-alkyl simple



Acylation d'énamine

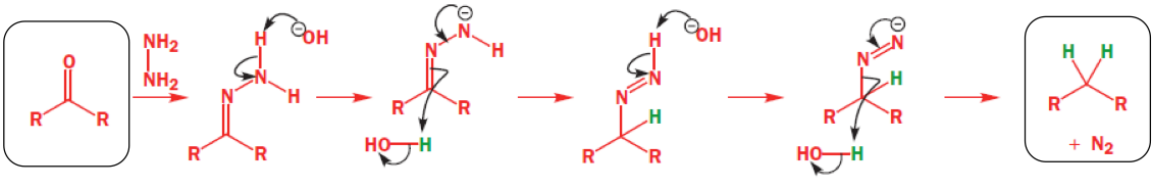


Addition conjuguées et directe

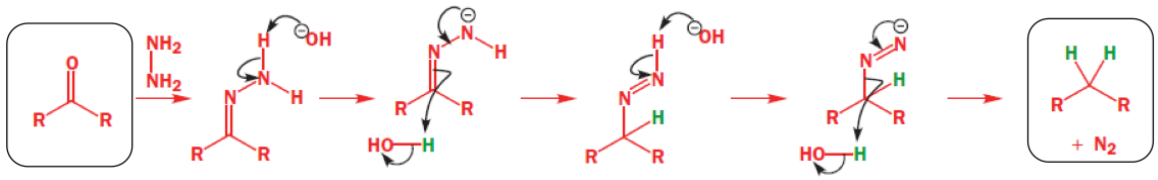


Addition conjuguée = Addtion de michael, on parle d'accpeteur de michael

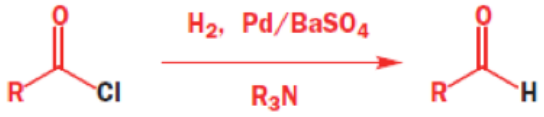
- Addition 1,4 des amines (on garde la double liaisons c=o)
- Addition 1,4 des thiols (nucléophile mou) versus 1,2 des organomagnésiens (nucléophile dur)
- Addition 1,4 des alcools (en milieu acide ou basique)



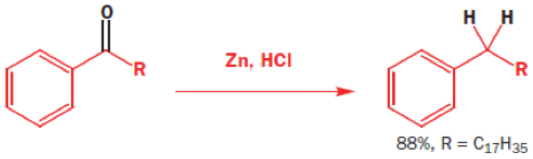
Reduction de Wolf-Kishner



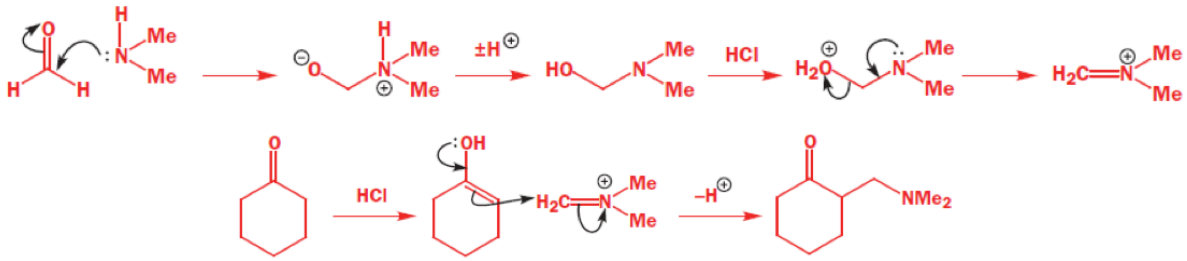
Reduction de Rosenmund



Reduction de Clemmensen, métal se dissous et donnes des électrons



Reaction de Mannich



Composé aromatiques

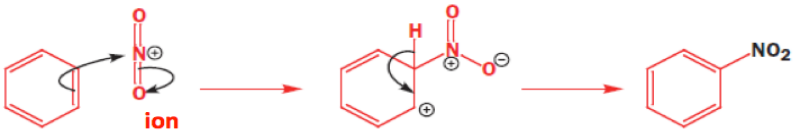
Reactivité du benzène *, SEar (fort electrophile nécéssaire, par ex pas de Br2 sauf si accompagné ac lewis (alcl3),*

1) Nitration

Formation réactif de nitration

acide nitrique **acide sulfurique** **ion nitronium**

Substitution électrophile du benzène



ion nitronium

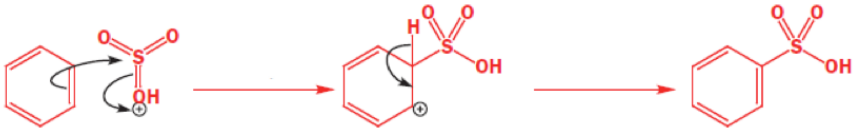
2) Sulfonation

Formation réactif de sulfonation

acide sulfurique

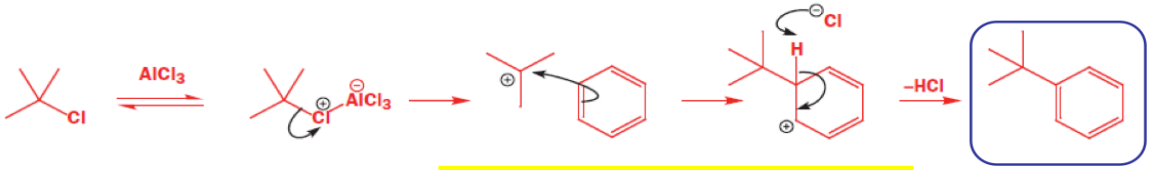
ou (SO$_3$ + H$_2$SO$_4$) = Oléum

Substitution électrophile du benzène



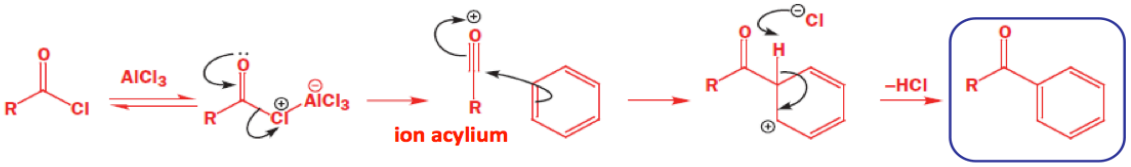
étape cinétiquement déterminante

3) Alkylation ou Aclylation de Friedel Craft

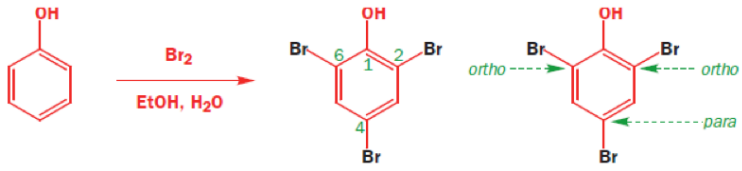


Formation réactif de d'alkylation/d'acylation

Alkylation de Friedel-Crafts
(Substitution électrophile du benzène)
Acylation de Friedel–Crafts

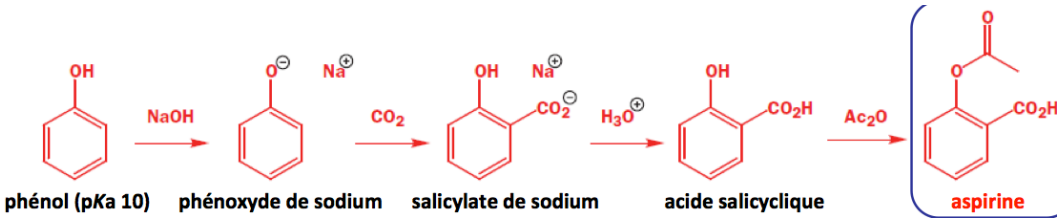


Reactivité du phénol

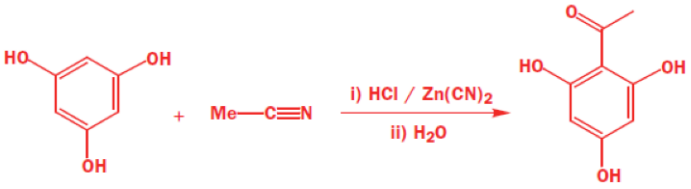


- OH electro-donneur, reaction facile sans acide de lewis
- Obtention de composé monobromé possible

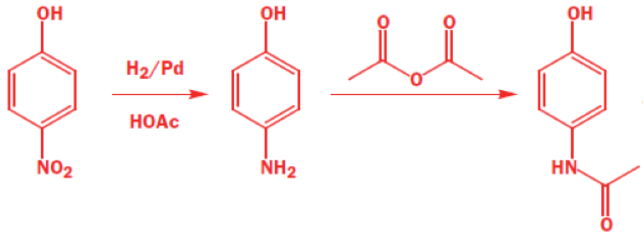
1) Procédé Kolbe-Schmidt (CO2 faible E+)



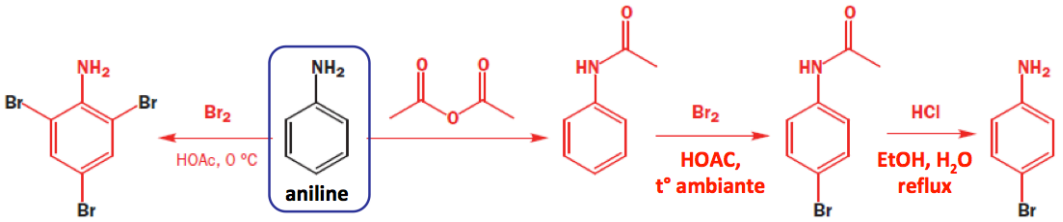
2) Reaction de Gatterman (R-CN ->R-C=O)



3) Synthèse paracetamol

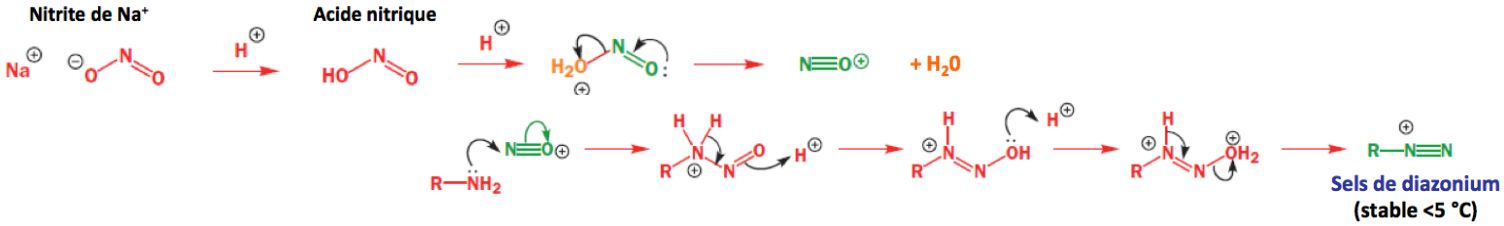


Réactivité de l'aniline et sels de diazonium

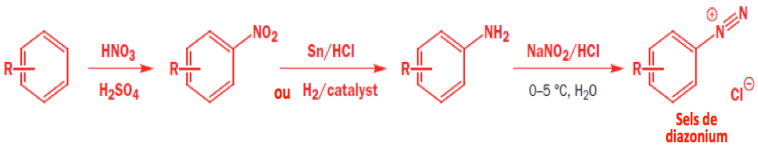


Reactivité plus forte de l'aniline (NH2 meilleur electro-donneur), possibilité de formation de composés tri-bromés.
On peut baisser la réactivité du composé

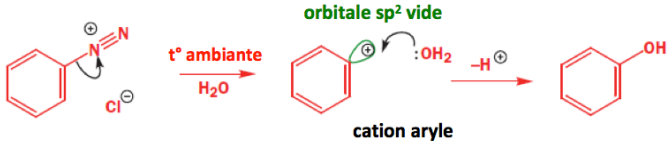
Formation du sel de diazonium



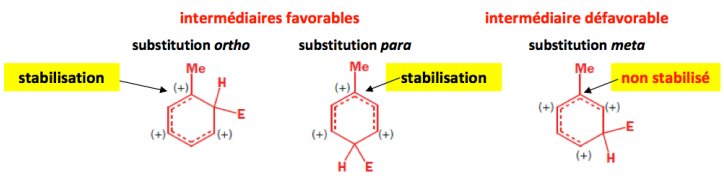
Sel de diazonium, sans perte du diazo



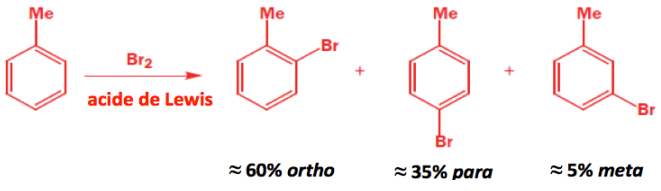
Sel de diazonium, avec perte du diazo SN1



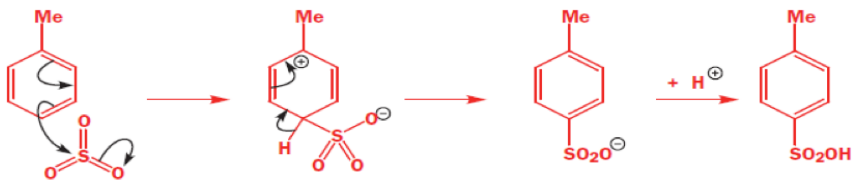
Réactivité des alkylbenzènes



Bromation

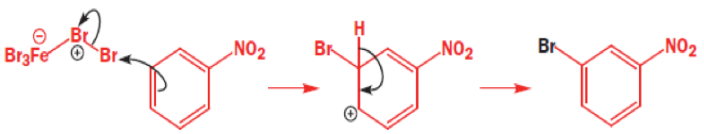


Sulfanation

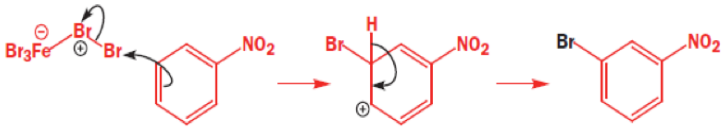


Réactivité des (NR3+/PR3+/CF3+)-Benzène *(Liason très polarisée)*

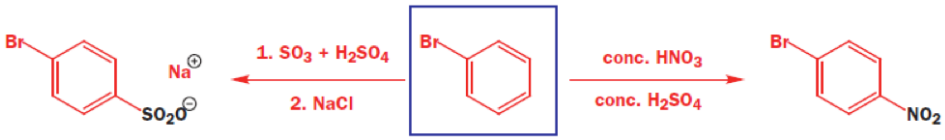
Nitration



Bromation



Halogénobenzène : *-I et +M ortho/para directeur*



Composé Hétérocyclique

→ **Dénomination des hétérocycles**

Un préfixe est attribué à chaque hétéroatome
Ces préfixes sont ordonnés comme suit :

Exemple **:**
hétérocycle comportant 1 atome d'oxygène et 1 atome d'azote : O > N ⇒ OXAZA (1 seul A)

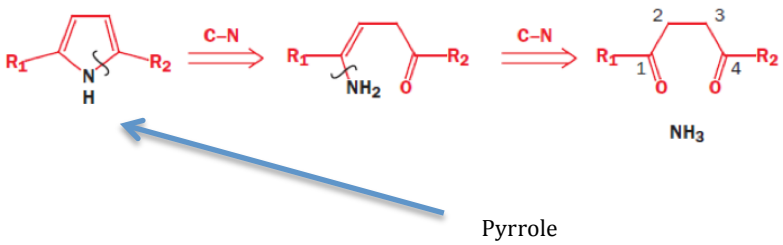
Élément	Préfixe	Élément	Préfixe
O	oxa	Sb	stiba
S	thia	Bi	bisma
Se	selena	Si	sila
Te	tellura	Ge	germa
N	aza	Sn	stanna
P	phospha	Pb	plumba
As	arsa	B	bora
		Hg	mercura

→ **Taille des cycles : Déterminée par un suffixe (≠ pour cycle saturé ou insaturé)**
6A et 6B : Dépend du dernier hétéroatome dans le nom

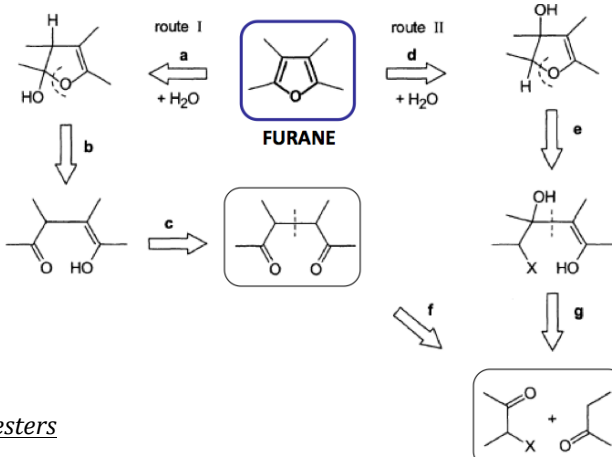
Taille	Insaturé	Saturé
3	irène (N : irine)	irane (N : iridine)
4	ète	étane (N : étidine)
5	ole	olane (N : olidine)
6A (S, O)	ine	ane
6B (N)	ine	inane

Cycle à 5 chainons, 1 hétéroatome

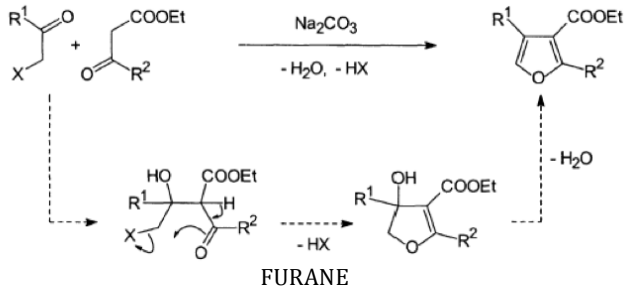
Retrosynthèse



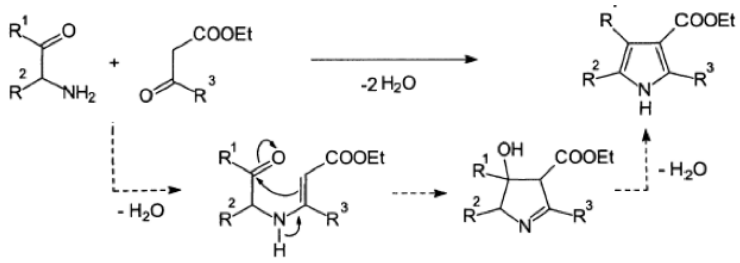
Pyrrole



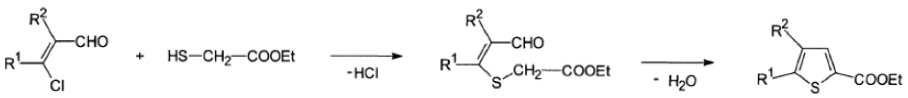
Synthèse de Feist-Benary et Knorr : Composés a-halocarbonylés avec des b-céto-esters



FURANE

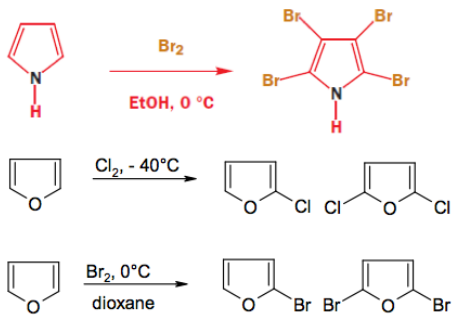


THIOPHENE

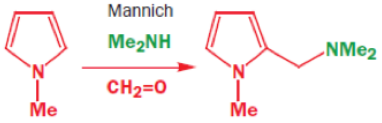


PYRROLE

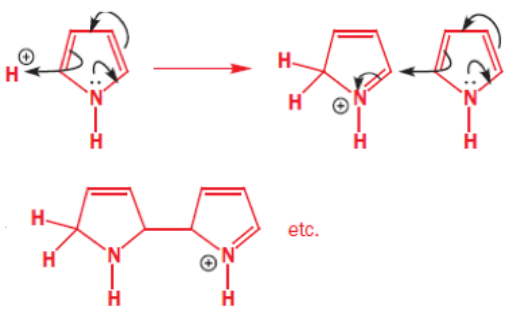
Substitution E+: *1) Halogénation*



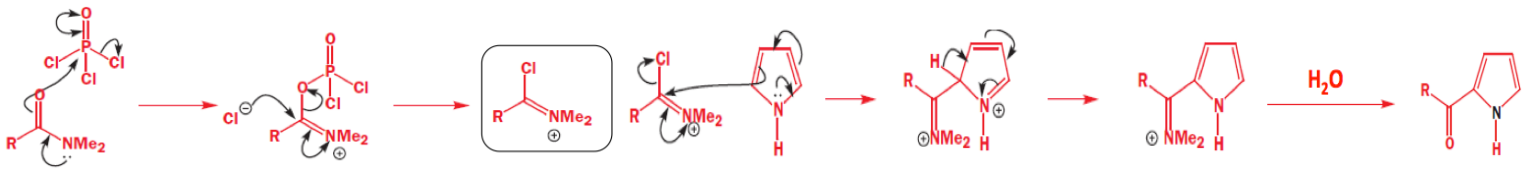
2) Reaction de Mannich



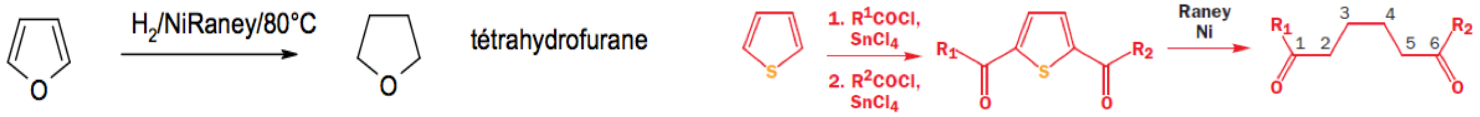
3) Acylation Friedel Craft



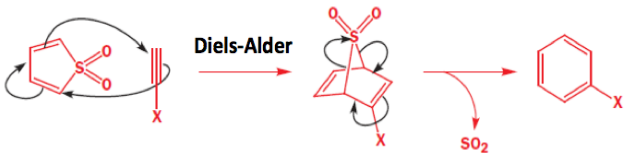
4) Reaction de Vilsmeier-Haack



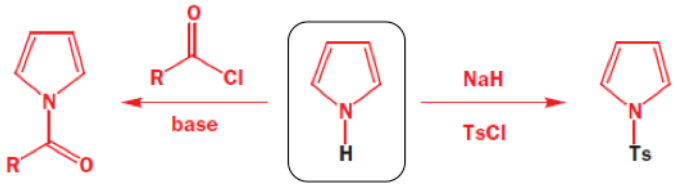
5) Reduction



6) Reaction diénique de Diels-Alder



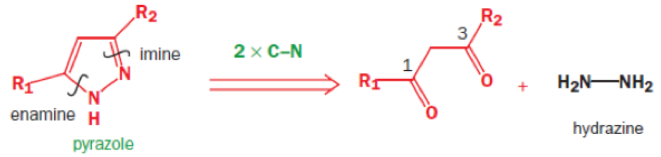
7) Reaction à l'azote, Pyrole



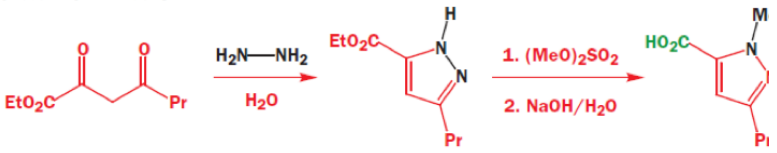
Cycle à 5 chainons, 2 hétéroatome

1) Pyrazole et Isoxazole

RETROSYNTHESE PYRAZOLE

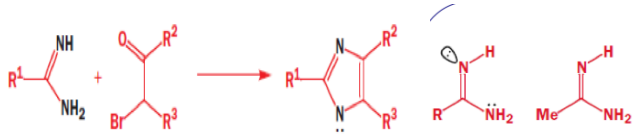


SYNTHESE PYRAZOLE

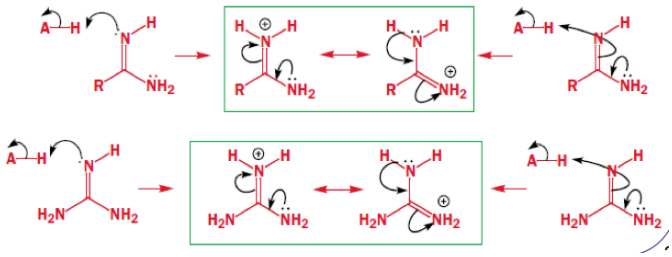


2) Imidazol

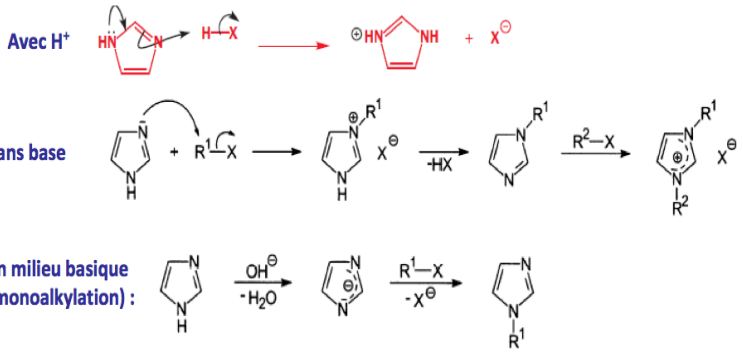
Synthèse :



Nota sur amidine et guanidine

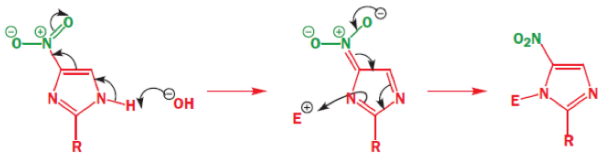


Reaction avec les E+

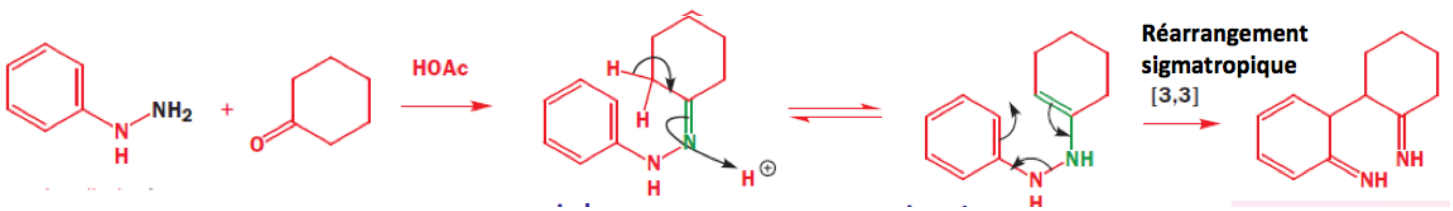


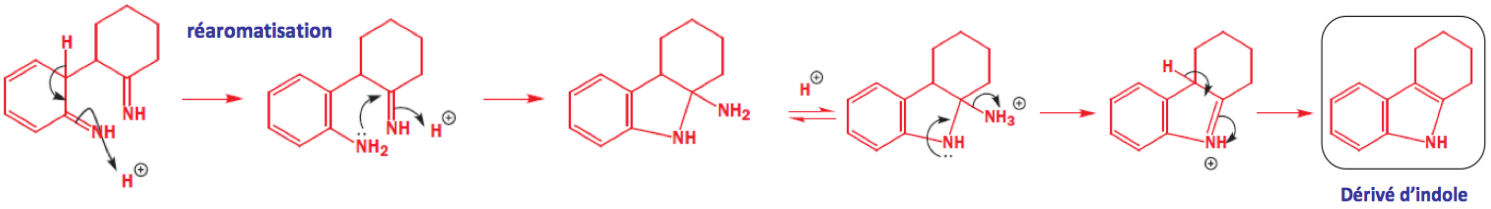
**** Nitration :***

...puis attaque électrophile

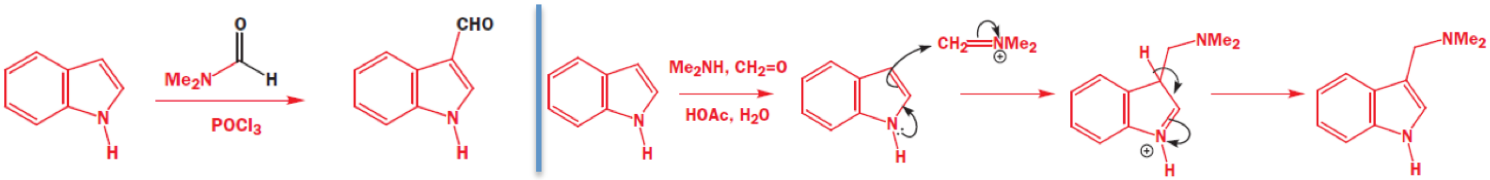


***Indole** : synthèse*





<u>Reactivité : en position 3</u> *Vilsmeier-Haack* *Mannich*



***<u>Pyridine</u>**: synthèse de Hantzsch*