X orga

Oxydo - réduction

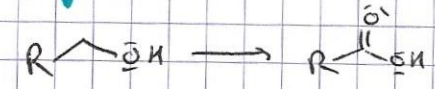
Biblio : - Mécanismes réact° en X orga, Brückner (chap 14)
- Chimie organique avancée tome 2, Carey (chap 12) +5
- (Clayden)
- ICO, Dromin ~~(chap 18.10 et 9.5 et 14.1)~~
- Strategic applications of named reactions in organic chem., Kürti
- Chimie Tout-en-un PCSI, Fosset (chap 18)
- Rabasso

I) Généralités

* Degré et classe d'oxydation (cf Brückner p485-489)
* Oxydat° ménagée ; coupure oxydante ; totale

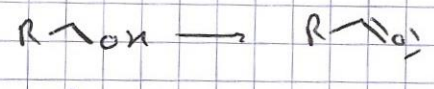
* Différents réactifs d'oxydant. cf fiche cours

Oxydations (ICO chap 13.8.4)

*  Carey tome 2 p 618

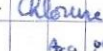
- $H_2Cr_2O_7$, H_2SO_4 dilué

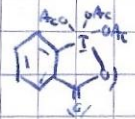
Jones - CrO_3, H_2SO_4 dilué Kürti p 229

* 

- 2 Pyr. CrO_3 → ds pyr Sarett Carey p 618
  → ds CH_2Cl_2 Collins

Corey - Pyr-H^+. Cl^-, CrO_3 (PCC) Carey p 618 - $(2\,Pyr, H^+)$, $Cr_2O_7^{2-}$ Corey-Fuchs

Swern - Chlorure d'oxalyle () ; NEt_3 ; DMSO (ICO p 413 ; Kürti p 450-451

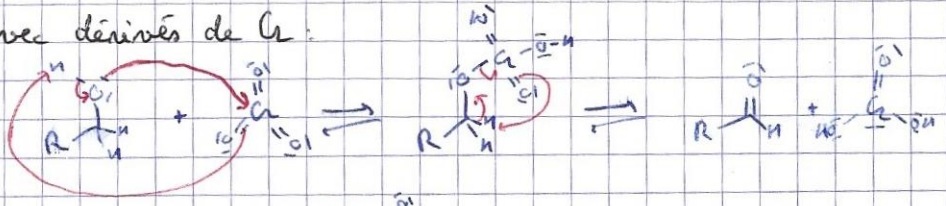
Dess-Martin :  (Kürti p 136)

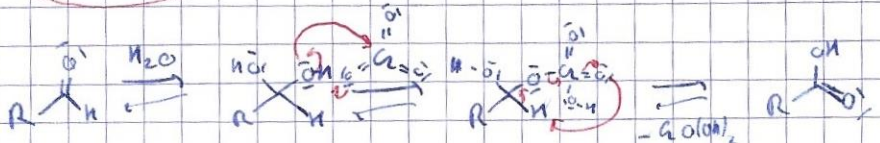
Ley-Griffith - Pr_4N^+, RuO_4^- cat.,  oxyde de N-méthyl morpholine (NMO) (Kürti p 262

* Au manganèse : ICO p 414

Mécanismes :

Avec dérivés de Cr :

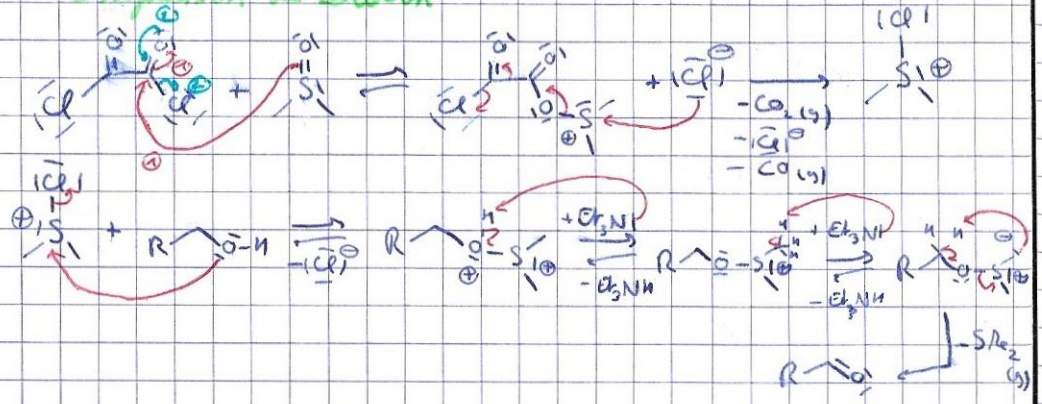
dans eau : 

de eau : 

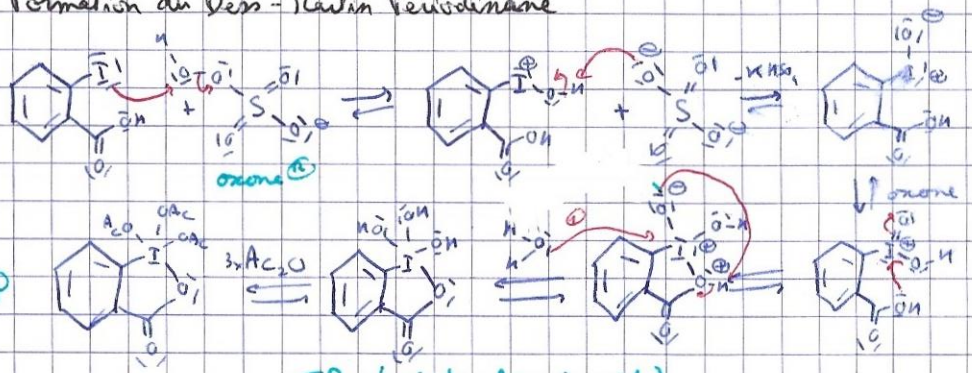
Dismutation du Cr : $3\,Cr(OH)_2 \longrightarrow Cr_2O_3 + CrO_3 + 3H_2O$
(instable)

IV III VI

Oxydation de Swern



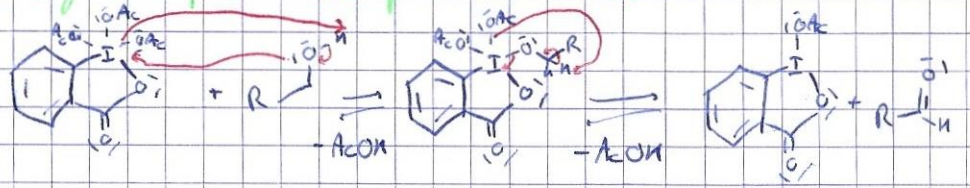
Formation du Dess-Martin Periodinane



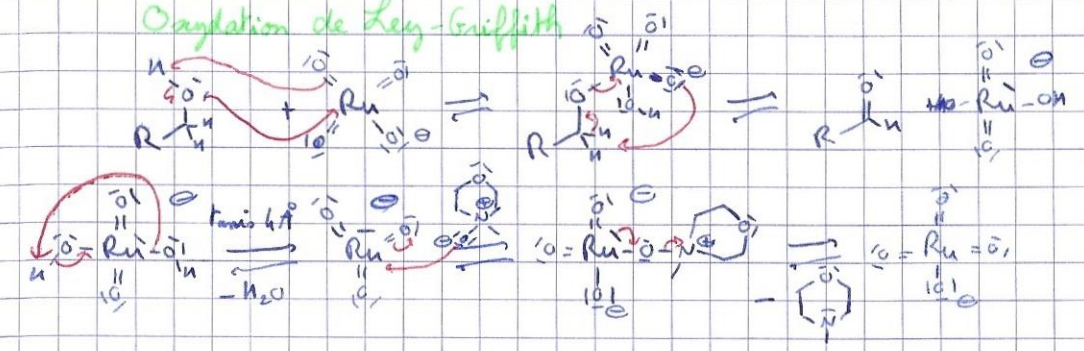
DMP

IBX (= iodoxybenzoic acid)
↳ ≠ DMP mais peu soluble ds solvant org classiq (ex soluble ds DMSO = polaire)

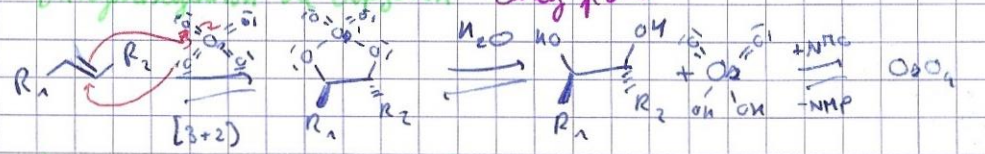
Oxydation par le réactif de Dess-Martin



Oxydation de Ley-Griffith



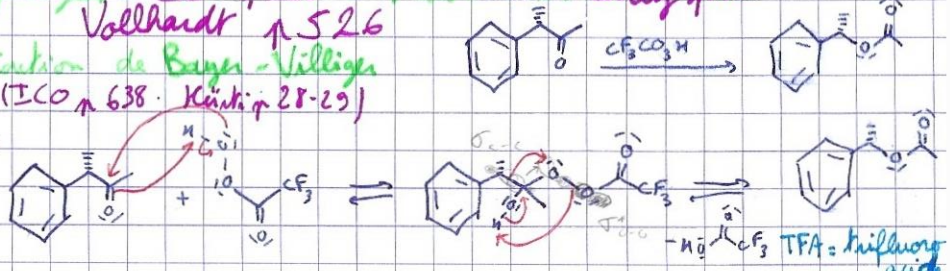
Dihydroxylation de Upjohn Carey p626



Syn-dihydroxylat°: ICO p208 | diol anti: Carey p633
Vollhardt p526

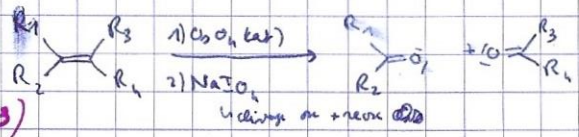
Réaction de Bayer-Villiger
(ICO p638 · Kürti p28-29)

Rem:

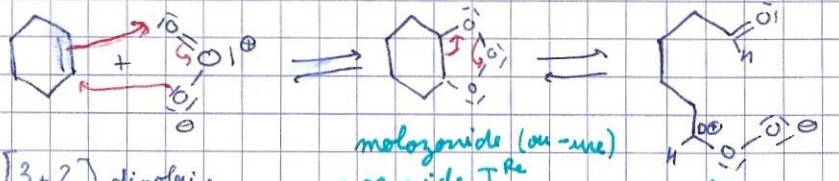


TFA = trifluoroacide

Lemieux-Johnson:
(ICO p415, Brückner p502-503)



Ozonolyse (Brückner p507 ; Carey p647 ; ICO p212-215)

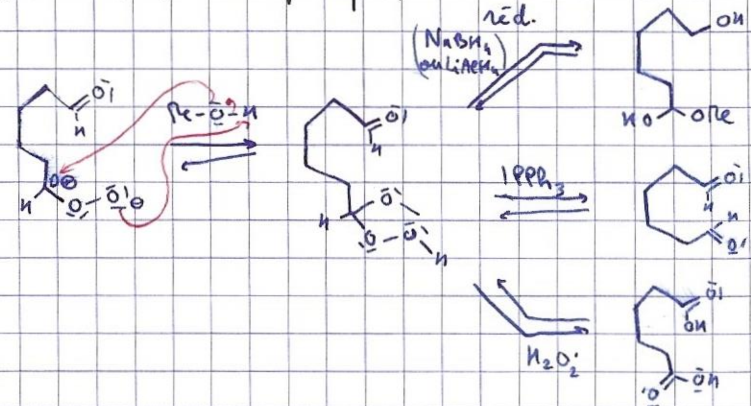


[3+2] dipolaire

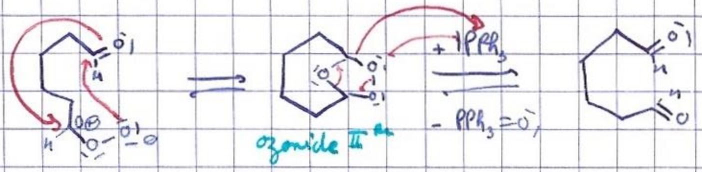
molozonide (ou -ane) = ozonide I^re

Zwitterion de Criegee

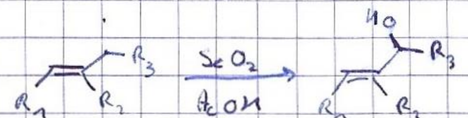
* MeOH (milieu protique)



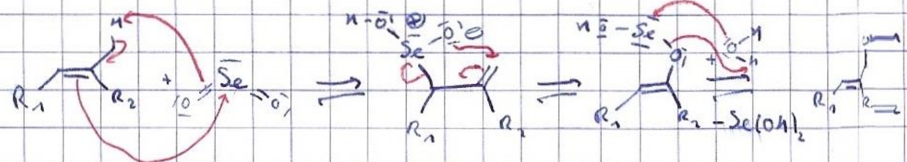
* CH_2Cl_2 (aprot.)



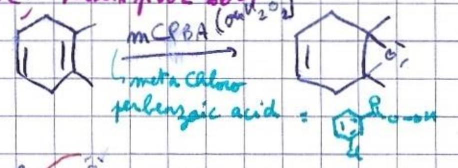
* Oxydat° position allyliq : (Clayden p1270;



Réca :

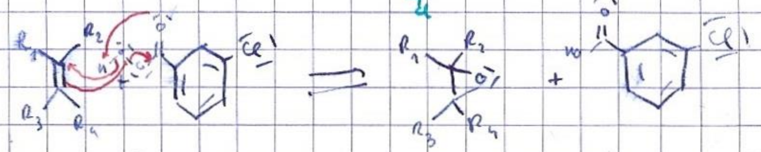


Epoxydat° (∅ chgt classe d'oxydat°) - Prilezhaev
(Carey p632. Kürti p662-663)



régiosélect (région ⊕ riche en e⁻)

Réca

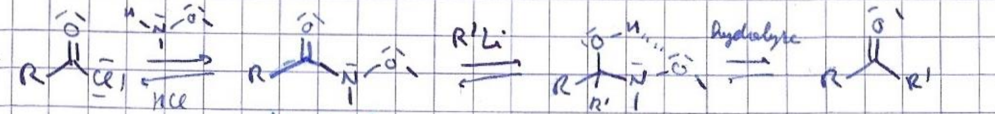


Réductions (Clayden p622 ; ICO p707-709) + Fosset PCSI ?

— = lent

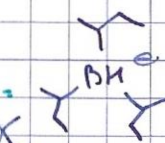
	ester R-CO-OR'	R-CO-R' (H)	R-COOH	amide R-CO-NR1R2	nitrile R-C≡N	imine
$LiAlH_4$	R⌒OH	R⌒OH	R⌒OH	R⌒NH2 (R⌒N si BT)	R⌒NH2	amine
$LiBH_4$ ↳ ester	R⌒OH	R⌒OH				
$NaBH_4$ ↳ sélect. cétone/ald.	R⌒OH	R⌒OH				amine
DIBAL-H ↳ ester → ald. possible	R-CHO ou R⌒OH (dpd solv., T°, sub)	R⌒OH	R⌒OH	R⌒NH2 (R-CHO si BT)	R-CHO (BT)	amine
BH_3 ↳ ac. carbox.	R⌒OH	R⌒OH	R⌒OH	R⌒NH2	R⌒NH2	amine
$NaBH_3CN$ ↳ sélect. imines		R⌒OH				amine

*

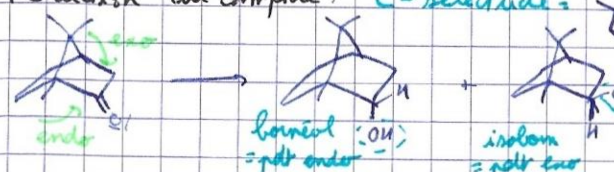


amide de Weinreb

* Réduction du camphre : L-sélectride =

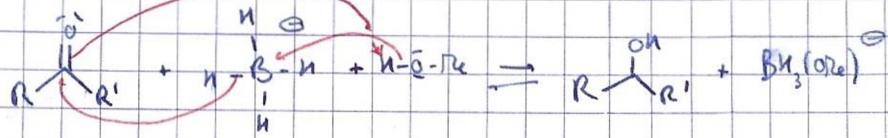


(ICO p583, Brückner p276)



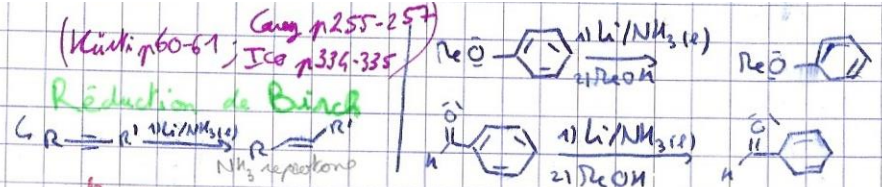
attq selon angle de Bürgi-Dunitz (≈ 107°)

Réca

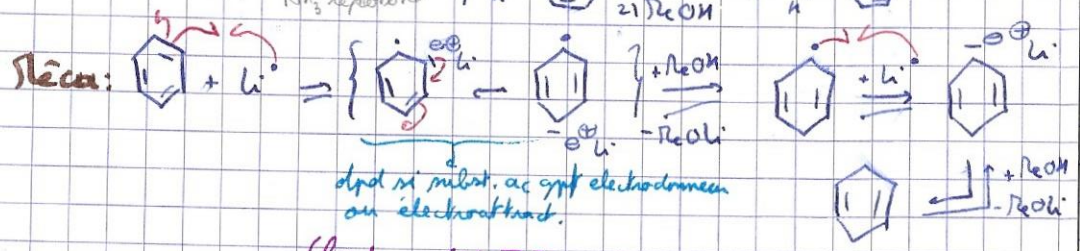


Réduction de Birch

(Küntz p60-61 ; Carey p255-257 ; ICO p334-335)



Réca :



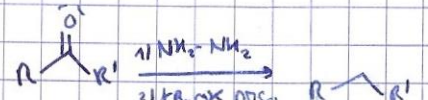
dépot si substit. ac gpt électrodonneur ou électroattract.

(Clayden p626 ; ICO p264)

Cat. de Lindlar = Pd sur $CaCO_3$ empoisonnée par $BaSO_4$ (et parfois quinoléine)

Réaction de Wolff-Kishner

(Küntz p496-497)



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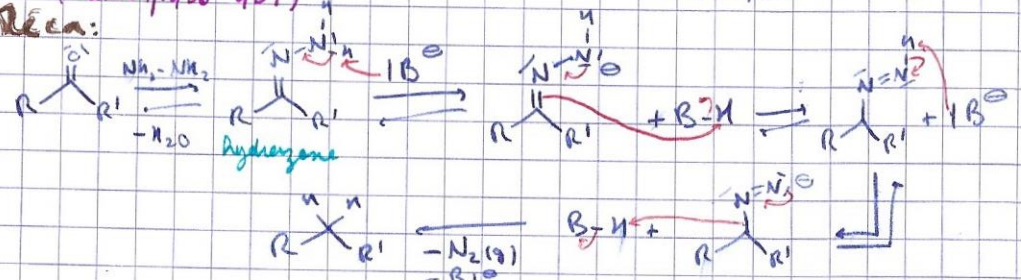
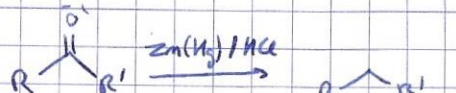
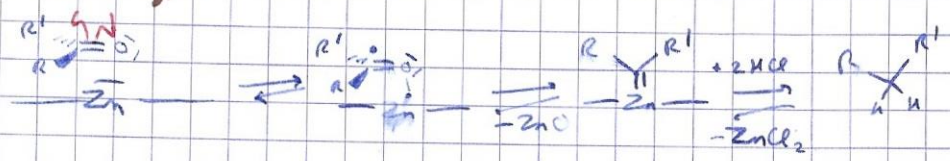


Réaction de Clemmensen

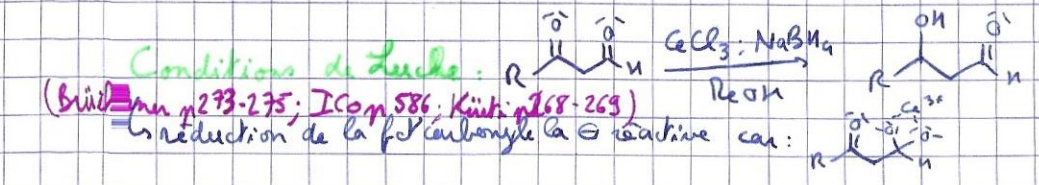
(Carey p267 ; ICO p611)



Réca (hyp) :



Conditions de Luche

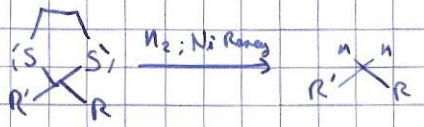


(Brückner p273-275 ; ICO p586 ; Küntz p268-269)

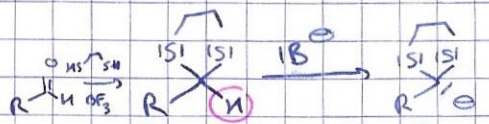
↳ réduction de la fct carbonyle la + réactive car :

Réduction de Mozingo (1943)

(Clayden p1254)

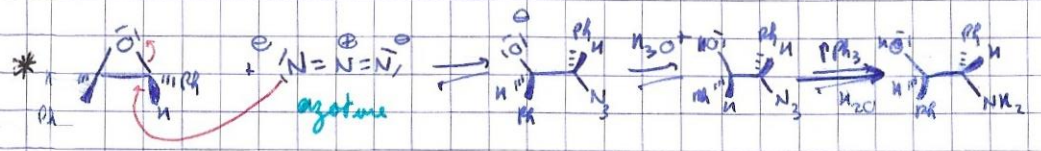


Réaction de Corey-Seebach



pKa ≈ 30

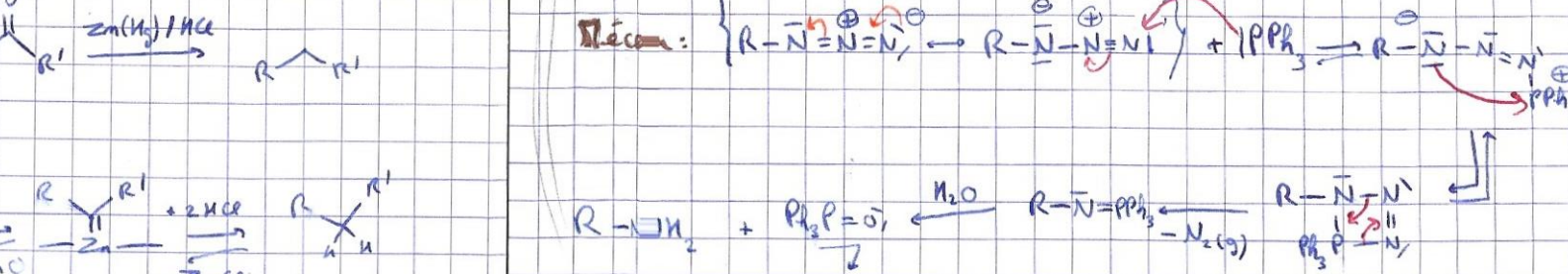
Umpolung = inversion de polarité



Réaction de Staudinger

(Küntz p428-429)

Réca :



Réduction des alcènes : ICO p187-191