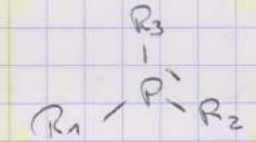
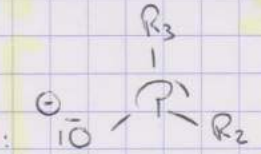
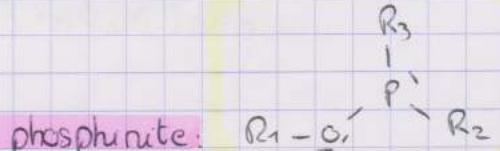
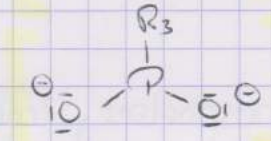
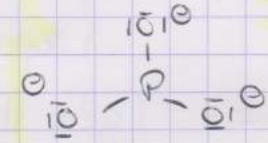
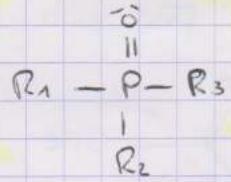
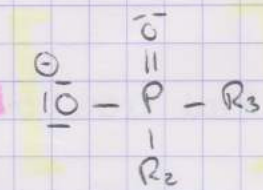
Fiche révision Heteroéléments I

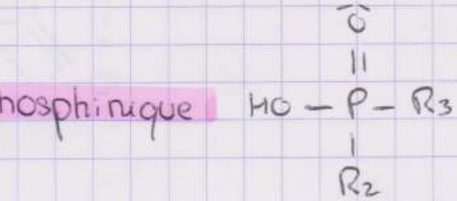
Le phosphore:

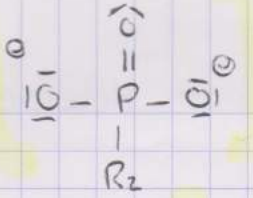
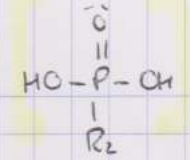
- $E(P-O) = 594\ kJ.mol^{-1}$
- $E(P=O) = 823\ kJ.mol^{-1}$ => moteur reaction

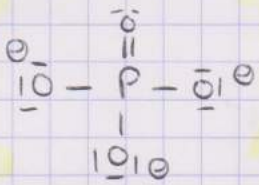
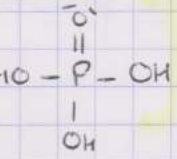
- 3 formes de phosphore :
  - noir : feuillets hexagonaux
  - blanc : P_4 tetraédrique (haute± inflammable, toxique)
  - rouge : Th bcp ⊖ long (allumettes)

* Nomenclature

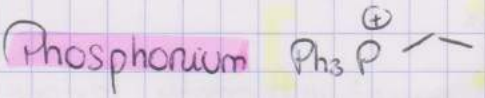
- Phosphane : 
- Phosphinite :  ester de phosphinite : 
- Phosphonite :  =
- Phosphite :  =
- Oxyde de phosphine 
- Phosphinate  ester ..

acide phosphinique 

- Phosphonate  acide phosphonique 

- Phosphate:  acide phosphorique 

- Ylures  Ylene

- Phosphonium 

⚠ Composés trivalents et pentavalent sont chiraux

↳ Barrière inversion > 100 kJ. mol⁻¹ : pas interconversion à Tamb

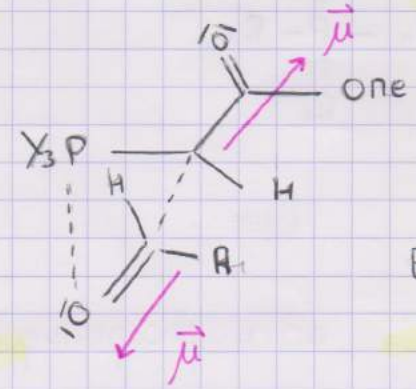
- Les phosphanes sont ⊕ Nu que les amines
- pKa(Me_3PH^+ / Me_3P) = 8,7

* Utilisation en chimie Organique :

- Wittig : formation oxaphosphetane { Supra-antara (on p) / Supra-Supra (on d)

↳ Supra antara par non stab (gêne stérique)

↳ Supra-Supra par stab (minimisation interaction dipôle)

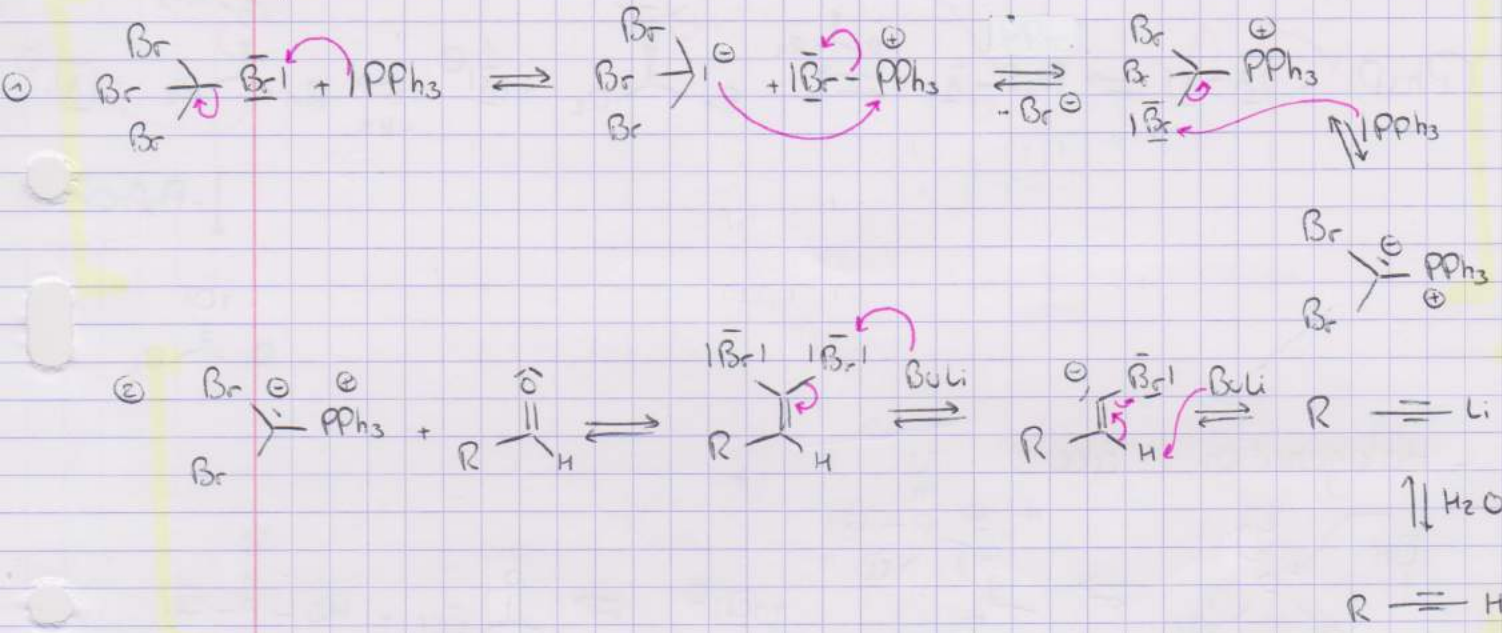


Etat transition plissé trans

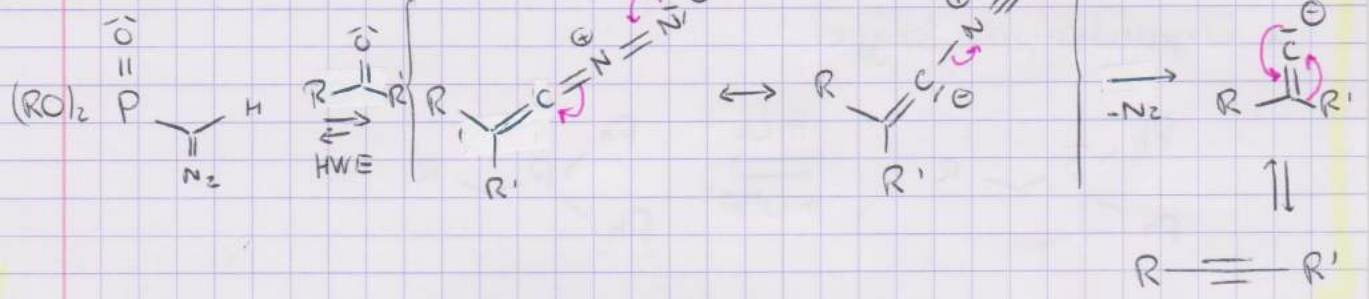
Fiche révision hétérocatalyse II.

• HWE : fermeture betaine trans est ⊕ rapide => alcene (E)

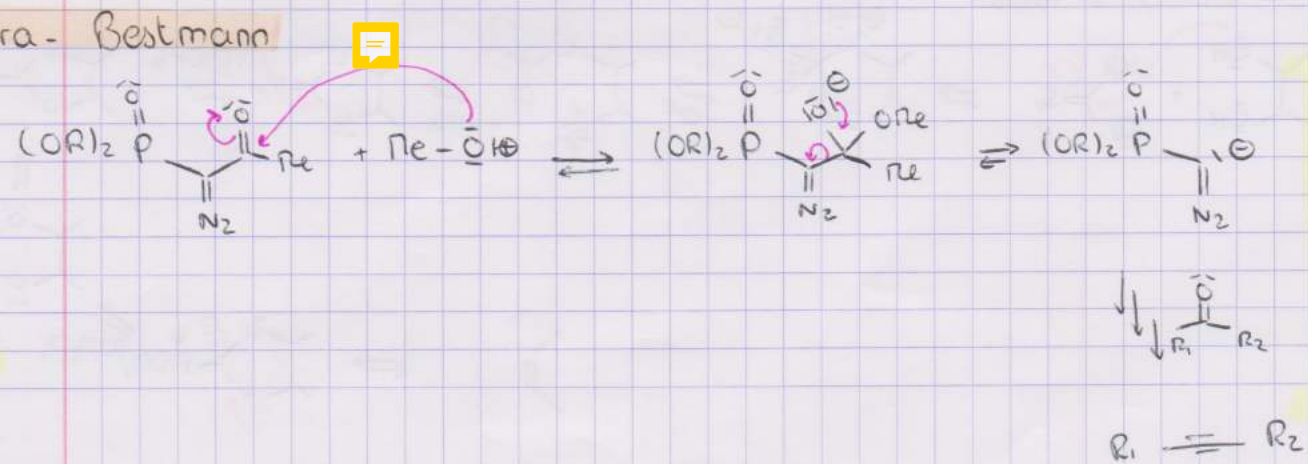
- Corey Fuchs



- Seyfert - Gilbert



- Ohira - Bestmann

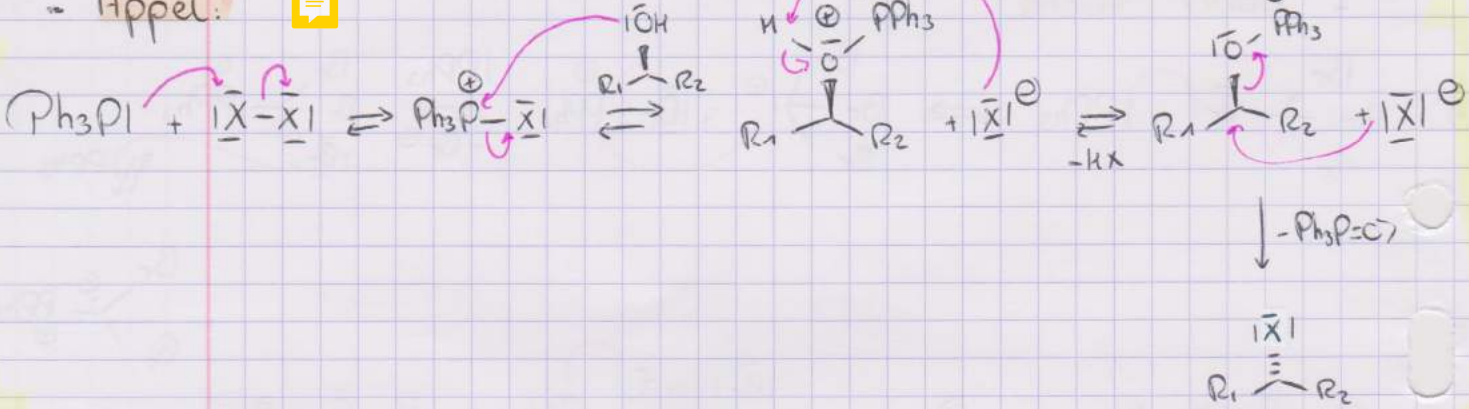


- Staudinger $R-N_3 + PPh_3 \xrightarrow{H_2O} R-NH_2$

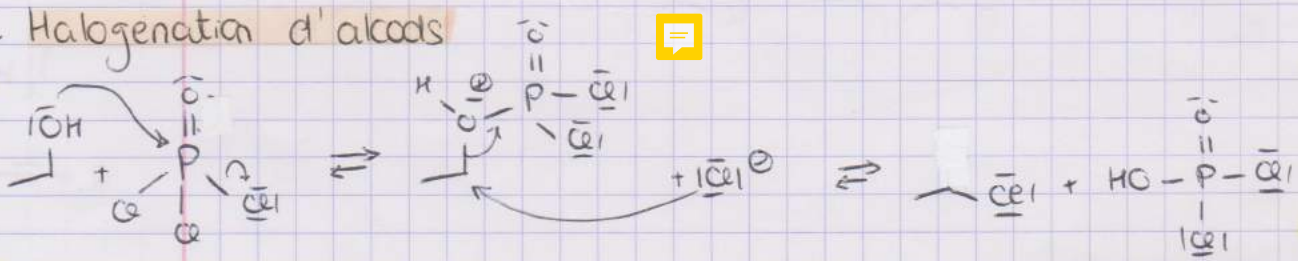
- Vilsmeier-Hach : $Ar-N< + POCl_3 \xrightarrow[H_2O]{DMF} HOC-Ar-N<$.

- Mitsunobu : $>OH + DEAD + PPh_3 \xrightarrow{YH} >\cdots Y$.

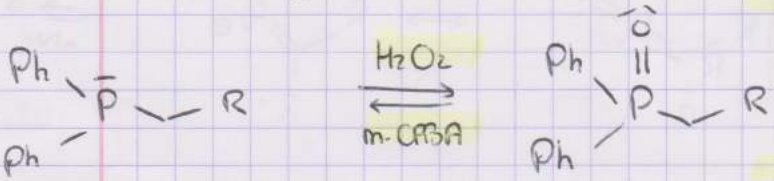
- Appel :



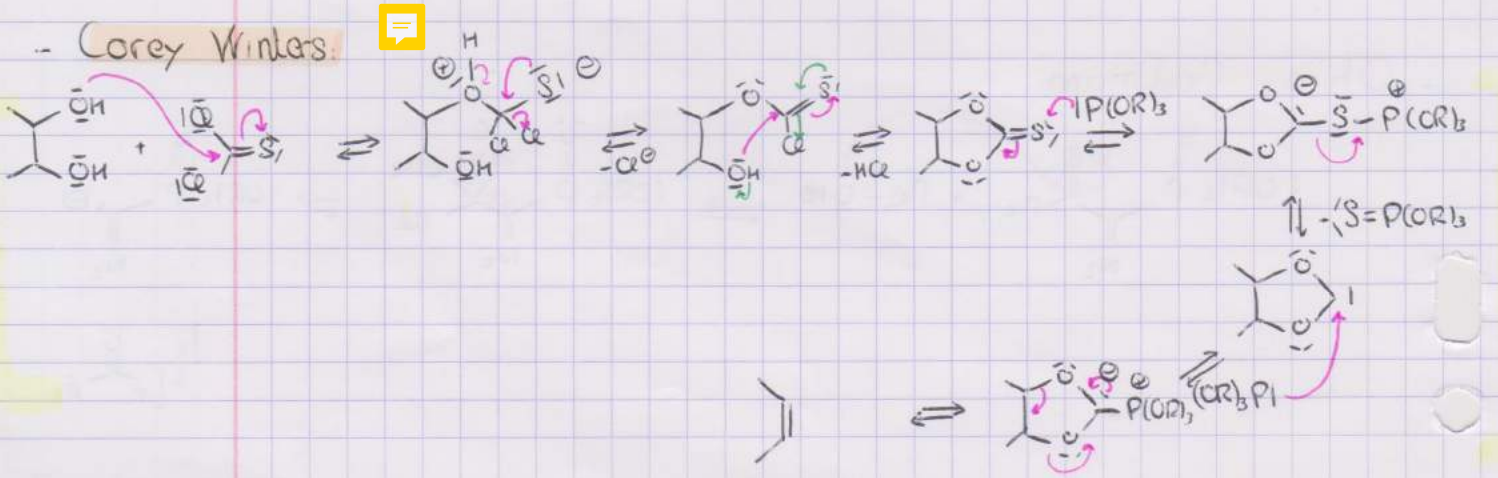
- Halogenation d'alcools



* Oxydation du soufre :



- Corey Winters :



Fiche révision hétéroéléments II

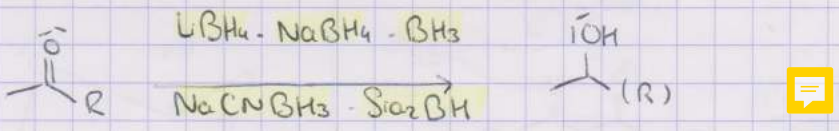
Le Bore :

* Nomenclature

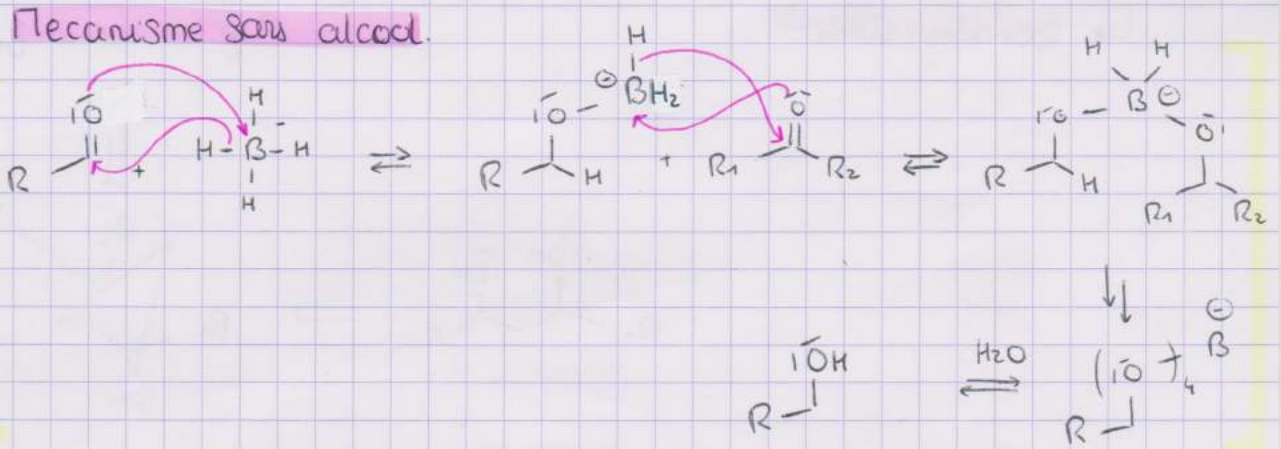
- boranes : BH_3 : non stable : Formation dimères
- alkylboranes BH_nR_{3-n}
- fluoroborane sont des très bons acide Lewis

- $R_2B(OH)$: acide borinique / borinate / ester borinate
- $RB(OH)_2$: acide boronique / boronate / ester boronique
- $B(OH)_3$: Acide borique / tetrahydroxyborate / ester borate

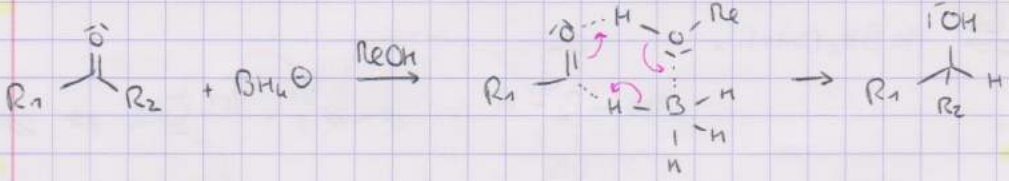
• Hydrure de Bore : reducteur



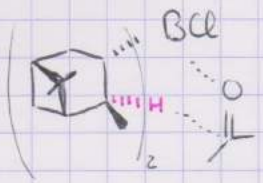
- Mécanisme sans alcool.



- Mécanisme avec alcool

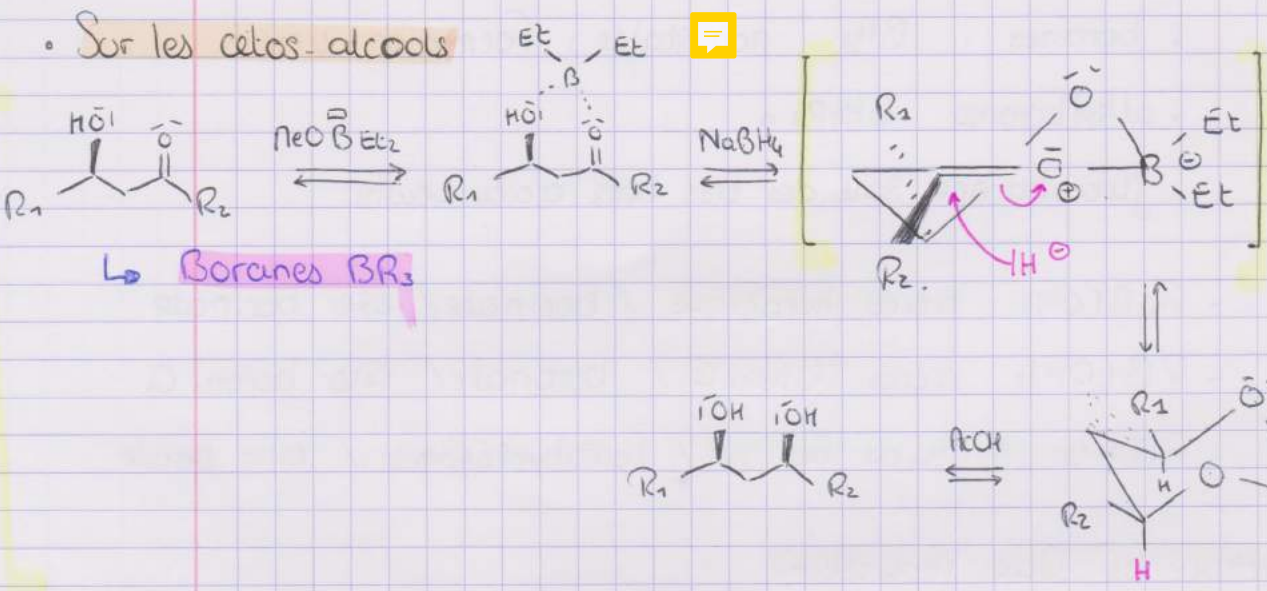


↳ On peut avoir stéréosélectivité avec borane sélective

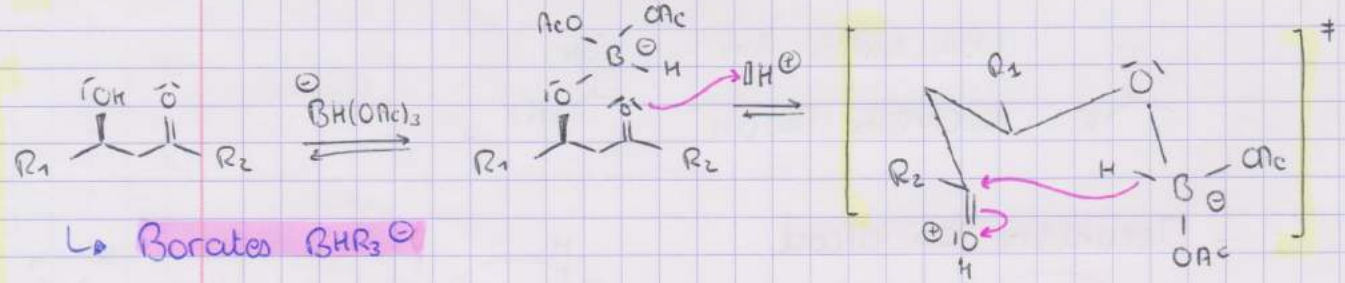


=> C'est le H en β qui réagit

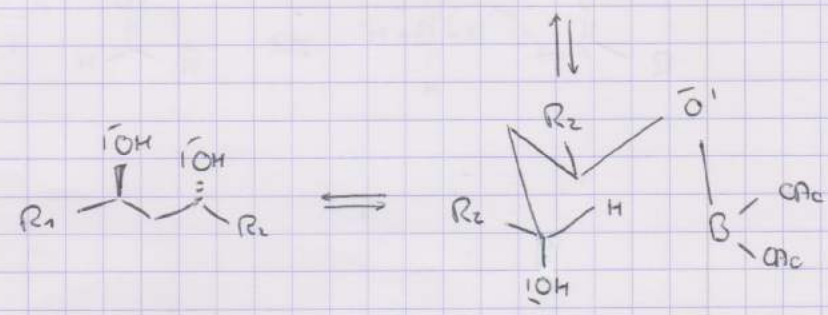
- Sur les cétos-alcools



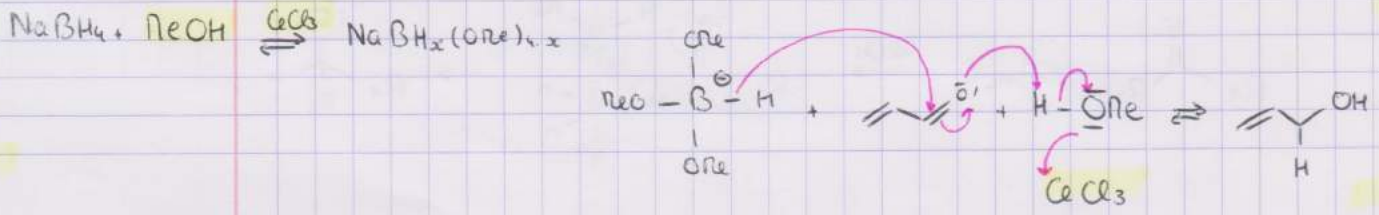
↳ Boranes BR_3



↳ Borates $BHR_3^{\ominus}$

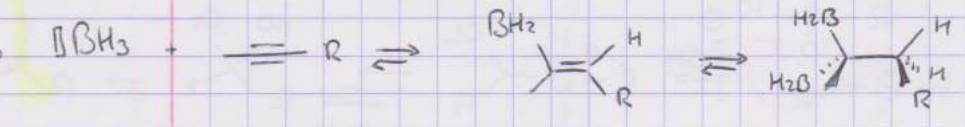


- Condition de Luche : addition 1,2 au lieu 1,4 (⊕ dur)



Fiche révision hétéroéléments III

• Hydroboration :

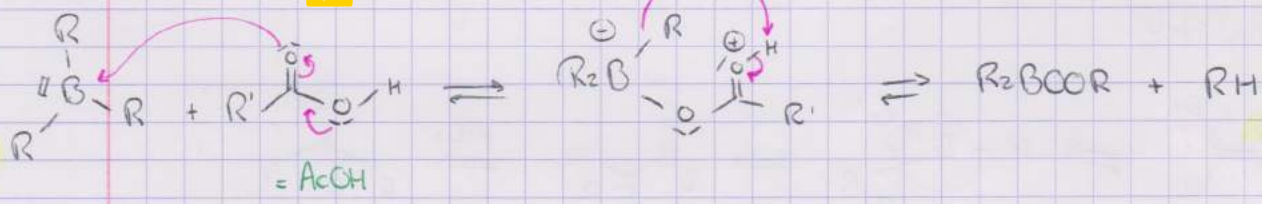


↳ di-addition si on a peu encombrement sur borane et alcène

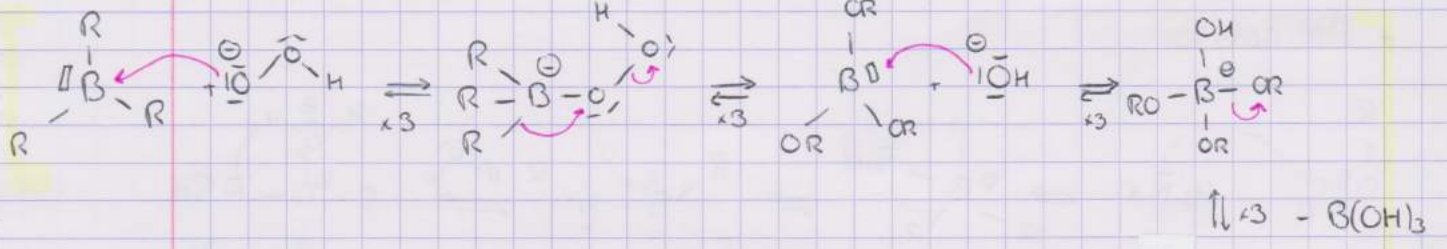
↳ addition du bore sur le carbone le moins encombré

↳ enantiosélectif avec borane chiraux

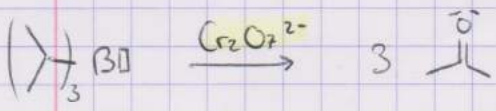
* Protonolyse :



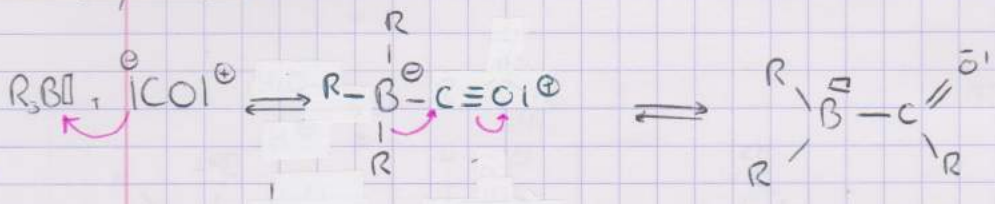
* Formation d'un alcool :



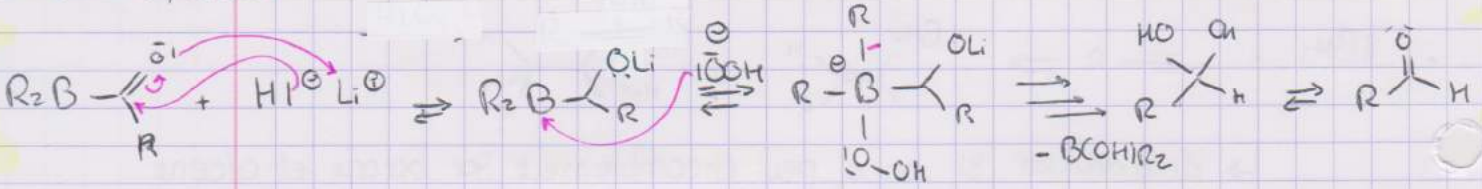
* Oxydation :



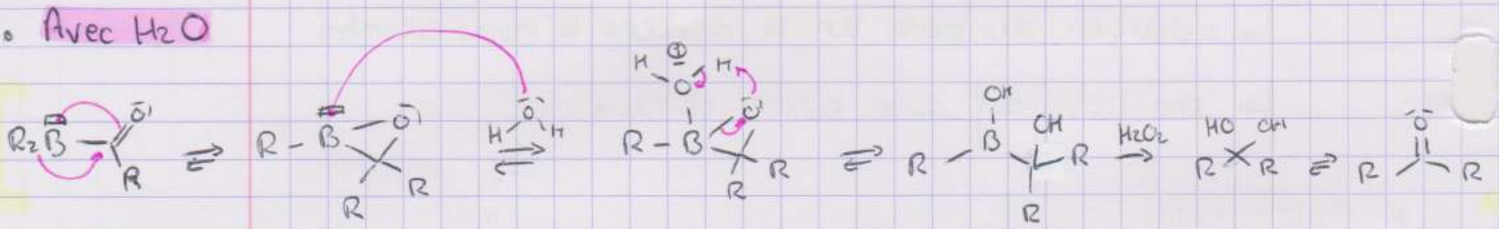
* Carbonylation



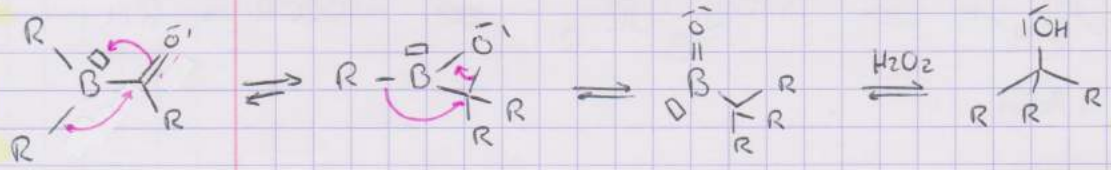
• Avec hydrure :



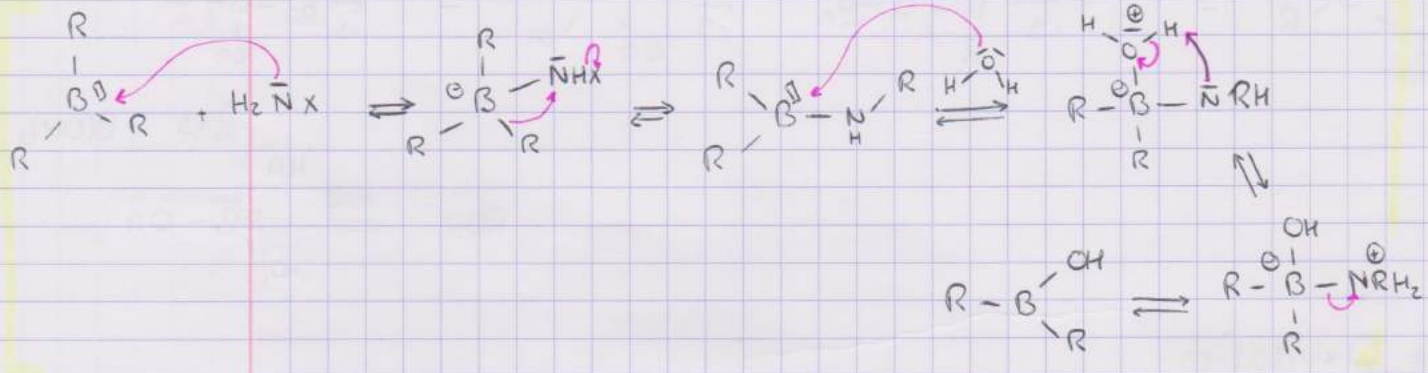
• Avec H_2O



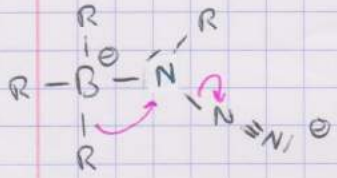
Sans $H_2O / H^\ominus$



* Aminolyse :

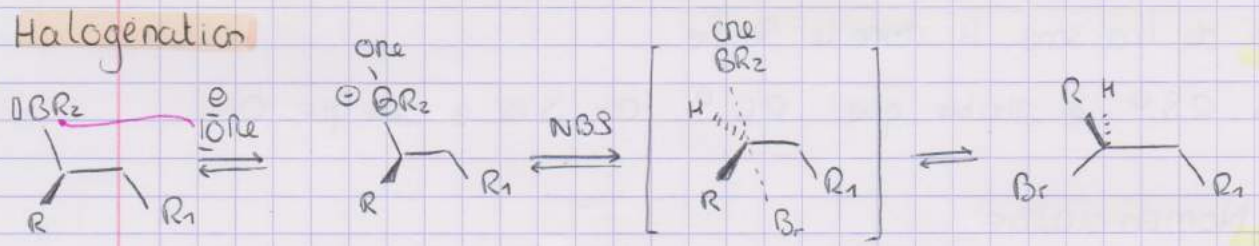


↳ Possible avec N_3 et départ N_2

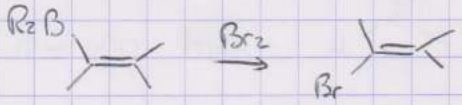


Fiche révision hetero elements V

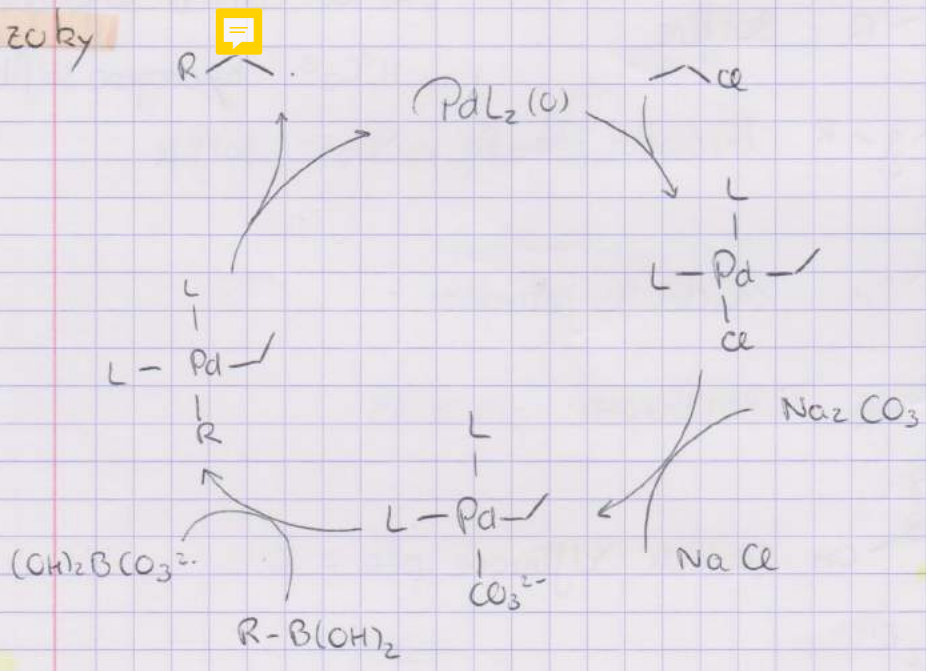
* Halogenation



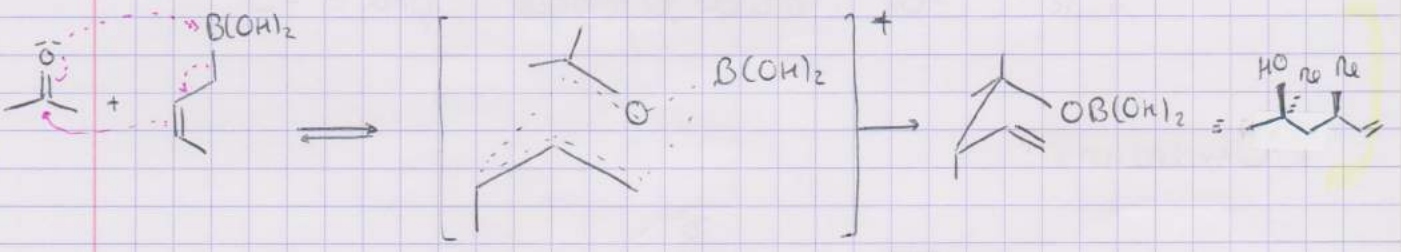
↳ Inversion configuration



* Suzuky



* allyl-boranes



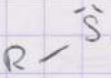
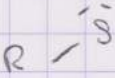
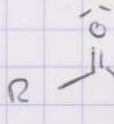
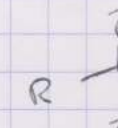
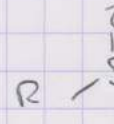
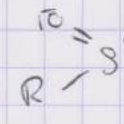
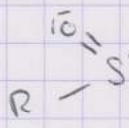
↳ Enantioselectivite avec copule chirale

Le Soufre

⚠ Pas de liaisons H avec le Soufre

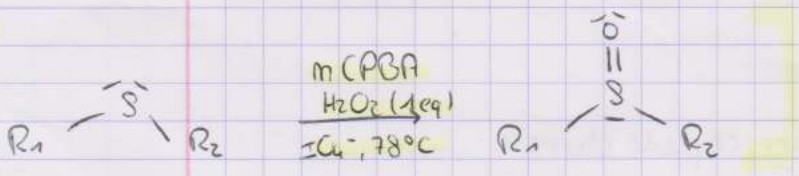
- $RS^{\ominus}$ ⊕ stable que $RO^{\ominus}$ car S est ⊕ mou que O

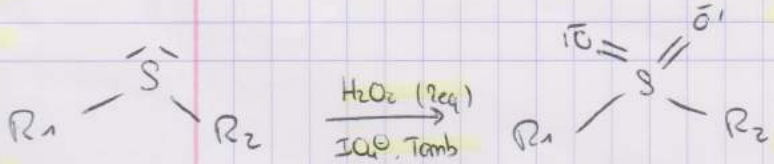
* Nomenclature

-  : thiol $pKa \simeq 11$
-  : Sulfure
-  : thioester $pKa \simeq 20$
-  : acides Sulféniques
-  : Sulfoxyde $pKa \simeq 35$ (Chiraux <=)
-  : acide Sulfinique $pKa \simeq 2$
-  : Sulfone
-  : acide Sulfonique $pKa \simeq -3$

- H_2SO_3 : acide Sulfureux
- H_2SO_4 : acide Sulfurique
- $HSO_3^{\ominus}$: hydrogéno Sulfite
- SO_3^{2-} : Sulfite

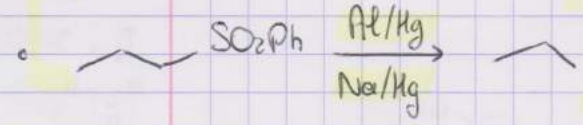
* Oxydations

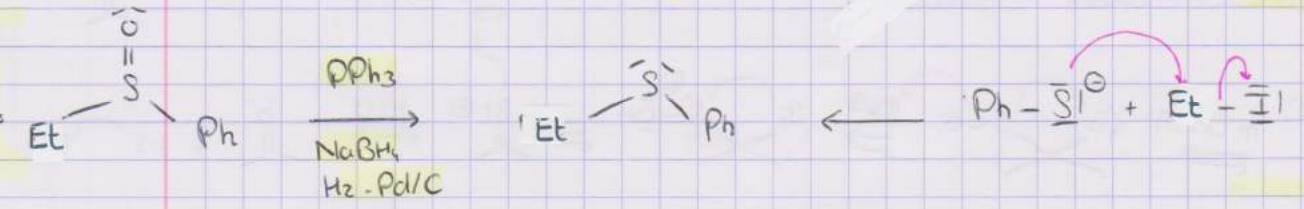




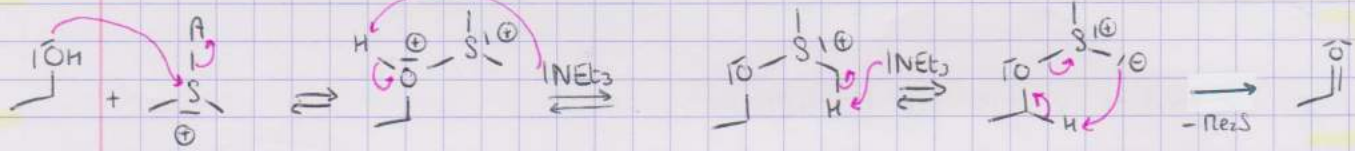
Fiche révision heteroelements VI

* Reductions :





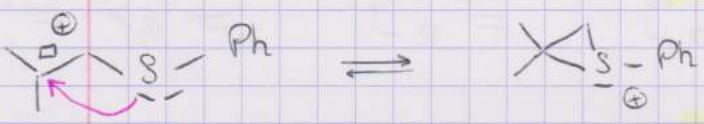
* Oxydations avec le soufre. (Swern ...)



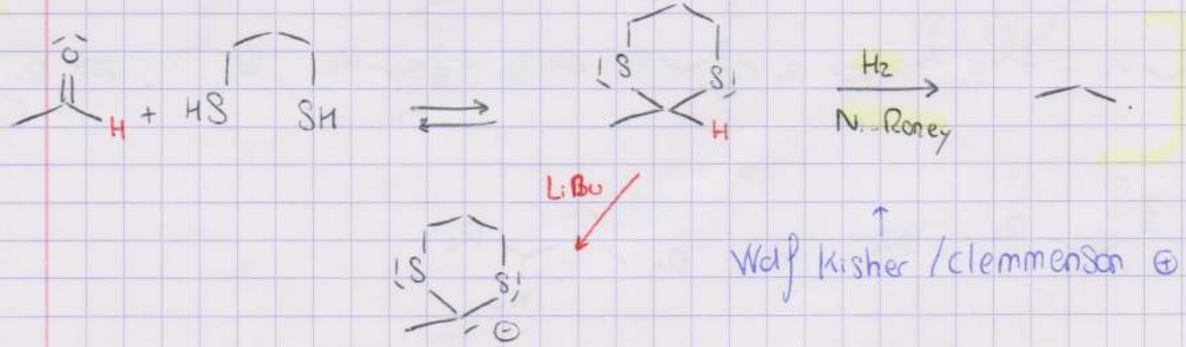
↳ Condi° douces / pas de Cr

↳ Pas de sur-oxydation en acide

* Reaction avec electrophile en β (Stabilisation carbocation)



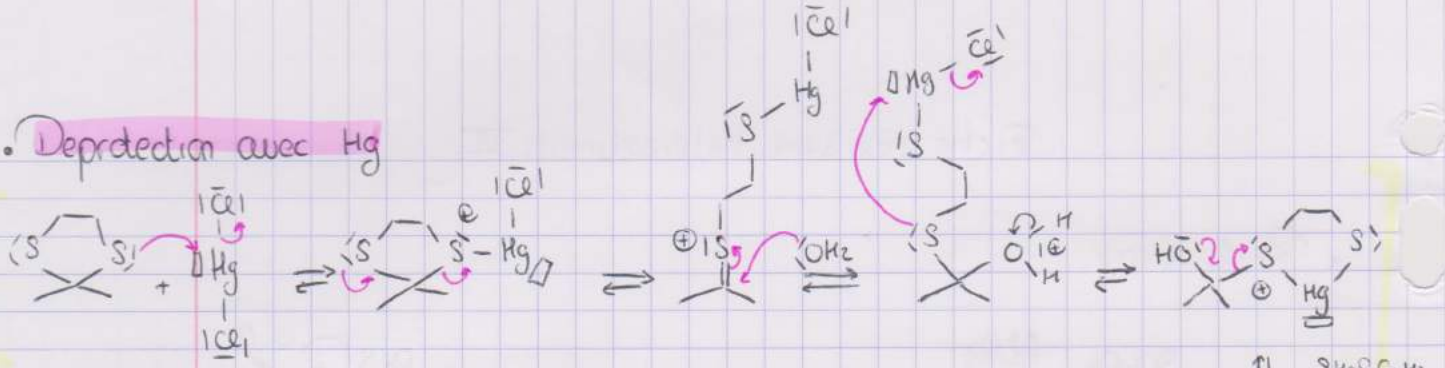
* Protection des carbonyles



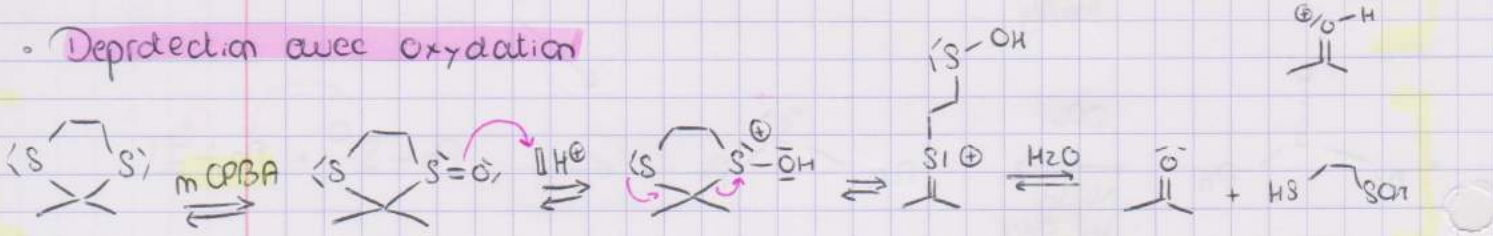
↑ Wolf Kisher / clemmenson ⊕ doux

Umpolung

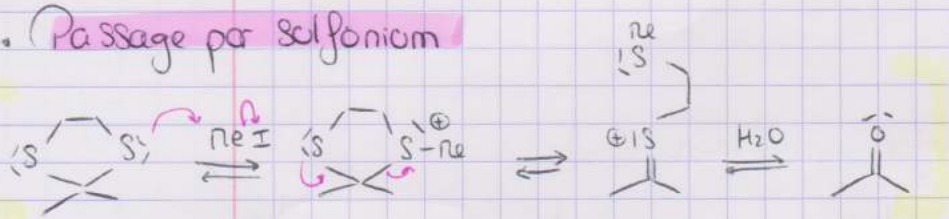
• Deprotection avec Hg



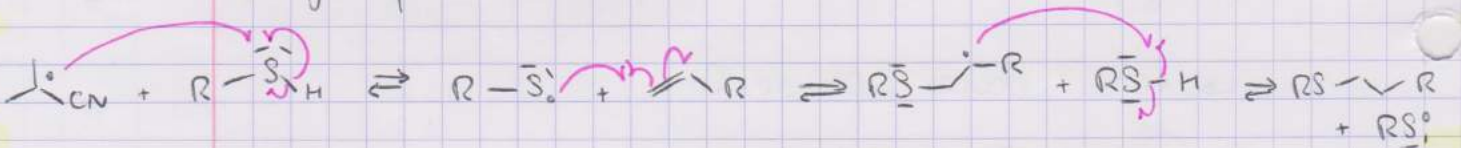
• Deprotection avec oxydation



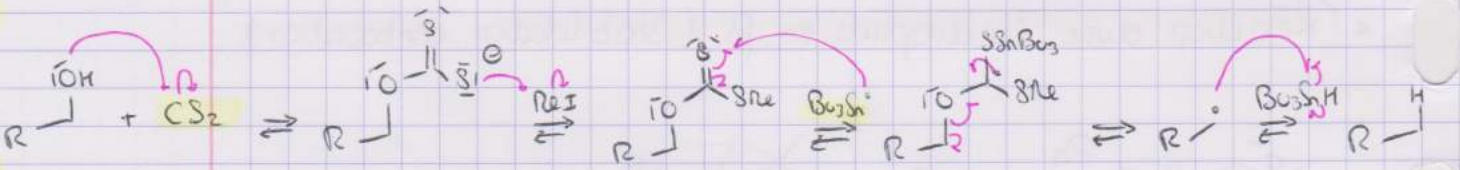
• Passage par sulfonium



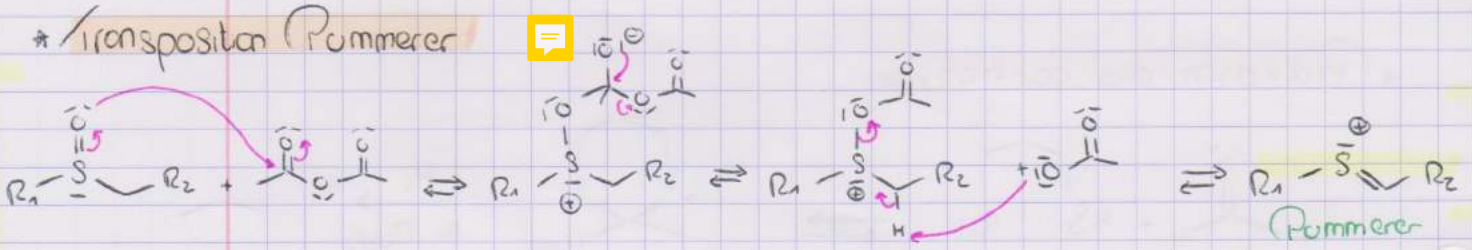
* Formation sulfure par radicaux

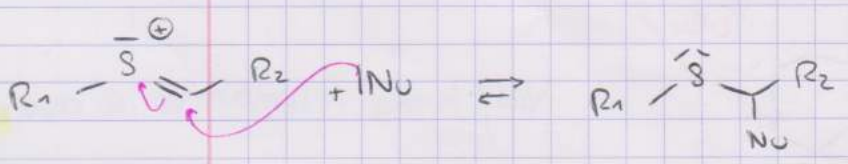


* Barton Mc Comby



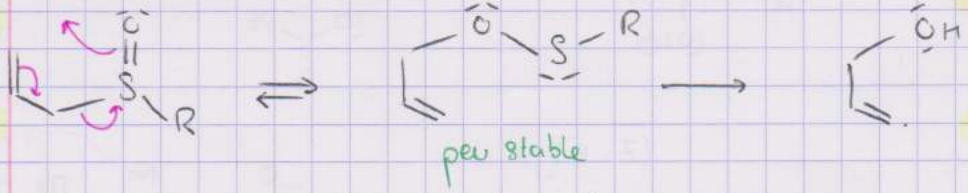
* Transposition Pummerer





Fiche révision heteroéléments VII

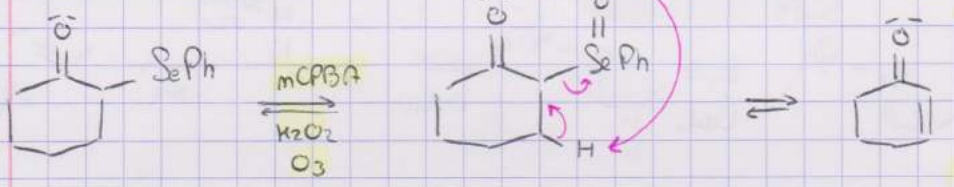
* Transpositions



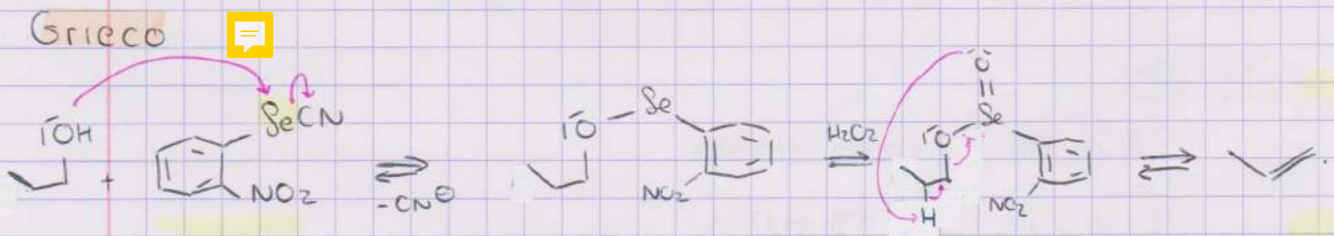
peu stable

↳ Fonctionne aussi avec Se

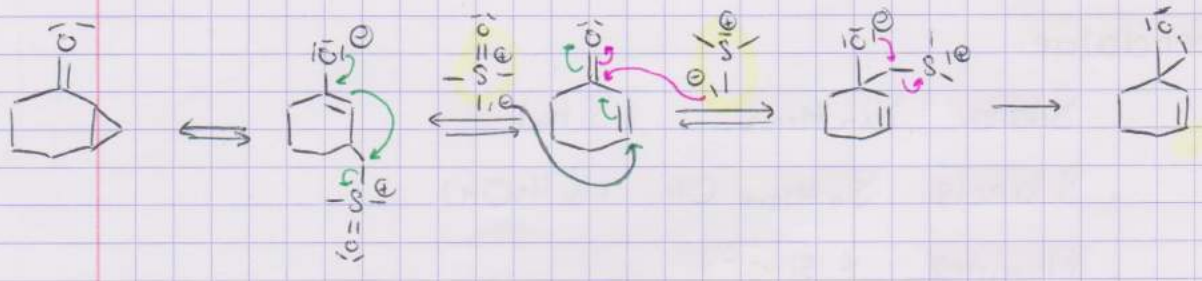
* Formation d'énones



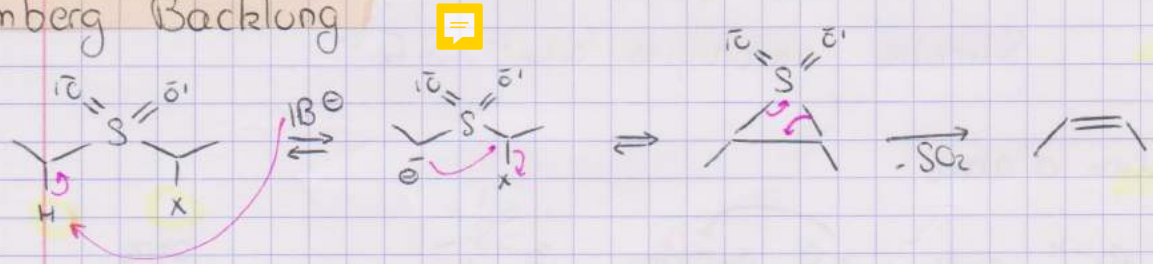
* Grieco



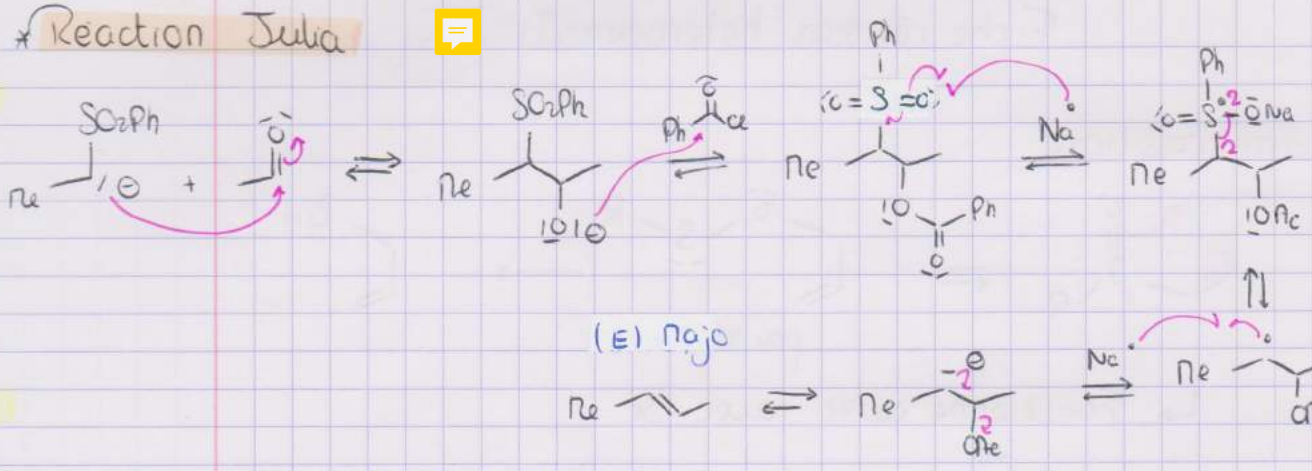
* Corey



* Ramberg Backlung

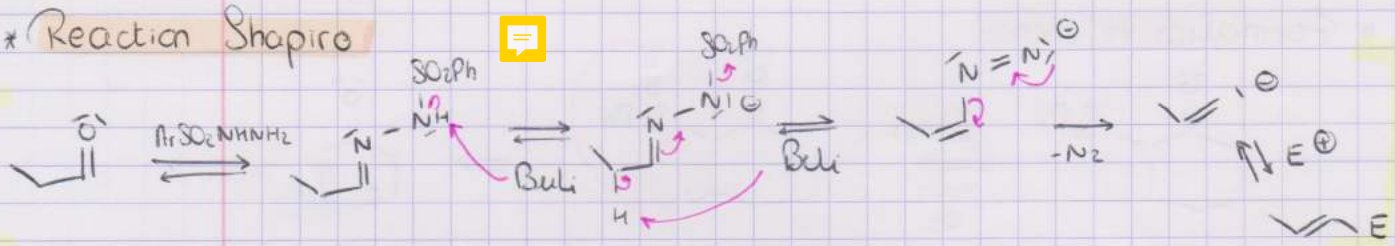


* Reaction Julia



(E) Najo

* Reaction Shapiro



Le Silicium :

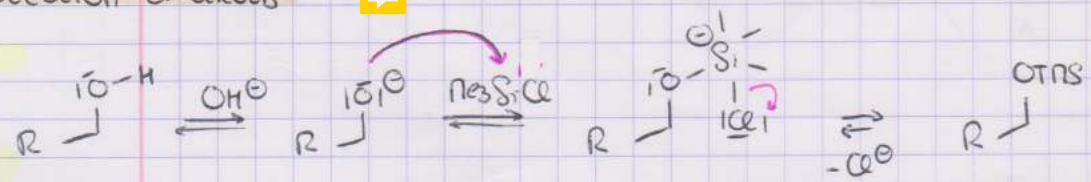
- 25 % de la croute terrestre
- E (Si O) = 530 kJ. mol^{-1}
- E (Si F) = 810 kJ. mol^{-1}

} Facteur reaction.

* Nomenclature :

- Silanes : $Si_n H_{2n+2}$. (SiH_4)
- Silanols : $Si_n H_{2n+1} OH$ (SiH_3OH)
- Siloxanes : $\left(Si(R)_2 - O \right)_n$.
- Silicates anioniques : SiO_4^{2-} ; SiF_6^{2-}

* Protection d'alcools

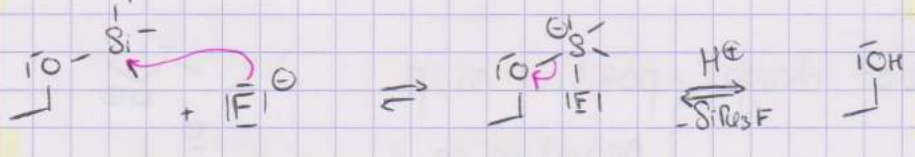


Fiche révision hétéroéléments VIII

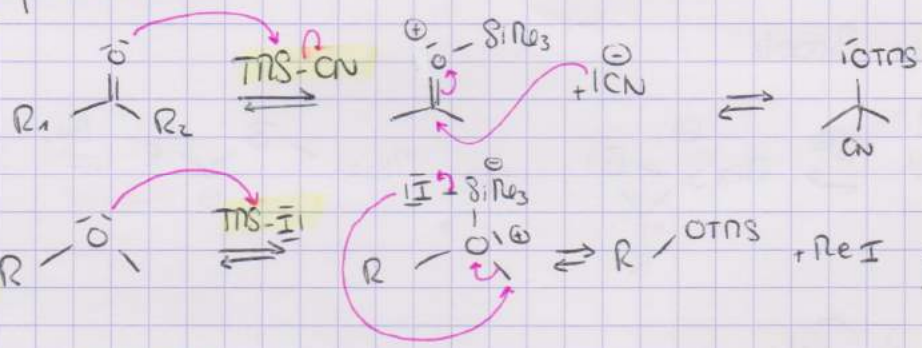
- éther Sylyles :

- Facilité déprotection dépend encombre ⁵ ⇒ "orthogonalité"

- Déprotection avec $F^{\ominus}$



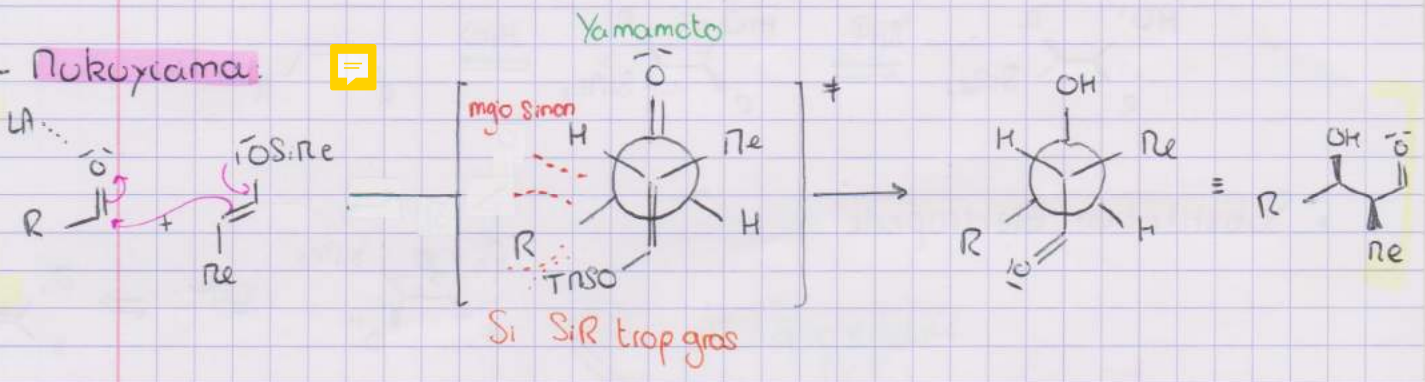
- Cas particulier



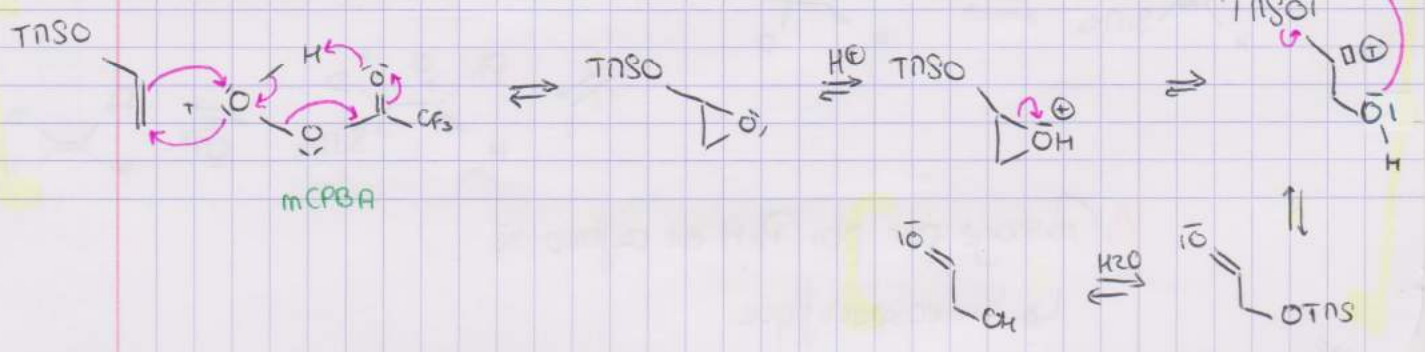
⇒ "$SiMe_3 = E^{\oplus}$"

* Ether d'ends Sylyles

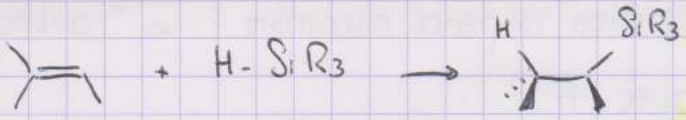
- Nukoyama



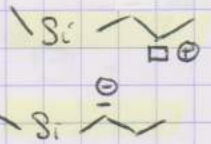
- Oxydation Robottom



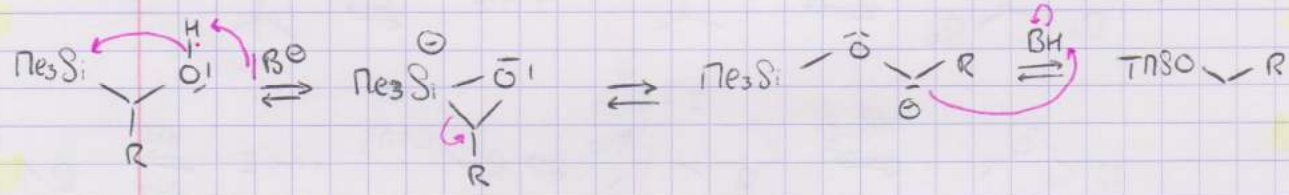
* Formation alkysilanes

- $R-MgX + X-SiR_3 \longrightarrow RSiR_3$
-  (hydrosilylation) aussi avec alcynes

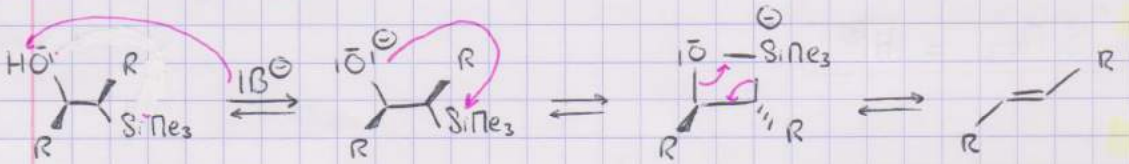
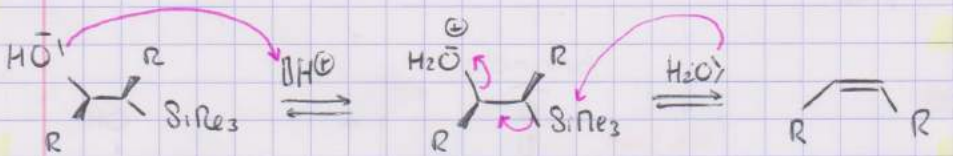
- Stabilisation charge { positive en β / negative en α



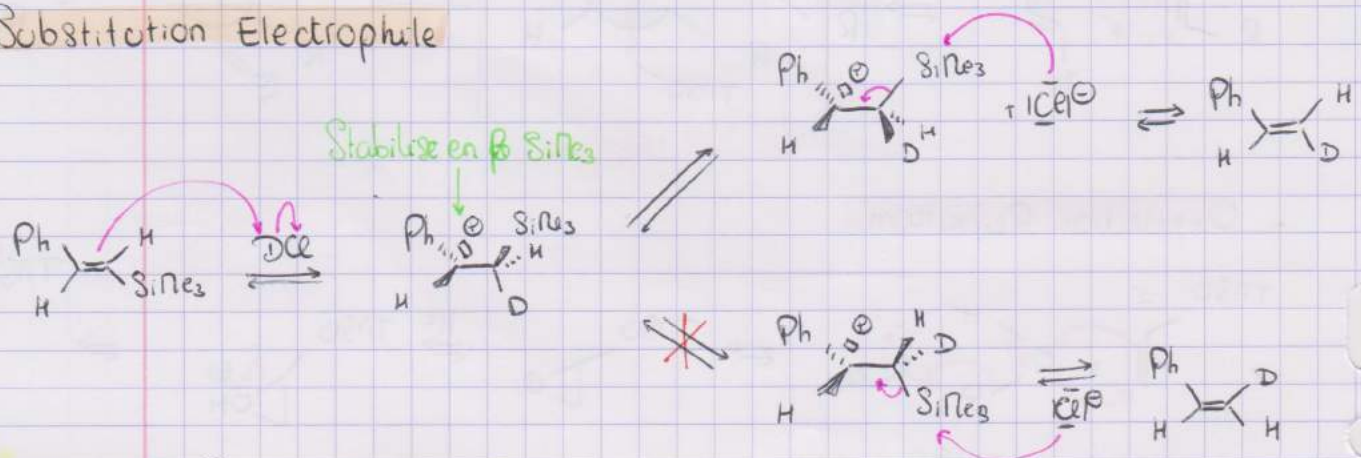
* Rearrangement Brook



* Elimination de Peterson:

- 
- 

* Substitution Electrophile

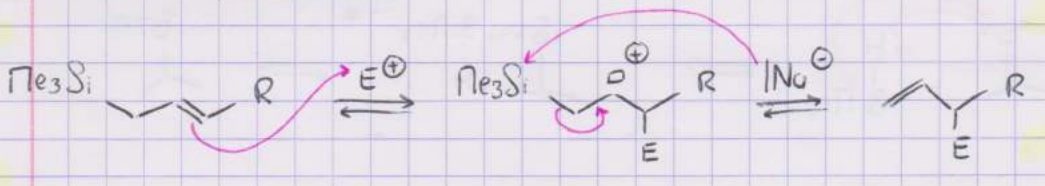


⚠ Passage par plan PhH est défavorisé

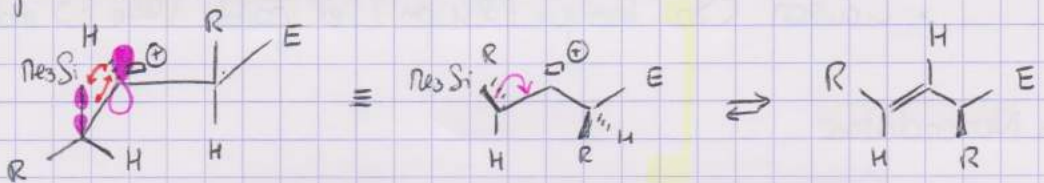
↳ Stereospecifique

Fiche révision heteroelements IX

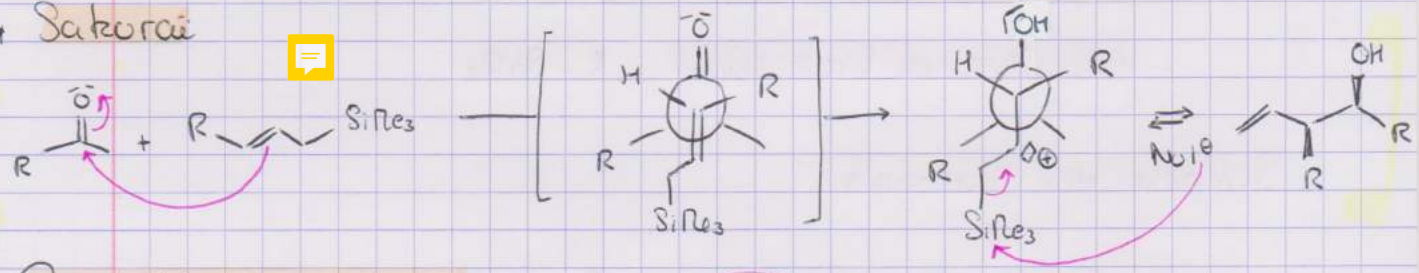
* Reactivité Allylsilanes:



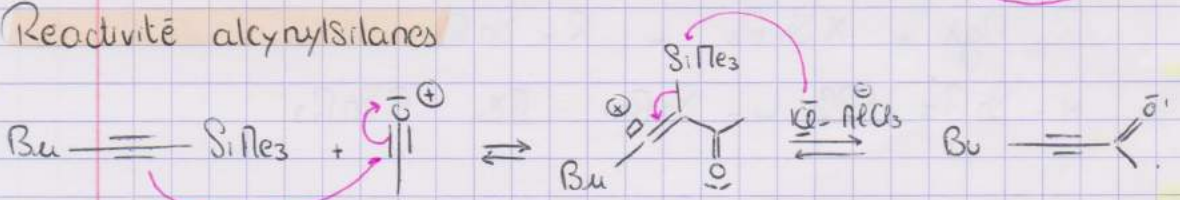
↳ il faut $SiMe_3$ en stabilisa ≤ au $C^{\oplus}$



* Sakurai

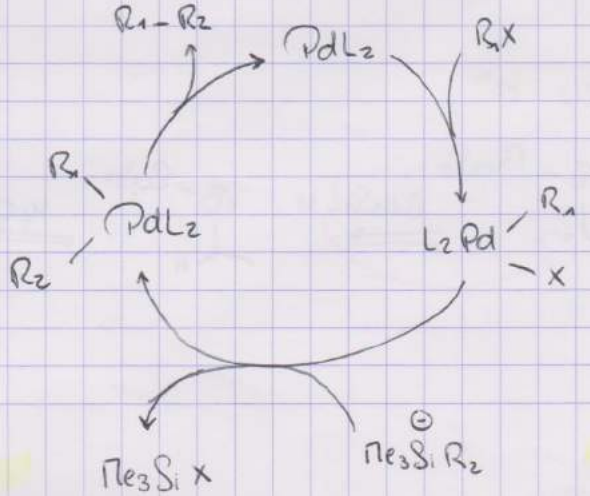


* Reactivité alcynylsilanes



* Hiyama.

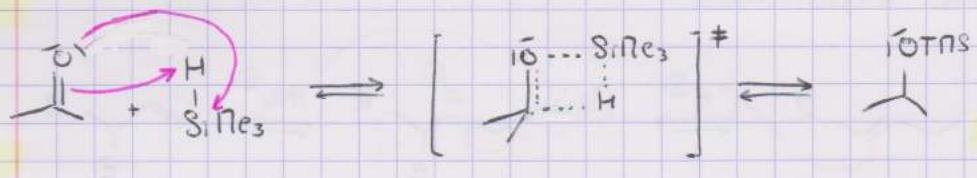
. $R_1X + R_2SiMe_3 \xrightarrow[\text{Base}]{Pd(0)} R_1-R_2$



Transmetallation

* Reduction par les hydrosilanes

- $R_3Si\,H$ sont des donneurs hydrures " $SiR_3^{\oplus}$; $H^{\ominus}$ "



L'Etain

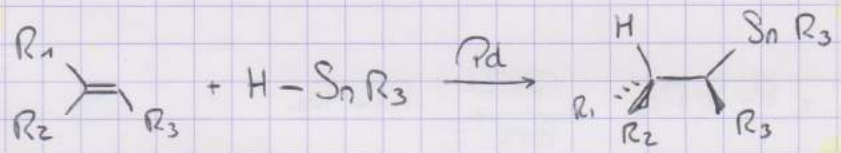
- Liaison CSn longue (210 pm) et faible (240 kJ.mol⁻¹) => polarisable

* Nomenclature

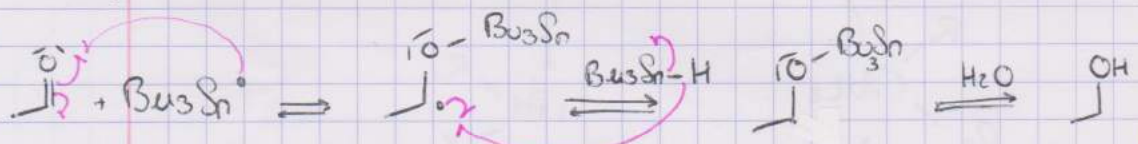
- Stannanes : $R_3Sn\,H$
- Oxyde de dialkyl etain : $\backslash O{=}SnR_2$
- Halogenure de trialkyletain : $X-SnR_3$

* Synthese des Stannanes:

- $R-MgX + XSnR_3 \rightarrow R-SnR_3$
- $H-SnR_3 \xrightarrow{LDA} Li-SnR_3 \xrightarrow{RX} RSnR_3$
- hydrostannation:



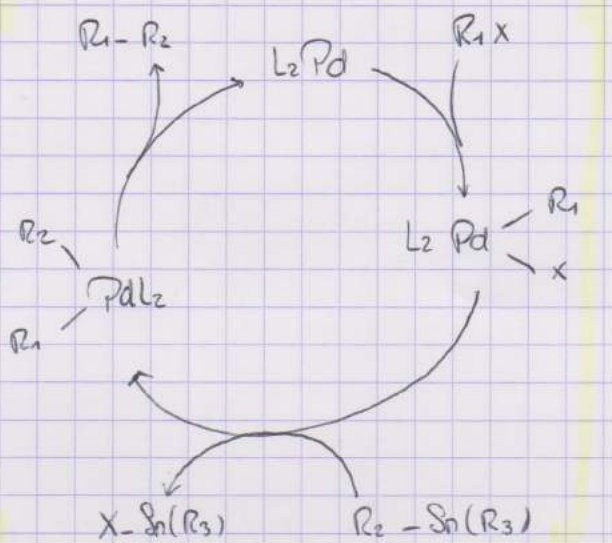
* Reactif comme donneur H°



Fiche révision hétéroéléments X

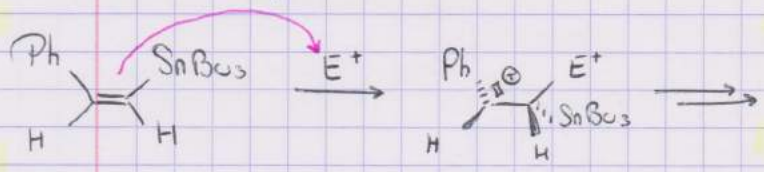
* Couplage Stille

- $R_1X + R_2Sn(R)_3 \xrightarrow{Pd} R_1R_2$

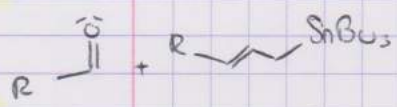


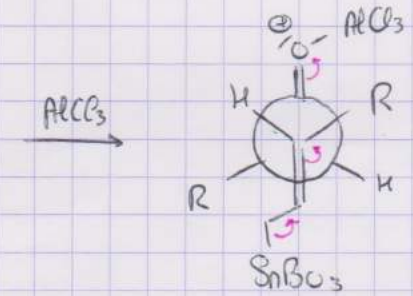
Transmetallation

* Addition électrophile



* Allylstananes

- 



-