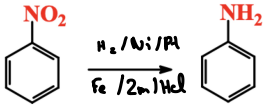
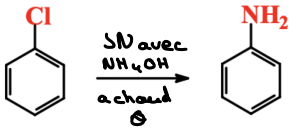
Amines aromatiques

1. Preparation

- Reduction



- Amination

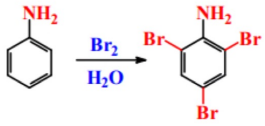


- Amination

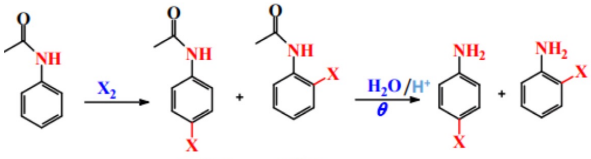
2. Halogenation

1. halogénation

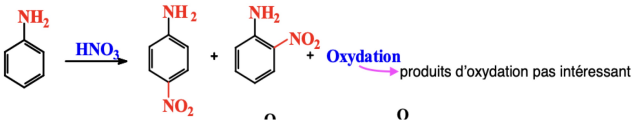
a. brome



b. brome et chlore sur l'acétanilide

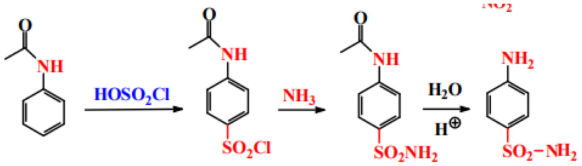


3. Nitration



préférable sur de l'acétanilide

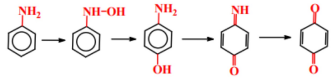
4. Sulfochloration



p-acétamidobenzène sulfochlorure

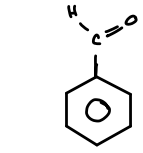
5. Oxydation

oxydants dilués :



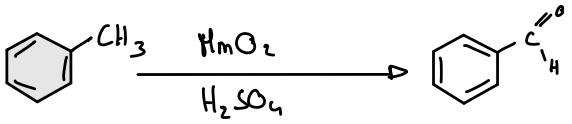
p.benzoquinone

Carbonylés aromatiques

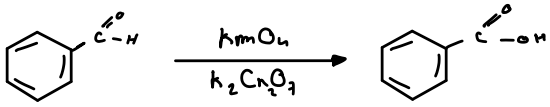


benzaldéhyde

1. Préparation

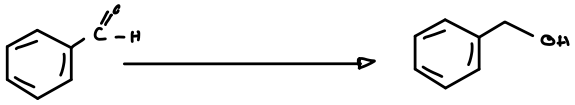


2. oxydation

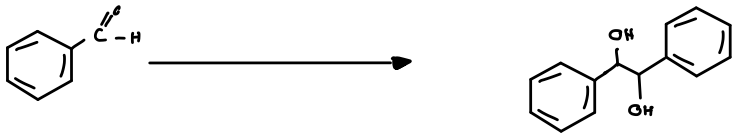


3 Reduction

- par les hydrures LiAH (réducteur chimique) H_2/Ni (réducteur catalytique)



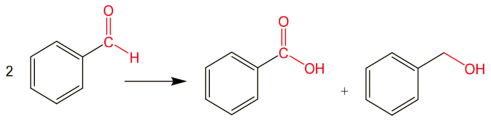
- par les métaux en milieu acide : Zn / H^+



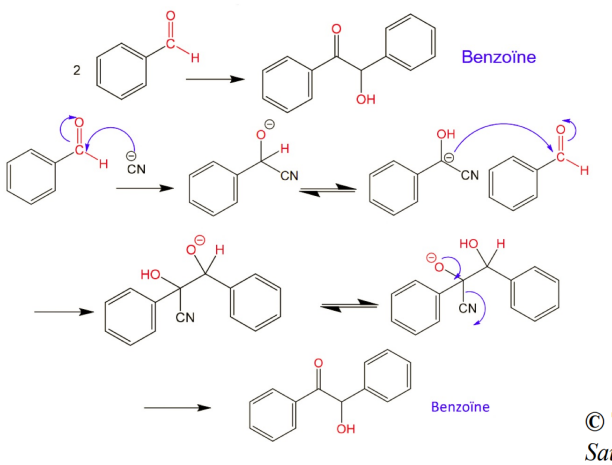
hydrobenzoïne
a-diols

4 Oxyda-reduction couplées

- Réduction de Cannizzaro : KOH / H_2O

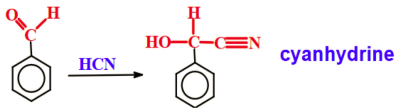


- Condensation benzoïnique : KCN/ Et OH /chaud

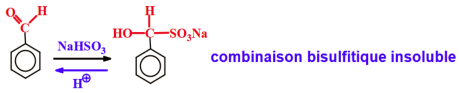


5. Réaction d'addition sur le carbonyle

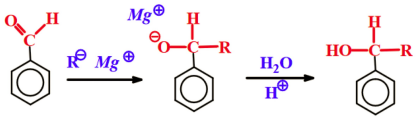
- D'acide cyanhydrique



- de l'hydrogénosulfite de sodium

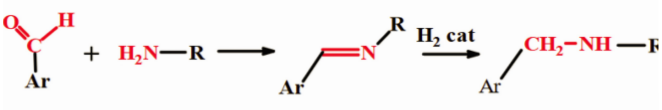


- des organomagnésiens

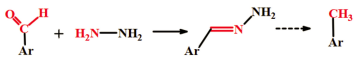


6. Condensations avec les molécules azotés

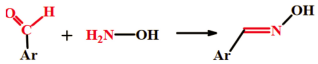
- Amines primaires : base de Schiff stable



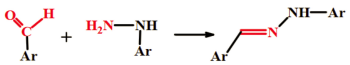
- Hydrazines : hydrazones puis reduc. selon Wolff Kishner



- Hydroxylamines : oximes

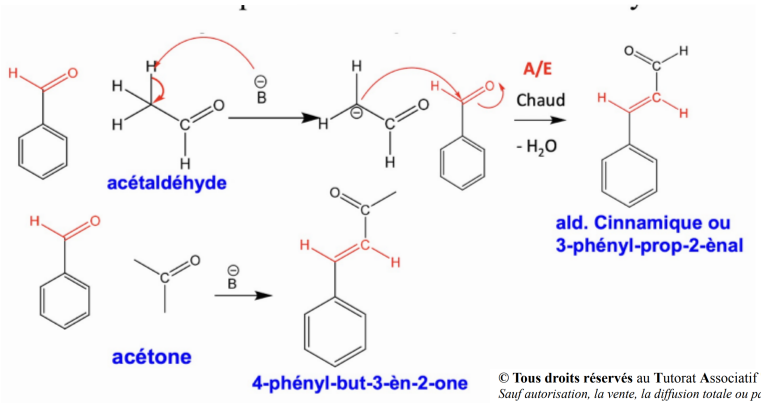


- Phénylhydrazine :

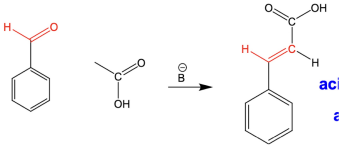


7. Condensation avec des C porteurs d'H mobiles

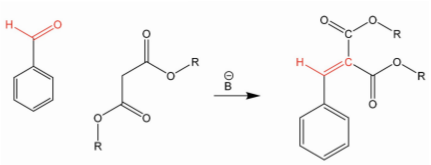
- Réaction de Claisen - Schmidt

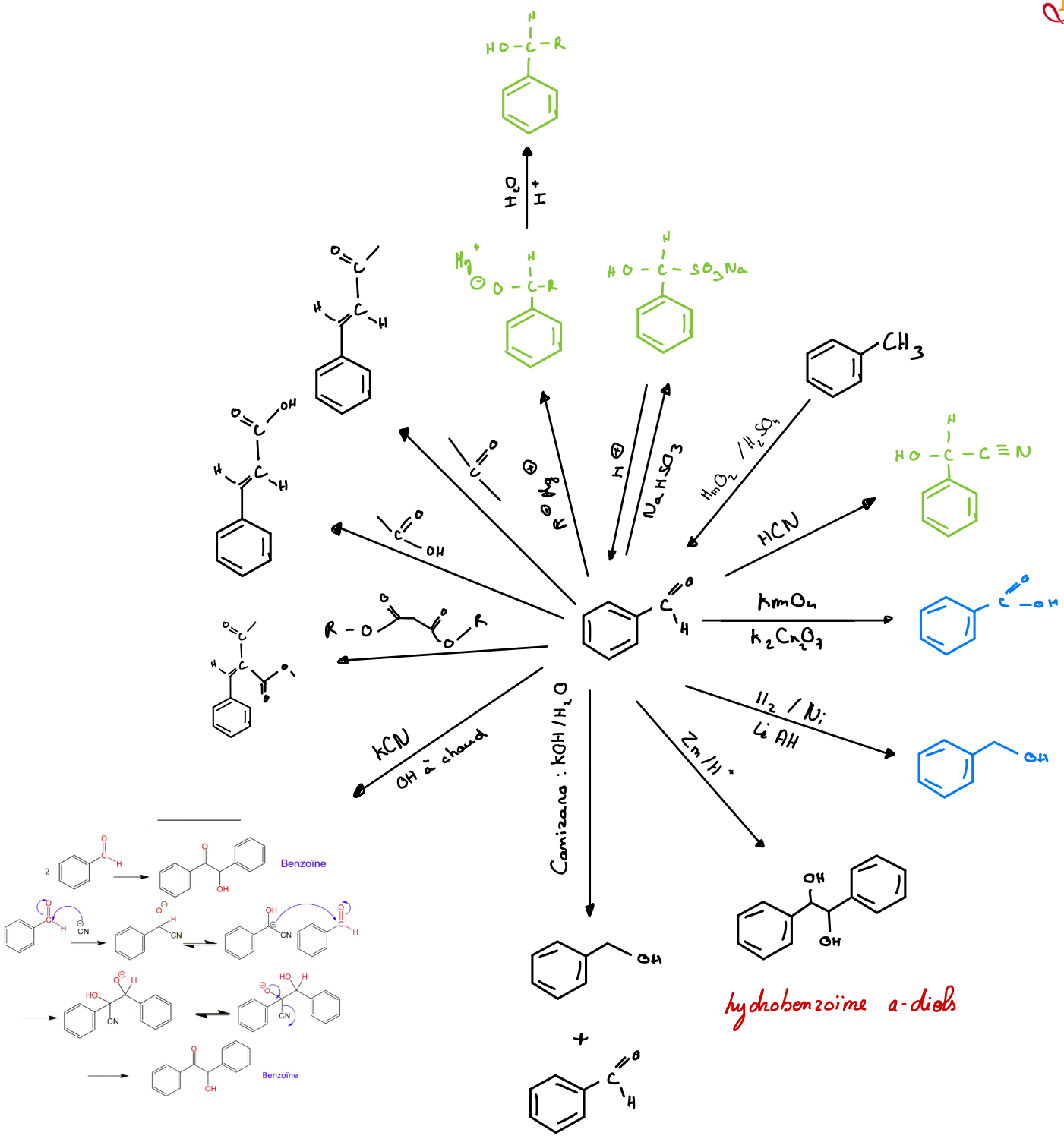


- Réaction de Perkin



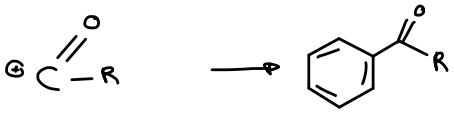
- Réaction Knoevenagel



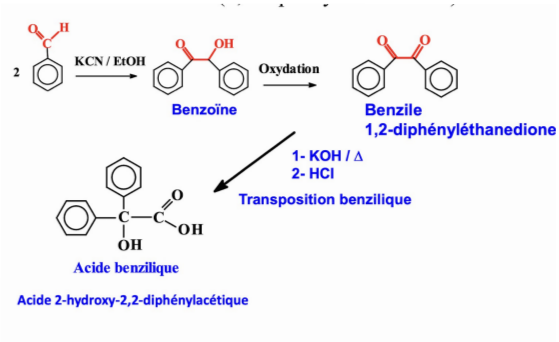


Cétones aromatiques

1. Préparation avec acylation des carbures aromatiques selon Friedel - Crafts : avec $AlCl_3$ et RCOX



2 Préparation alpha dicarbonylées aromatique

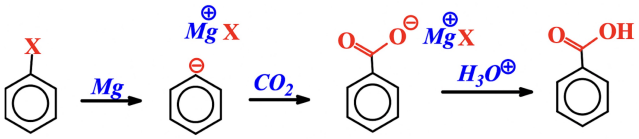


Acides et dérivés aromatiques

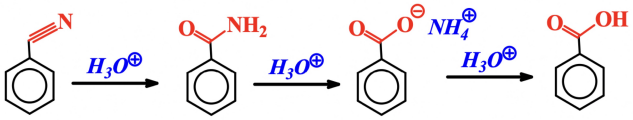
1. Préparation

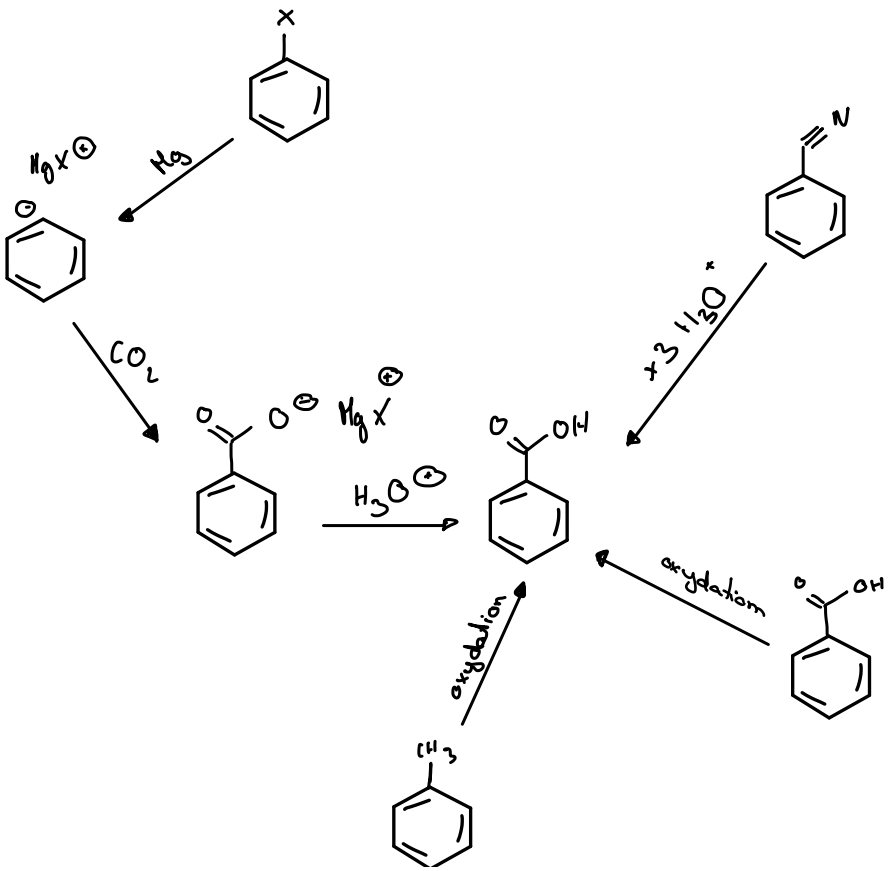
- oxydation des alkylbenzènes

- carbonation des organomagnésiens



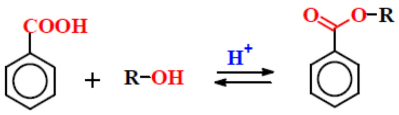
- Hydrolise totale des nitriles : H_2O / H^+

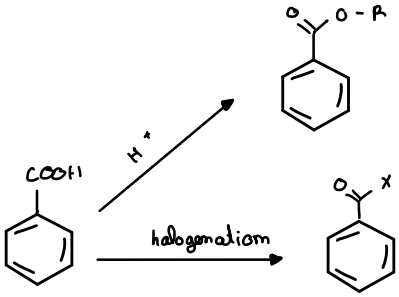




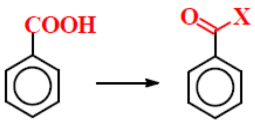
Acides carboxyliques et dérivés aromatiques

1. Estérification

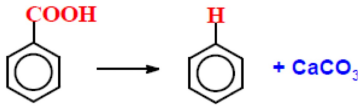


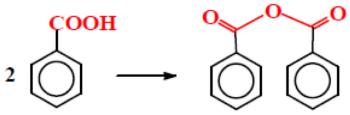


2. Halogénation

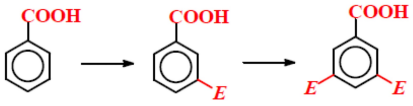


3. Elimination portant sur le carboxyle

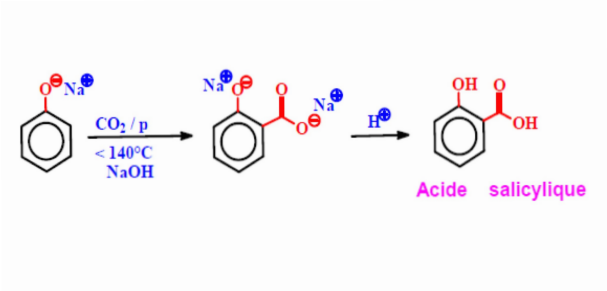




4. Propriété des noyaux aromatiques



5. Préparation selon Kolbe Schmit



Hétérocycles

Hétérocycles aromatiques

- **Pyrrole**

=> suit règle de Huckel
=> acide

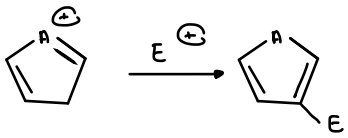
- **Pyridine**

=> suit les règles de Huckel
=> Azote à un sommet + électronégatifs

Heterocycle non aromatiques

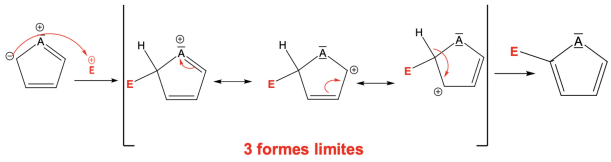
- **Heterocycles pentagonaux :**

1. Substitution en β



passe par 2 formes limites

2. Substitution en α



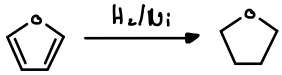
3 formes limites
=
+ grande délocalisation
=
niveau energetique bas

- **Furane et dérivés**

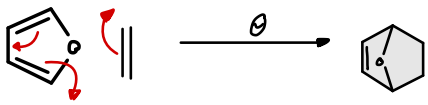
furane => prioritaire

furyl => en substituant

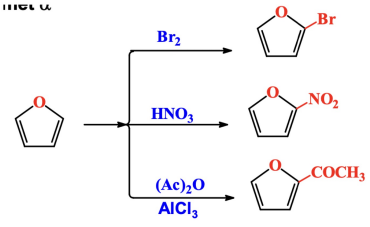
1. hydrogénation



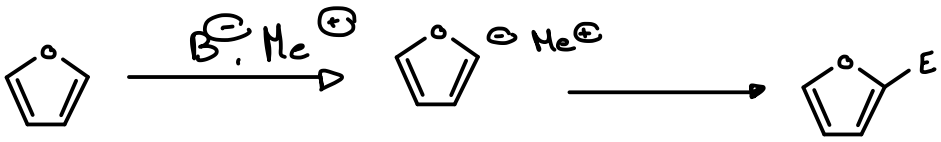
2. Réaction de Diels - Alder



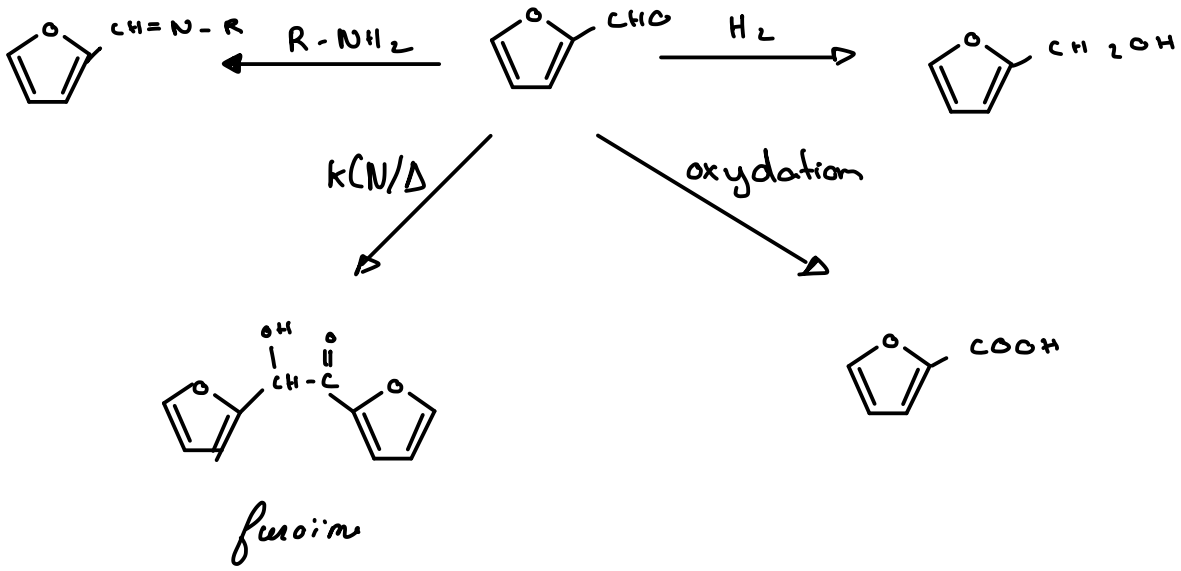
3. Substitutions électrophiles



4.. Action des organo-métalliques



5. Réac sur du Furfural

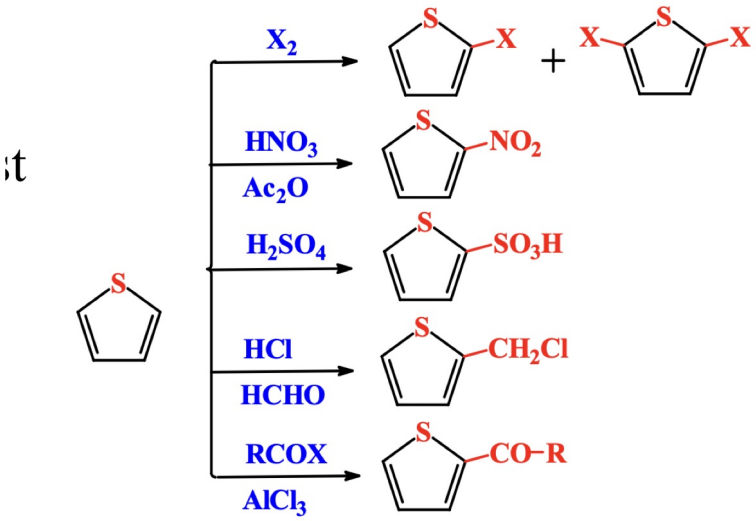


furoïne

Thiophène et dérivés

thiophène

thiemyl => thiophène en substituant

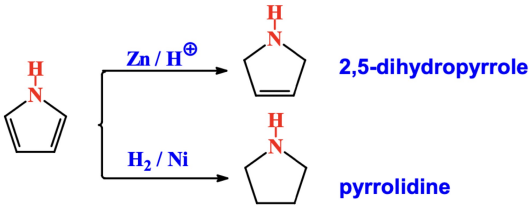


Pyrroles et dérivés

pyrrole

pyrrole en substituant => pyrrolyl

1. Addition

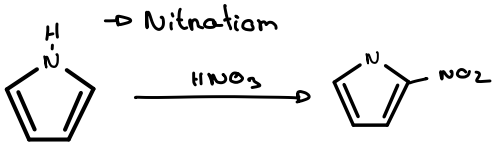


Basicité d'amines secondaires

2. Substitutions électrophiles

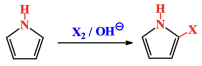
• Milieu acide fort

→ Nitration

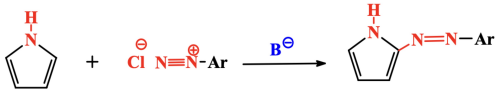


• Milieu basique

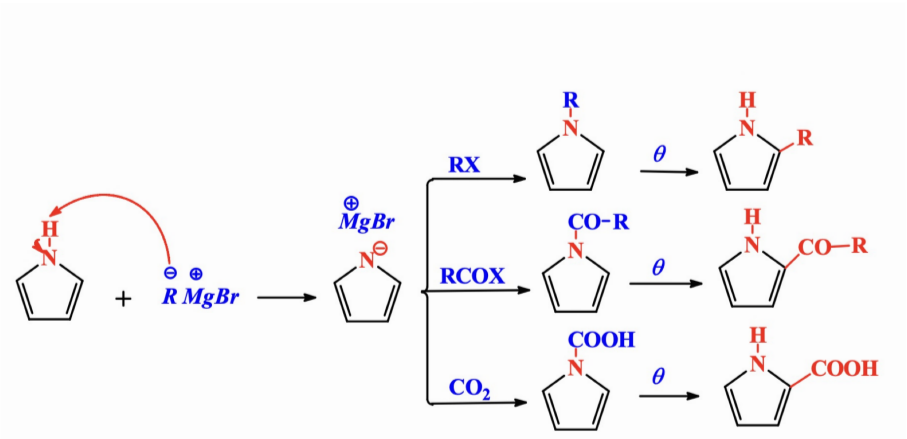
→ halogénation

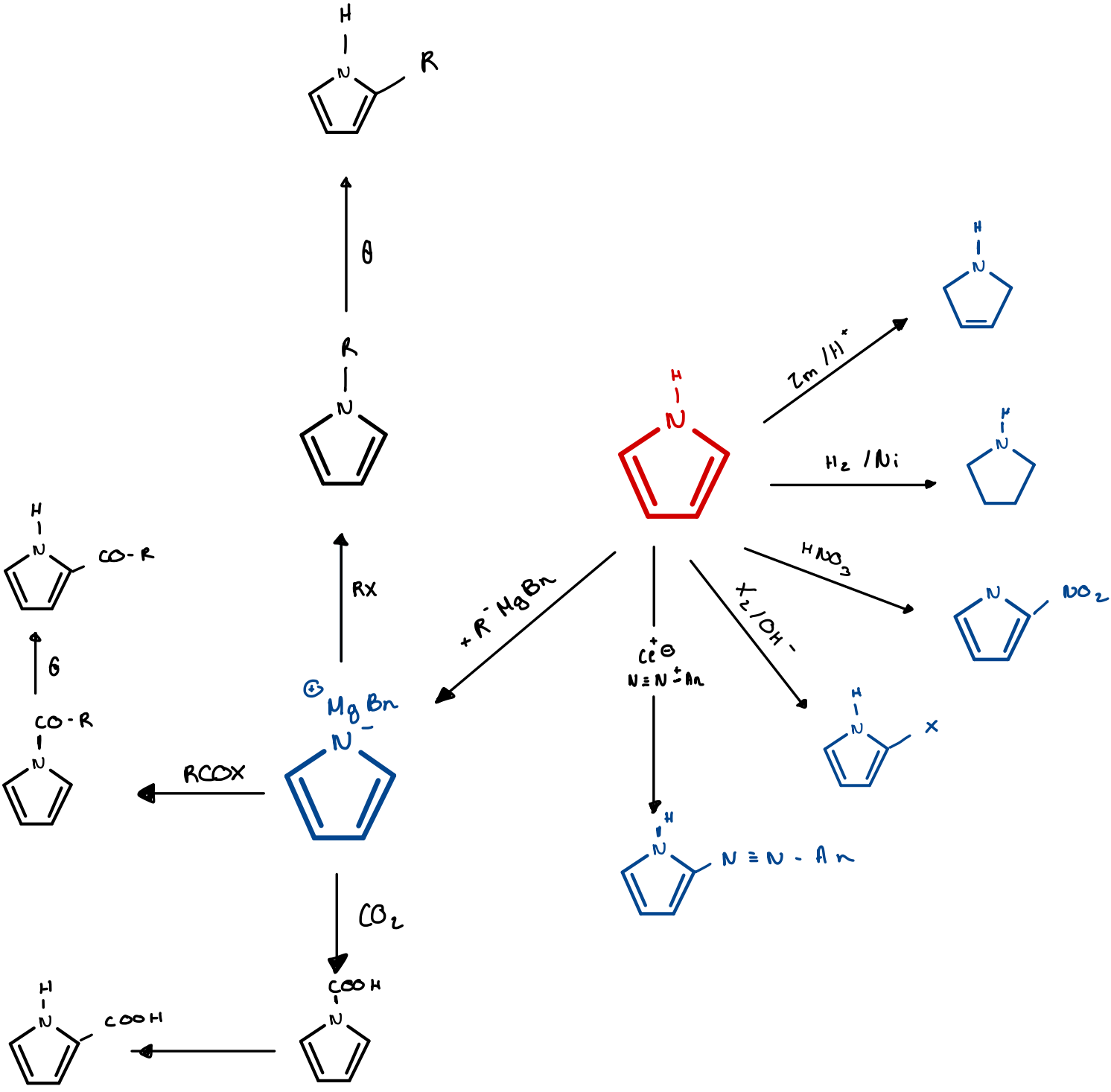


→ formation d'azoïque colorié

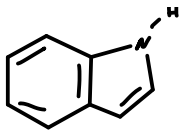


• Réaction de dérivé magnésien





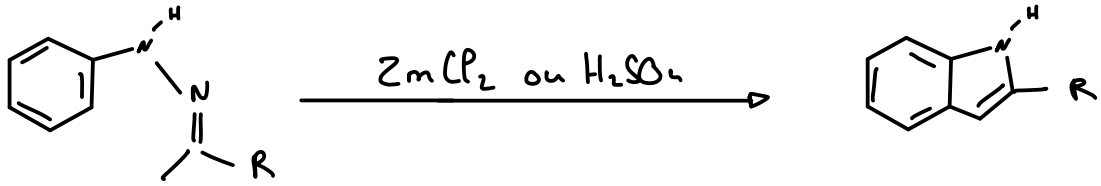
Indole



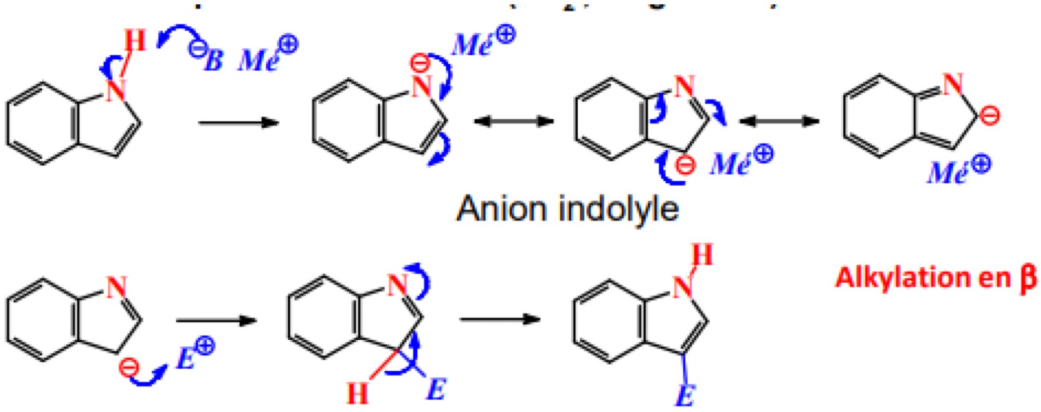
indole

indole en substituant : indolyl

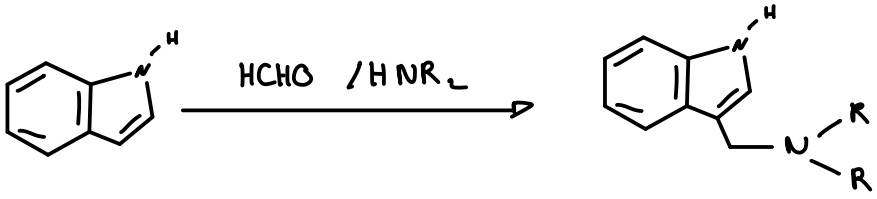
1. Synthèse des indoles selon Fisher



2. Métallation par les bases fortes



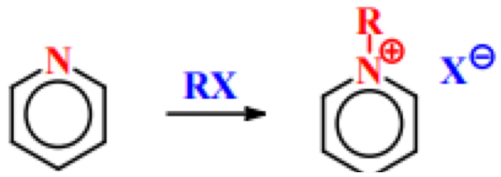
3. Aminométhylation de Mannich



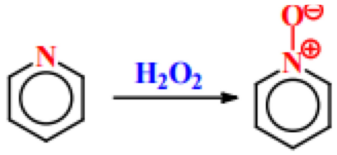
Cycles hexagonaux à des hétéroatomes

Pyridine

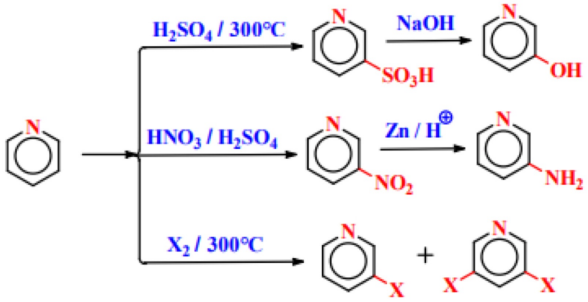
1. N - alkylation

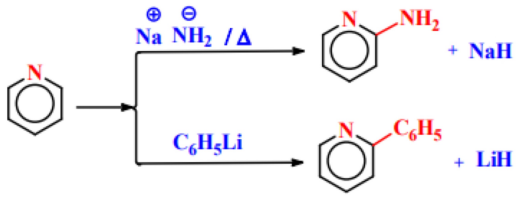


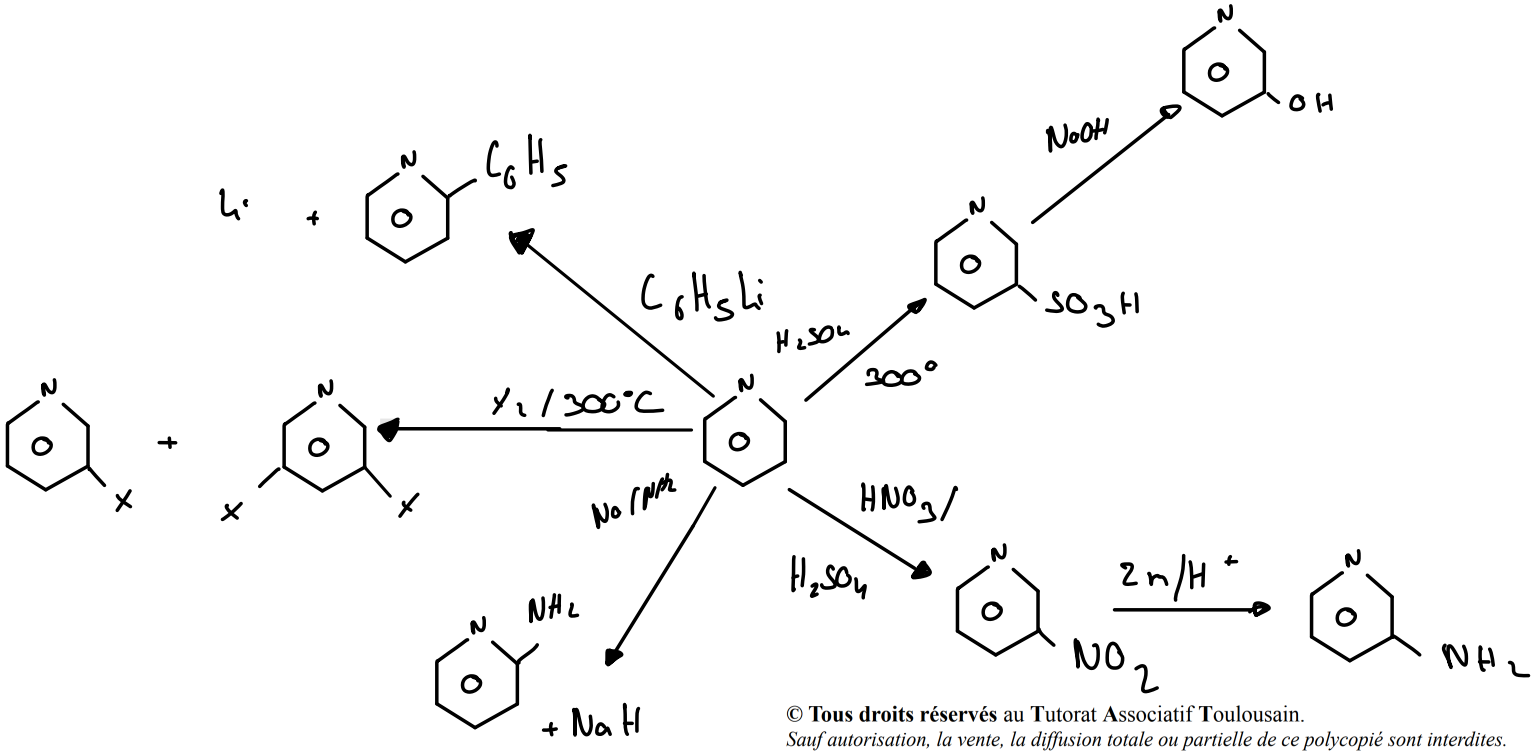
2. Formation de N - oxyde



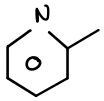
3. Réaction du au noyau

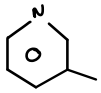


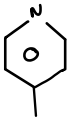




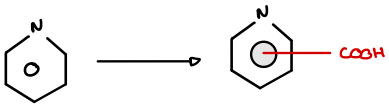
Picoline et methylpyridine


α-picoline


β-picoline

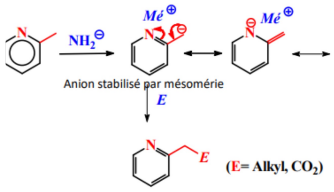

γ-picoline

1. Oxydation

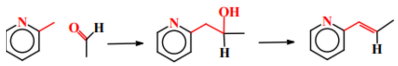


2. Hydrogenation acides des 2-4 picolines

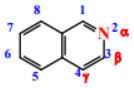
• Formation des organométalliques

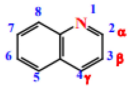


• Condensation avec les aldéhydes



Nomenclature


isoquinoléine
benzo[c]pyridine


quinoléine
benzo[b]pyridine

Présence d'une fonction -COOH en ortho, méta et para :

ac. picolique
ac. pyridine-2-carboxylique

ac. nicotique
ac. pyridine-3-carboxylique

ac. isonicotique
ac. pyridine-4-carboxylique

Puis à partir de l'acide nicotique on peut réaliser des amides :

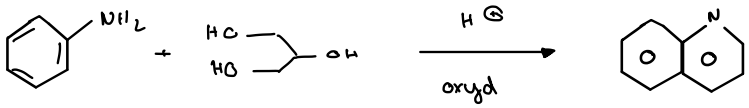
nicotinamide

diéthylnicotinamide

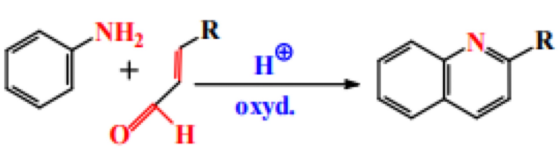
isoniazide
antituberculeux

Nicotinamide : intervient dans la structure des 2 coenzymes NAD, NADP qui jouent un rôle fondamental dans les processus biochimiques d'oxydo-réduction.

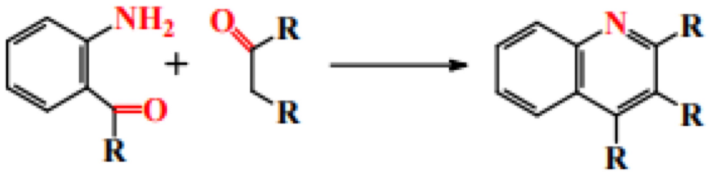
3. Synthèse de Skraup : permet d'avoir de la Quinoléine



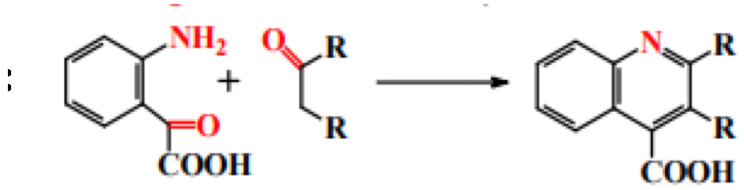
4. Synthèse de Döbner - Miller



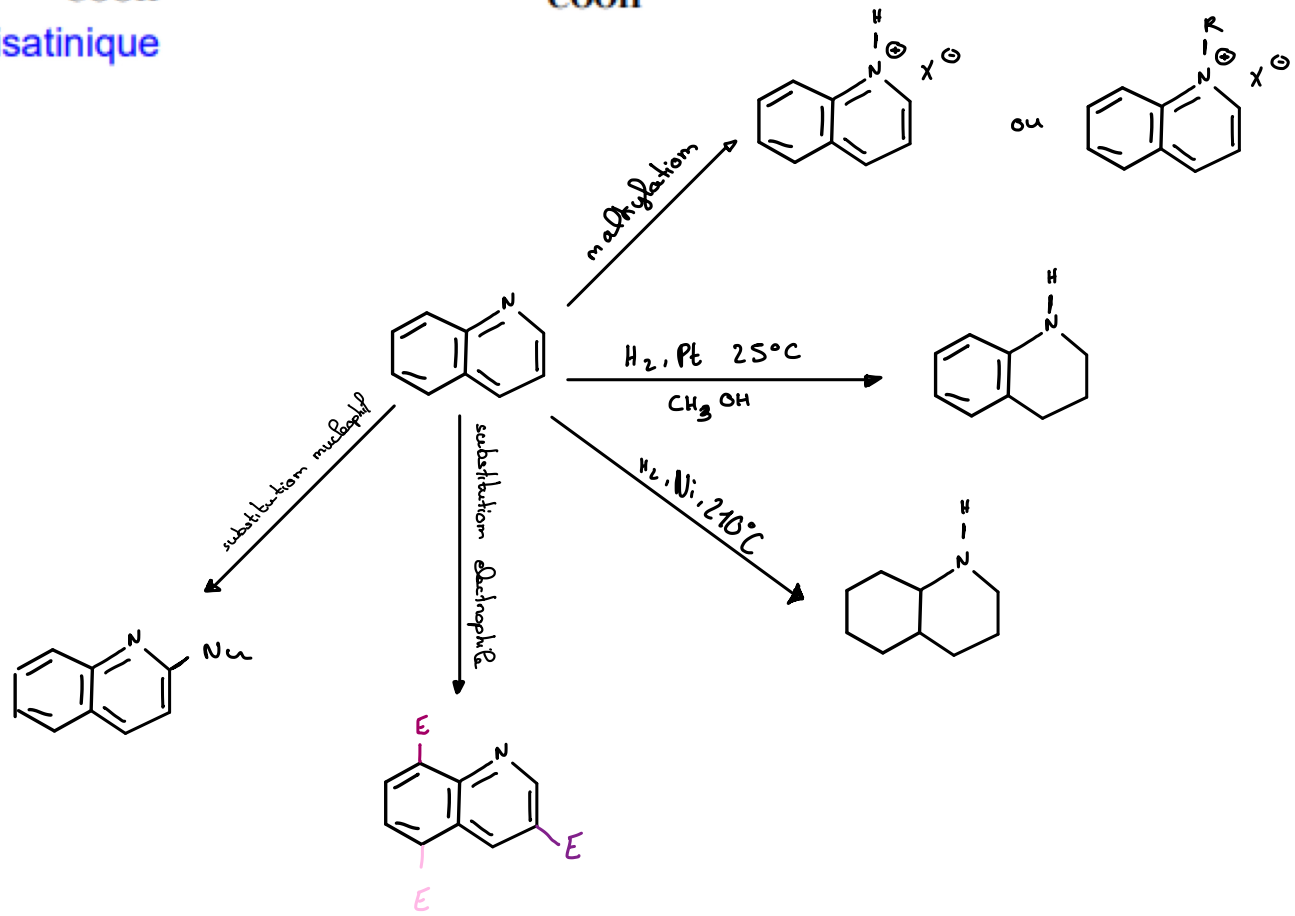
5. Synthèse de Friedländer



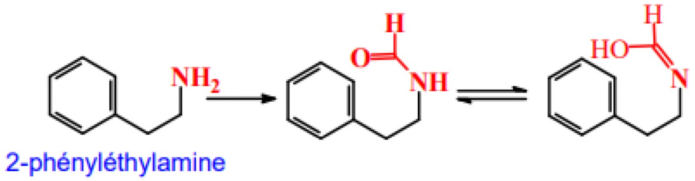
6. Synthèse de Pfitzinger



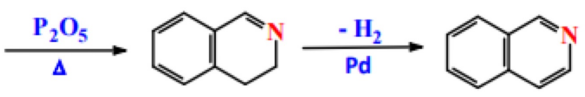
ac. isatinique



7. Synthèse de Bischler - Napieralski



2-phényléthylamine



Dihydroisoquinoléine