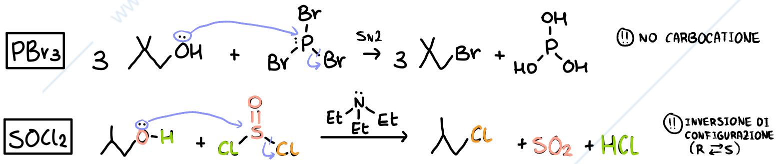
Chimica organica I secondo parziale

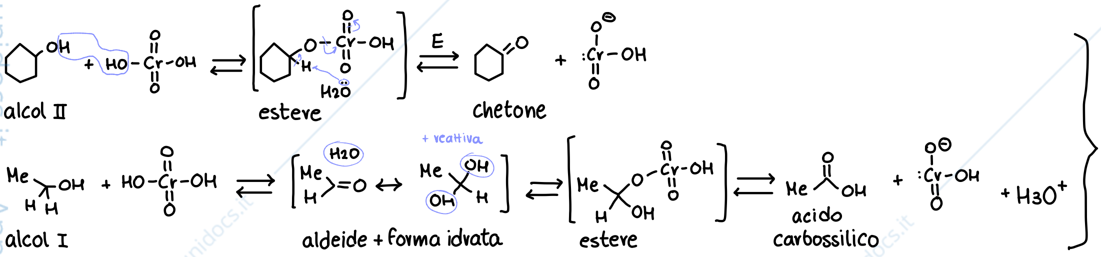
Alcoli

DA ALCOLI AD ALOGENURI ALCHILICI (Sn2)



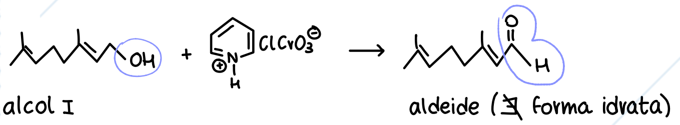
NOTE: HCl, HBr	SOCl2, PBr3
alcoli I Sn2 se ha ramificazioni in β si ha C⊕ e trasp.	alcoli I e II Sn2
alcoli II, III Sn1 con C⊕ e T	alcoli III → con questi NON reagiscono (si fa Sn1 con HCl, HBr)

OSSIDAZIONI: REATTIVO DI JONES

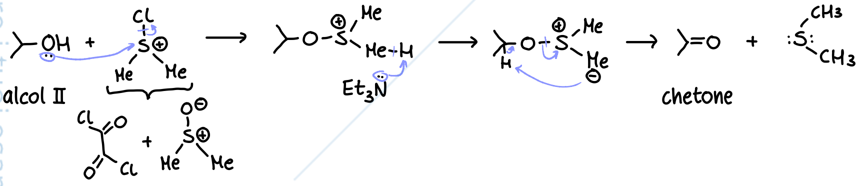


Quindi:
alcol II → chetone
alcol I → aldeide → acido carbossilico
+ forma idr.

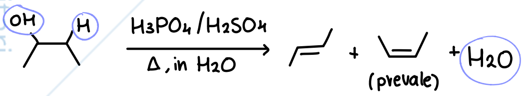
OSSIDAZIONI: PCC



OSSIDAZIONI: SWERN (DMSO) → carboanione + ilide

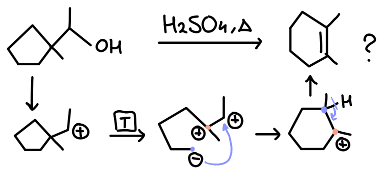


DISIDRATAZIONE ACIDO CATALIZZATA → carbocatione, Zaitsev



1) OH si protona con H^+ dell'acido → Gu → C⊕
2) E1 (trasposizione) → + prodotti

Es (ha detto che ci stava nel compito)



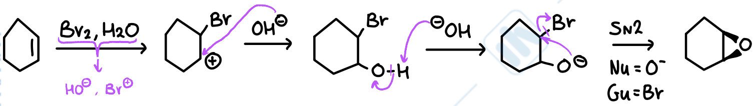
Eteri ed epossidi

SINTESI DI WILLIAMSON (eteri) → SN2, R_2 non ingombrato o si rischia competizione con E

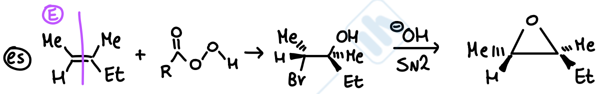
$R_1-O-R_2 \Rightarrow R_1-O^{\ominus} + R_2-X$

etere alcossido alogenuro alchilico

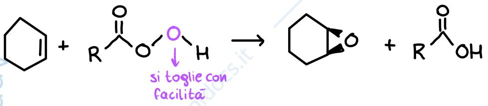
SINTESI CON BROMIDRINA E SN2 (epossidi) → Ⓜ, ANTI, C⊕, SN2 INTRAMOLECOLARE



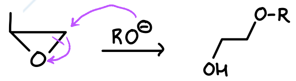
NOTA: basta $OH^{\ominus}$ come base pkK avviene facilmente



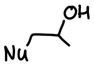
SINTESI CON PEROSSIACIDI (perossidi) → stereospecifica (stereochimica viene mantenuta)



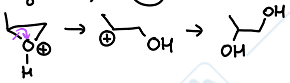
REATTIVITÀ (epossidi)



NOTA: apertura con Nu (SH^-, OH^-, $CH\equiv C^-$, NH_3) → Nu entra nel C - sostituito (+ sgombro) "Ⓐⓜ"

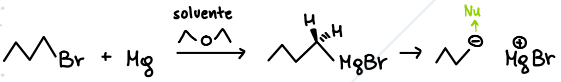


apertura con acidi (H_3O^+) → H_3O^+ entra nel C + sostituito Ⓜ



Composti organometallici

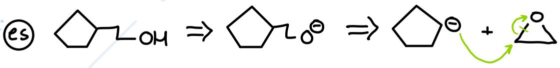
REATTIVI DI GRIGNARD

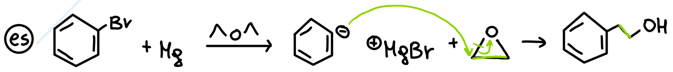


butil magnesio bromuro

NOTA: importante assenza di H_2O sennò $CH_2^{\ominus}$ da un alcano

butil-litio

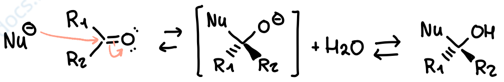




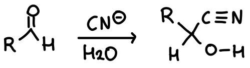
Aldeidi e chetoni

ADDIZIONE NUCLEOFILA ACILICA

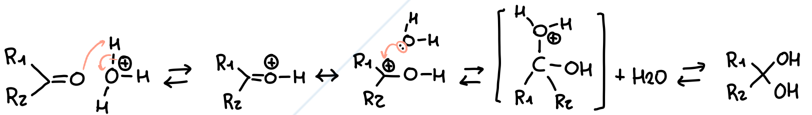
TIPO 1: $Nu^\ominus$

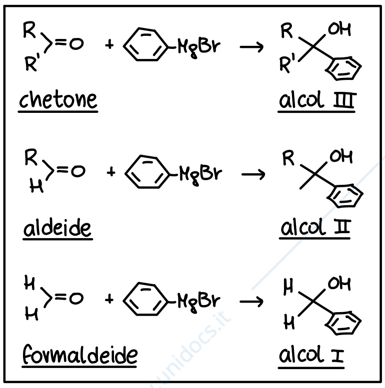


NOTA: se $Nu = {}^\ominus C \equiv N$ → racemo

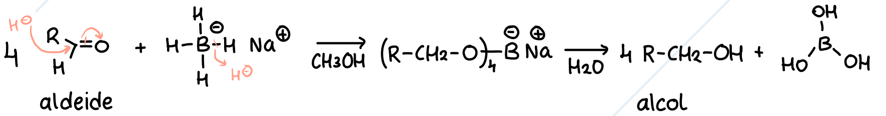


TIPO 2: Nu + catalisi acida





REAZIONE CON $H^\ominus$ → add. Nu acilica



1) entra H^- per ad.Nu.Ac. da $BH_4^\ominus$

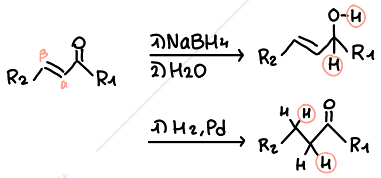
2) entra H^+ da H_2O

NOTA: $LiAlH_4$ + reattivo di $NaBH_4$, → selettivo: riduce C=O→C-OH ma non C=C

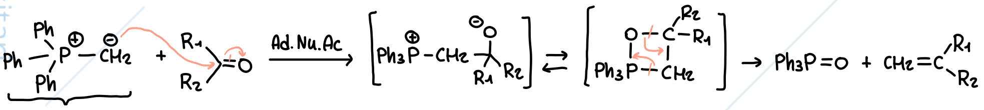
(!!) { $LiAlH_4$ riduce aldeidi, chetoni, esteri, acidi carbossilici
$NaBH_4$ riduce solo aldeidi e chetoni

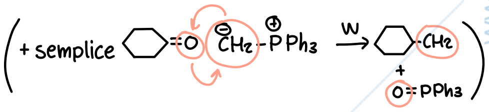
da racemo

selettività:



REAZIONE DI WITTIG → si passa da C=O a C=C, add. Nu acilica





$Ph_3P: + CH_3-I \xrightarrow{S_N2} Ph_3\overset{\oplus}{P}-CH_2-H \xrightarrow{\overset{\ominus}{Bu}\overset{\oplus}{Li}} Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}H_2$ ilide

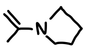
NOTA: da miscela di 2 alcheni

ilidi stabilizzanti ($P^+, C^- \leftrightarrow P^+, O^- \leftrightarrow$ P,C,O neutri) danno come prodotto solo Ⓔ (semi trans)

Emiacetali/acetali

EMIACETALI CICLICI

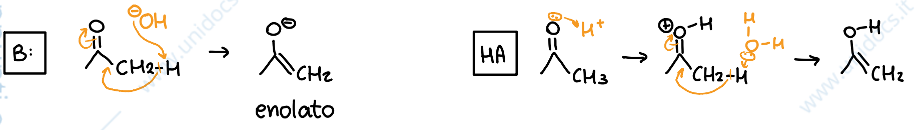
ADDIZIONE NUCLEOFILA ACILICA TIPO 2 (⁻)

→ no x ammine II →  enammina

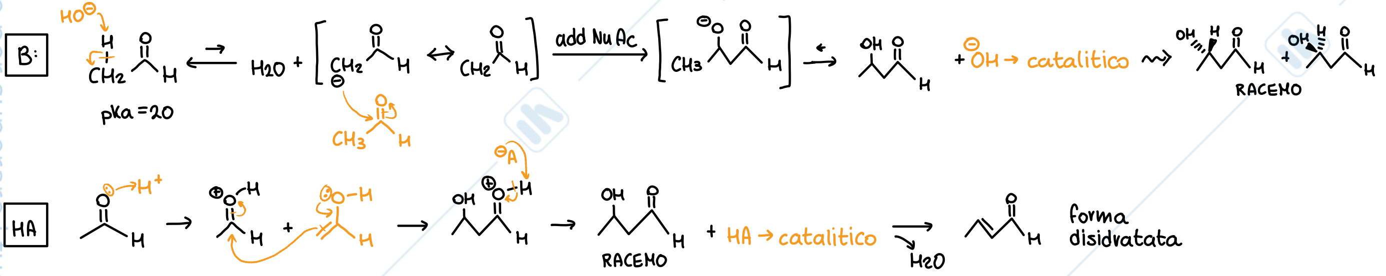
immina
↳ indica C=N } dette anche BASI DI SCHIFF

1) H⁺ attacca O
2) H3N: attacca forma risonanza $\overset{\oplus}{C}$-O
3) H⁺ di NH3⁺ e OH escono come H2O⁺ (Gu)
4) si forma C=N
5) H⁺ di NH2⁺ si stacca (preso da NH3)

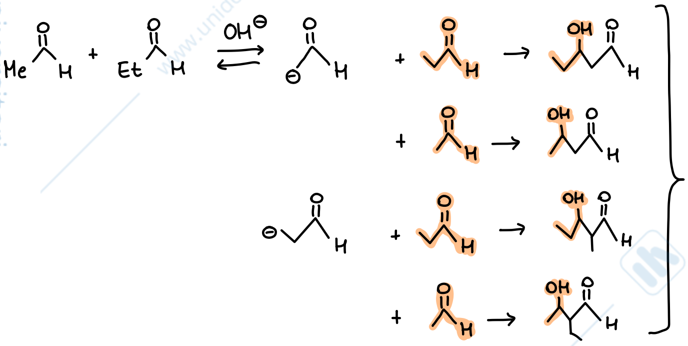
TAUTOMERIA CHETO-ENOLICA



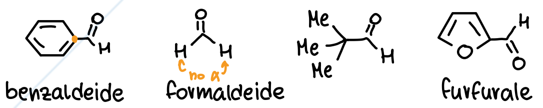
REAZIONE ALDOLICA (INTERMOLECOLARE)



ALDOLICA INCROCIATA

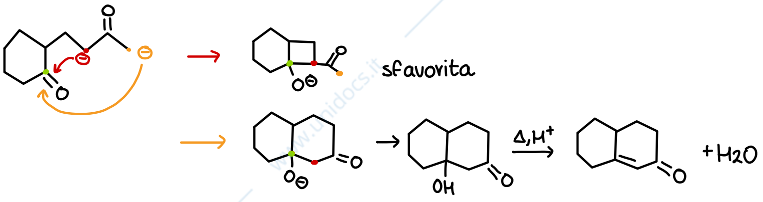


Questa reazione può essere spinta ad un unico prodotto se usiamo un'aldeide non enolizzabile come:



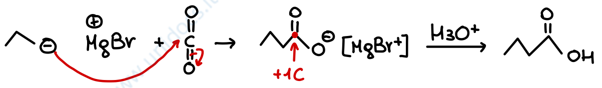
ALDOLICA INTRAMOLECOLARE

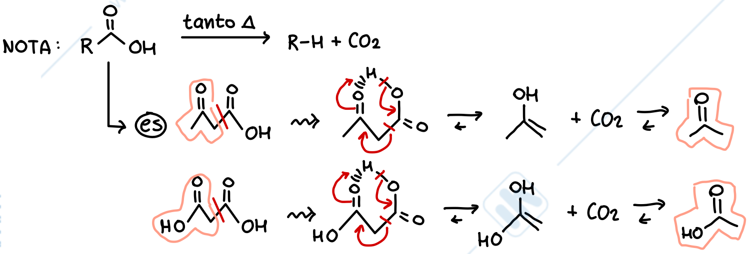
→ esce un ciclo (quelli a 5,6 = favoriti)



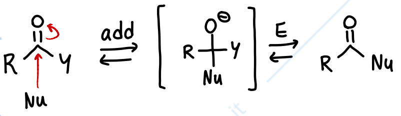
Acidi carbossilici e derivati

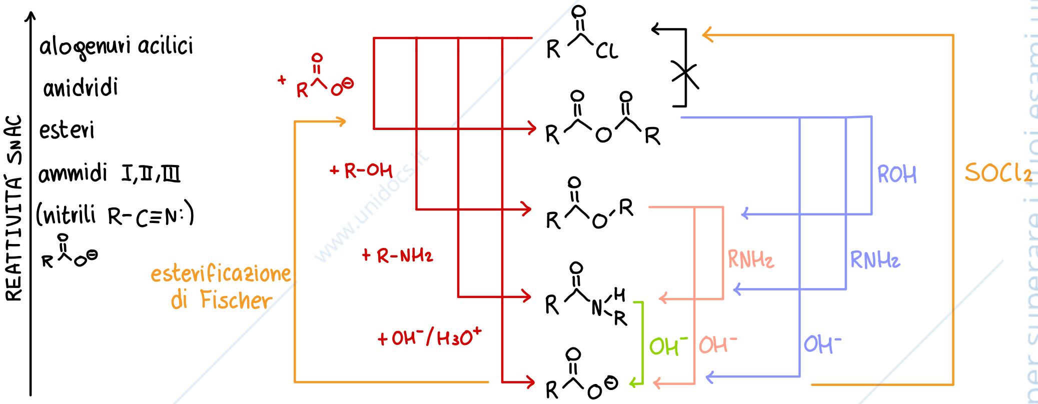
CARBONATAZIONE DEL GRIGNARD



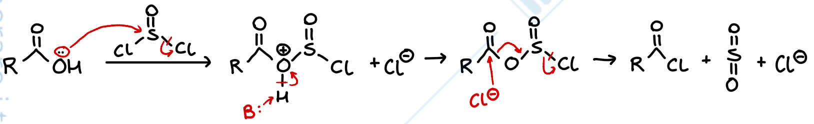


SOSTITUZIONE NUCLEOFILA ACILICA

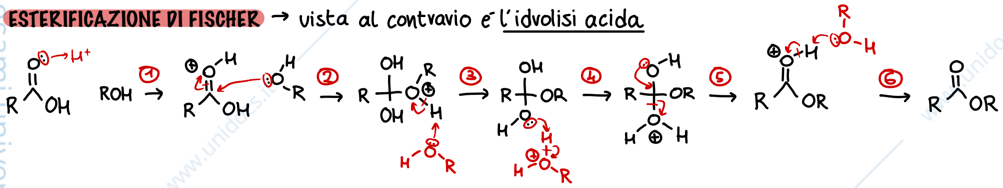




REAZIONE CON SOCL2

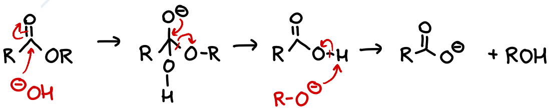


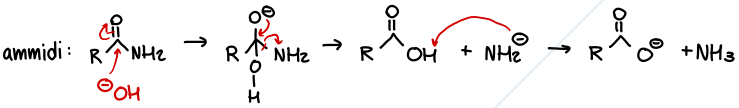
ESTERIFICAZIONE DI FISCHER → vista al contrario è l'idrolisi acida

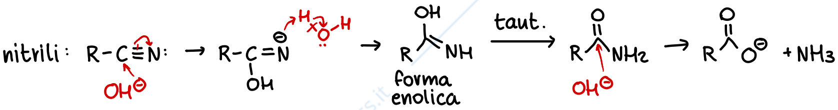


1) protonazione carbonile
2) entrata alcol
3) deprotonazione
4) protonazione OH
5) uscita H2O
6) deprotonazione

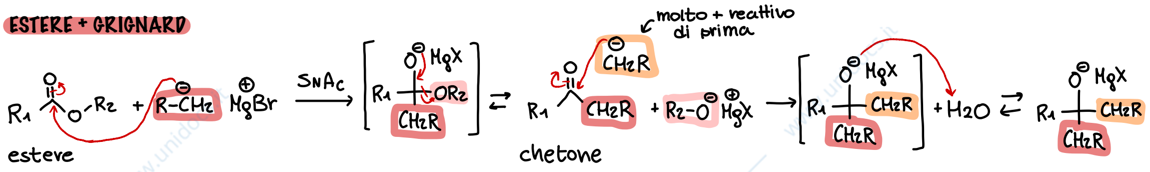
IDROLISI BASICA/SAPONIFICAZIONE



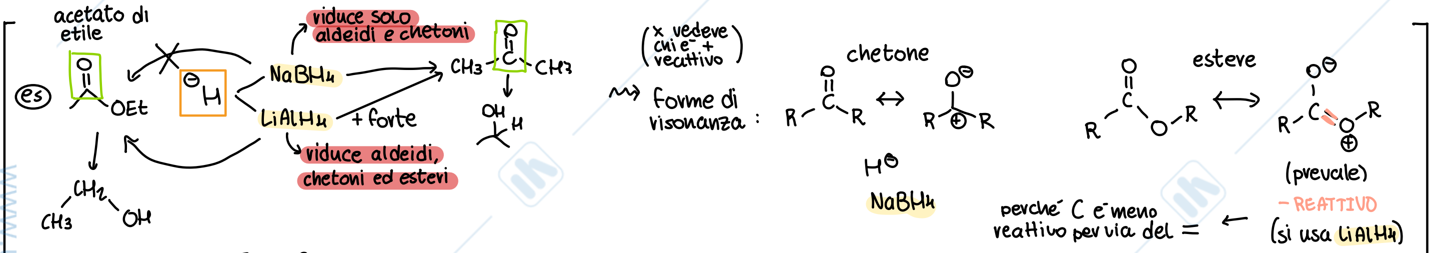


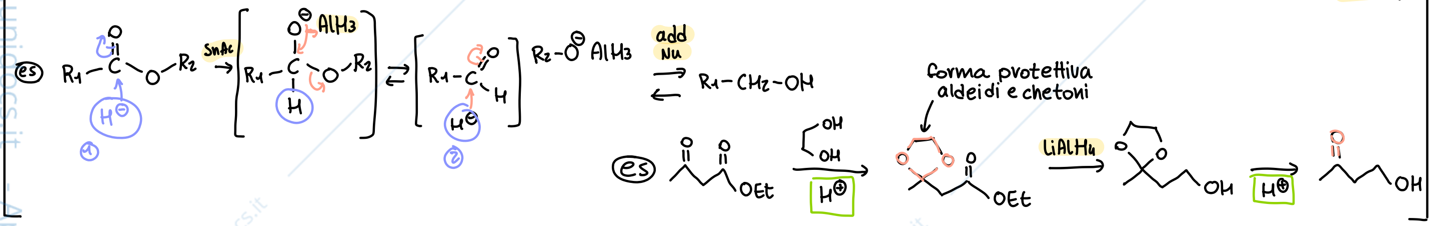


ESTERE + GRIGNARD

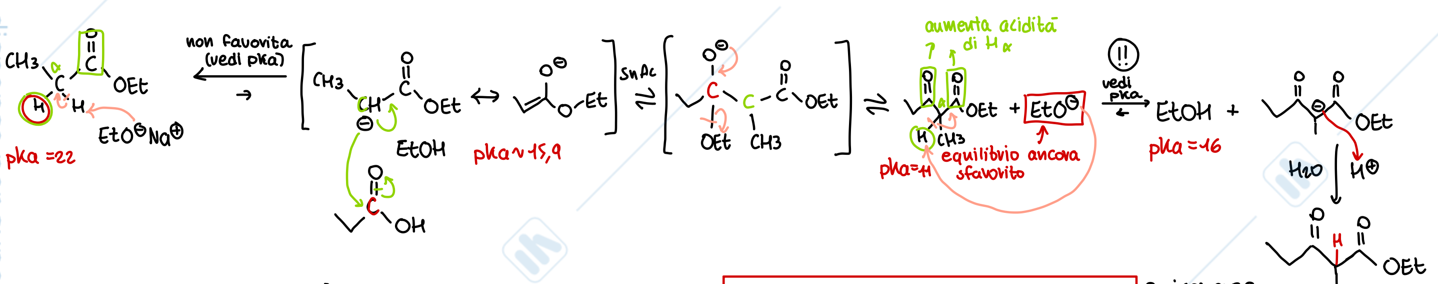


alcol III legato 2 volte al gruppo alchilico a cui era legato il Grignard

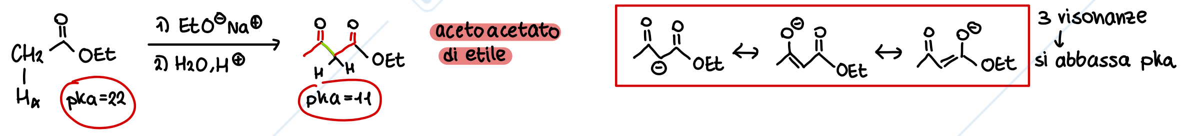




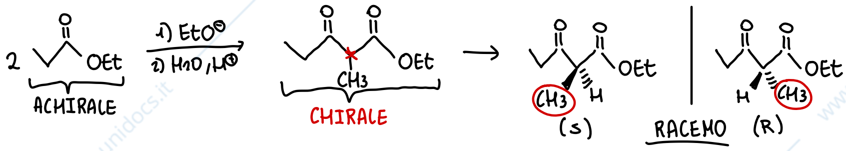
CONDENSAZIONE DI CLAISER



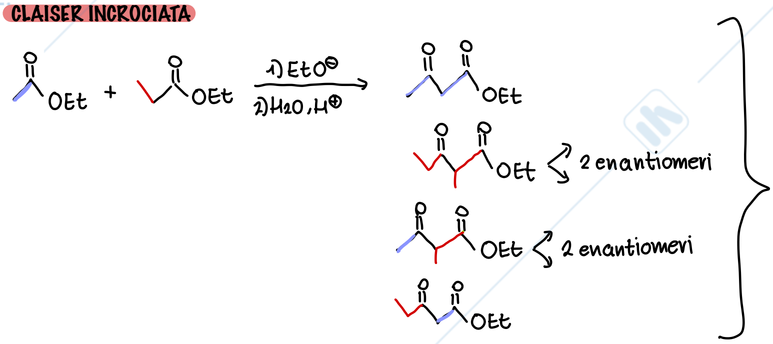
in breve:



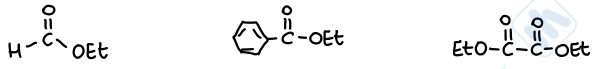
NOTA:



CLAISER INCROCIATA



∃ esteri non enolizzabili:

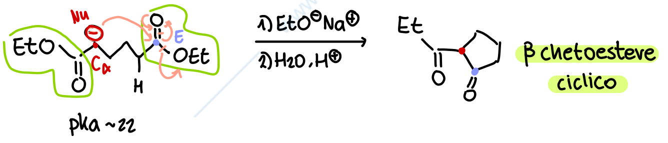


formiato di etile (non ha H in α)

benzoato di etile

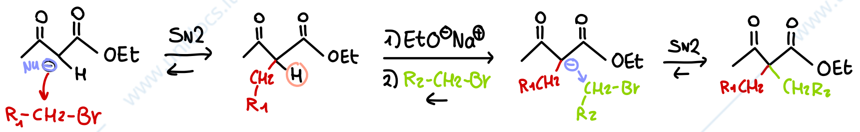
ossalato di etile [SWERN]

CLAISER INTRAMOLECOLARE → ciclo, prevale su inter in condizioni di iperdiluizione

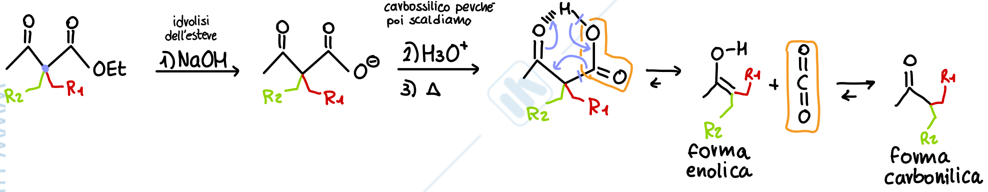


SINTESI ACETOACETICA

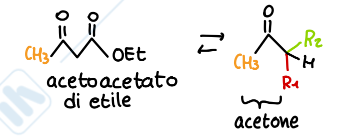
1° fase = 2 volte SN2



2° fase = decarbossilazione

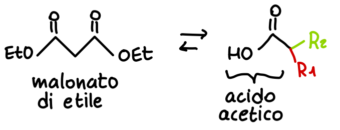


SINTESI ACETOACETICA



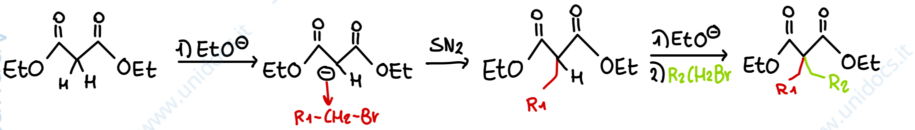
VS

SINTESI MALONICA

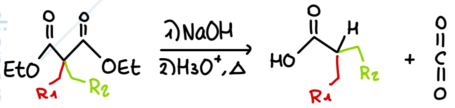


SINTESI MALONICA

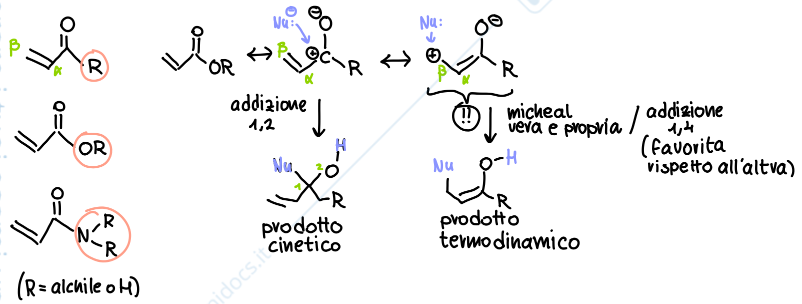
1° fase = 2 volte SN2

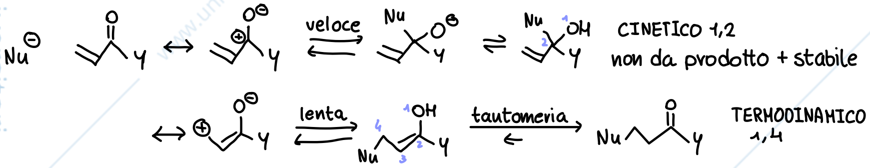


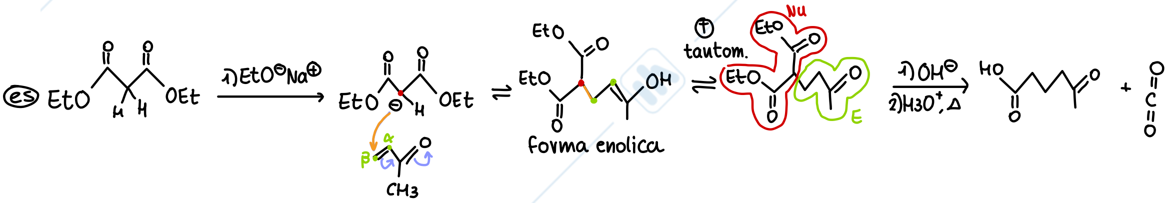
2° fase = decarbossilazione



REAZIONE DI MICHAEL

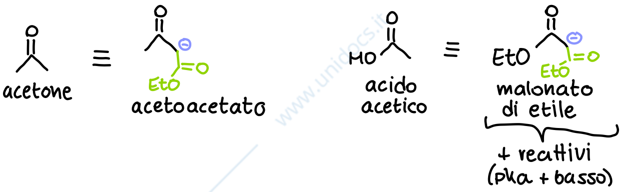


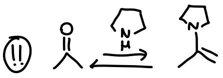




EQUIVALENTI SINTETICI

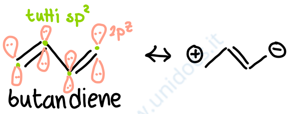
→ sono + reattivi, hanno pka + basso, si possono interconvertire nel rispettivo (tramite decarbossilazione)



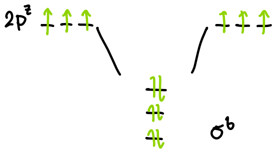


enammina è un equivalente sint. del chetone

Composti aromatici



+ lunga la catena, + è stabile

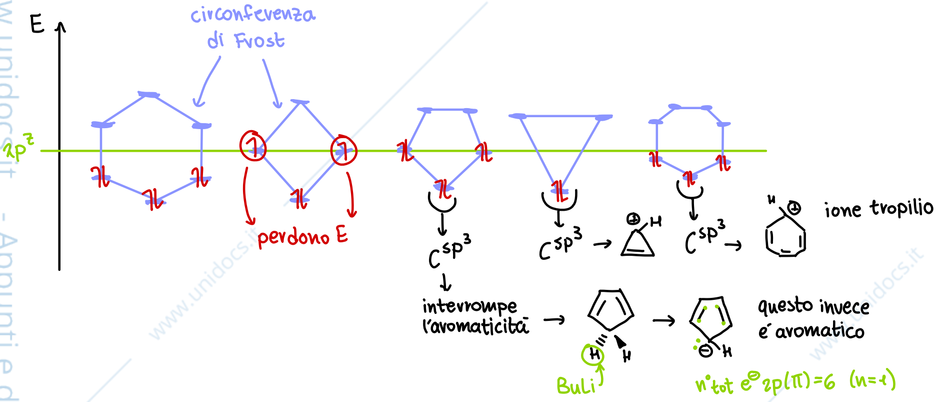


REGOLE DI HUCKEL PER AROMATICITÀ

1) deve essere ciclico e planare
2) deve avere 1 orbitale 2p per atomo di C
3) deve avere un n° di e^- $2p = 4n+2$ $(n=0,1,2\ldots)$

(!!) antiaromatico: rispetta tutte le regole tranne la 3

non aromatico: non rispetta 3 e un'altra



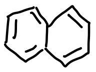
In sintesi:
- ciclopropene: ar. (forma ionica)
- ciclobutandiene: anti-ar.
- ciclopentandiene: ar. (forma ionica)
- benzene: ar.
- cicloeptantriene: ar. (forma ionica)

Ci sono delle eccezioni alle regole di Huckel

** ciclo a 10

ciclico, non planare → non aromatico

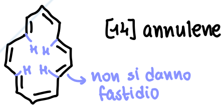
[10] annulene monociclico



biciclico, aromatico

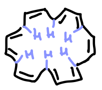
naftalene

** ciclo a 14



[14] annulene, aromatico

** ciclo a 18



[18] annulene, aromatico

Schema generale: reazioni chimica organica

conversione alcoli → alogenuri alchilici

alcol I,II + PBr_3 → Br-R S_N2, no C⊕

$SOCl_2$ → Cl-R S_N2, no C⊕, inversione di configurazione (R⇆S)

↳ I con ramificazioni in β + HBr, HCl S_N2, Ⓣ

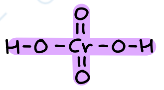
III + HBr, HCl S_N1, C⊕, Ⓣ

disidratazione acido-catalizzata

alcol + H_3PO_4/H_2SO_4, Δ, H_2O → alchene   C⊕, Ⓣ, E1, Ⓩ

ossidazioni

alcol I / II + reattivo di Jones

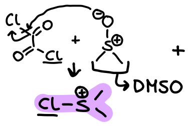


$\xrightarrow{H_2O}$ aldeide + FORMA IDRATA (reattiva) + H_2CrO_4 $\xrightarrow{H_2O}$ acido carbossilico

$\xrightarrow{H_2O}$ chetone

alcol I / II + PCC → aldeide / → chetone } no presenza H_2O

alcol I / II + swern



+ ammina III (genera C⊖) → aldeide / → chetone   C⊖, ilide

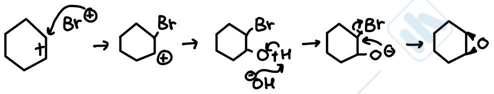
sintesi di Williamson

alcossido + alogenuro alchilico I (non ingombrato) → etere (R-O-R)

---

sintesi con SN2 nelle aloidrine

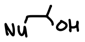
alchene $\xrightarrow[HO^{\ominus}\ Br^{\oplus}]{Br_2, H_2O}$ bromoidrina (C⊕, Ⓜ, ANTI) $\xrightarrow[2)\,S_N2\text{ interna}]{1)\,OH^{\ominus}}$ epossido



sintesi con perossiacidi

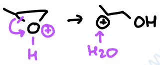
alchene + perossiacido → epossido + acido carbossilico   (cis→cis), 1 passaggio (pull-push)

apertura epossidi con → $Nu^{\ominus}$: entra nel C - sostituito



(AM)

↳ H^+, H_2O: entra nel C + sostituito Ⓜ



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sintesi dei reattivi di Grignard

alogenuri + Mg $\xrightarrow{Et_2O}$ $R-\overset{\ominus}{C}H_2$ + $\overset{\oplus}{Mg}-X$

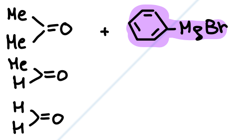
2Li → $R-\overset{\ominus}{C}H_2$ + $\overset{\oplus}{Li}$ + Li-X

---

addizione nucleofila acilica

aldeide/chetone + $Nu^{\ominus}$ $\xrightarrow{H_2O}$ composto tetraedrico

+ Nu (catalisi acida)   composto tetraedrico + forma idrata



→ alcol III   racemo se Nu ≠ R_1, R_2

alcol II

alcol I

riduzione

aldeide/chetone + $LiAlH_4/NaBH_4$ $\xrightarrow{H_2O}$ alcol   AdNuAc

(!!) $\xrightarrow[2)\,H_2O]{1)\,NaBH_4}$ riduce C=O in C-OH

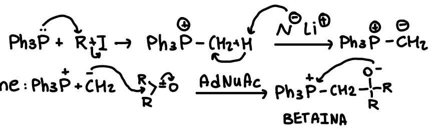
$\xrightarrow[Pd]{1)\,H_2}$ riduce C=C in CH_2-CH_2

reazione di Wittig

aldeide/chetone + $Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}H_2$ (ILIDE) → alchene + $Ph_3P=O$

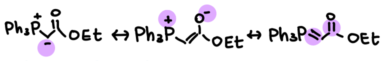
1) formazione ilide:

2) formazione alchene:



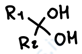
miscela E,Z

ilidi stabilizzanti danno +E



idratazione

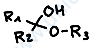
maggiore
aldeide/chetone + H^+/OH^- $\xrightarrow{H_2O}$ dioli germinali



H^+, OH^- CATALITICI

sintesi emiacetale e acetale

aldeide/chetone + alcol $\xrightarrow{H^+/OH^-}$ emiacetale



2 alcol $\xrightarrow{H^+}$ acetale (x favorirne la formazione, si allontana H_2O grz alla trappola di Dean-Stark)

$\xrightarrow{H^+}$

+ H_2O (acetale) (GRUPPO PROTETTIVO)

sintesi delle immine ed enammine

aldeide/chetone + ammina I / NH_3 $\xrightarrow{H^+}$ immina (C=N)

1) Ad Nu 2 composti
2) deprotonazione NH_3^+ grz a NH_3/ammina I → $R-\overset{+}{N}-H_3$
3) protonazione O^- grz a $R-N-H_3$
4) protonazione OH grz a $H_3\overset{+}{O}^+$
5) uscita OH_2^+ e formazione $C=N^+$
6) deprotonazione $\underset{+}{N}RH$ grz a $R-N-H_2$

+ ammina II $\xrightarrow{H^+}$ enammina (C=C-N<)

6) deprotonazione CH_3 grz a NH_3 → $\bar{C}-C=\overset{+}{N}<$
7) formazione C=C-N<

+ $H_2\ddot{N}-\ddot{N}H_2$ (IDRAZINA) → >=N-NH₂ (IDRAZONE)

$H_2\ddot{N}-\ddot{O}-H$ (IDROSSILAMMINA) → >=N-OH (OSSIMA)

tautomeria cheto-enolica

aldeide/chetone $\xrightarrow{H^+/OH^-}$ forma enolica

>=O   >-O-H

BASE CAT.:
1) deprotonazione $\overset{\alpha}{C}H_3$ grz a OH^-
2) formazione enolato
3) protonazione O^- grz a H-B

ACIDO CAT:
1) protonazione =O grz a H-A
2) deprotonazione $\underset{\alpha}{C}H_3$ grz a A^- (o H_2O)
3) formazione C=C e rottura C=O

reazione aldolica

2 aldeidi/chetoni $\underset{H_2O}{\overset{H^+/OH^-}{\rightleftharpoons}}$ idrossialdeide/chetone $\downarrow H^+$ aldeide/chetone α-β insaturo + H_2O

BASE CAT: (non favorita)
1) deprot. di $C_\alpha H_3$ grz a B^-
2) ad. Nu enolato + 2° molecola
3) prot. di O^- grz a H_2O

ACIDO CAT:
1) prot. =O grz a H-A
2) tautomeria della 2° molecola
3) add. Nu.
4) deprot. $=\overset{+}{O}-H$ grz a A^-

(!!) miscela racemica

reazione aldolica incrociata → unico prodotto se si ha:

intramolecolare →
1) deprot. $C_\alpha H_3$ grz a KOH
2) legame tra C⊖ e C di C=O → ciclo

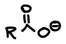
---

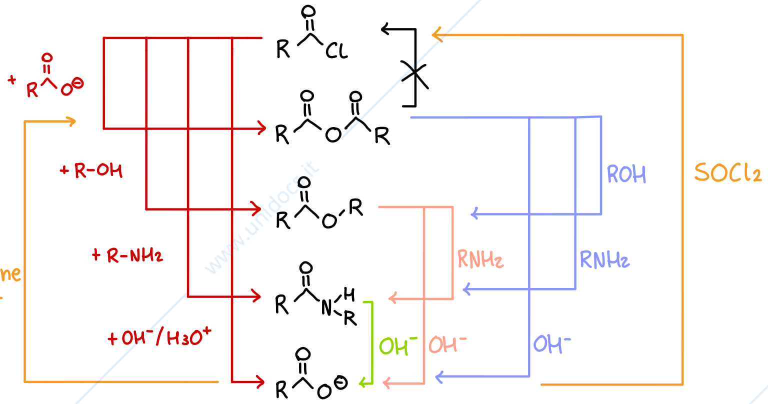
carbonatazione del Grignard

reattivo di Grignard + $O=C=O$ $\xrightarrow{H^+}$ acido carbossilico

sostituzione nucleofila acilica

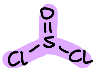
REATTIVITÀ SnAC ↑
- alogenuri acilici
- anidridi
- esteri
- ammidi I, II, III
- (nitrili $R-C\equiv N:$)





conversione in cloruri acilici

acido carbossilico +



$\xrightarrow{B:}$ cloruro acilico

esterificazione di Fischer

acido carbossilico + alcol $\xrightarrow{H^+}$ estere

1) prot. =O grz a H^+
2) add. alcol + acido carb. e rottura – di $=\overset{+}{O}-H$
3) deprot. di $-\overset{+}{O}{<}^{R}_{H}$
4) prot. O-H grz a $H-\overset{\overset{R}{|}}{\overset{+}{O}}-H$
5) uscita $H-O-H$ e formazione $=\overset{+}{O}-H$ (quello di 2))
6) deprot. $=\overset{+}{O}-H$ grz a ROH

idrolisi delle anidridi

anidride (

) $\xrightarrow{H_2O}$ 2 acidi carbossilici

idrolisi cloruro acilico

cloruro acilico $\xrightarrow{H_2O}$ acido carbossilico + HCL

NO CAT. BASICA/ACIDA:
1) H_2O lega con C di C=O → rottura – di C=O
2) deprot. di $H-\underset{+}{O}-H$ grz a H_2O
3) rottura legame con CL e formazione C=O

idrolisi estere

estere $\xrightarrow{H_3O^+, H_2O}$ acido carbossilico

$\xrightarrow{^-OH, H_2O}$ acido carbossilico

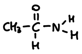
ACIDO CAT:
1) prot. =O grz a H_3O^+
2) H_2O attacca C di C=O → rottura – di $C=\overset{+}{O}-H$
3) deprot. di $H-\overset{+}{O}-H$ grz a H_2O
4) prot. O-R grz a H_3O^+
5) esce R-O-H e si forma $=\overset{+}{O}-H$ (quello in 2))
6) deprot $=\overset{+}{O}-H$ grz a H_2O

(!!)
BASE (SAPONIFICAZIONE):
1) ^-OH lega con C di C=O → si rompe – di C=O
2) esce O-R e si riforma C=O
3) deprot. acido carb. grz a O-R

idrolisi ammide

ammide $\xrightarrow{H_3O^+, H_2O}$ acido carbossilico

$\xrightarrow{^-OH,\ H_2O}$ acido carbossilico



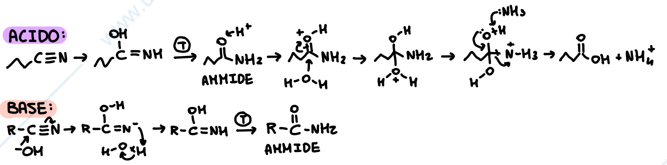
ACIDO:
1) prot. =O grz a H_3O^+
2) entra H_2O nel C di C=O → rottura - di C=O
3) deprot. di H-O-H e prot. di NH_2
4) rottura legami –OH e $-NH_3^+$
5) deprot. =O-H grz a NH_3

BASE:
1) ⁻OH attacca C di C=O → rottura - di C=O
2) deprot. OH grz a ⁻OH
3) prot. NH_2 grz a H_2O → rottura C-N e formazione C=O

idrolisi nitrile

nitrile $\xrightarrow{H_3O^+, H_2O}$ acido carbossilico

$\xrightarrow{^-OH,\ H_2O}$ acido carbossilico



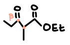
reazione estere e Grignard

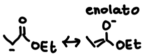
estere + 2 reattivi di Grignard ⟶ alcol III (tranne se si usa il formiato allora è II)

1) CH_2^- lega con C di C=O → rottura - di C=O
2) esce –OR e si riforma C=O
3) 2° CH_2^- lega con C di C=O → rottura - di C=O
4) prot. $-O^-$ grz a H_3O^+

condensazione di Claiser

2 esteri $\xrightarrow[2) H_2O, HCl]{1) EtO^- Na^+}$ β-chetoestere (racemo)





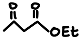
1) deprot. CH_3 grz a EtO^- → si forma enolato ⓘ eq a SX pKa(H⁺)=22 → pKa ≅ 15,9
2) add. tra CH_2^- e C di C=O → rottura - di C=O della molecola senza CH_2^- all'inizio
3) esce OEt^- e si riforma C=O di prima
4) deprot di CH_2 tra i 2 C=O grz a EtO^- → ⓘ eq. a DX per pKa di EtOH = 16 (prima era 11)
5) prot. CH^- grz a H_3O^+

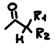
Claiser incrociata ⟶ unico prodotto se si ha

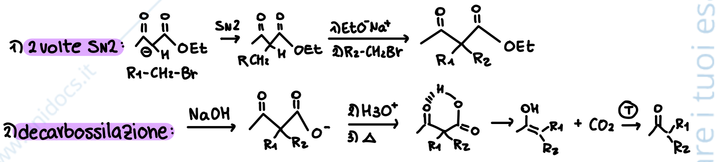
intramolecolare (Dieckmann) ⟶ 1) Cα attacca C=O → esce OEt^-
2) β-chetoestere ciclico

sintesi aceto-acetica

aceto-acetato di etile $\xrightarrow[4) HCl, H_2O \ 5) \Delta]{1) EtO^-Na^+ \ 2) R-CH_2Br \ 3) NaOH, H_2O}$ derivato dell'acetone

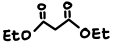


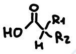




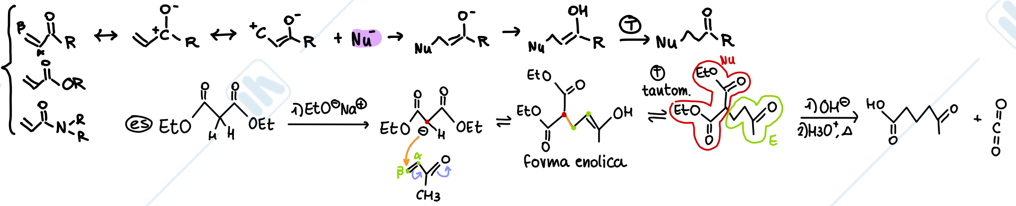
sintesi malonica

malonato di etile $\xrightarrow[4) HCl, H_2O \ 5) \Delta]{1) EtO^-Na^+ \ 2) R-CH_2Br \ 3) NaOH, H_2O}$ derivato dell'acido acetico (vedi sopra)





reazione di Micheal

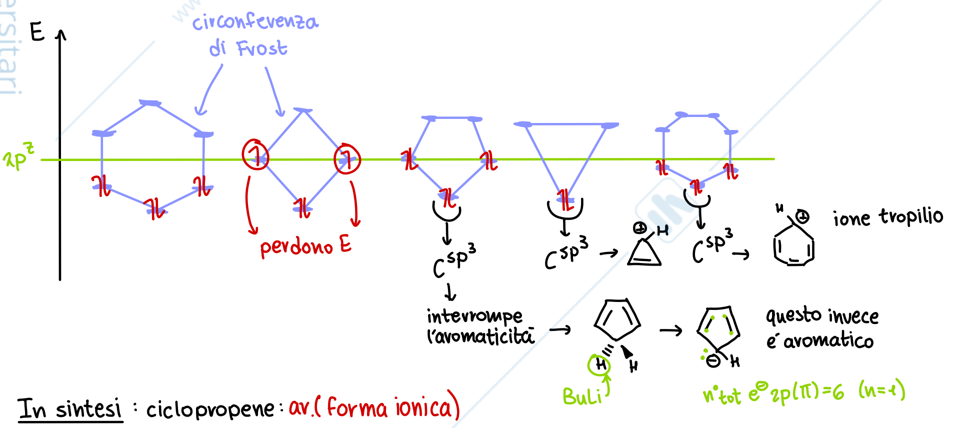


REGOLE HÜCKEL PER AROMATICITÀ

1) deve essere ciclico e planare
2) deve avere 1 orbitale 2p per atomo di C
3) deve avere un n° di e⊖ 2p = 4n+2 (n=0,1,2…)

ⓘ antiaromatico: rispetta tutte le regole tranne la 3

non aromatico: non rispetta 3 e un'altra



In sintesi: ciclopropene: ar. (forma ionica)
ciclobutandiene: anti-ar.
ciclopentandiene: ar. (forma ionica)
benzene: ar.
cicloeptantriene: ar. (forma ionica)

ETERI