FICHES
SPE - PHARMA
Volume II

L'armée sait remonter le moral de ses troupes

De moins en moins de déserteursapparemment

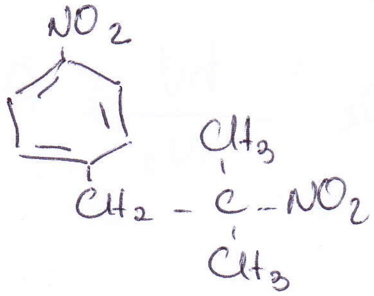
DERIVES NITRES

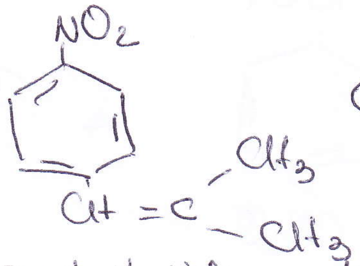
S_NAr :

A = 

B = HCl

SRN_1 = Substitution nucleophile radicalaire unimoleculaire "monoelectrique"

A = 

B = 

produit d'eliminat°

C = HCl

4 etapes en chaine :

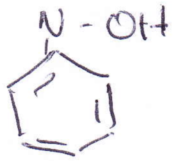
1. etape d'initiation : transfert monoelectrique = Saut d'é
2. Decomposition du radical anion.
3. Couplage du radical avec l'anion
4. 2ème Saut electronique

Reduction :

A = 

aniline

Reduction :

A = 

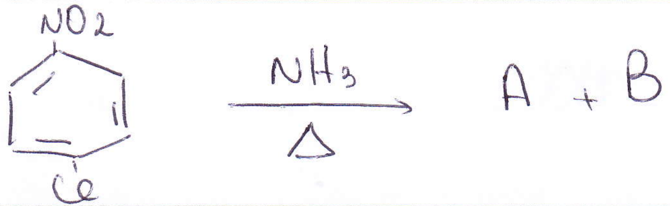
phenylhydroxyamine.

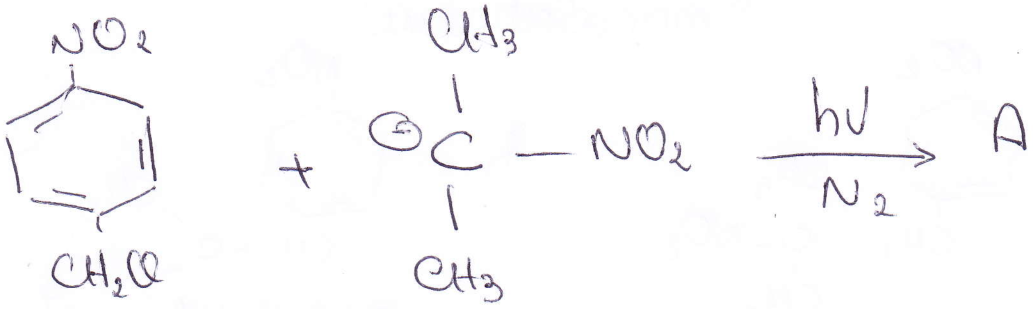
Reduction :

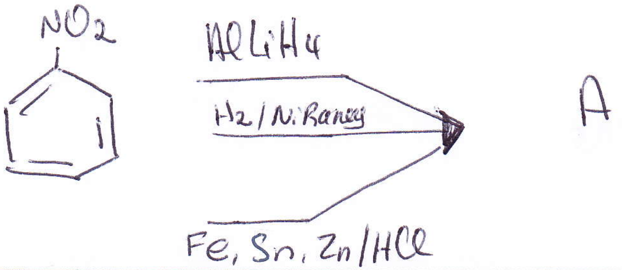
A = 

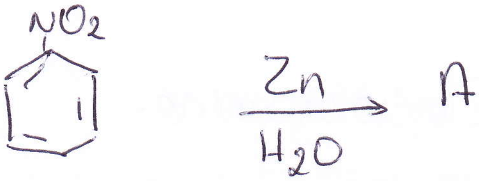
Cyclohexylamine.

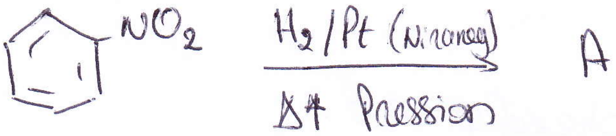
DERIVES NITRES (2)







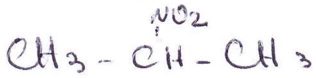




DERIVES NITRES

Preparation des nitro-aliphatique : Substitution radicalaire

$A = CH_3NO_2$ $B = CH_3CH_2NO_2$ $C = CH_3-CH_2-CH_2-NO_2$

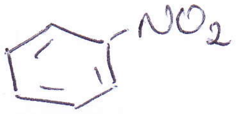
D =

$CH_3-\overset{NO_2}{CH}-CH_3$

mecanisme radicalaire.

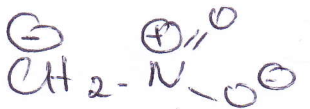
Oxydation des amines :

$A = CH_3-CH_2NO_2$ nitroethane

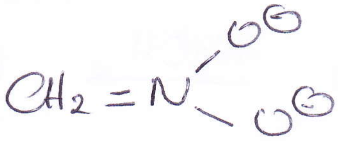
nitration du benzene.

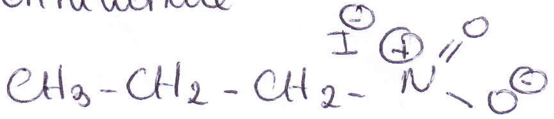
A =


SN :

A =

$\overset{\ominus}{C}H_2-\overset{\oplus}{N}(=O)-O^{\ominus}$

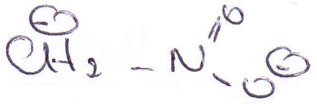
anion nitronate

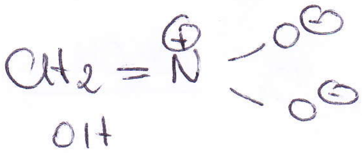
⟷ B =

$CH_2=N(-O^{\ominus})-O^{\ominus}$

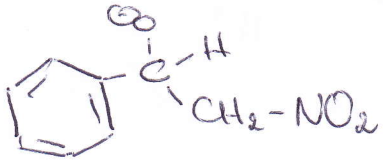
C =

$CH_3-CH_2-CH_2-\overset{\oplus}{N}(=O)-O^{\ominus}$ $\overset{\ominus}{I}$

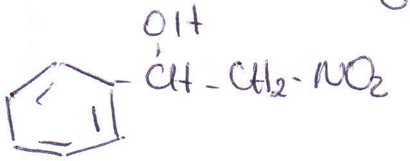
nitropropane

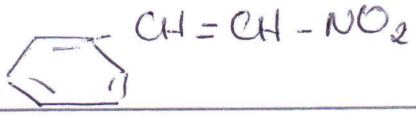
SN :

A =

$\overset{\ominus}{C}H_2-N(=O)-O^{\ominus}$

B ⇒

$CH_2=\overset{\oplus}{N}(-O^{\ominus})-O^{\ominus}$

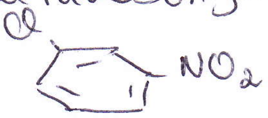
C =


D =


E =


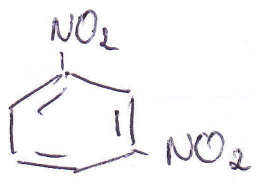
nitrostyrene.

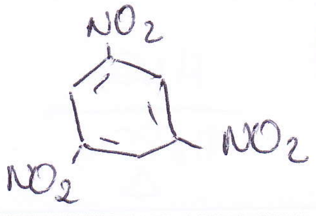
Chloration du nitrobenzene SE :

A =


appauvrissement des sommets ortho et para.

Nitration :

A =


B =


trinitrobenzene

A = rien

Le nitrobenzène peut être utilisé comme solvant dans la reaction de Friedel et Craft.

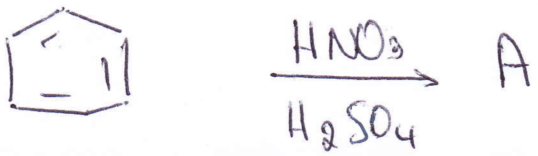
DERIVES NITRES

(1)

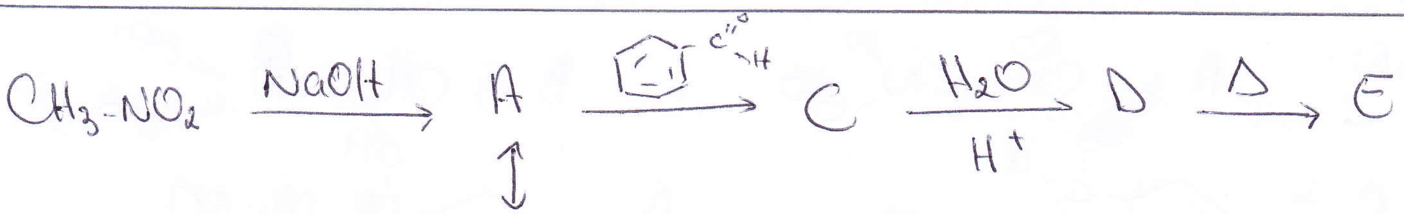
$$CH_3-CH_2-CH_3 \xrightarrow[400°C]{HNO_3} A + B + C + D$$

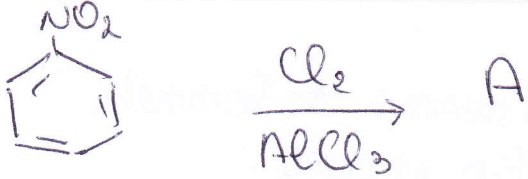
$$CH_3-CH_2-NH_2 \xrightarrow[McPB]{Peracide} A$$

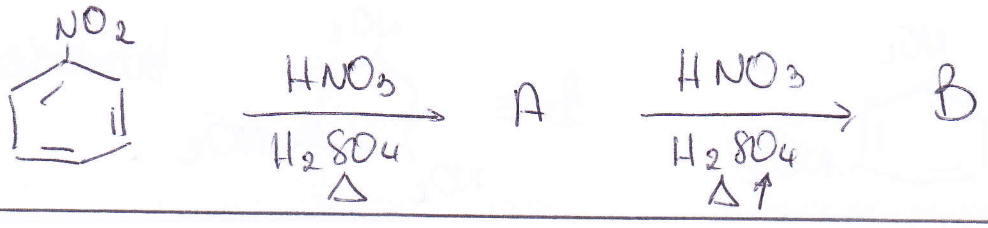
acide meta chloro perbenzoique

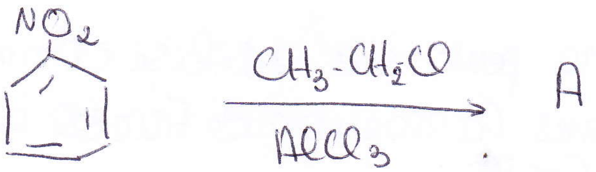


$$\begin{tikzcd} CH_3-NO_2 \arrow[r, "NaOH"] & A \arrow[r, "CH_3-CH_2-I"] \arrow[d, leftrightarrow] & C \\ & B & \end{tikzcd}$$









DERIVES DIAZOIQUES

Reaction d'oxydo-reduction :

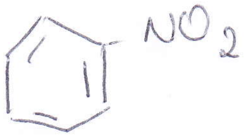
A = 

B = $N_2\uparrow$ C = HCl

D = 

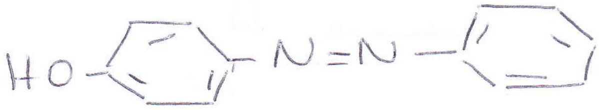
$CH_3-\overset{O}{\overset{\|}{C}}-H$ ethanal

- reduction du nitrobenzene en benzene
- Oxydation de l'alcool en ethanal

A = 

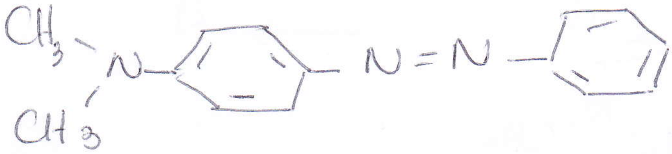
B = $N_2\uparrow$ C = HCl

Reaction de copulation avec un phenol :

A = 

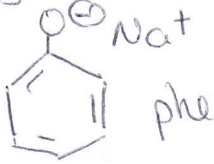
azobenzene (colorant)
- Système hyperconjugué

Reaction de copulation avec ~~un~~ une amine aromatique :

A = 

Helianthine

Hydrolyse alcaline des halogenures d'aryles :

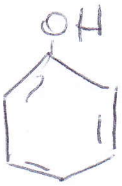
A = 

phenate de Na

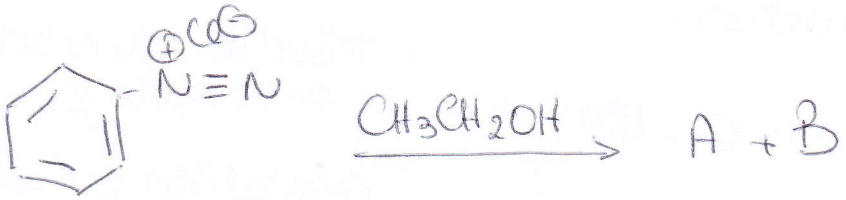
B = 

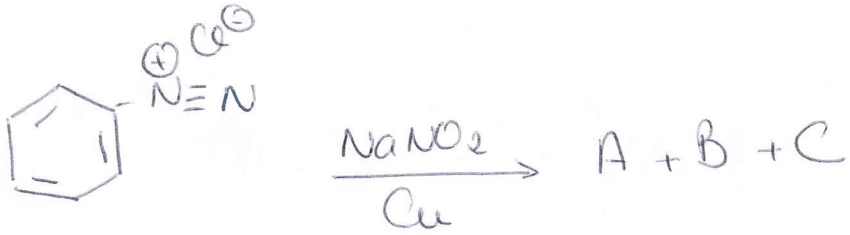
phenol (reprotonation)

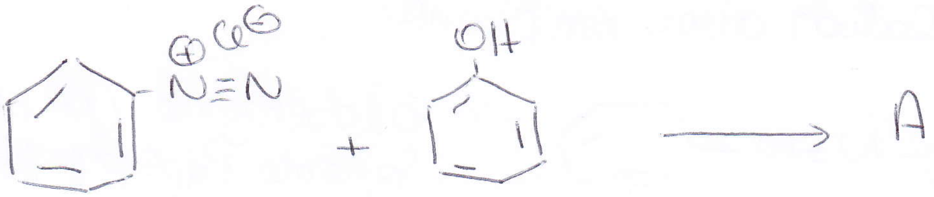
Decomposition des diazoniums :

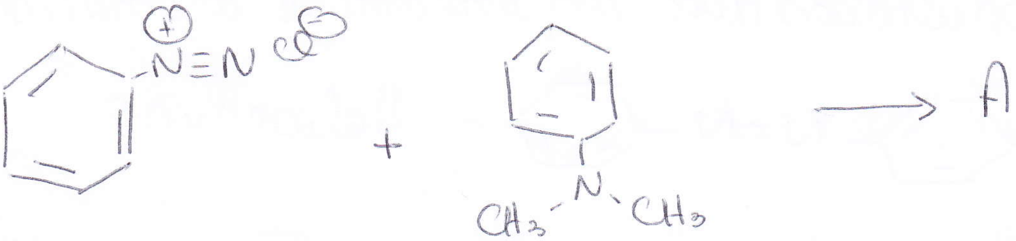
A = 

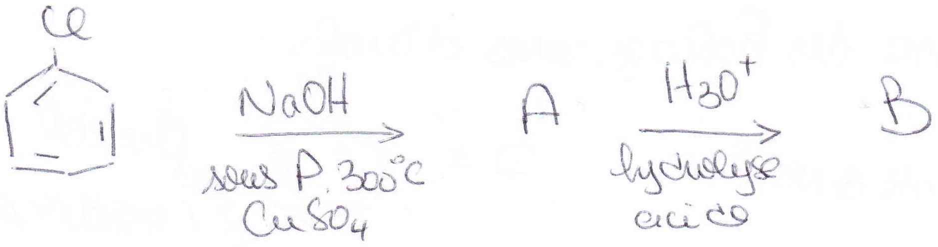
DERIVES DIAZOIQUES (2)

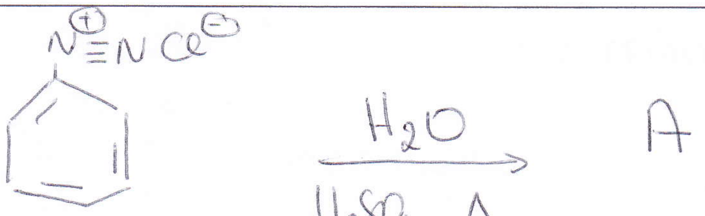




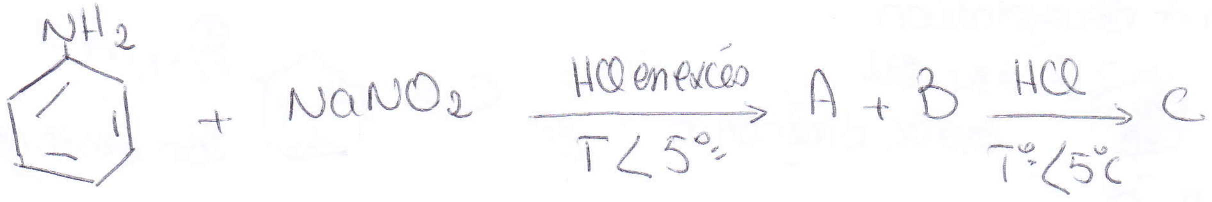


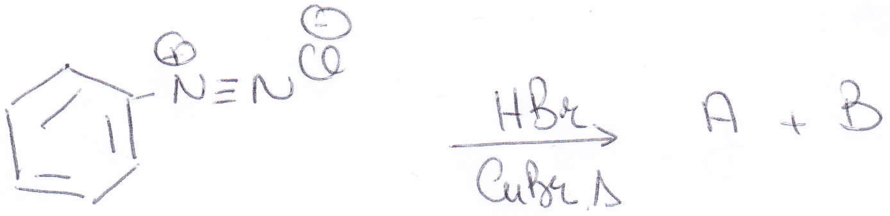


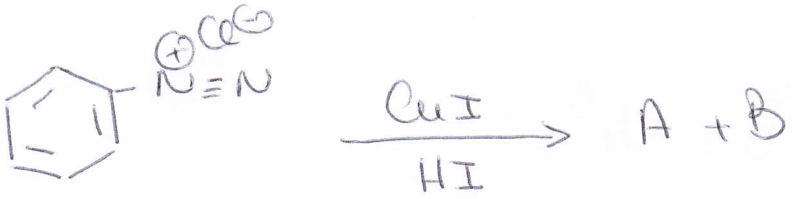


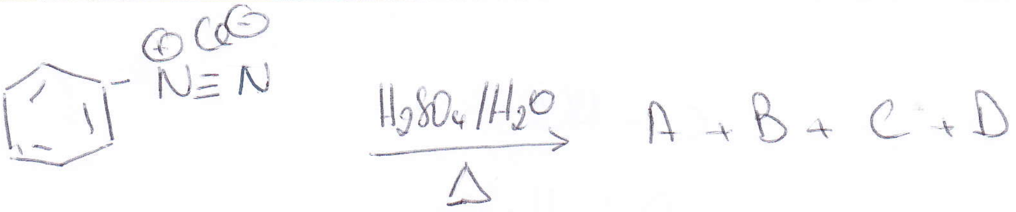


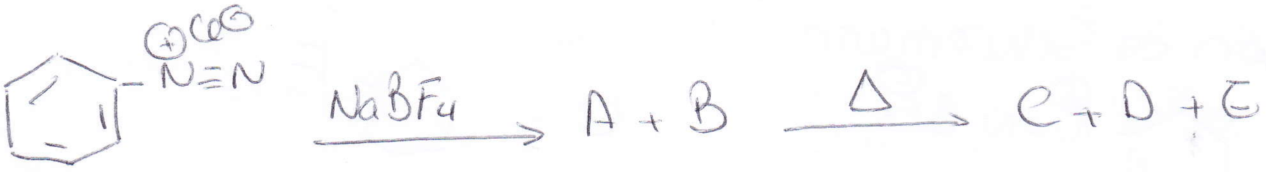
DERIVES DIAZOIQUES (1)

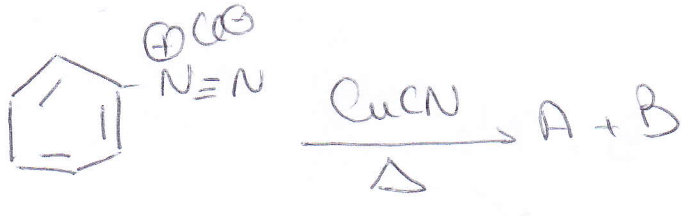






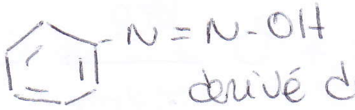




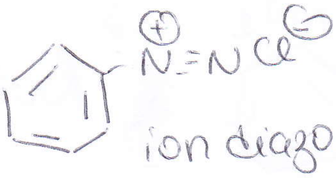


DERIVES DIAZOIQUES

Reaction de diazotation :

A =


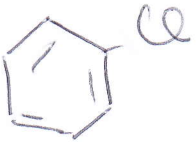
dérivé diazoique

C =


ion diazonium.

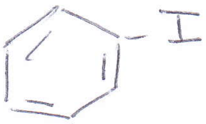
B = H_2O

Reaction de Sandmayer :

A =


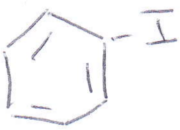
B = N_2 ↑

Reaction de Sandmayer :

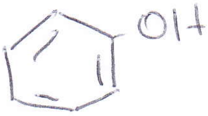
A =


B = N_2 ↑

Reaction de Sandmayer

A =


B = N_2 ↑

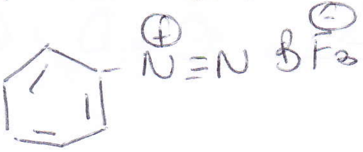
A =


C = HCl

B = N_2 ↑

D = H_2SO_4

Reaction de Schiemann.

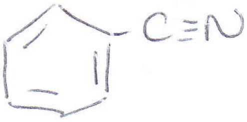
A =


C =


B = NaCl

D = N_2 ↑

E = BF_3

A =


B = N_2 ↑

AMINES AROMATIQUES:ANILINE

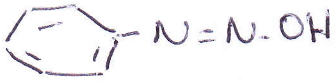
Condensation avec les aldehydes :

A =

imine.

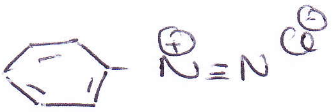
Diazotation

A :



diazoïque covalent aromatique

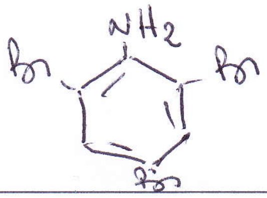
B =



diazonium stable à 5°C

Bromation : SE

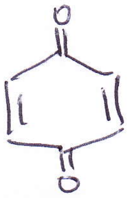
A =



tribromoaniline

Oxydation :

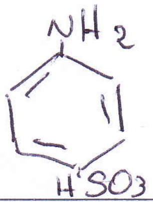
A =



benzoquinone

Sulfonation :

A =

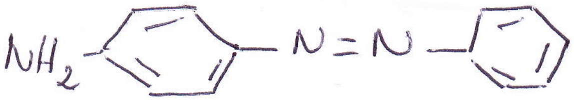


acide sulfanilique

SE propre aux noyaux activés

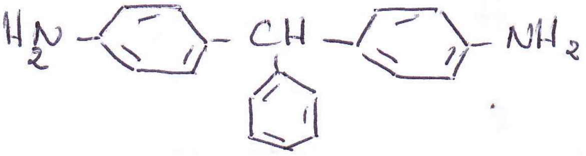
⚠ Substitution en para.

A =

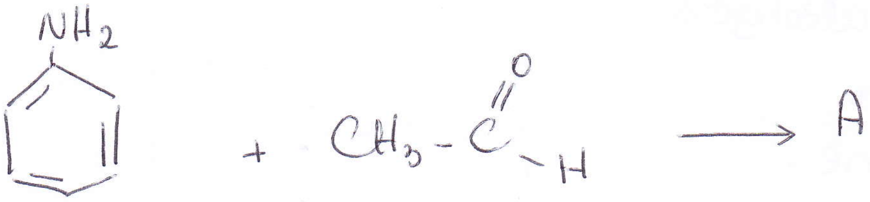


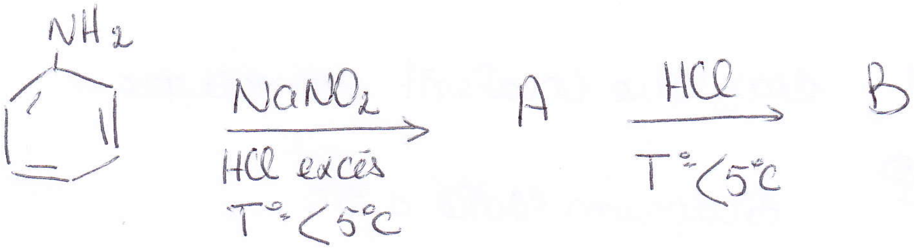
azobenzene

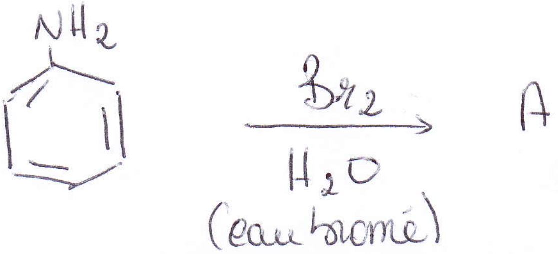
Condensation avec les aldehydes aromatiques :

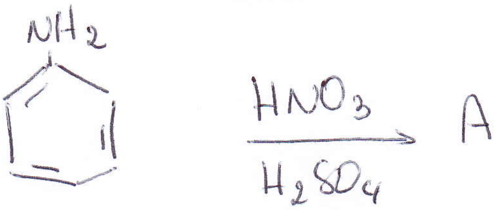


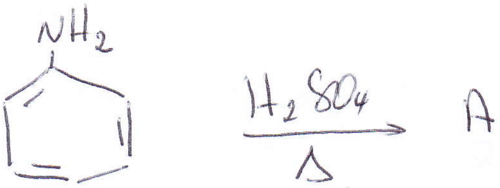
AMINES AROMATIQUES:ANILINE (3)

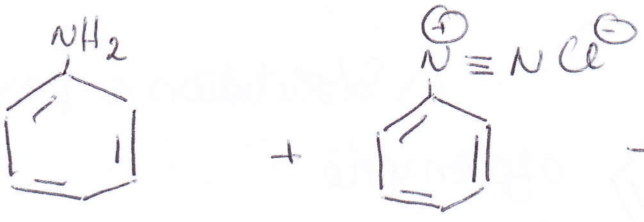


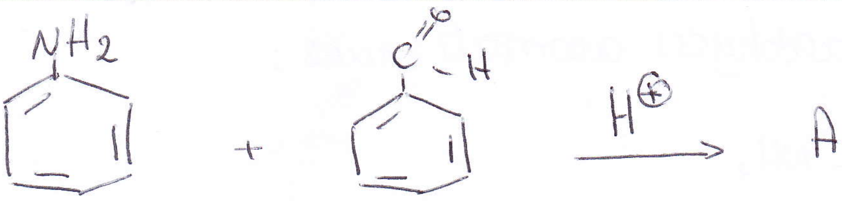








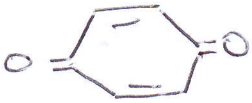




AMINES AROMATIQUES:ANILINE

Oxydation de l'aniline

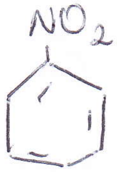
A =



benzoquinone

Oxydation de l'aniline :

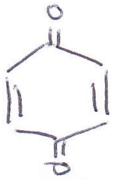
A =



nitrobenzène

Oxydation du phenol :

A =

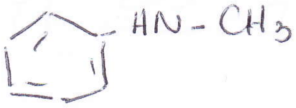


benzoquinone

⚠ l'oxydation des cycles activés par $KMnO_4/[H^+]$ donne une benzoquinone

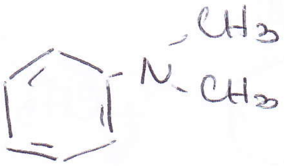
Alkylation :

A =

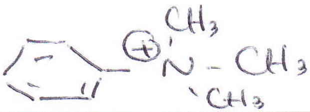


B = HI

C =

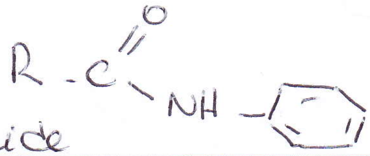


D =



Acylation :

A =

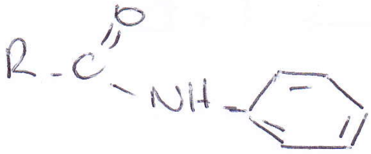


amide

B = HCl

Acylation :

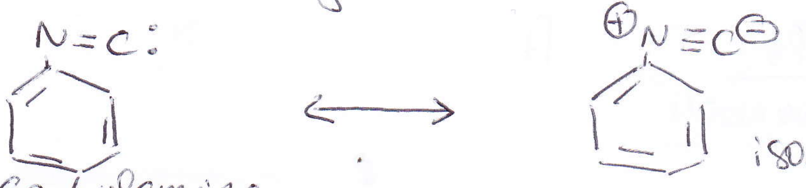
A =



B = R - COOH

formation de la Carbylamine (isonitrile)

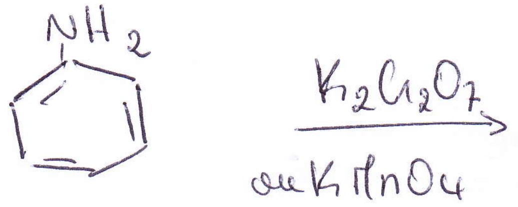
A =

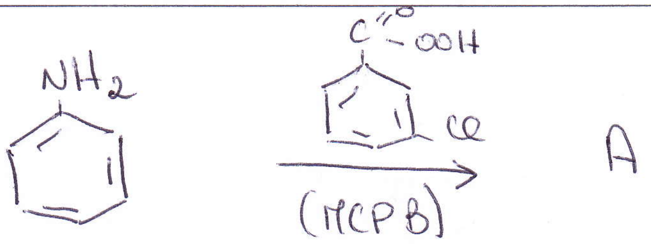


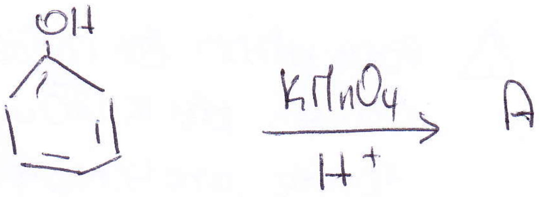
Carbylamine

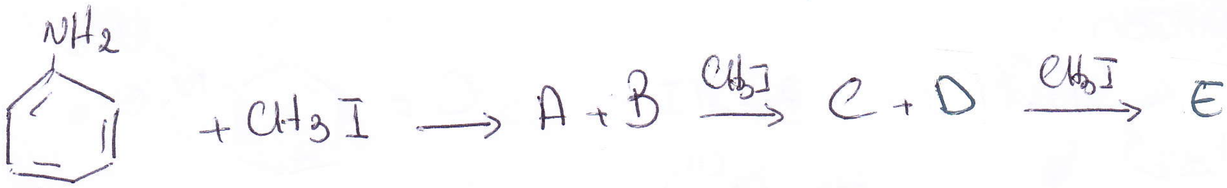
isonitrile

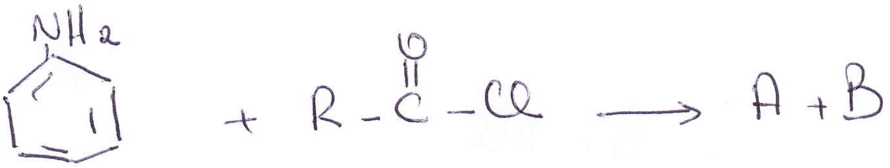
AMINES AROMATIQUES:ANILINE (2)

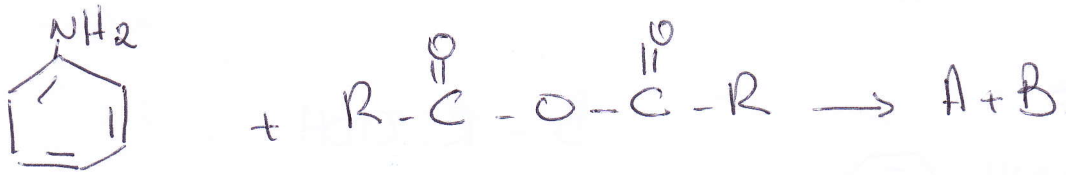


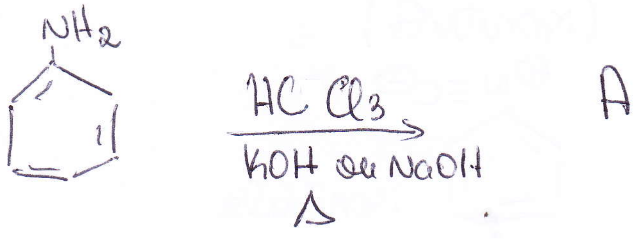








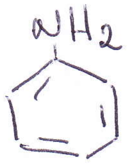




AMINES AROMATIQUES:ANILINE

Degradation d'Hoffman : (decarboxylation)

A =



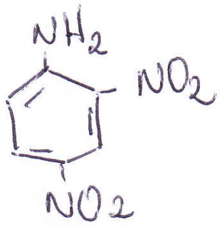
B = CO_2

C = NaBr

⚠ NaOBr = hypobromate de sodium .

Amination sur derivés halogenés :

A =



B = HCl

S_NAR favorisée car :

- Cl est activé par NO_2
- Pas de base forte

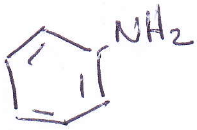
A = Rien

SN ne se fait pas

- Cl n'est pas actif
- Cl n'est pas mobile

Amination des halogenures d'aryle : E/A

A =



B = HCl

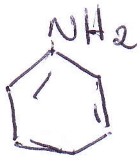
intermediaire aryne = benzyne

E/A favorisée car :

- $NaNH_2$ base forte
- Cycle non activé

Amination du Phenol :

A =



B = H_2O

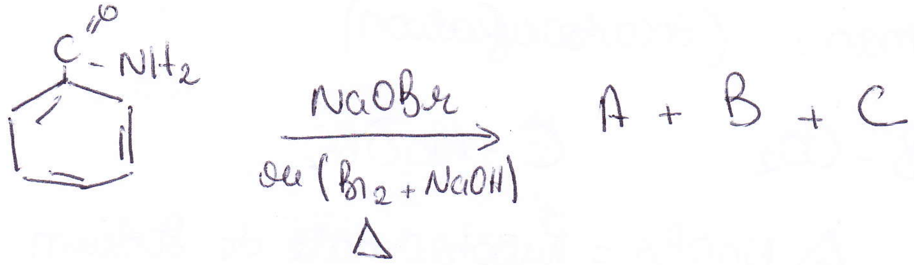
Reduction des derivés nitrés

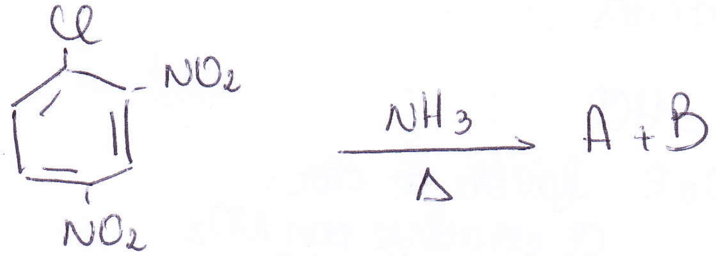
A =

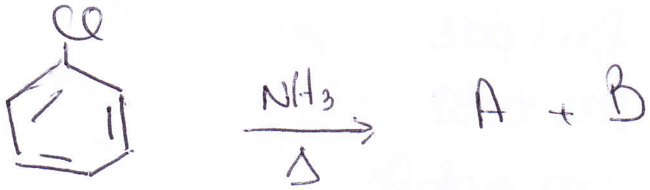
Reduction des derivés nitrés

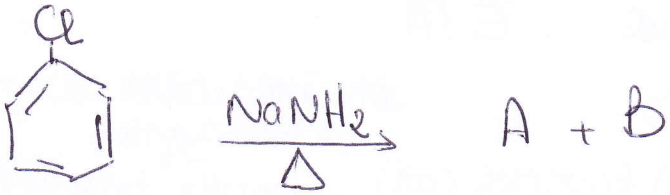
A =

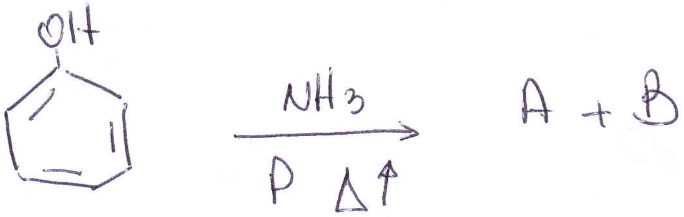
AMINES AROMATIQUES:ANILINE (1)

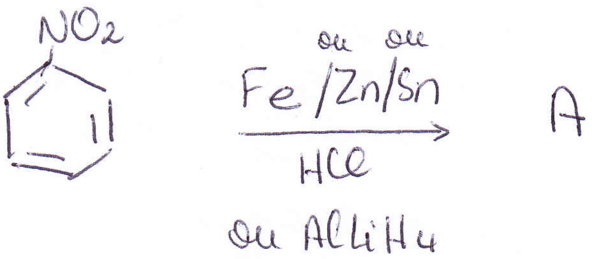


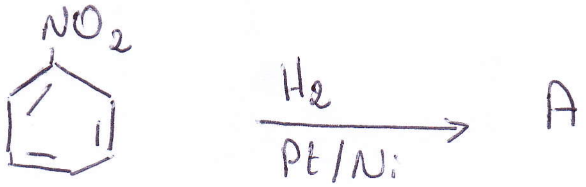












Addition Sur chlorure d'acide

$A = R-\underset{R'}{\overset{Cl}{C}}-\overset{\ominus}{O}MgX$ $B = R-\overset{R'}{C}=O$ $C = ClMgX$

$D = R-\underset{R}{\overset{R}{C}}-OH$ $E = HOMgX$

Addition Sur nitrile imine

$A = R-\underset{R}{C}=\overset{\ominus}{N}MgX$ $B = R-\overset{R'}{C}=NH$ $C = HOMgX$

$D = {}^{R}_{R'}{>}C=O$ $E = NH_3\uparrow$

cetone n'evolue pas vers alcool III^{aire}

---

addition sur derives satene = epoxyde.

$A = R-CH_2-CH_2-OMgX$ $B = R-CH_2-CH_2-OH$

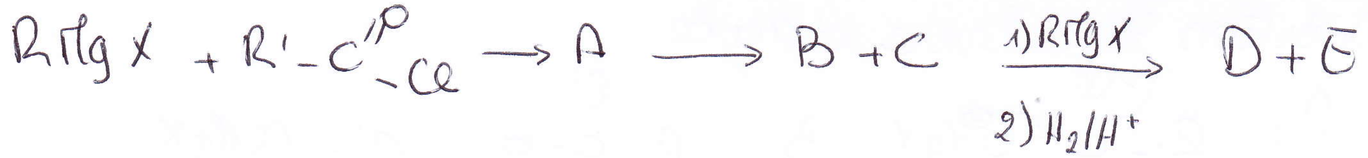
---

addition sur derivés Salinés

$A = R-CH_2-\underset{OMgX}{CH}-CH_3$ $B = R-CH_2-\underset{OH}{CH}-CH_3$

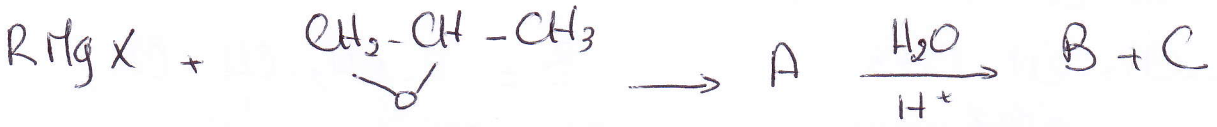
$C = HOMgX$

Regioselectivité : Nucleophile attaque le carbone le moins Substitué : il se forme l'alcool le (+) substitué



$$RMgX + R'-C(=O)-Cl \longrightarrow A \longrightarrow B + C \xrightarrow[2)\ H_2O/H^+]{1)\ RMgX} D + E$$

$$RMgX + R-C\equiv N \longrightarrow A \xrightarrow[H^+]{H_2O} B + C \xrightarrow[H^+]{H_2O} D + E$$



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organomagnesiens (3)

ORGANOMAGNESIENS

reaction de substitution avec des derivés halogenés.

$A = R-CH_2-CH=CH_2$ $B = MgCl_2$

Substitution avec halogenures metalliques :

$A = RHgCl$ $B = MgCl_2$

organomercurique mixte.

$A = RHgR$ $B = 2MgCl_2$

organomercurique symetrique .

$A = RCdCl$ $B = MgCl_2$

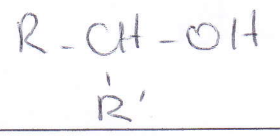
$A = RCdR$ $B = 2MgCl_2$

Addition sur derivé carbonylé : formol = formaldehyde

$A = CH_2-OMgX$ $B = CH_2-OH$ $C = HOMgX$ $D = \frac{1}{2} MgOH_2$

$E = \frac{1}{2} MgX_2$

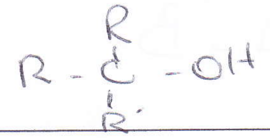
Addition avec aldehyde :

A =


$R-\underset{R'}{\underset{|}{CH}}-OH$

alcool II^{aire} $B = HOMgX$

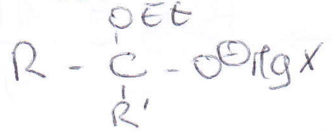
Addition avec une cetone.

A =


$R-\overset{R}{\underset{R'}{\underset{|}{C}}}-OH$

$B = HOMgX$

Sur un ester

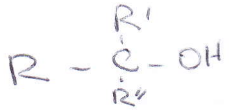
A =


$R-\overset{OEt}{\underset{R'}{\underset{|}{C}}}-OMgX$

$B = EtOMgX$

C =


$R-\overset{O}{\overset{\|}{C}}-R'$

D =


$R-\overset{R'}{\underset{R''}{\underset{|}{C}}}-OH$

$E = HOMgX$

ORGANOMAGNESIENS (2)

$R-MgCl + Cl-CH_2-CH=CH_2 \longrightarrow A + B$

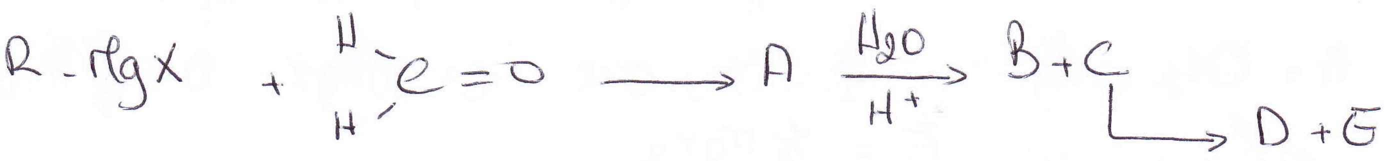
$RMgCl + HgCl_2 \longrightarrow A + B$

$\underline{\underline{2}}\, RMgCl + HgCl_2 \longrightarrow A + B$

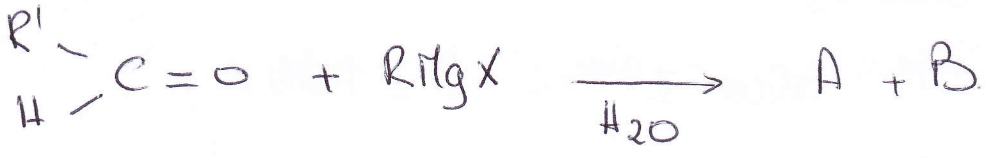
(si excès)

$RMgCl + CdCl_2 \longrightarrow A + B$

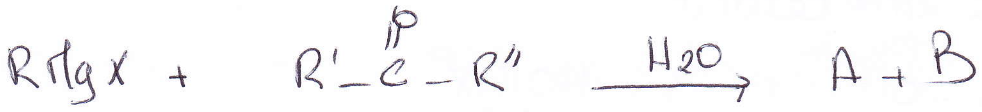
$\underline{\underline{2}}\, RMgCl + CdCl_2 \longrightarrow A + B$



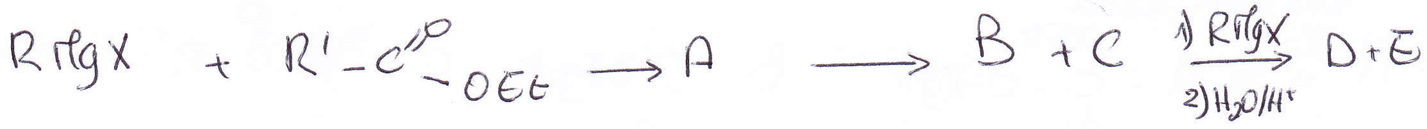
$R-MgX + H_2C=O \longrightarrow A \xrightarrow[H^+]{H_2O} B + C$; $C \longrightarrow D + E$



$R'HC=O + RMgX \xrightarrow[H_2O]{} A + B$



$RMgX + R'-CO-R'' \xrightarrow{H_2O} A + B$



$RMgX + R'-COOEt \longrightarrow A \longrightarrow B + C \xrightarrow[2)\ H_2O/H^+]{1)\ RMgX} D + E$

ORGANOMAGNESIENS (1)

$$RX \xrightarrow[\text{etheranhydre}]{Mg} A$$

$$RMgX + H_2O \longrightarrow A + B$$
$$B \longrightarrow C + D$$

$$RMgX + O_2 \longrightarrow A \xrightarrow{RMgX} B \xrightarrow{H_2O/H^+} C + D$$

$$RMgX + CO_2 \longrightarrow A \xrightarrow{H_2O/H^+} B + C$$

$$RMgX + AH \longrightarrow A + B$$

$$AH + CH_3MgI \longrightarrow A + B$$

$$HO-H + CH_3MgI \longrightarrow A + B$$

$$R-OH + CH_3MgI \longrightarrow A + B$$

$$R-C\equiv C-H \xrightarrow{CH_3MgI} A + B$$

$$R-\bar{N}\begin{matrix} /H \\ \backslash H \end{matrix} + CH_3MgI \longrightarrow A + B$$

$$R-MgX \xrightarrow{I_2} A + B$$
$$B \longrightarrow C + D$$

ORGANOMAGNESIENS

Preparation des organomagnesiens

$A = RMgX$ l'ether sert à stabiliser l'organomagnesien par des liaisons de coordination

---

Precaution sion reactions parasites : ① milieu anhydre.

$A \Rightarrow RH$ $B \Rightarrow XMg\text{-}OH$ (instable se dissoue) $C = \frac{1}{2} Mg(OH)_2$

$D = 1/2\ MgX_2$

---

② atmosphere inerte.

$A = R\text{-}O\text{-}O\text{-}MgX$ (instable)

peroxyde de magnesium

$B = 2\ ROMgX$

$C = 2\ ROH$

$D = HO\text{-}MgX$.

$A = R\text{-}C(=O)\text{-}OMgX$ $B = R\text{-}C(=O)\text{-}OH$ $C = HOMgX$

methode de preparation d'acides carboxyliques

Reaction de substitution = Methode de Zirivitinoff.

$A = RH$ (alcane) $B = AMgX$

$A = CH_4 \uparrow$ $B \Rightarrow AMgI$

$A = CH_4 \uparrow$ $B \Rightarrow HOMgI$

$A = CH_4 \uparrow$ $B \Rightarrow RO\text{-}MgI$

$A = CH_4 \uparrow$ $B = R\text{-}C \equiv C\text{-}MgI$

$A = CH_4 \uparrow$ $B = R\text{-}\underset{H}{\bar{N}}\text{-}MgI$

methode de Zirivitinoff.

Substitution avec des halogenes

$A = RI$ $B = IMgX$ $C = \frac{1}{2} MgI_2$ $D = \frac{1}{2} MgX_2$