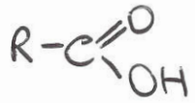
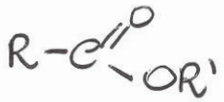
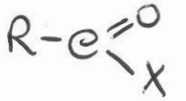
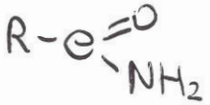
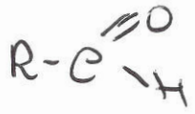
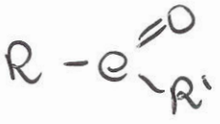
PRIORITA' NOMENCLATURA

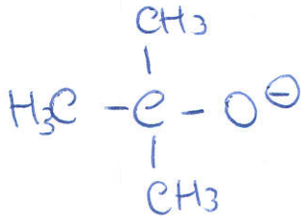
GRUPPO FUNZIONALE		suffisso	prefisso
acidi carbossilici		Acido ...-oico	carbossi
esteri		...oato di ...-ile	ossicarbonil
alogenuri acilici		alogenuro di ...-ile	alocarbonil
ammidi		...-ammide	carbamoil
nitrili	$R-C\equiv N$	...-nitrile	ciano
aldeidi		...-ale	osso/formil
chetoni		...-one	osso
alcoli	$R-OH$	...-olo	idrossi
tioli	$R-SH$	...-tiolo	mercapto
ammine	$R-NH_2$	...-ammina	ammino

Ricapitolando

Metilico CH_3X	S_N2	Non si osservano reazioni S_N1 da parte degli alogenuri metilici. Il catione metilico è così instabile che non si osserva nei comuni solventi.
Primario RCH_2X	S_N2	Reazione principale con buoni nucleofili/basi deboli, come I^- e CH_3COO^-.
	E2	Reazione principale con basi forti ed ingombrate, come $(CH_3)_3CO^-$.
	~~S_N1/E1~~	I cationi primari si formano raramente in soluzione e, quindi, le reazioni S_N1 ed E1 degli alogenuri primari sono improbabili.
Secondario R_2CHX	S_N2	Reazione principale con basi/nucleofili (deboli, buoni) in cui il pK_a dell'acido coniugato è minore o pari a 11, per esempio I^- e CH_3COO^- (ione carbossilato), RS^- (tiolato), ^-CN
	E2	Reazione principale con basi/nucleofili (forti) in cui il pK_a dell'acido coniugato è maggiore o pari a 11, per esempio OH^- e $CH_3CH_2O^-$.
	S_N1/E1	Comuni nelle reazioni con nucleofili deboli in solventi protici polari, come l'acqua, il metanolo e l'etanolo. (Nu deboli → favoriscono S_N2; basi deboli → E1)
Terziario R_3CX	E2	Reazione principale con basi forti come HO^- e RO^-.
	(PREVALE) S_N1/E1	Reazioni principali con nucleofili deboli/basi deboli se il solvente è protico polare.
	~~S_N2~~	Le reazioni S_N2 degli alogenuri terziari non si osservano mai, a causa dell'elevato ingombro intorno al carbonio 3°.

Non tutte le basi forti sono dei buoni nucleofili!

(dal 2-metil-2-butanolo)



ANIONE TERZ-BUTOSSIDO

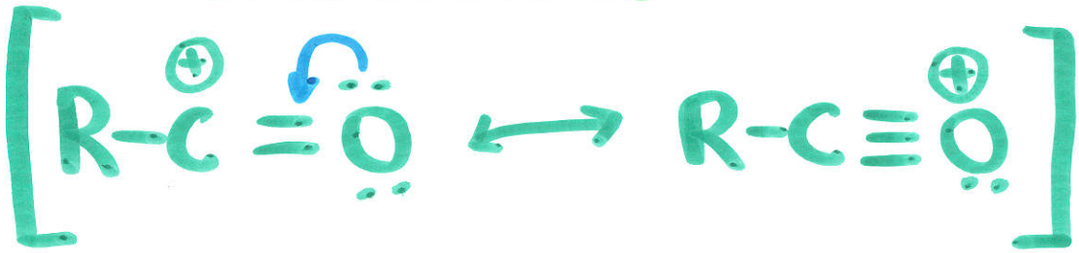
- è una base forte
- è un nucleofilo debole

Ciò a causa di fattori di natura sterica

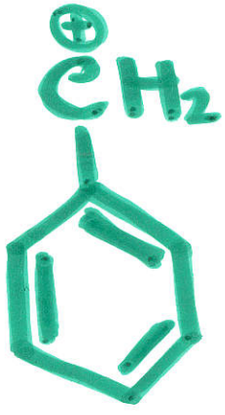
I gruppi $-CH_3$ legati al carbonio determinano un INGOMBRO STERICO che impedisce l'avvicinamento dell'ossigeno carico negativamente ad un sito elettrofilo

→ Quando la specie si deve comportare da Base non ci sono problemi di natura sterica.

CATIONE ACILICO

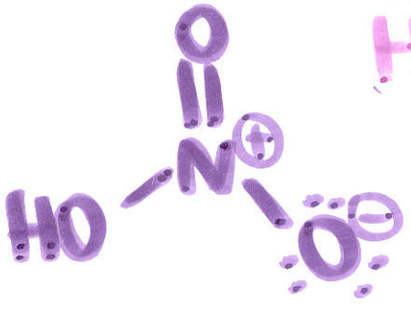


CARBOCATIONE BENZILICO



CLORURO di ALLILE

ACIDO NITRICO

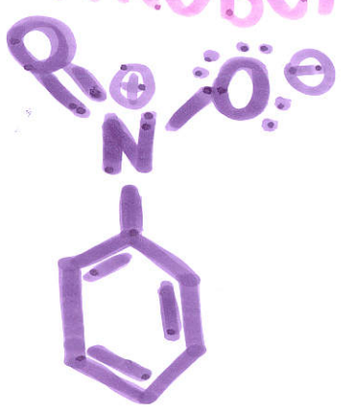


HNO_3

IONE NITRONIO

NO_2^+

NITROBENZENE



ACIDO CIANIDRICO

IONE CIANURO

ALCHINO

IONE ACETILURO

GRUPPI FUNZIONALI

IDROLISI
ANIDRIDI

- Alogenuri Alchilici R-$\ddot{X}$:
- Alcoli R-$\ddot{O}$H
- Tioli R-$\ddot{S}$H
- Eteri R-$\ddot{O}$-R

- alogenuri + eteri
- alcheni + H_2O (DISIDRATAZ.)

SINTESI:

- ALDEIDI e CHETONI + H_2O
- ALDEIDI e CHETONI + 2 volte GRIGNARD

ALCOLI

$-\overset{\delta-}{\ddot{O}}-\overset{\delta+}{H}$

$-\overset{\delta+}{C}-\overset{\delta-}{\ddot{O}}-$

LEGAMI POLARIZZATI

- legami ad H
- interazioni intramolecolari (DIPOLO-DIPOLO)
- Teb più alte di ALCANI

* OH è ACCETTORE o DONATORE di legami a H

REAZIONI

① - con ACIDI (si comportano da BASI)

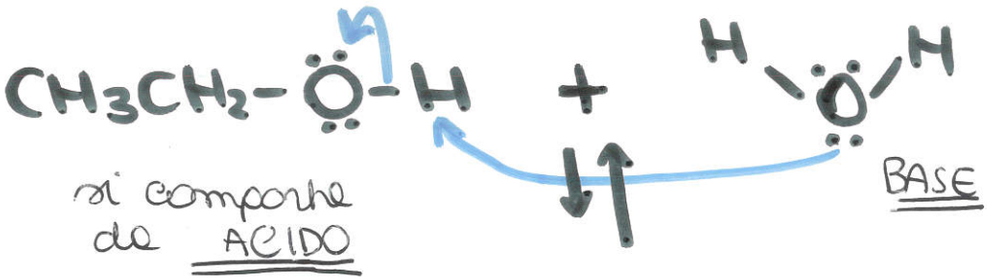
② - con BASI (si comportano da ACIDI)

③ - CONVERSIONE in ALOGENURI ALCHILICI

④ - DISIDRATAZIONE acido catalizzata

⑤ - OSSIDAZIONE di ALCOL 1° e 2°

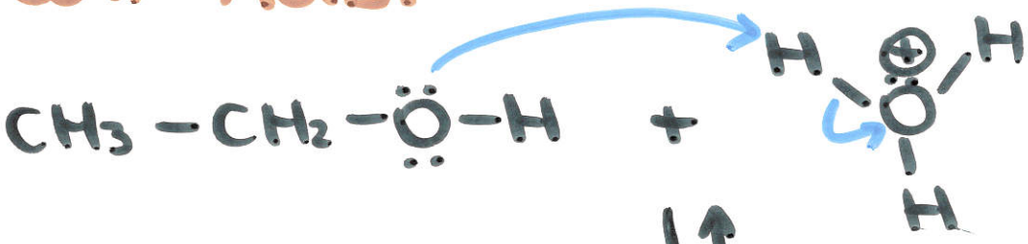
② - con BASI

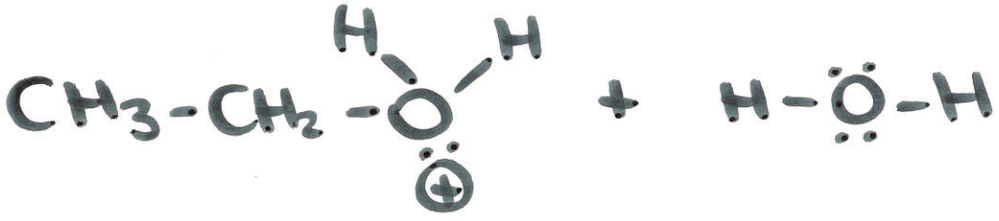


anione etossido

ALCOL + BASE → ANIONE ALCOSSIDO

① - con ACIDI



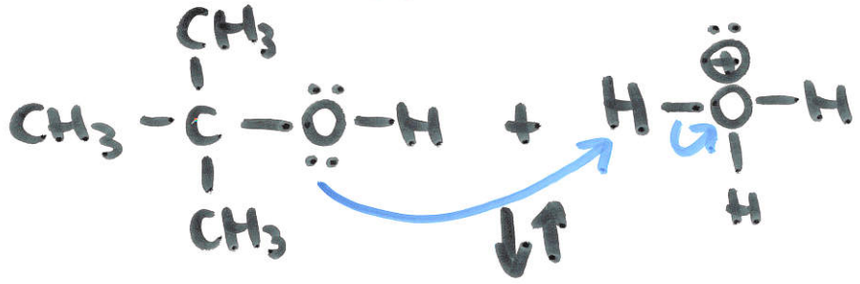


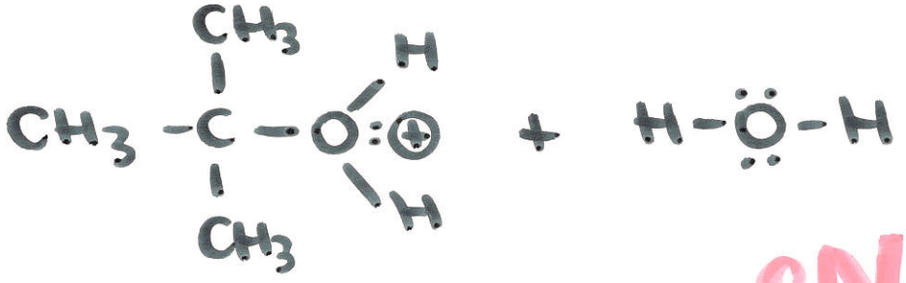
catione ossonio

ALCOL + ACIDO → CATIONE OSSONIO

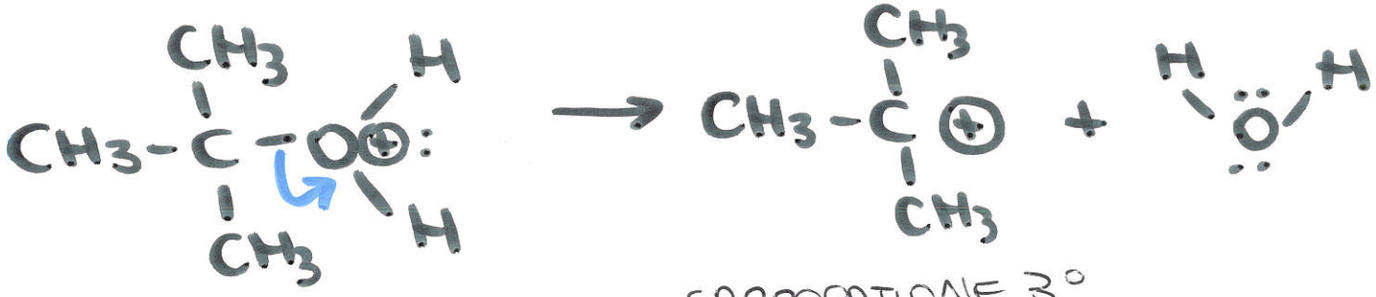
③ CONVERSIONE in ALOGENURI ALCHILICI

Stadio 1:



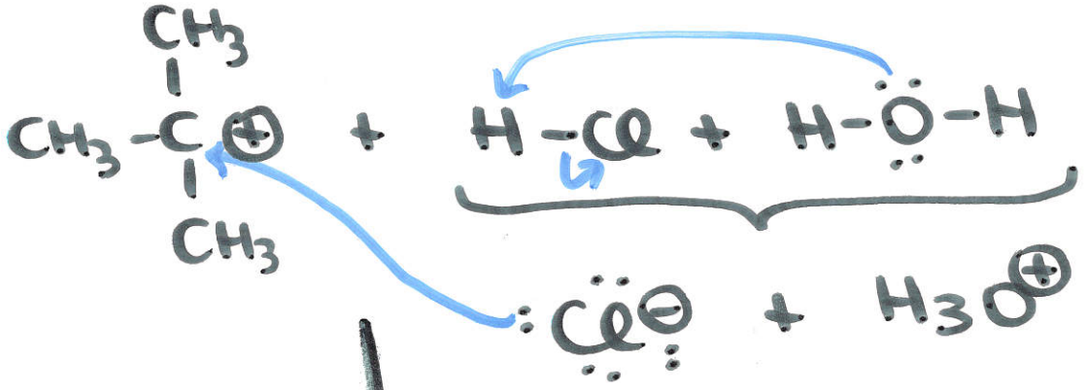


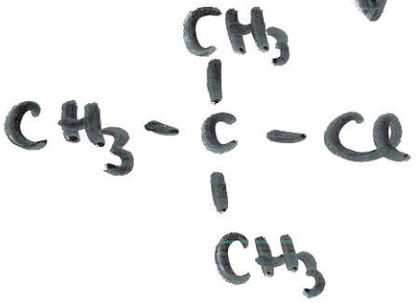
Stadio 2: **SN1**



CARBOCATIONE 3°

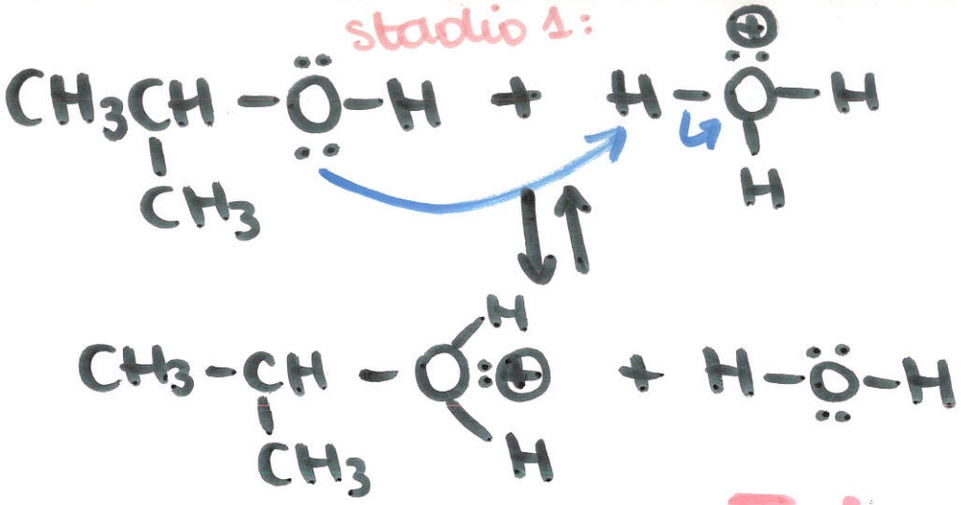
Stadio 3:



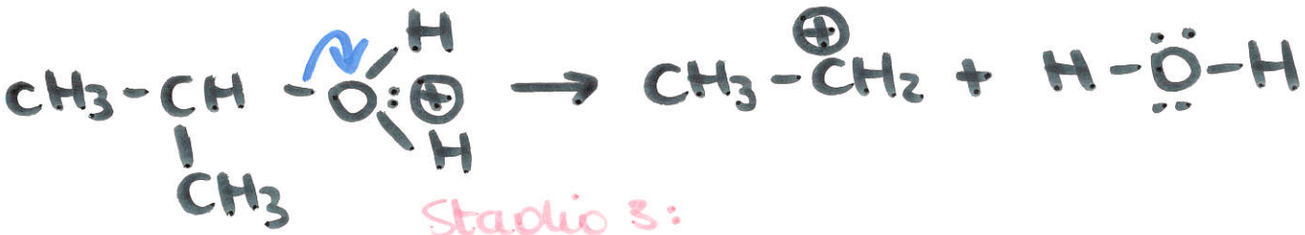


④ DISIDRATAZIONE acido catalizzata

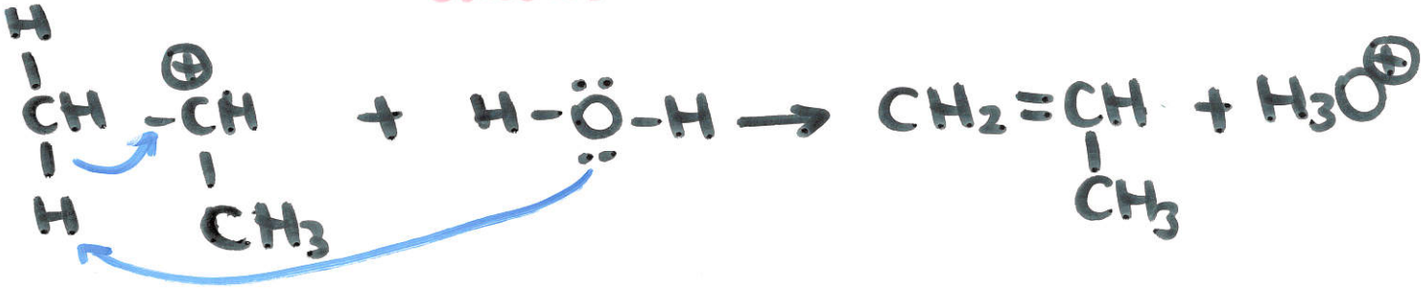
Stadio 1:



Stadio 2: **E1**

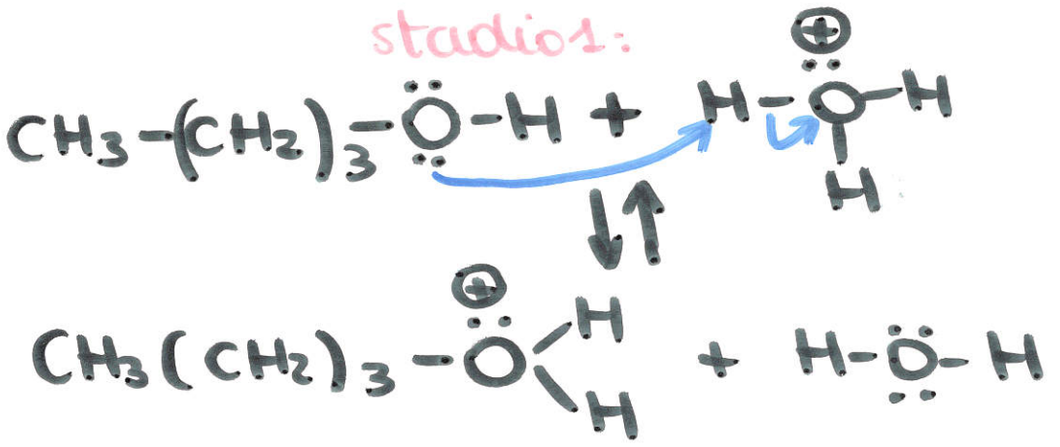


Stadio 3:

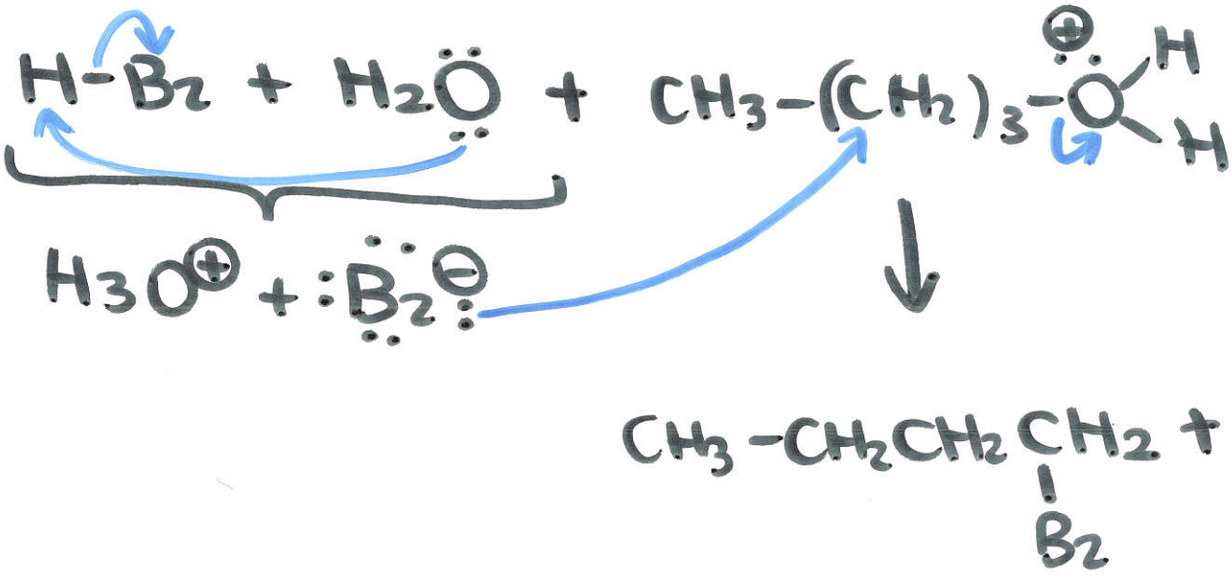


③ CONVERSIONE in ALOGENURI ALCHILICI

stadio 1:



stadio 2: SN2



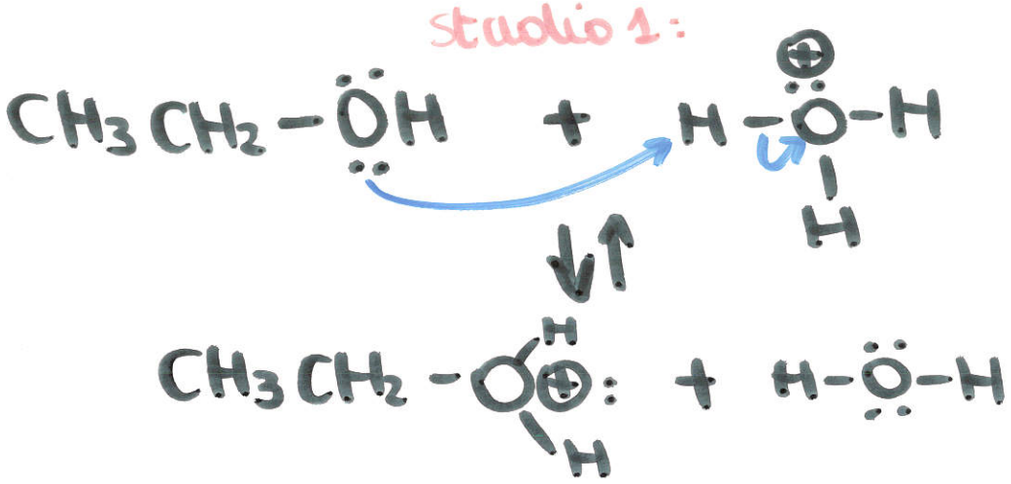
ALCOL + $H^{\oplus}$ + H-X

↓

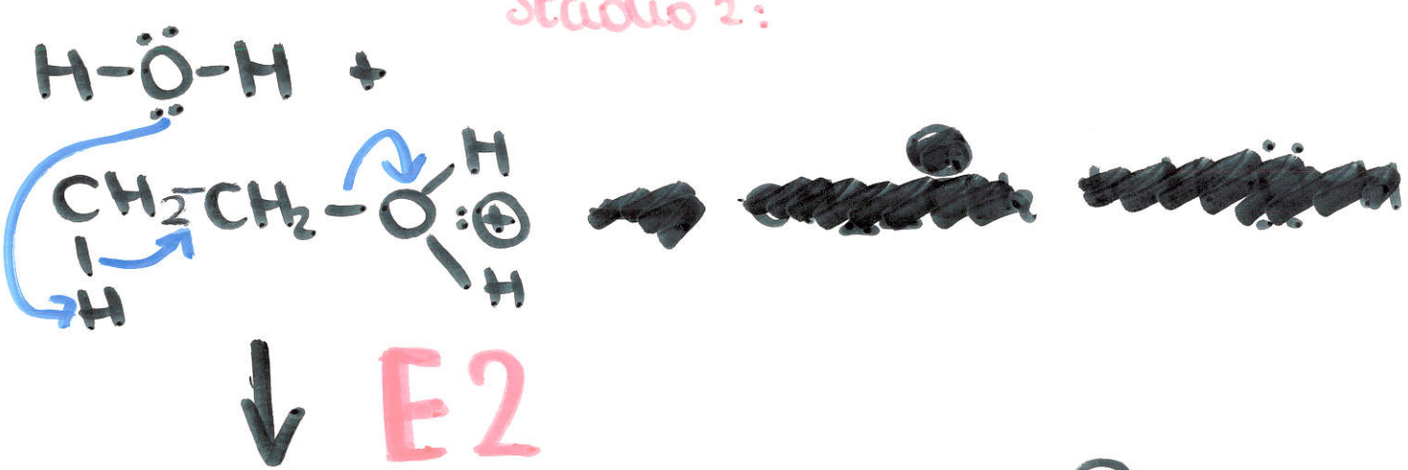
H_2O + ALOG. ALCHILICO

DISIDRATAZIONE Acido catalizzato

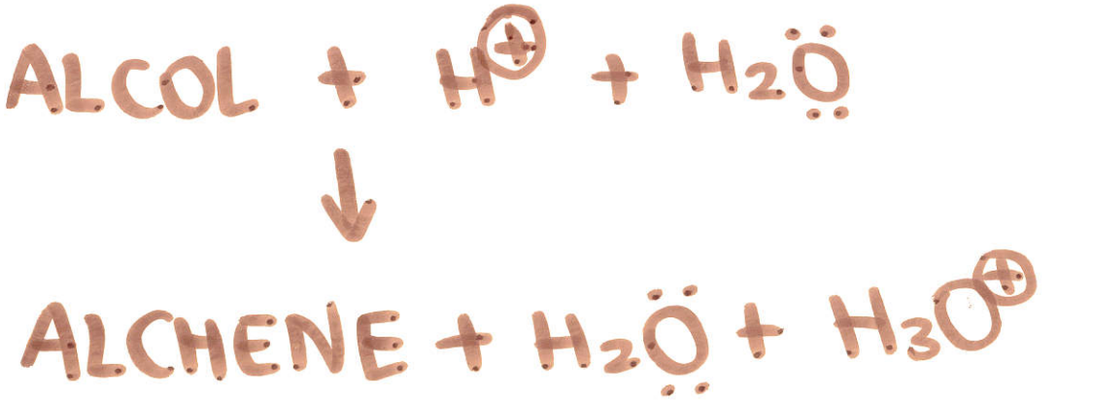
Studio 1:



Studio 2:

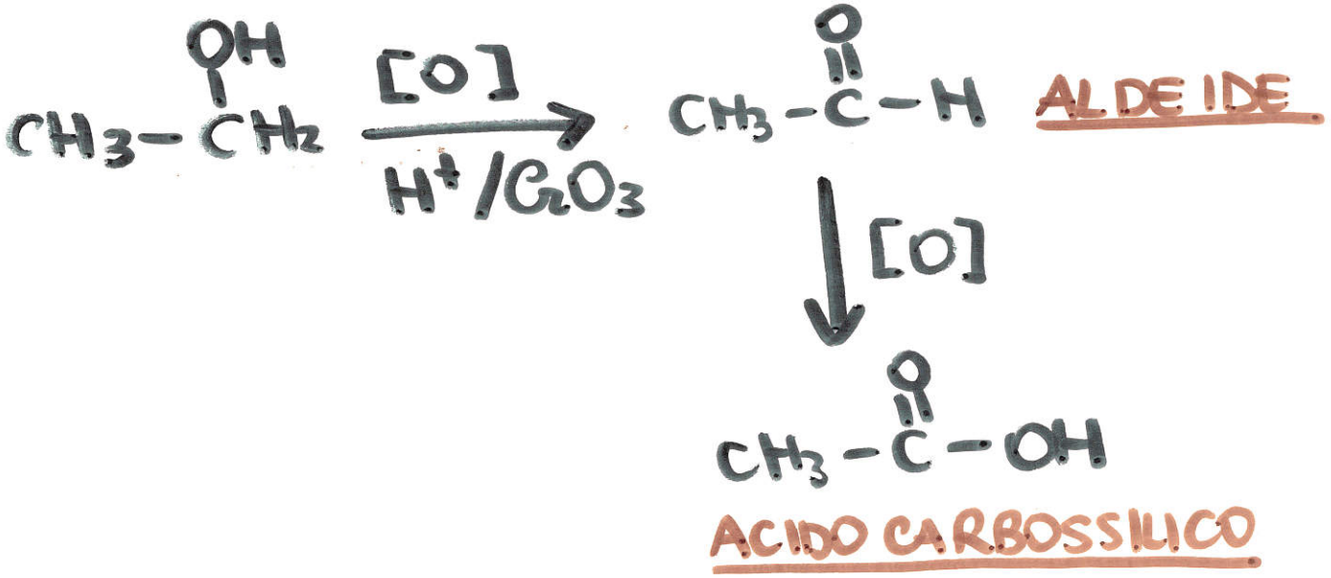


E2

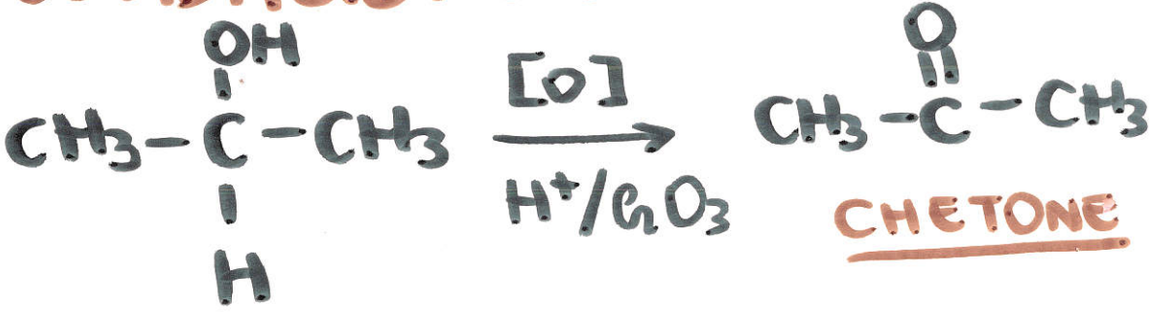


⑤

- OSSIDAZIONE di ALCOLI 1°



- OSSIDAZIONE di ALCOLI 2°



ETERI

Sintesi

1. SINTESI di Williamson

ALCOSSIDO + ALOGENURO ALCHILICO

↓

ETERE

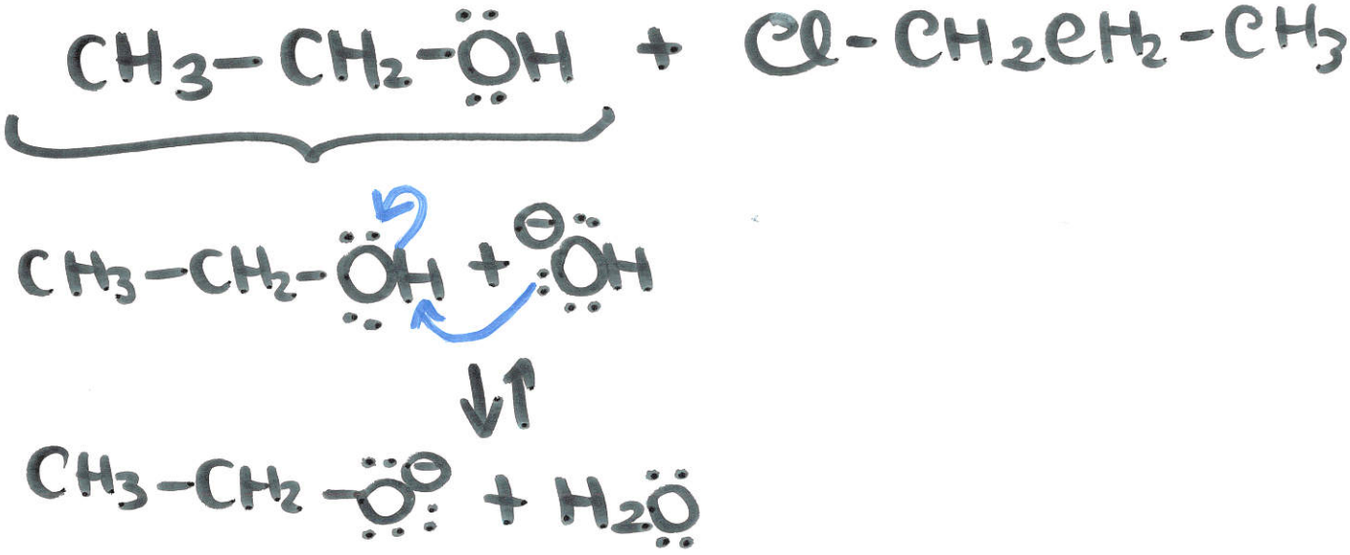
2. DISIDRATAZIONE acido catalizzata
   - dagli ACIDI degli ALCOLI
   - ~~dagli Acidi degli Alcheni~~

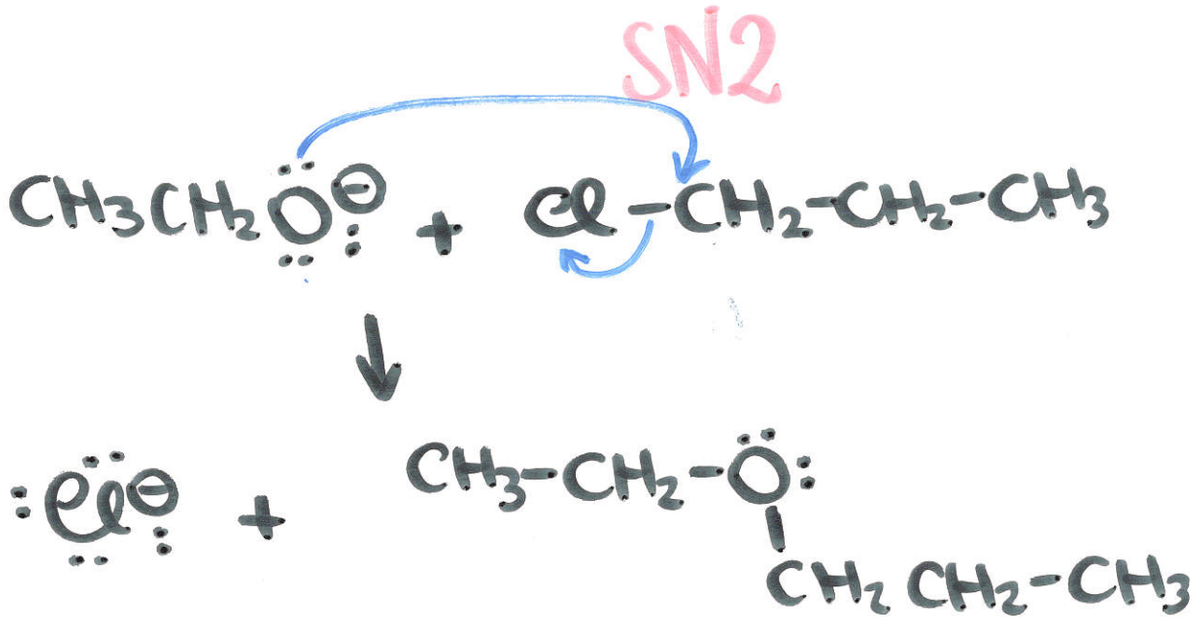
3. ADDIZIONE acido catalizzata
   - di ALCOLI ad ALCHENI

Reazioni

4. SCISSIONE Acido Catalizzata con HX

① Sintesi di Williamson SN2





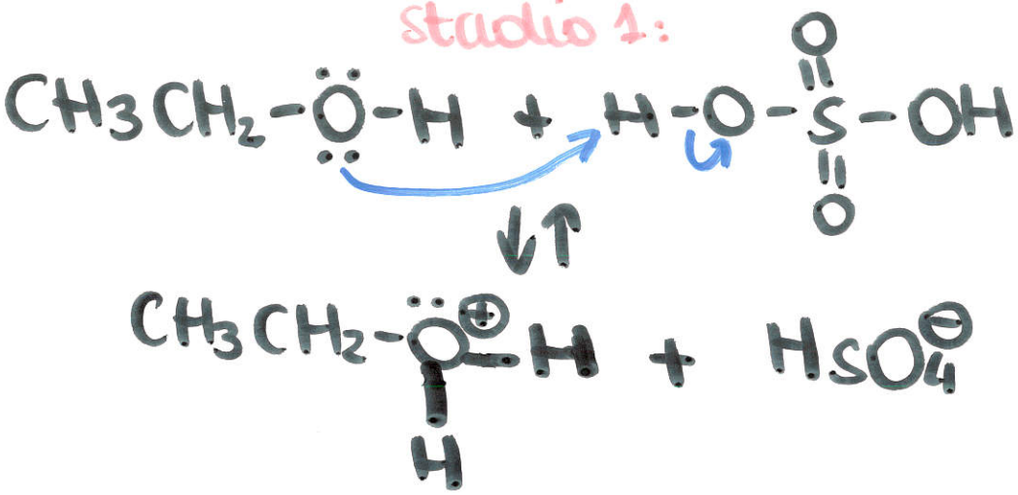
ALCOSSIDO + ALOG. ALCHILICO

↓

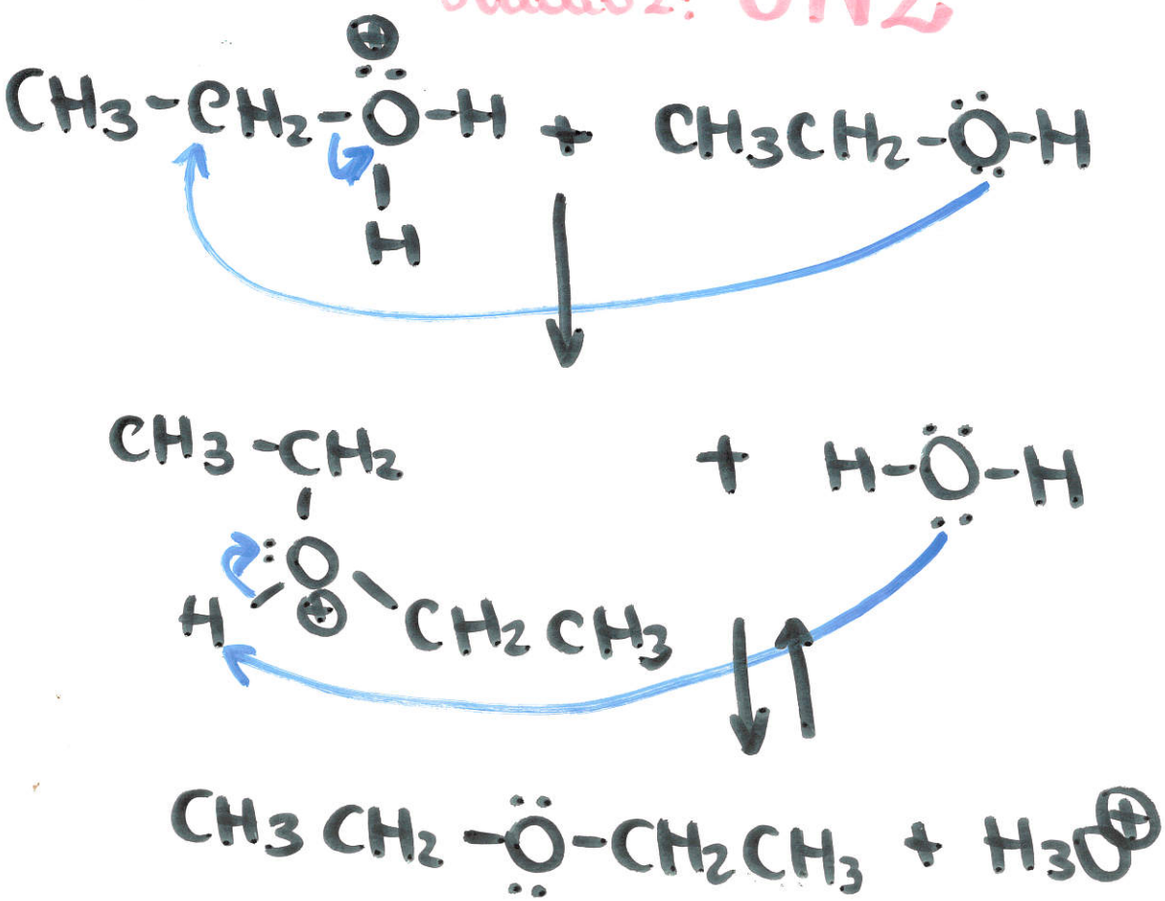
ETERE

(2) DISIDRATAZIONE Acido Catalizzata
ALCOL PROTONATO + ALCOL (SN2)

stadio 1:



stadio 2: SN2

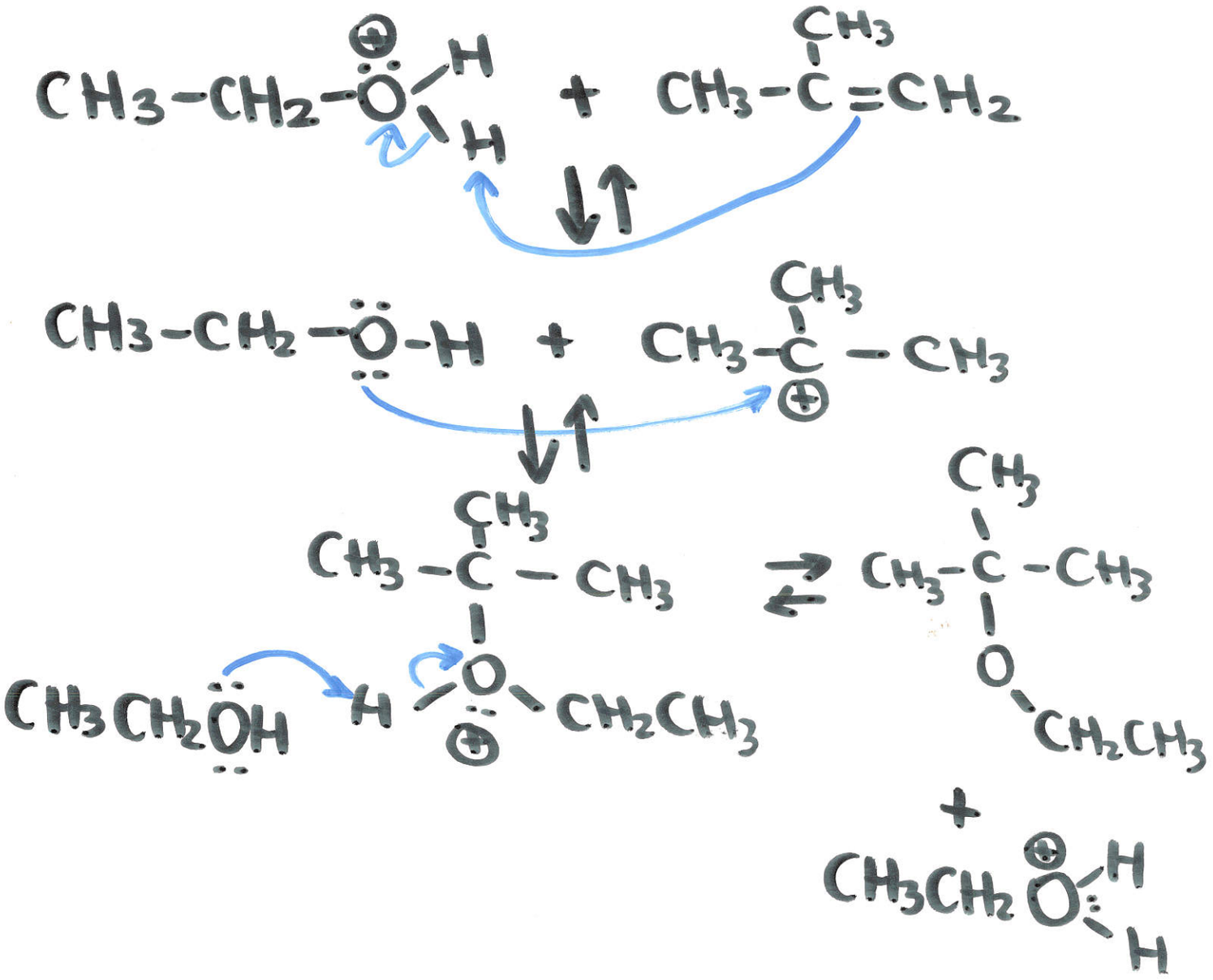


ALCOL + ALCOL PROTONATO

↓

ETERE

③ ADDIZIONE acido catalizzato
ALCHENI + ALCOLI PROTONATI

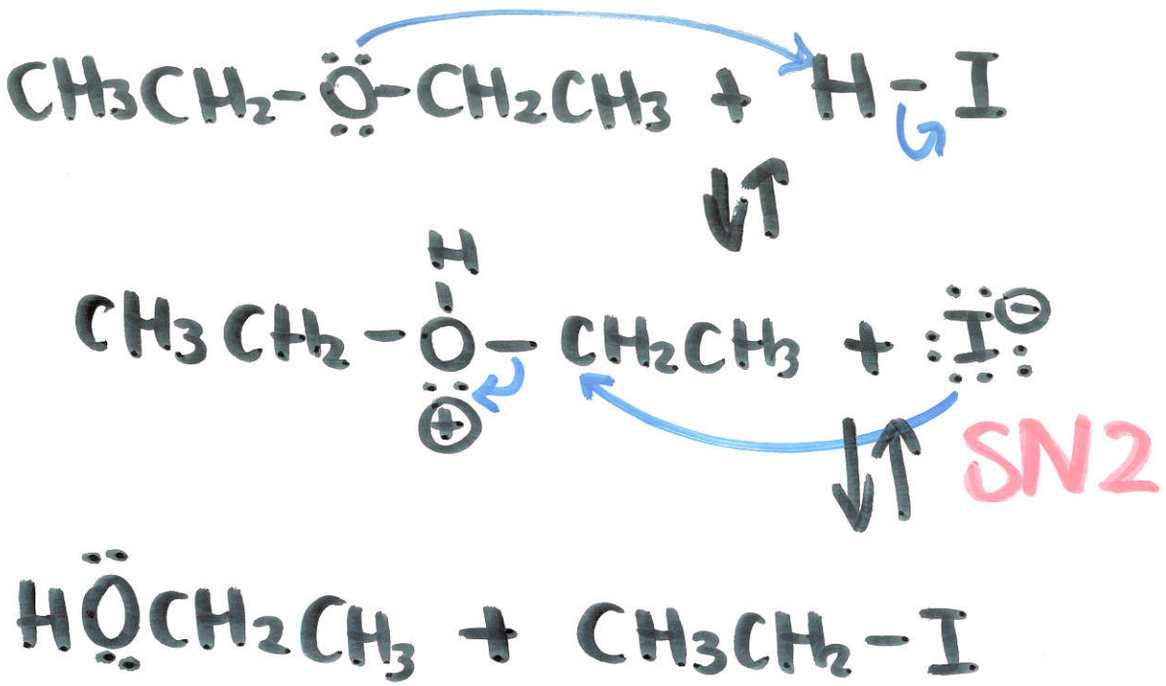


ALCOL PROTONATO + ALCHENE

↓

ETERE

④ SCISSIONE Acido catalizzata con HX



ETERE + HX → ALOGEN. ALCHILICO + ALCOOL

(FORMAZIONE di un ALCOL)

EPOSSIDI

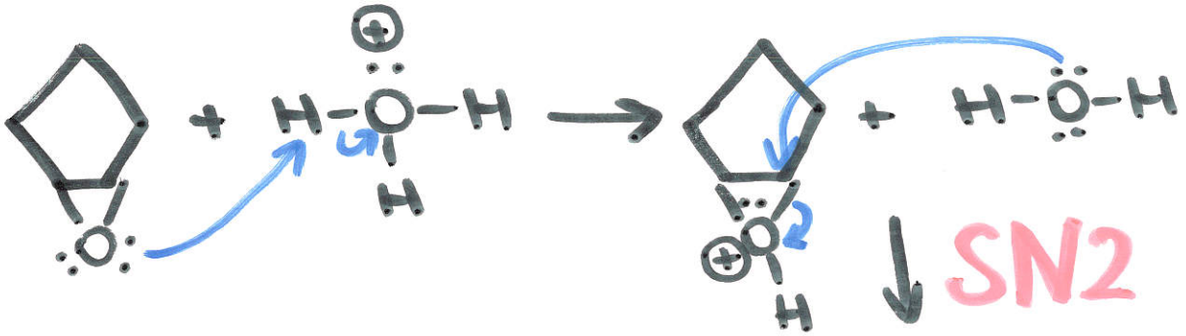
Sintesi:

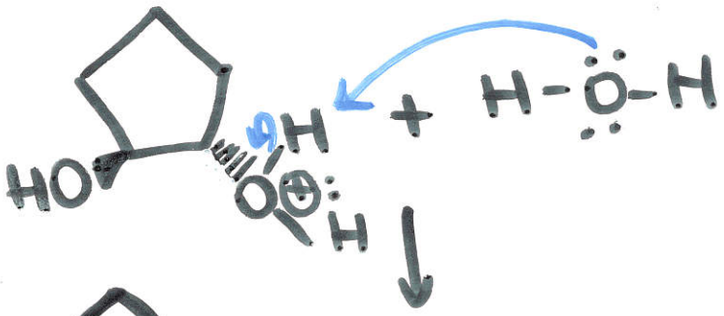
- OSSIDAZIONE degli ALCHENI con PERACIDI

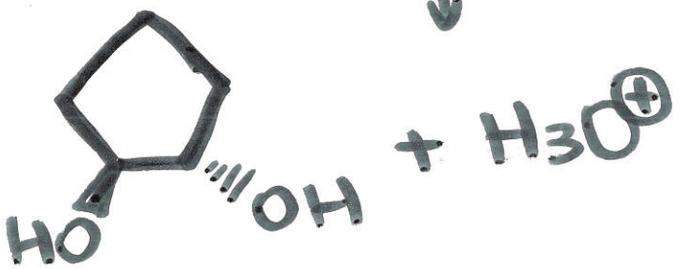
- SOSTITUZIONE NUCLEOFILA INTERNA nelle ALOIDRINE

Reazioni:

- APERTURA dell'ANELLO (idrolisi acido catalizzata)

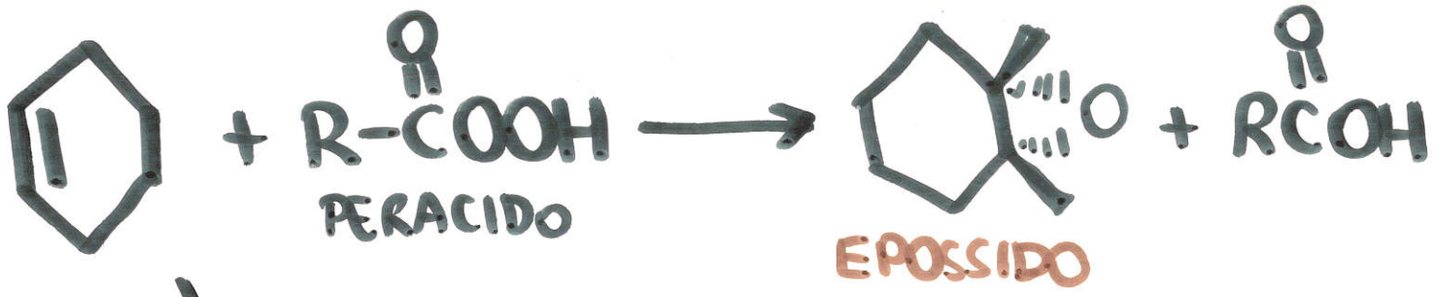




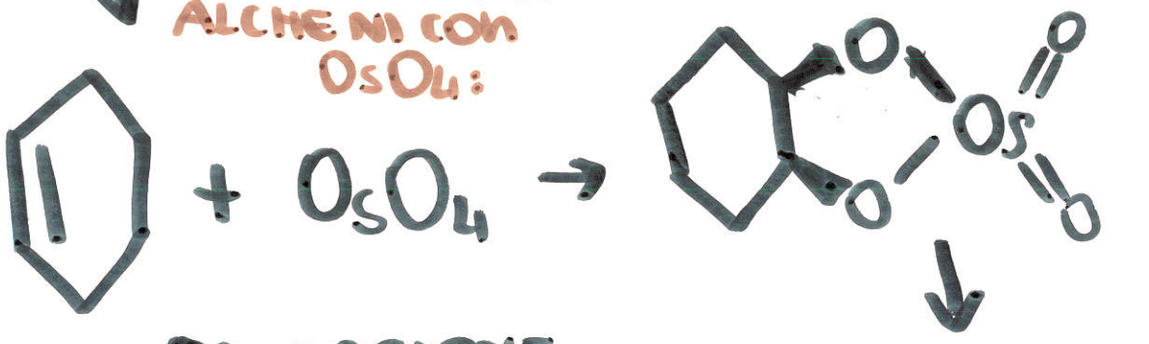


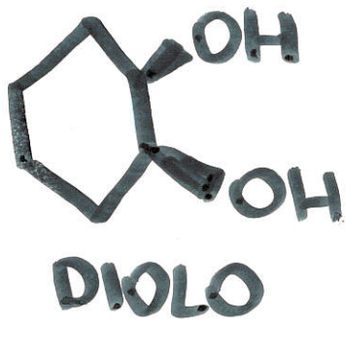
DIOLO TRANS

-OSSIDAZIONE di ALCHENI con PERACIDI

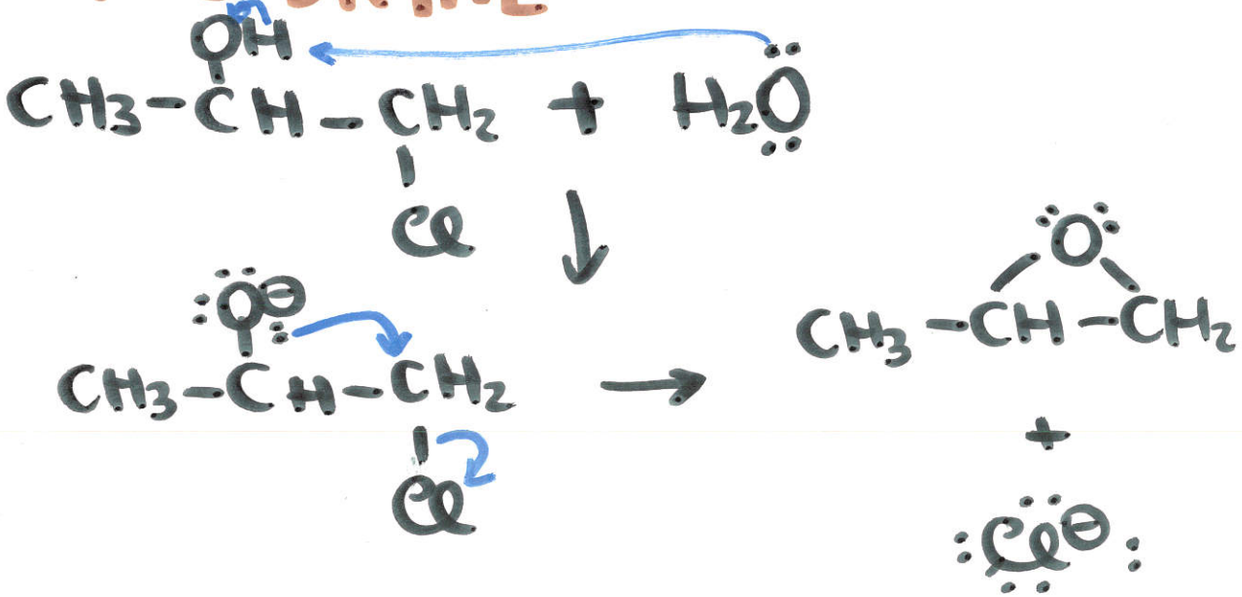


OSSIDAZIONE di ALCHENI con OsO_4:





-SOSTITUZIONE N_u INTERNA nelle ALOIDRINE



BENZENE C_6H_6

IDROCARBURO AROMATICO (INSATURO)

- CLORURAZIONE: Cl_2, $FeCl_3$
- NITRAZIONE: HNO_3, H_2SO_4
- SOLFONAZIONE: H_2SO_4
- ALCHILAZIONE: R-X, $AlCl_3$
- ACILAZIONE: $R-C(=O)-X$, $AlCl_3$

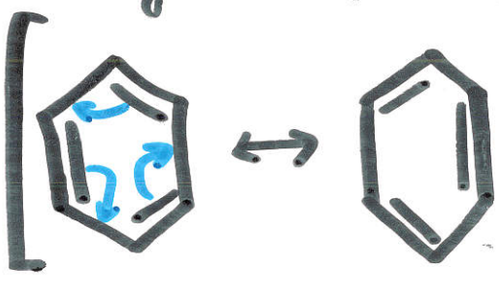
} SOSTITUZ. ELETTROFILA AROMATICA

C IBRIDATO sp^2 • $\alpha = 120°$

• legami C-C e C-H della stessa lunghezza

• 2 STRUTTURE LIMITE di RISONANZA ISOENERGETICHE

• legami σ sp^2-sp^2 e sp^2-1s



STRUTTURE di KEKULÉ (2ª PROPOSTA)

INTERCONVERSIONE ↳ EQUILIBRIO

1ª PROPOSTA:
- NON va bene:
  - atomo di C trivalente
  - non spiega l'equivalenza dei legami C-H e C-C.

AROMATICO: IDROCARBURO altamente INSATURO e NON REATTIVO verso i reagenti di Alcani ed Alcheni.

ARENI: IDROCARBURI AROMATICI

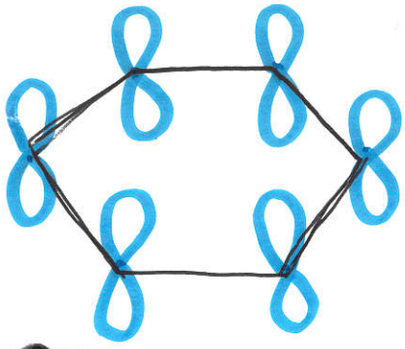
COMPOSTI AROMATICI:

Regola di Hückel

1. molecola ciclica
2. IBRIDAZIONE sp^2 con ORBITALI $2p$ ⊥ all'anello
3. $4n+2$ elettroni π
4. molecola PLANARE

1 MODELLO dell'ORBITALE MOLECOLARE

COMBINAZIONE dei 6 ORBITALI ATOMICI 2p MONOOCCUPATI PERPENDICOLARI al piano dell'anello: ottengo 6 ORBITALI MOLECOLARI



↳ 3 di LEGAME

↳ 3 di ANTI-LEGAME

STABILITA' ENERGETICA del BENZENE:

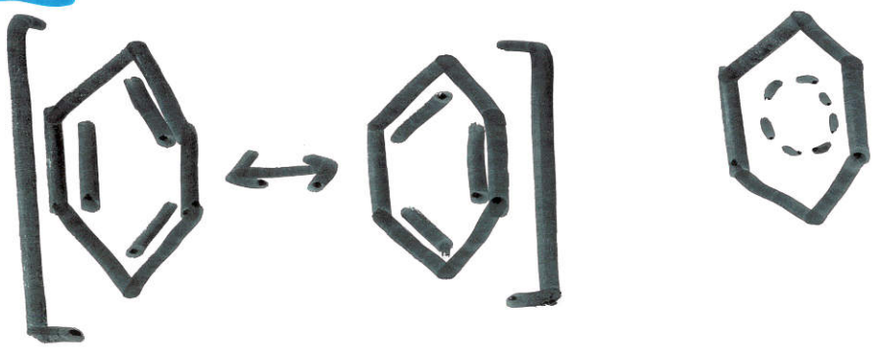
Energia M.O. di LEGAME ← ENERGIA più BASSA

LLL

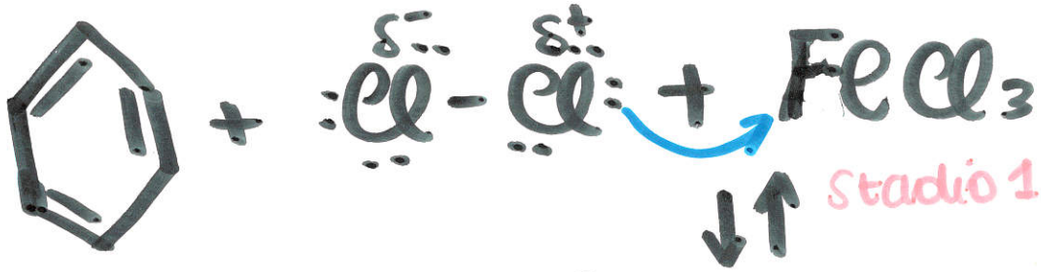
6 ORBITALI ATOMICI 2p non combinati

maggiore STABILITA' ENERGETICA.

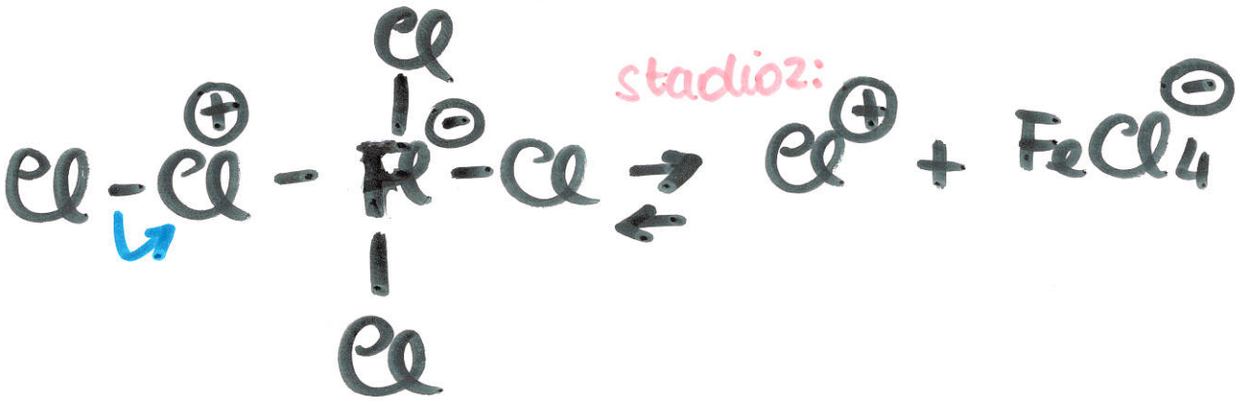
2 MODELLO della RISONANZA



molecola rappresentabile con 2 o più strutture nessuna delle quali singolarmente rappresenta in modo adeguato la molecola

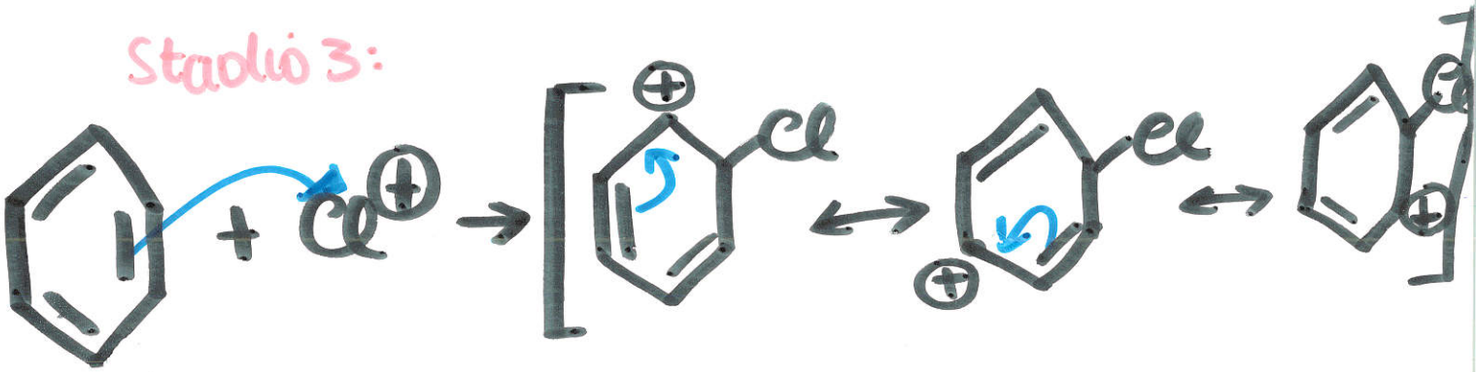


Stadio 1:



Stadio 2:

Stadio 3:



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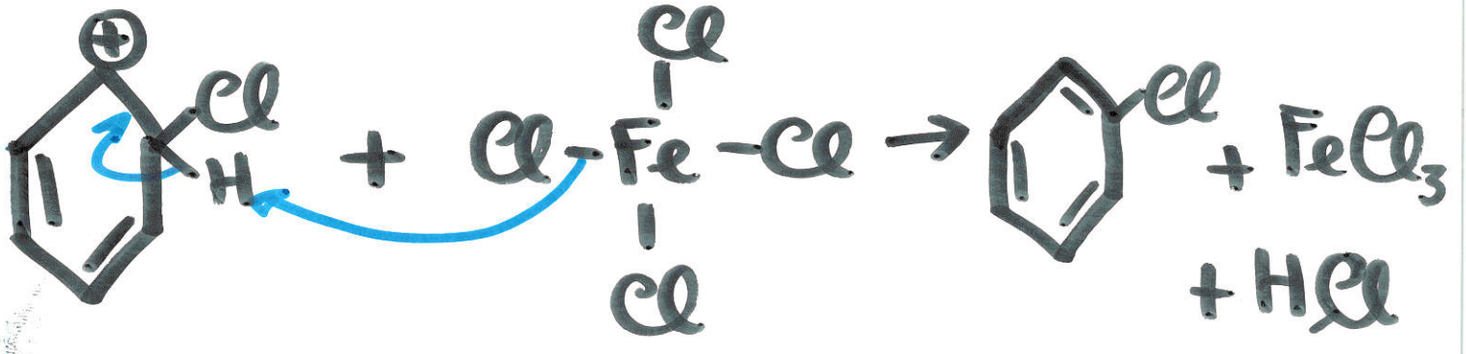
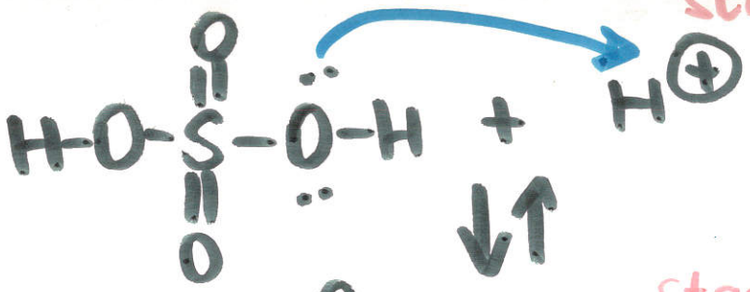


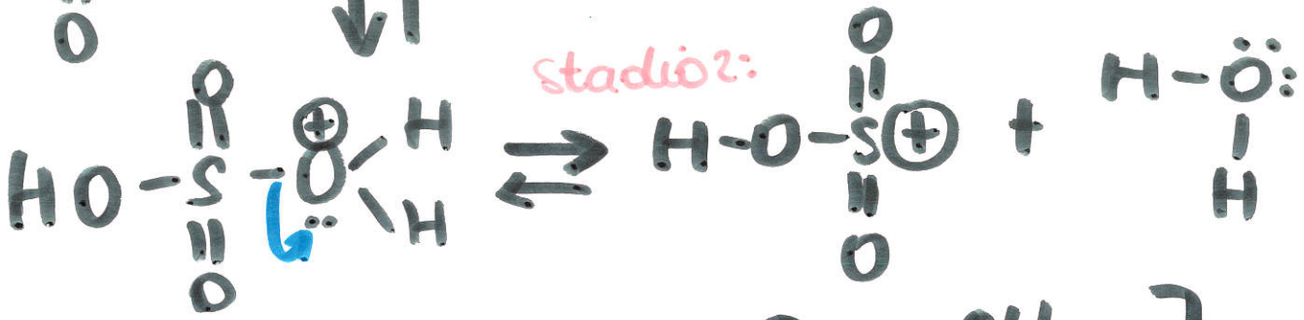
CLORURAZIONE

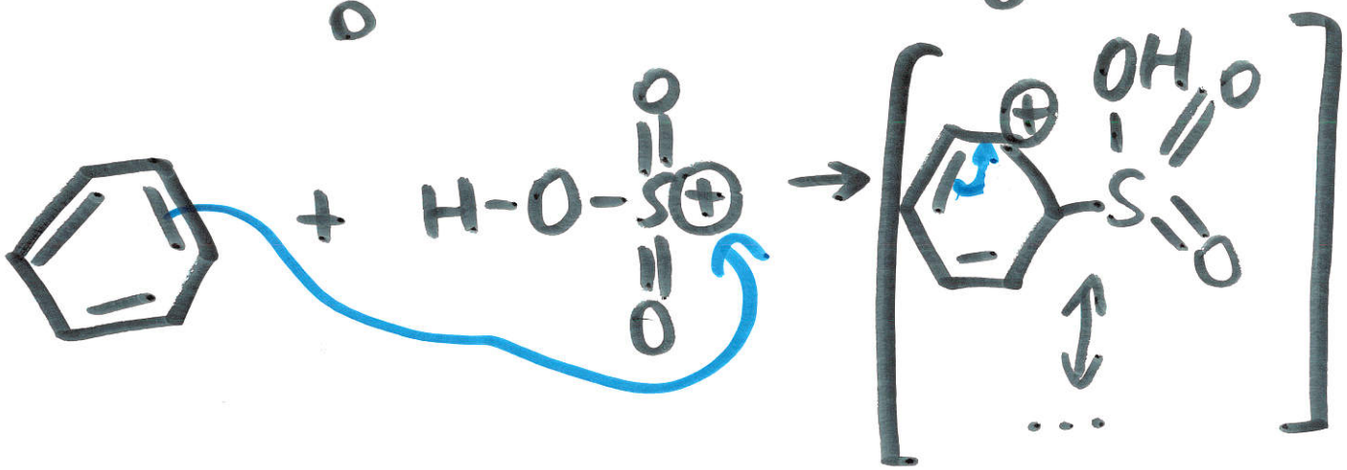
SOLFONAZIONE

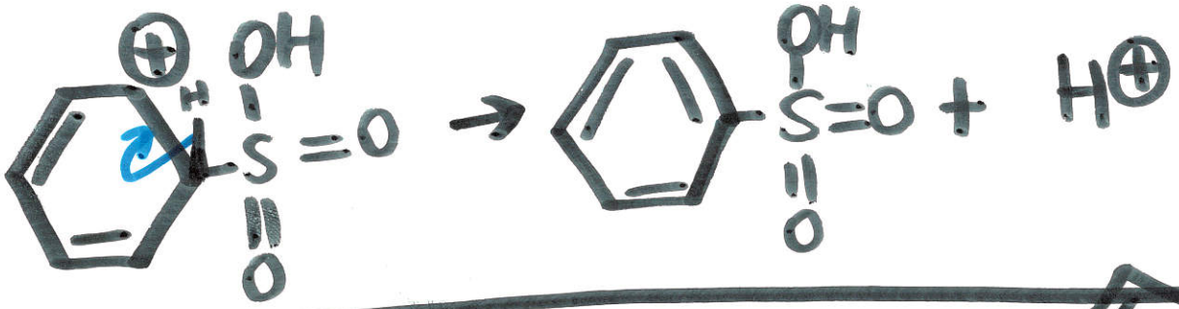
stadio 1:

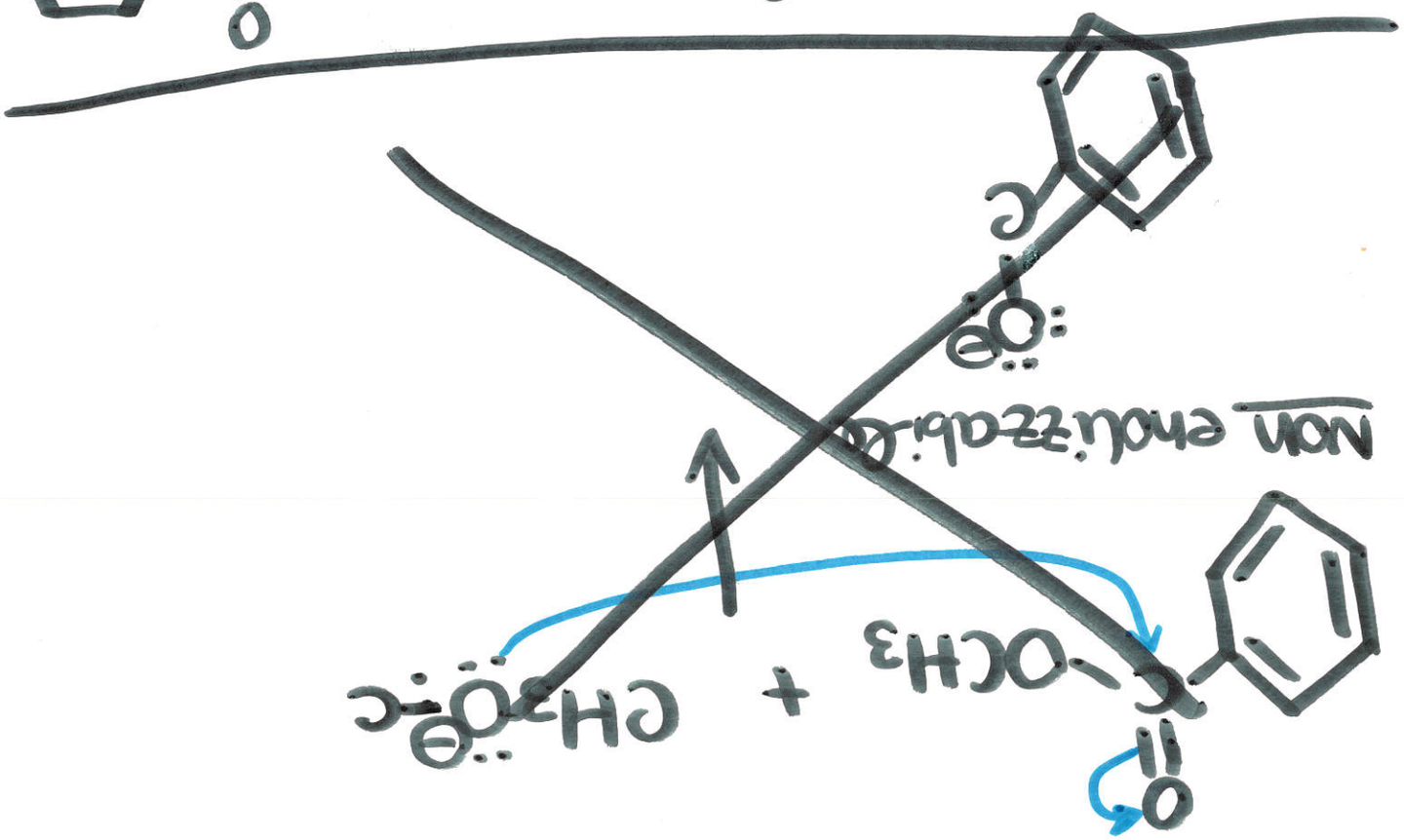


stadio 2:









NITRAZIONE

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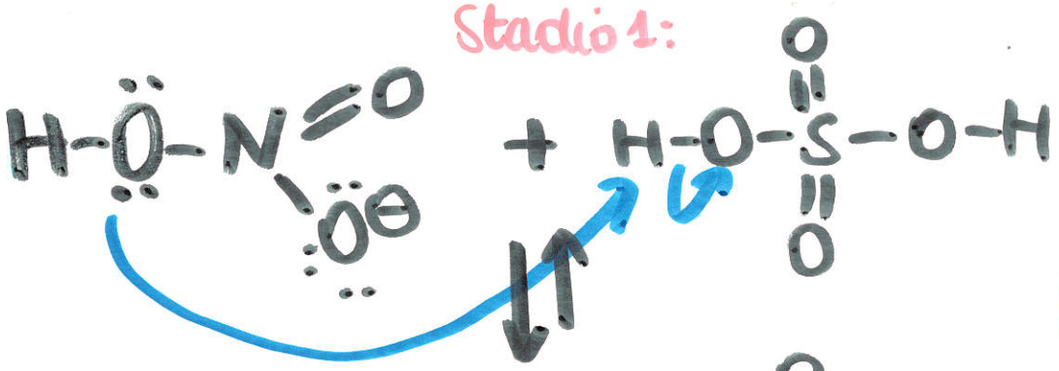
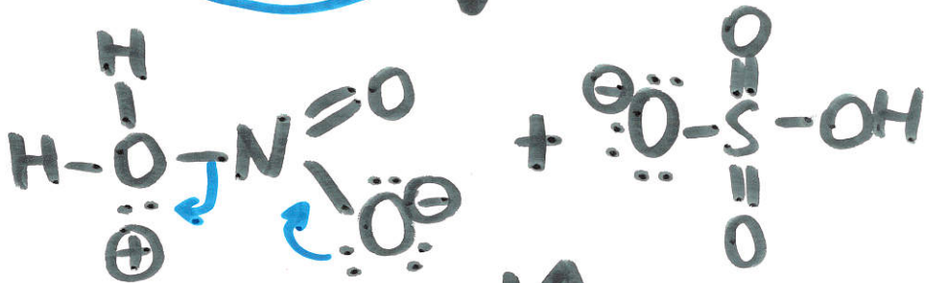
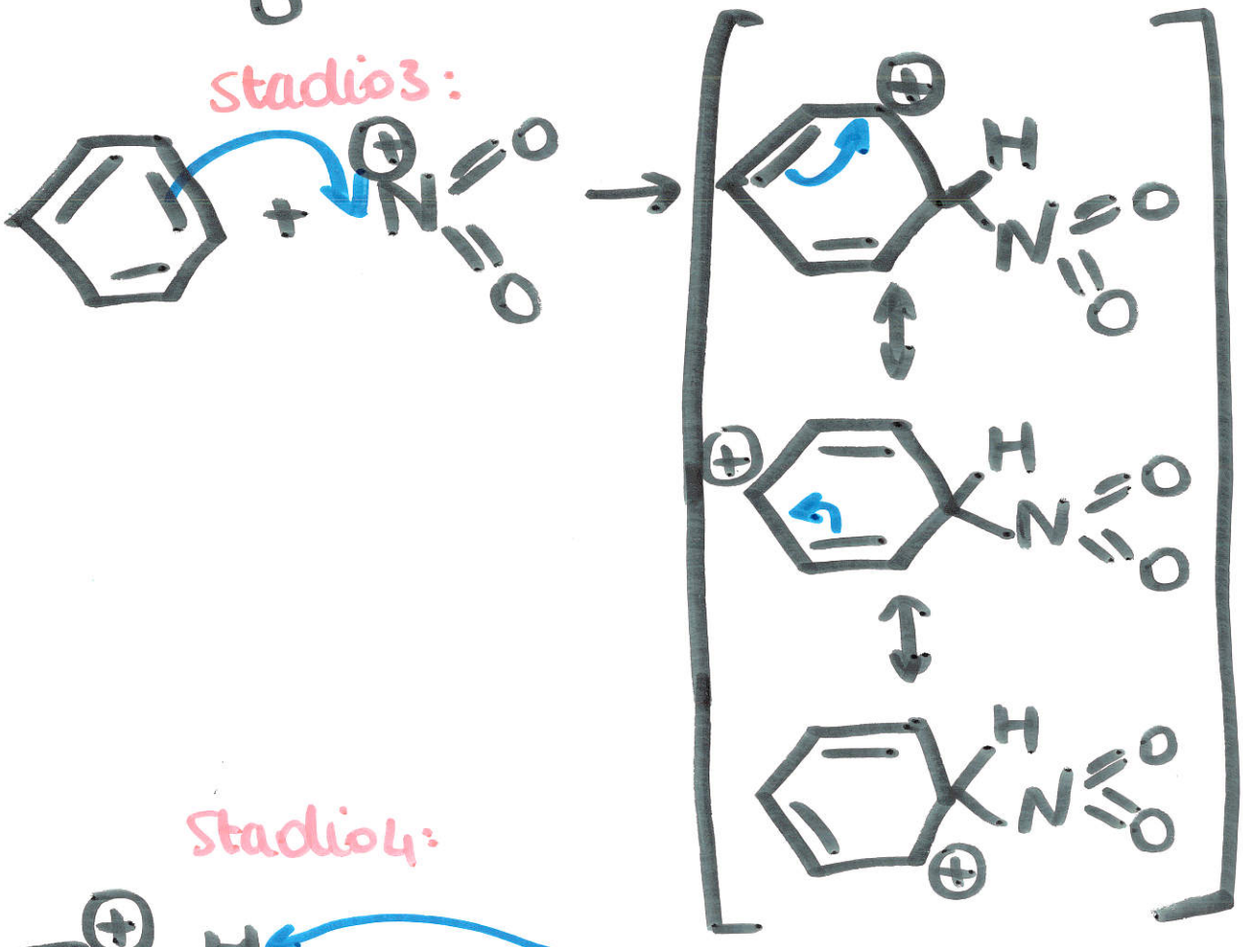


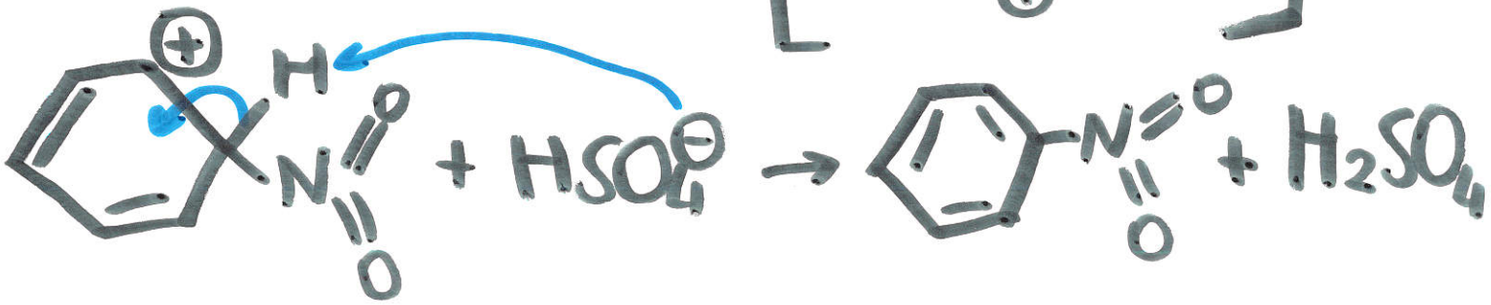


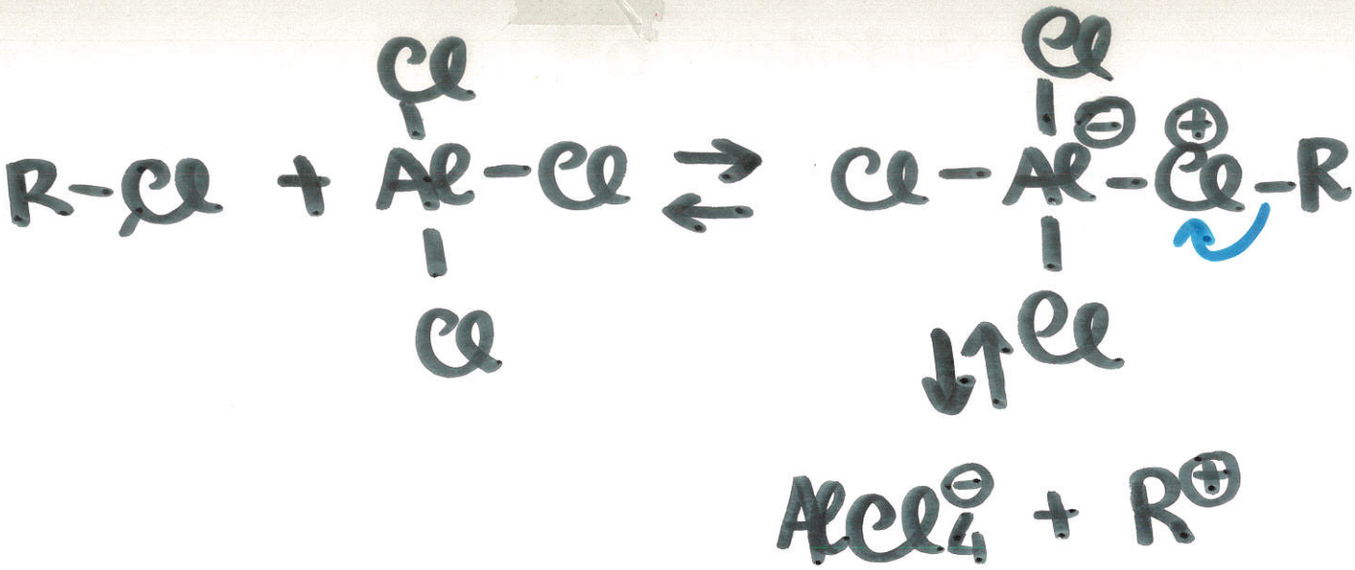
Stadio 2:

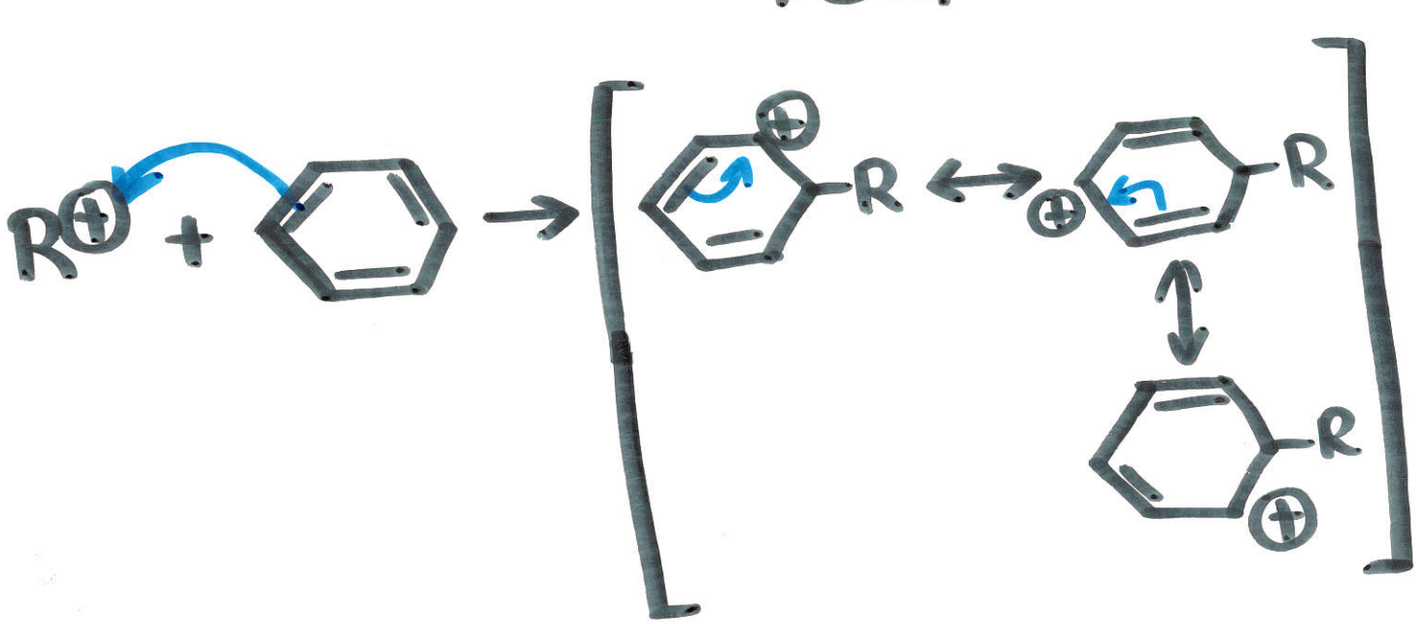
Stadio 3:

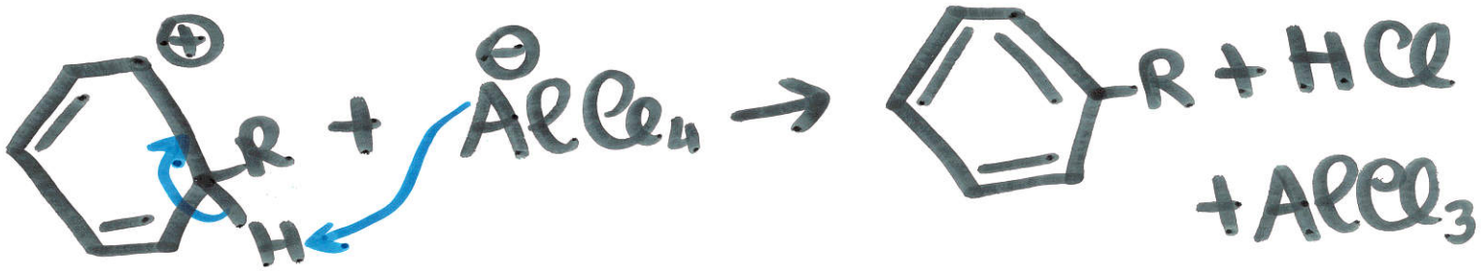


Stadio 4:



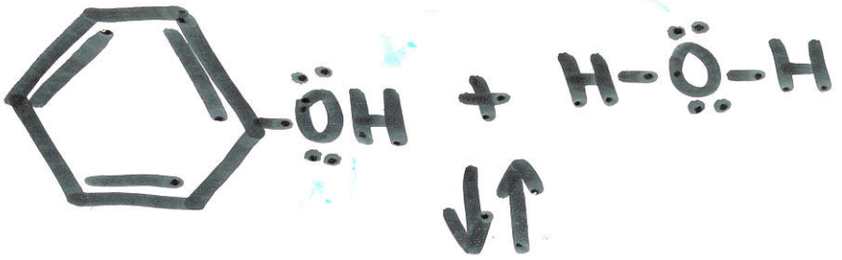


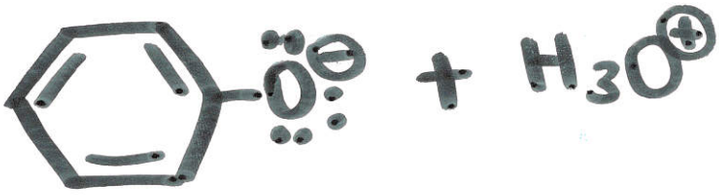


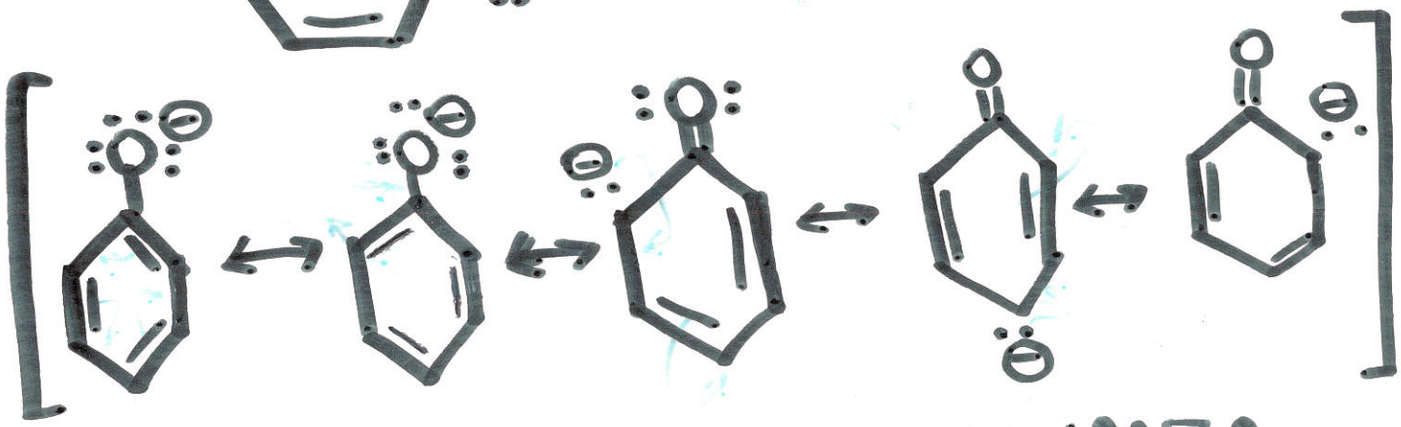


ALCHILAZIONE di FRIEDEL-CRAFTS

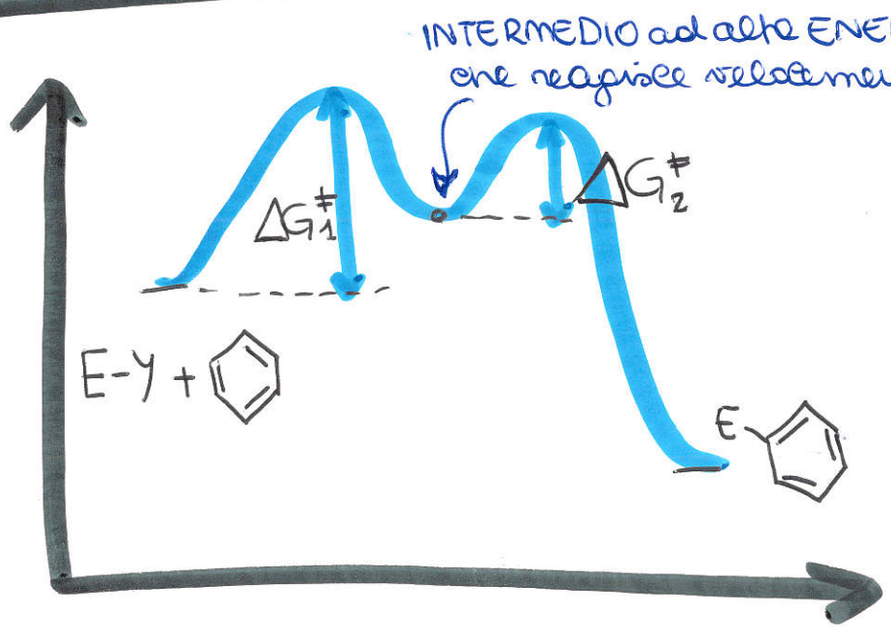
FENOLO



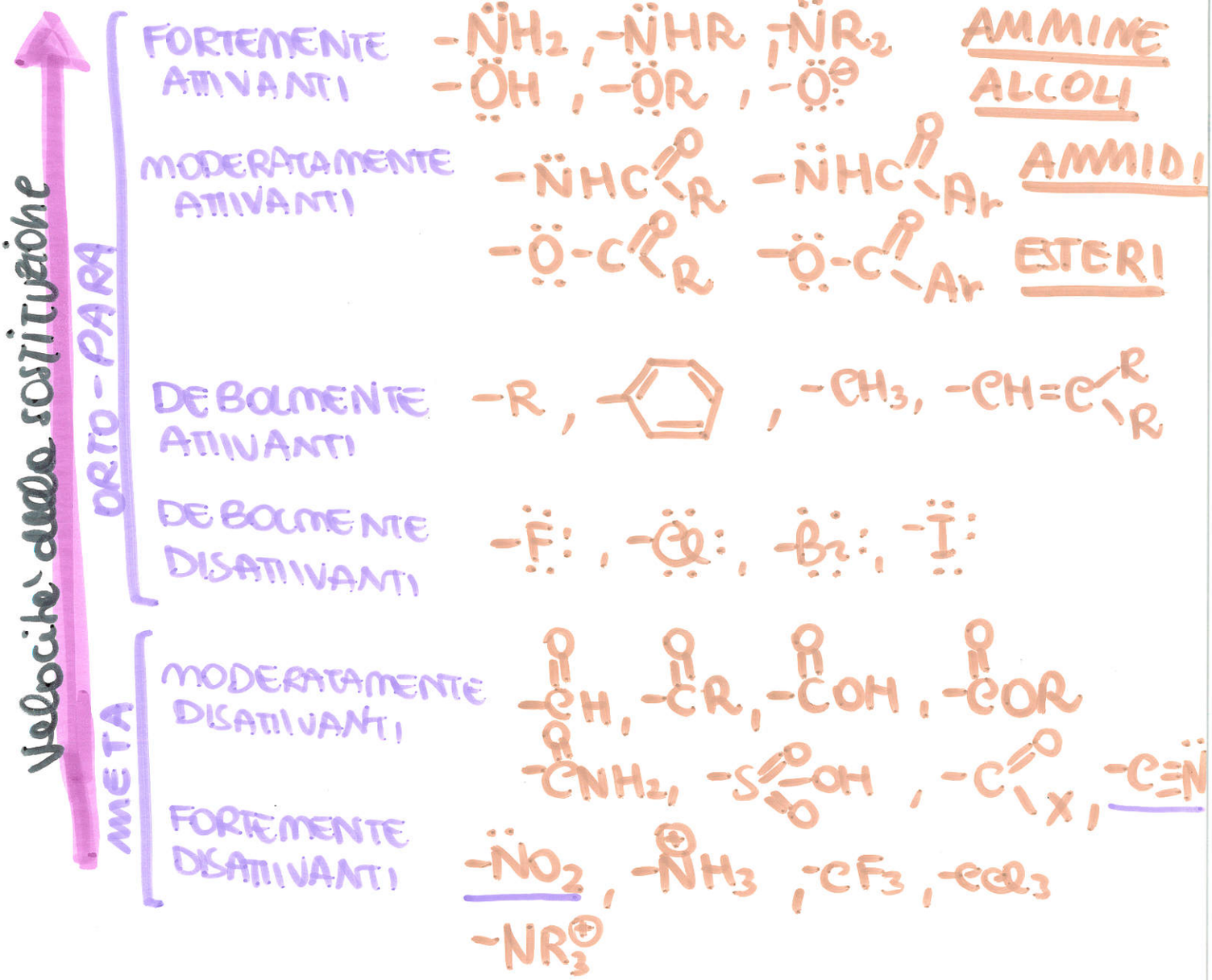




STRUTTURE LIMITE di RISONANZA
dello IONE FENOSSIDO



ACILAZIONE di FRIEDEL-CRAFTS



ELETTRON-ATTRATTORI: DISATTIVANTI

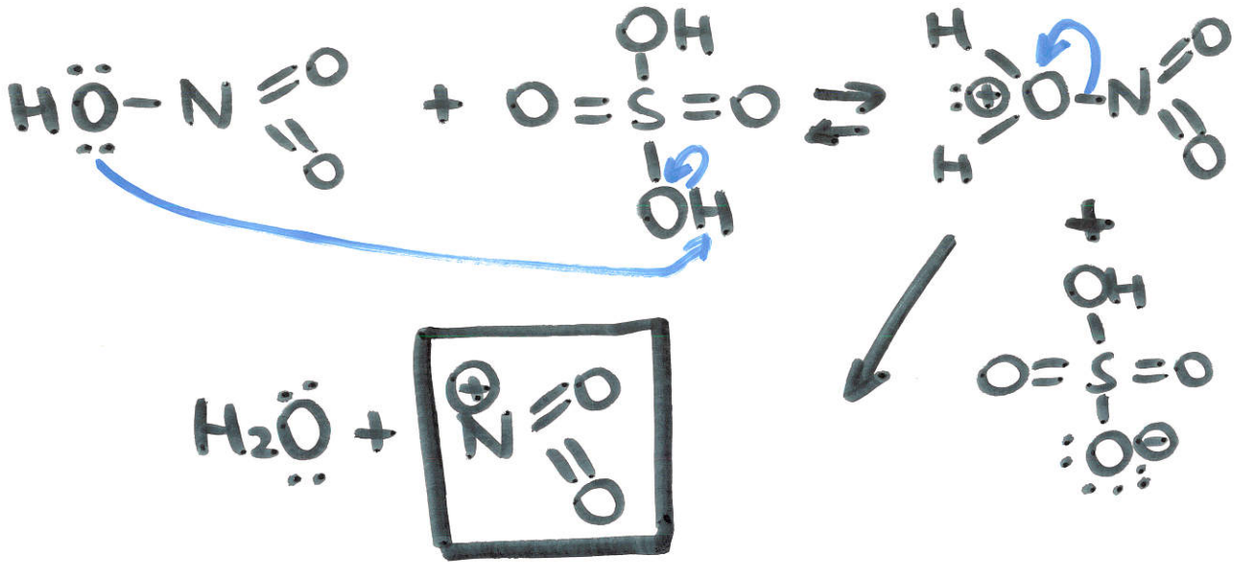
↳ impoveriscono l'anello di densità elettronica

ELETTRON-DONATORI: ATTIVANTI

↳ arricchiscono l'anello di densità elettronica

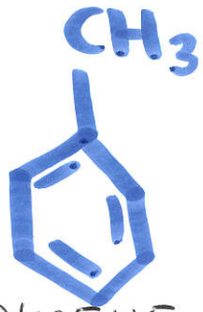
"Come si forma NO_2^+?"

$HNO_3 + H_2SO_4$

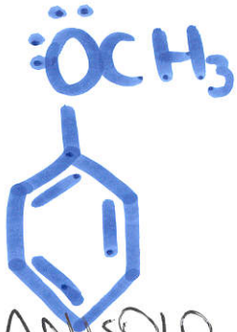


$H_2O +$

BENZENE

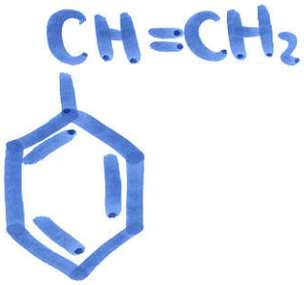


TOLUENE



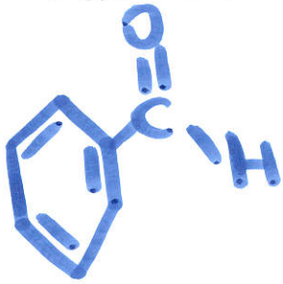
ANISOLO

ANILINA

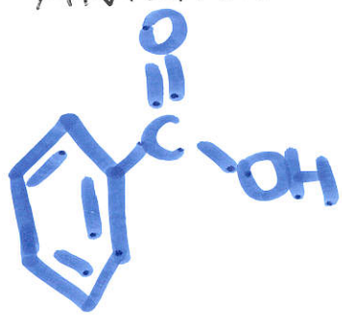


STIRENE

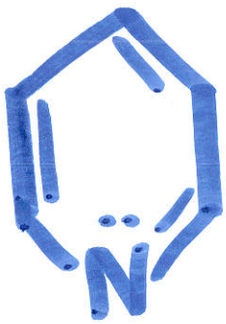
FENOLO



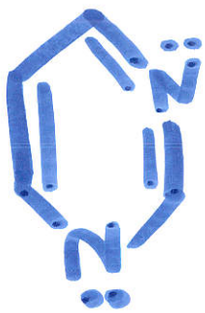
BENZALDEIDE



ACIDO BENZOICO

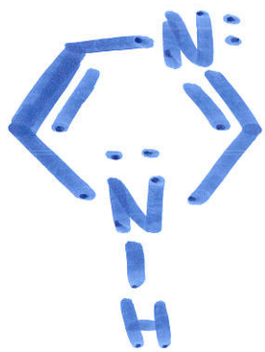


PIRIDINA



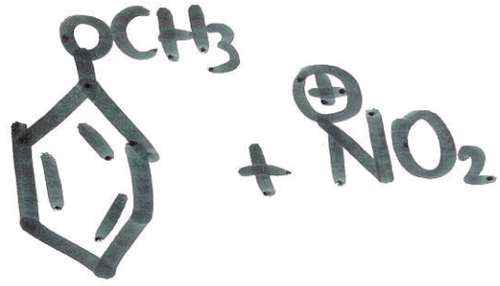
PIRIMIDINA

PIRROLO



IMIDAZOLO

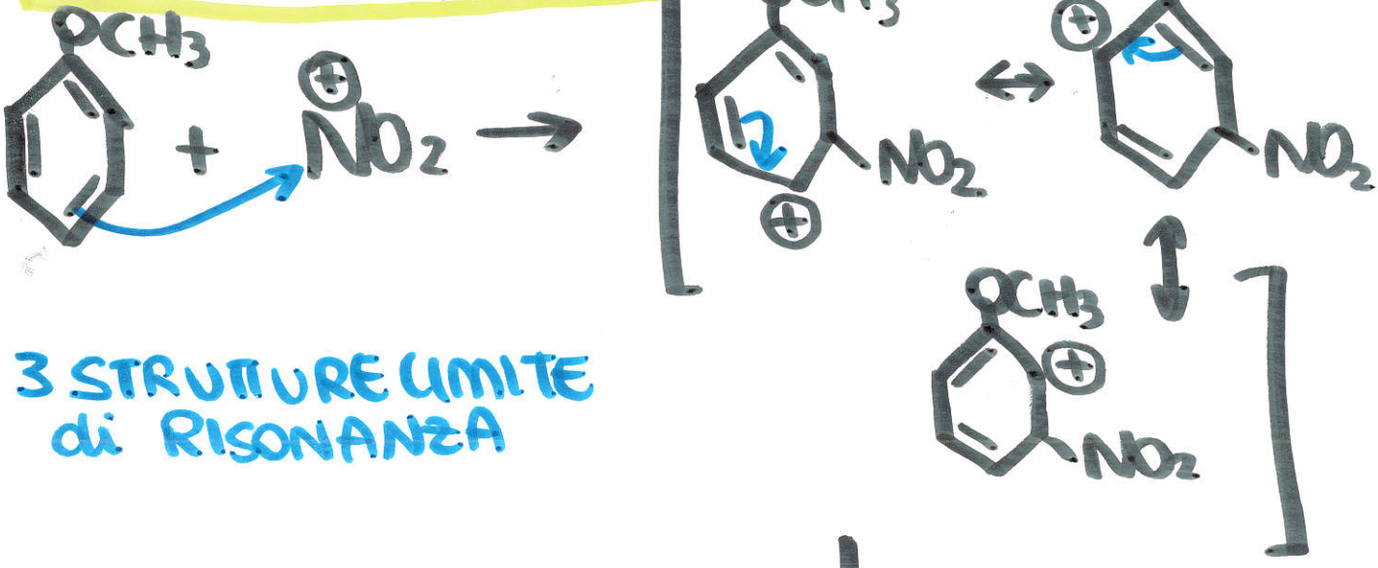
EFFETTO ORIENTAMENTO per un ATTIVANTE



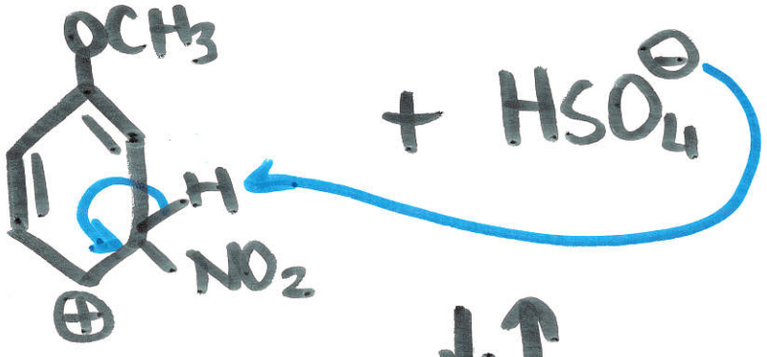
$-\ddot{O}CH_3$ E' ATTIVANTE,
E' **ORTO-PARA** ORIENTANTE.

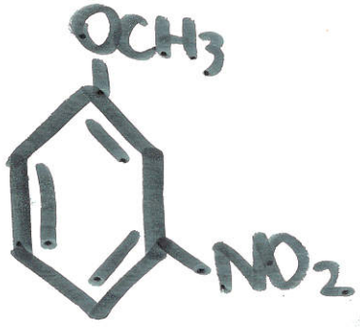
dim:

attacco in META:



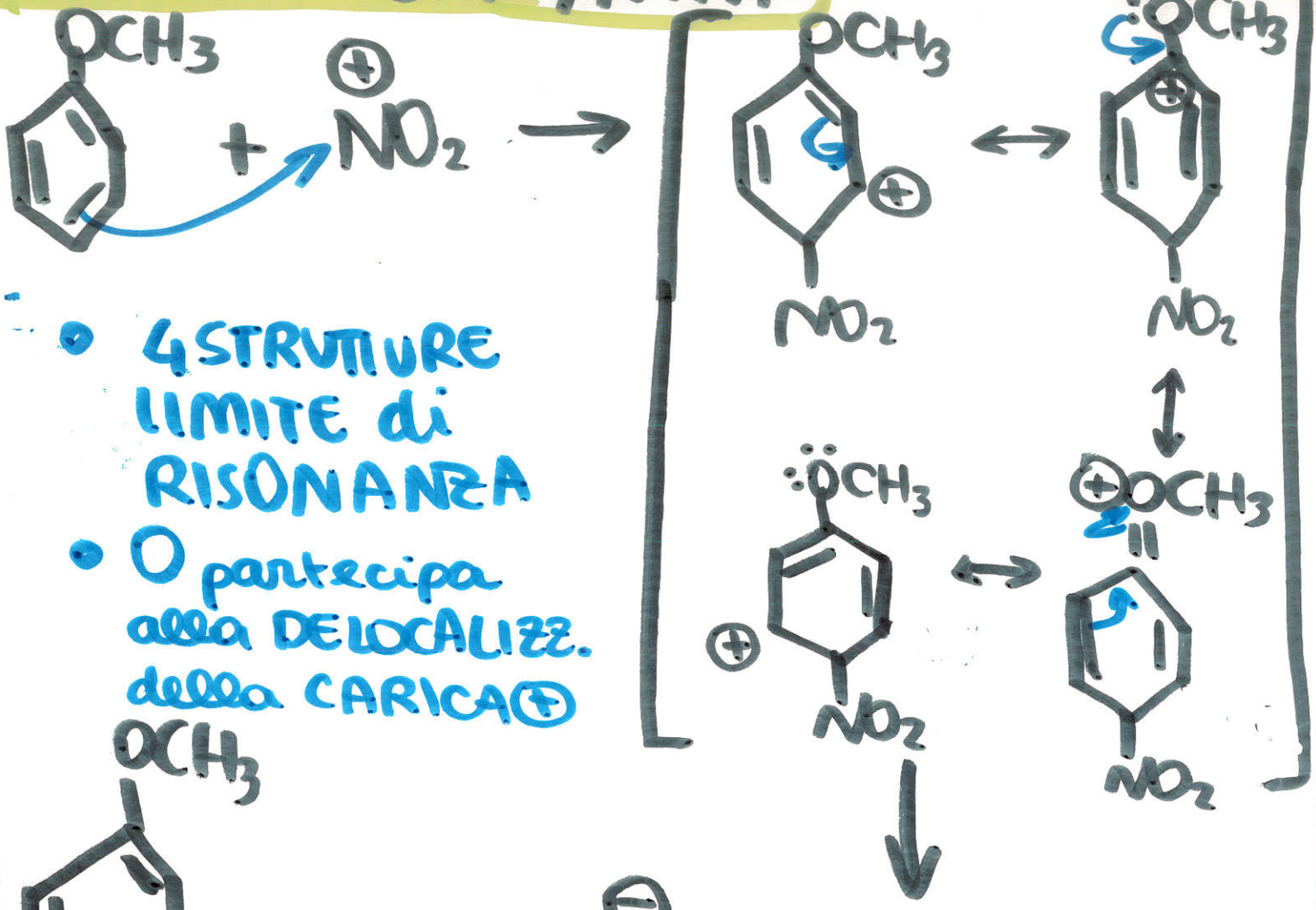
3 STRUTTURE LIMITE di RISONANZA



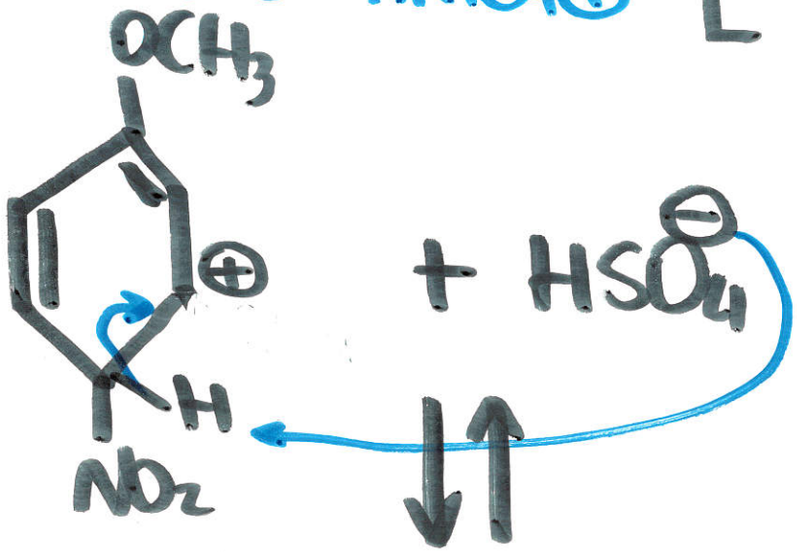


$+ H_2SO_4$

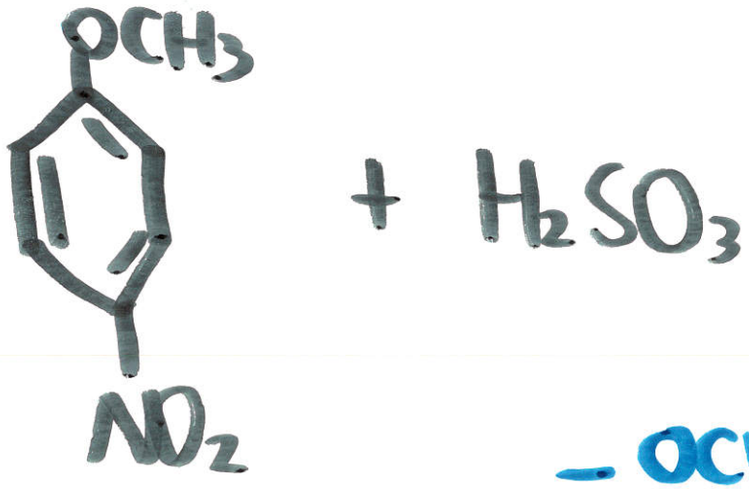
attacco in ORTO/PARA:



- 4 STRUTTURE LIMITE di RISONANZA
- O partecipa alla DELOCALIZZ. della CARICA ⊕



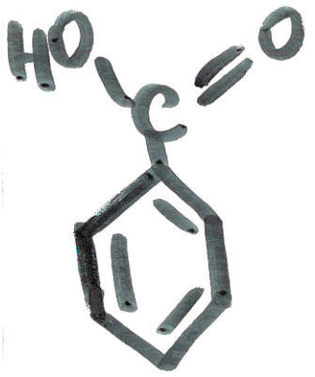
(attacco in PARA per motivi STERICI)



ARRICCHISCE l'anello di DENSITA' ELETTRONICA

- OCH_3 è elettron DONATORE, partecipa alla DELOCALIZZAZIONE della CARICA ⊕.

EFFETTO ORIENTAMENTO per un DISATTIVANTE



ACIDO BENZOICO

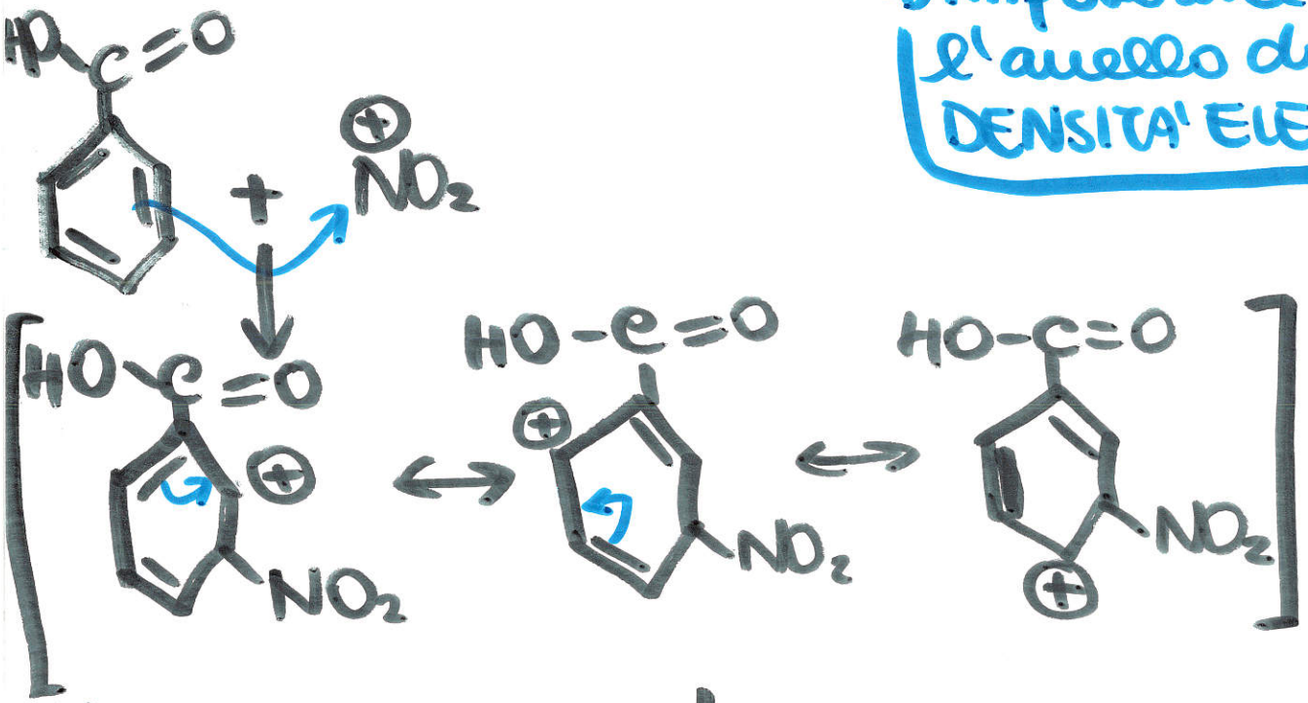
$-C(=O)OH$ è' DISATTIVANTE

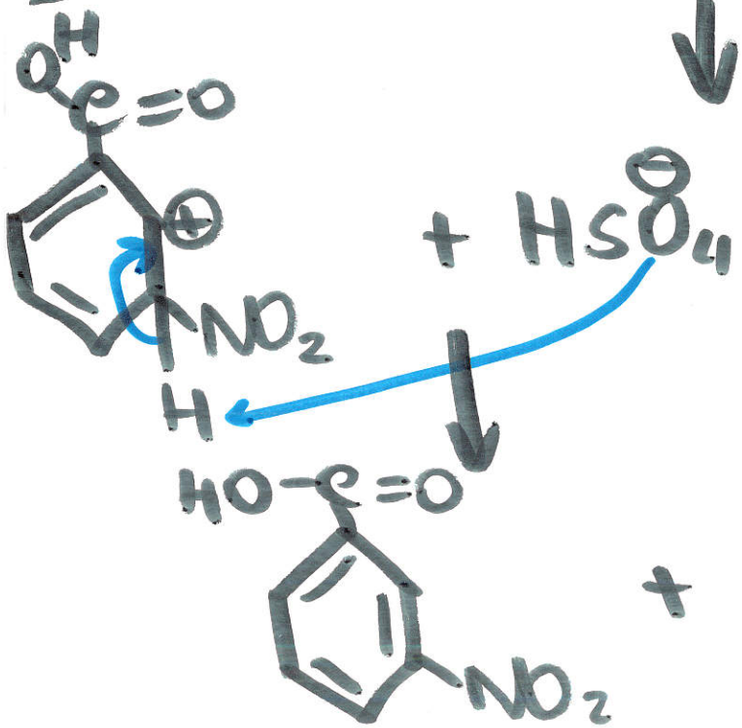
META ORIENTANTE

$-C(=O)OH$ è' elettron-ATTRATTORE

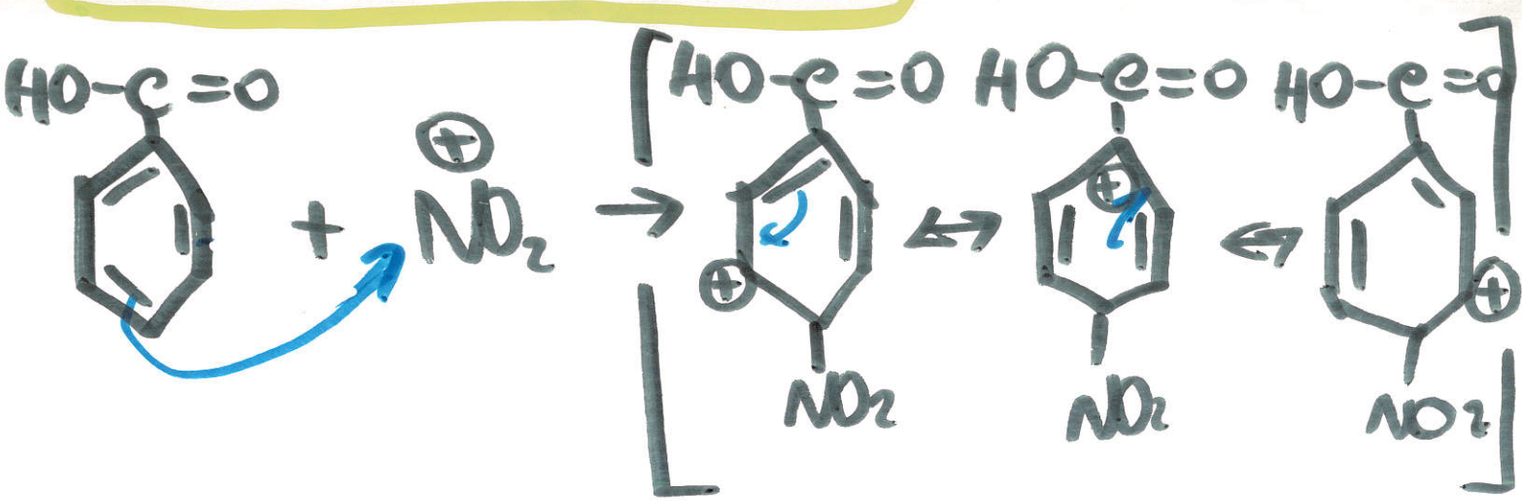
Impoverisce l'anello di DENSITA' ELETTRONICA

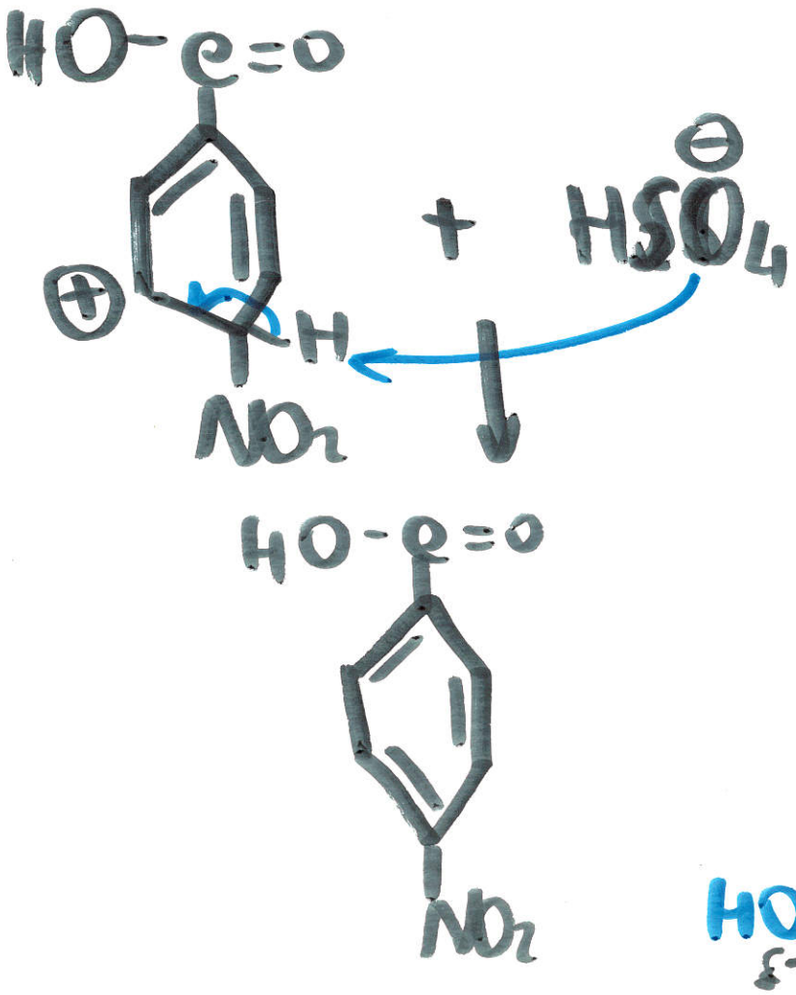
Attacco in META:





Attacco in ORTO/PARA:





N.B.

La CARICA ⊕ è' Delocalizzata adiacente ad un C con δ^+

CARBOSSILICO

Co effetto induttivo

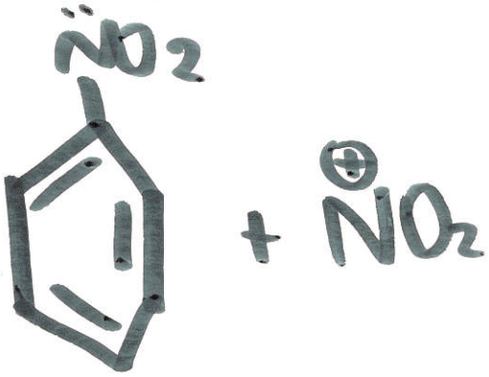
Co effetto di risonanza

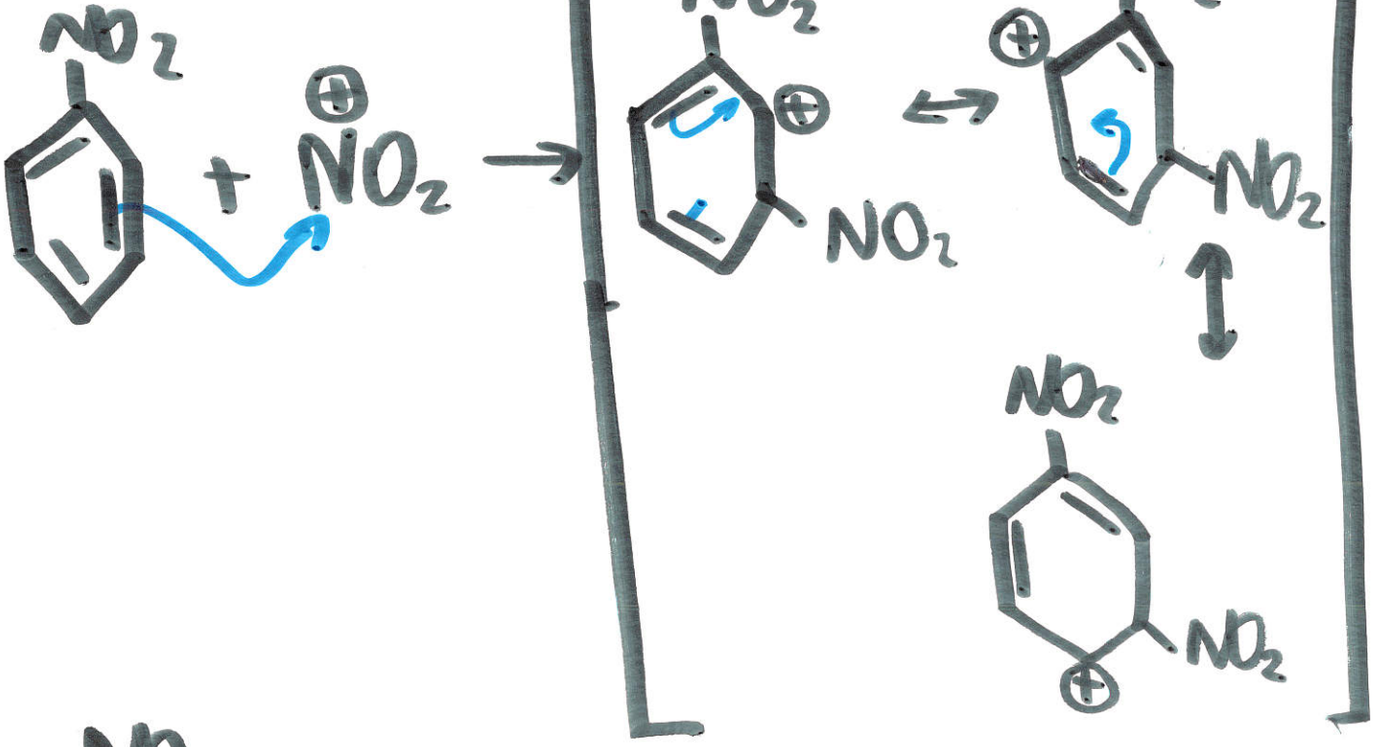
→ **INSTABILE**

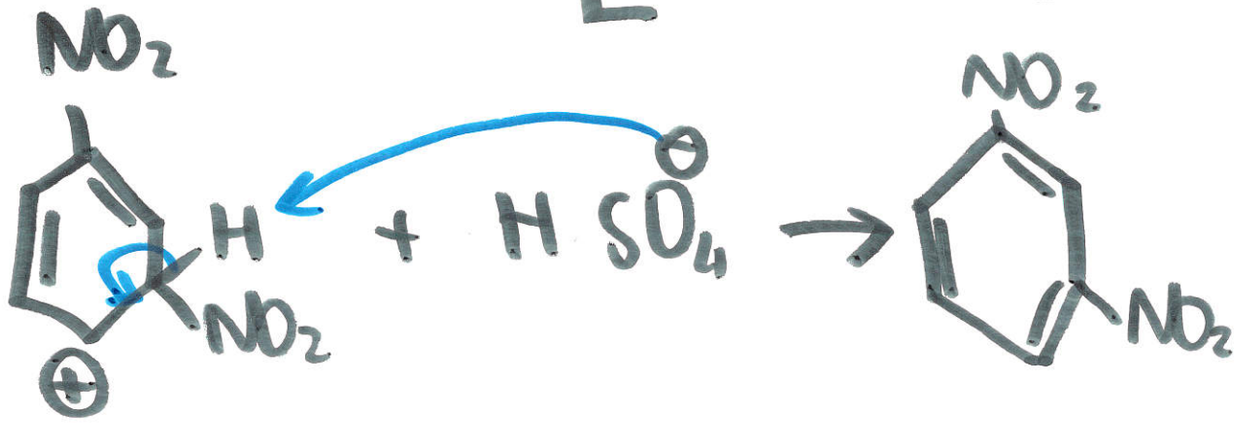
EFFETTO ORIENTAMENTO per un DISATTIVANTE

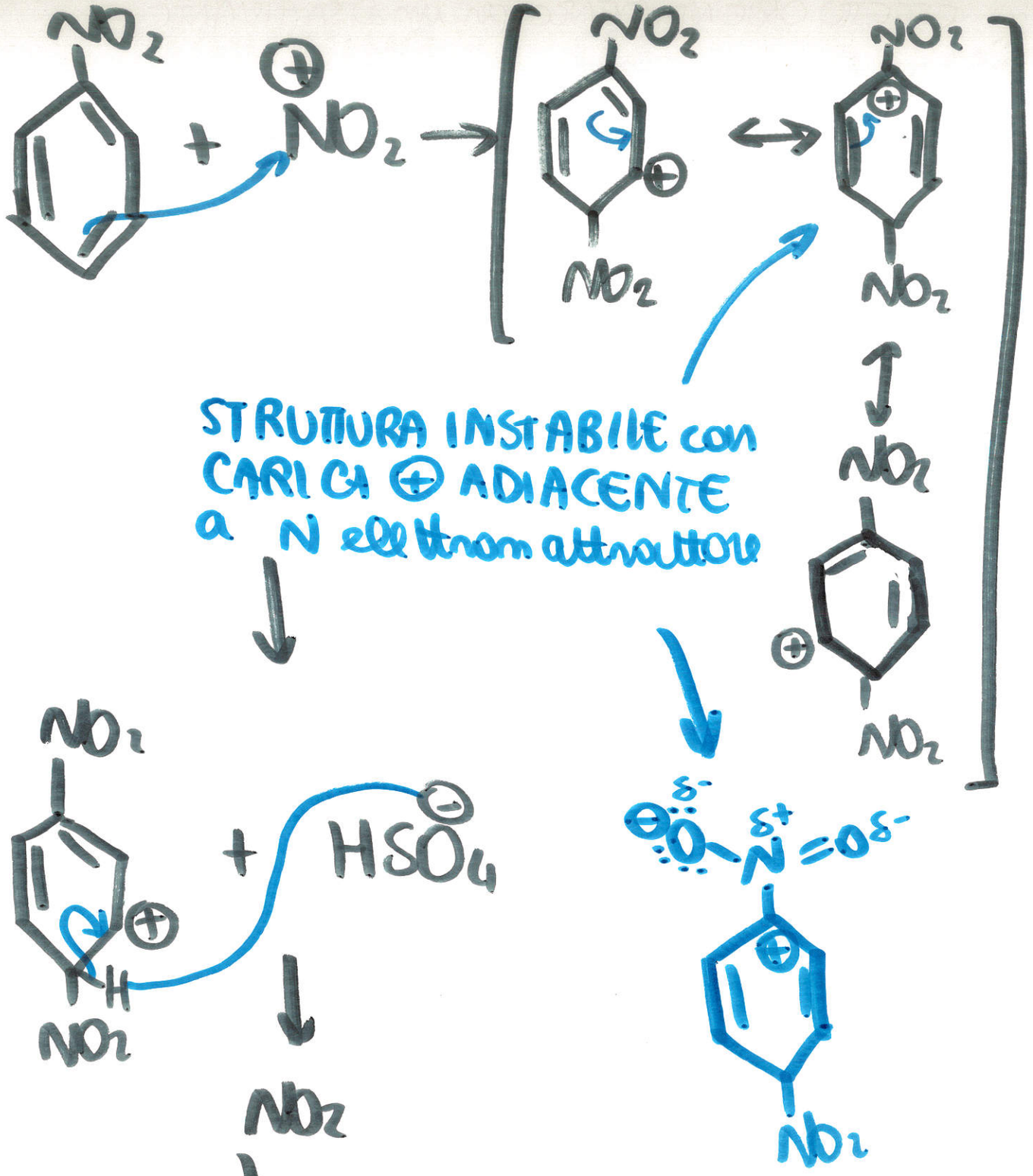
$-NO_2$ è' DISATTIVANTE

META ORIENTANTE








NO2
NO2
NO2
NO2
NO2
NO2
NO2
NO2
NO2
NO2
STRUTTURA INSTABILE con
CARICA ⊕ ADIACENTE
a N elettronattrattore
NO2
NO2
+ HSO4
H
NO2
δ-
δ+
δ-
NO2
NO2
+ H2SO4
NO2

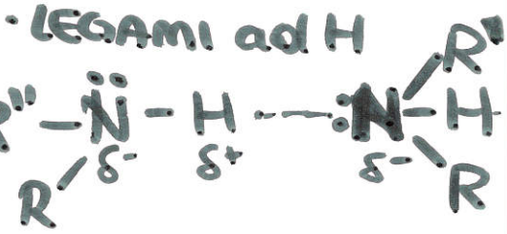
AMMINE

composti BASICI derivanti da $\ddot{N}H_3$ con uno o più H sostituiti da GRUPPI ALCHILICI E ARILICI.

N
- GEOM. PIRAMIDALE $\alpha = 107,5°$
- IBRIDATO sp^3
- coppia di ELETTRONI non condivisa che distorce la Geom. tetraedrica

$-\ddot{N}-$

CARATTERISTICHE:
- LEGAMI ad H



BASICITA' delle AMMINE →

MOLECOLE ETEROCICLICHE AROMATICHE

PIRIDINA

N sp^2

ORBITALE 2p MONOCCUPATO impiegato nei LEGAMI π dell'anello AROMATICO

→ coppia di elettroni sp^2 disponibile all'attacco → è una BASE

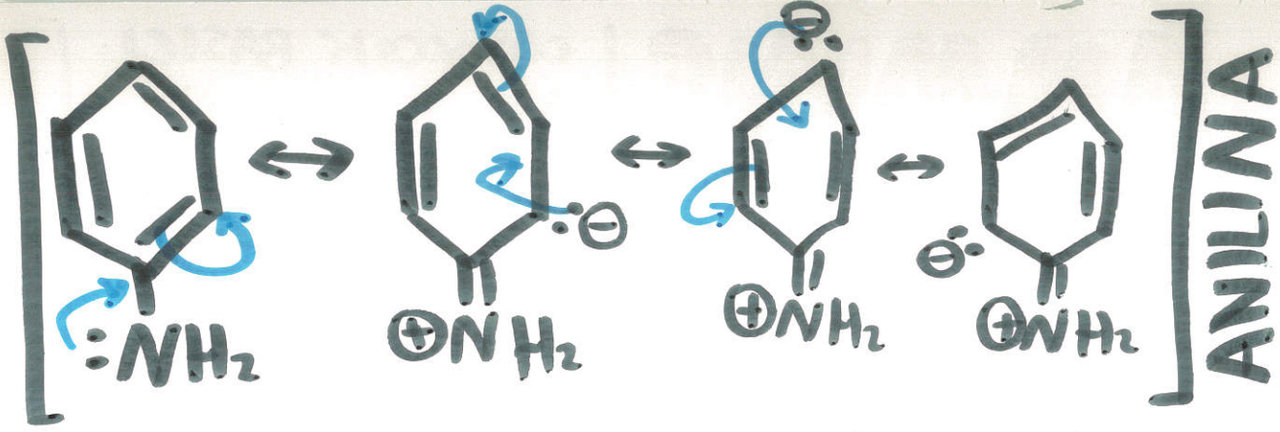
PIRROLO

N sp^2

ORBITALE 2p MONOCCUPATO - impiegato nel legame con H.

→ coppia di elettroni sp^2 che partecipa alla DELOCALIZZAZIONE della carica

→ non è una BASE

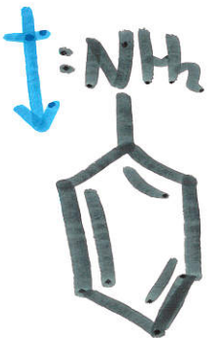


AMMINE AROMATICHE

meno BASICHE

- basi deboli
- doppietto elettronico non condiviso che partecipa alla DELOCALIZZ. della carica π dell'anello aromatico.

C sp^2 elettron-ATTRATTORE



AMMINE ALIFATICHE

- induttivo ELETTRON-DONATORE dei GRUPPI ALCHILICI

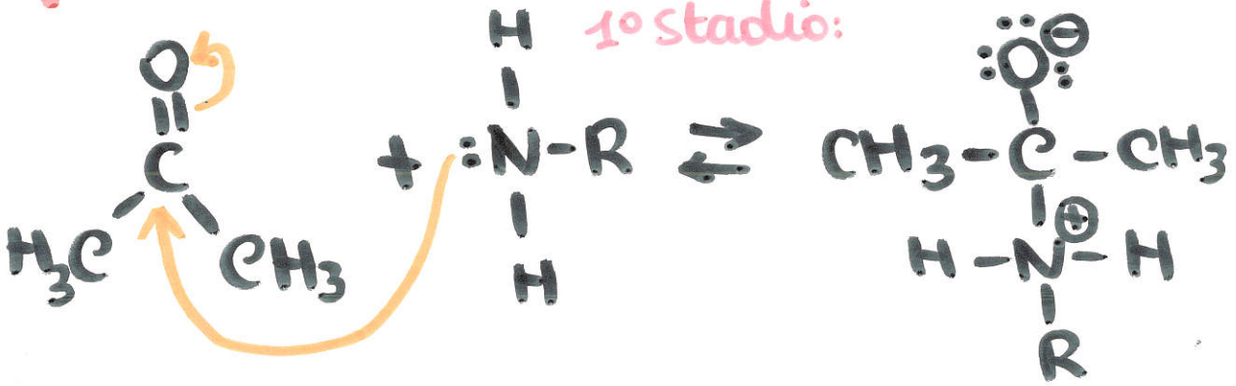
- induttivo ELETTRON-~~DONATORE~~ ATTRATTORE dell'N.

ALDEIDI / CHETONI + NUCLEOFILI AZOTATI

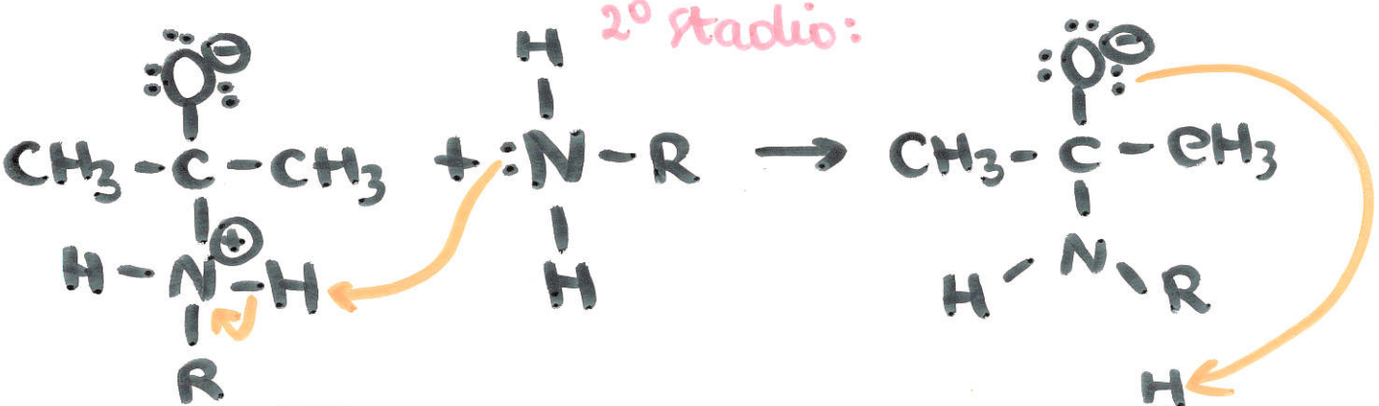
↓

IMMINE

1° stadio:

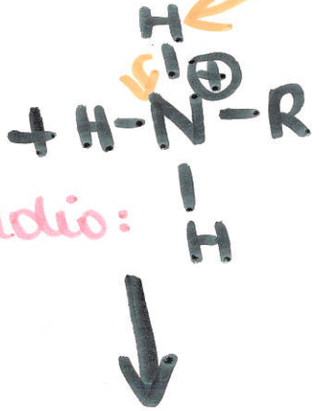


2° stadio:



DEPROTONAZIONE e PROTONAZIONE

3° stadio:



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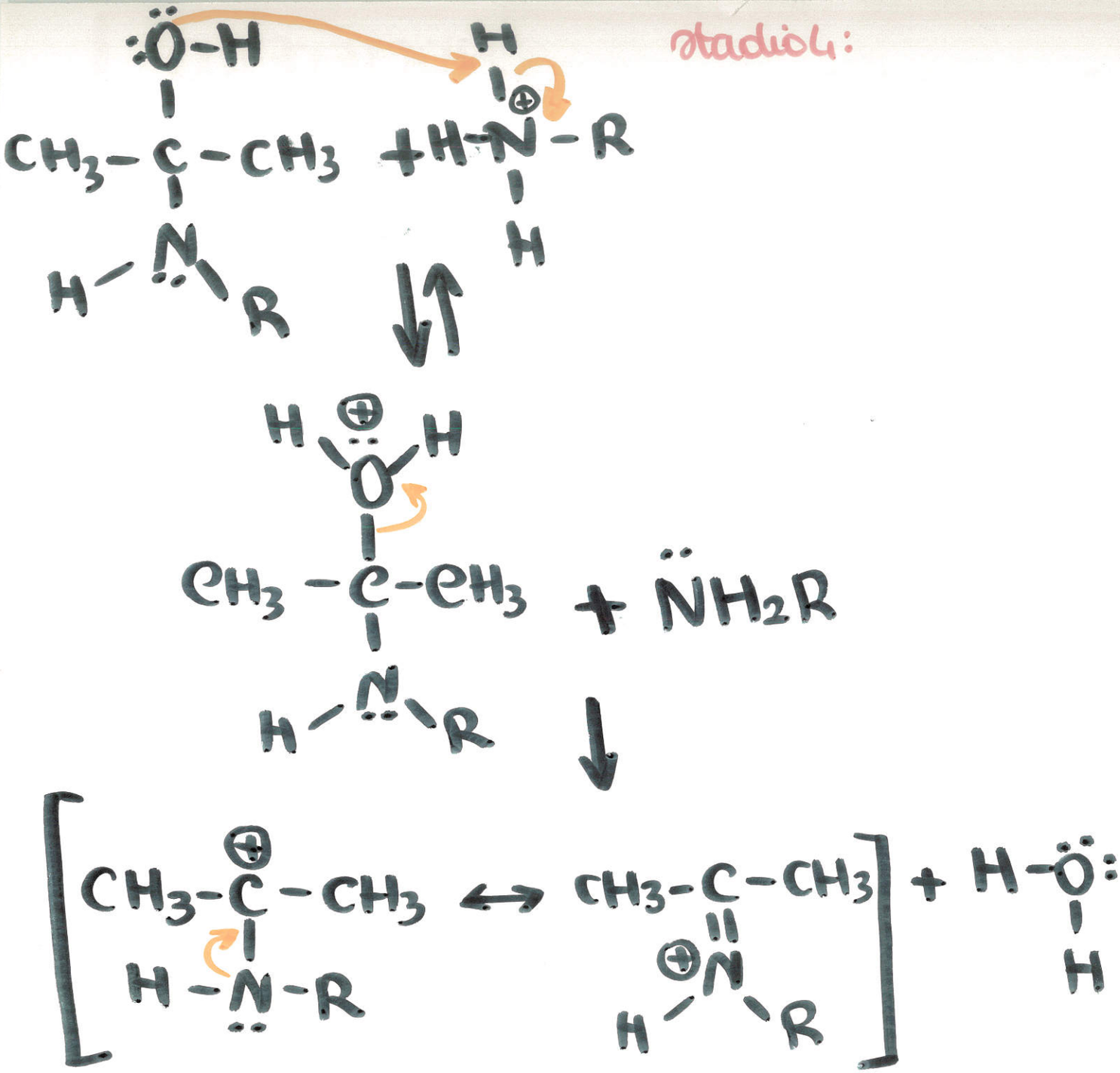
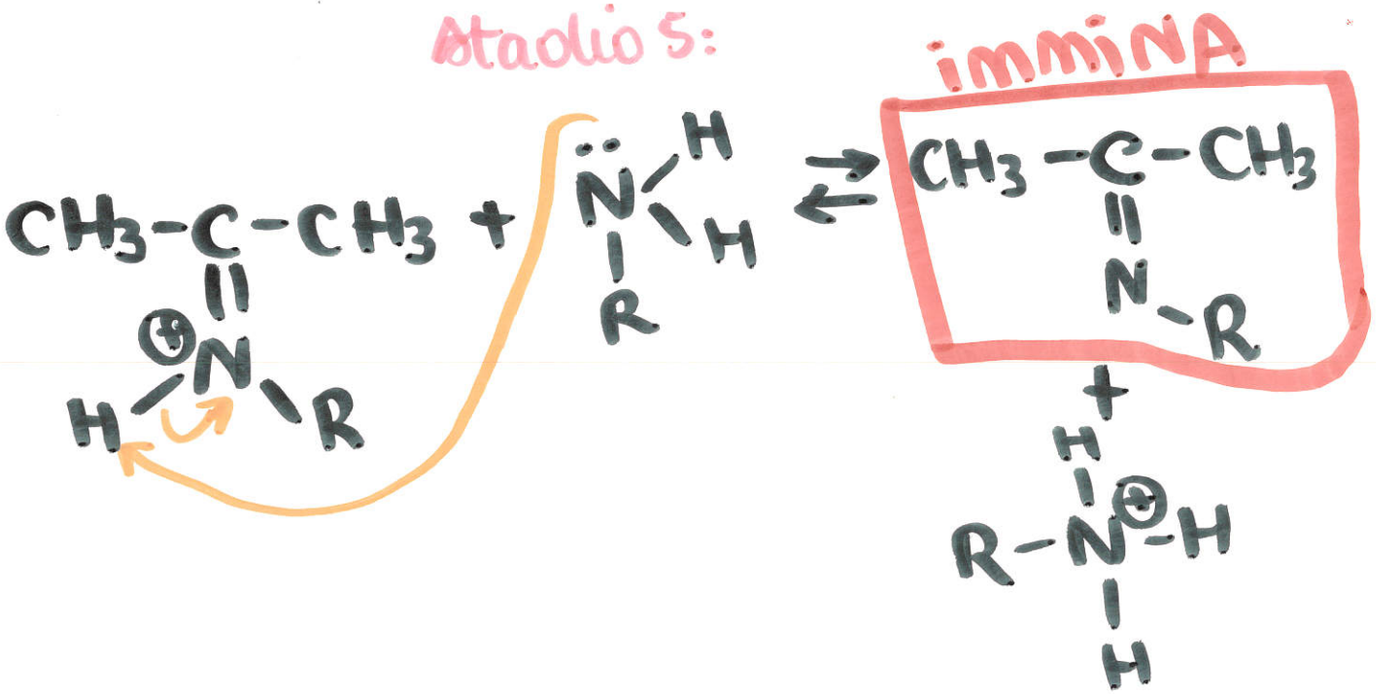
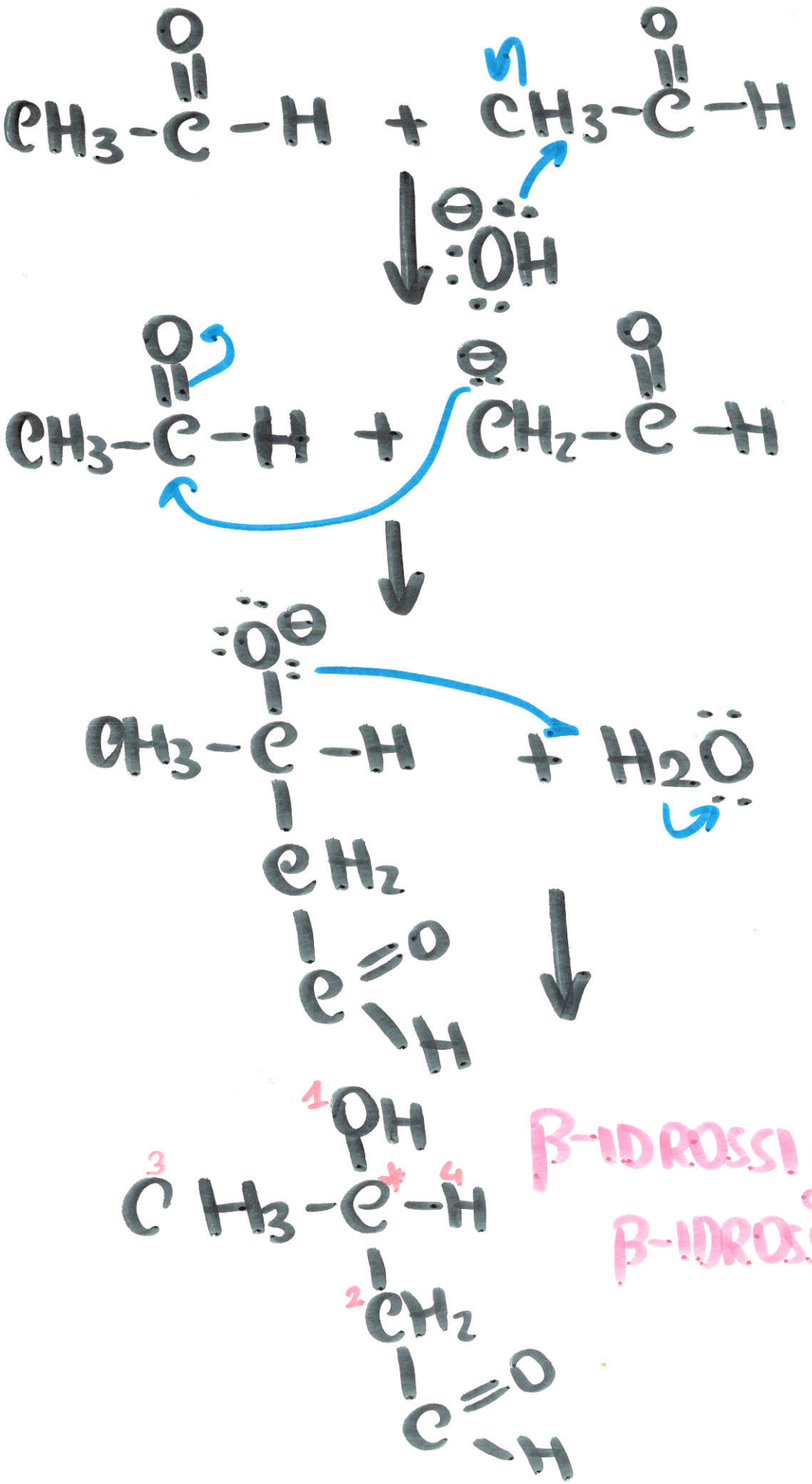
stadio 4:



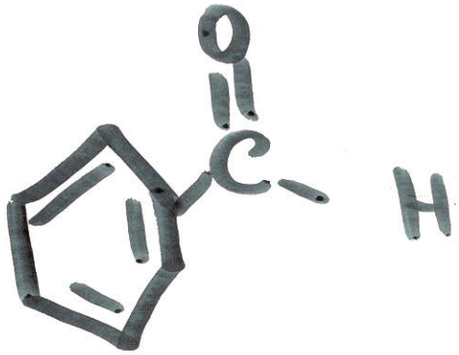
stadio 5:



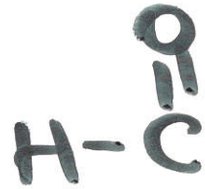
CONDENSAZIONE ALDOLICA



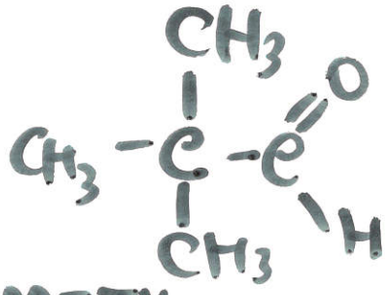
β-IDROSSI ALDEIDE
β-IDROSSI CHETONE



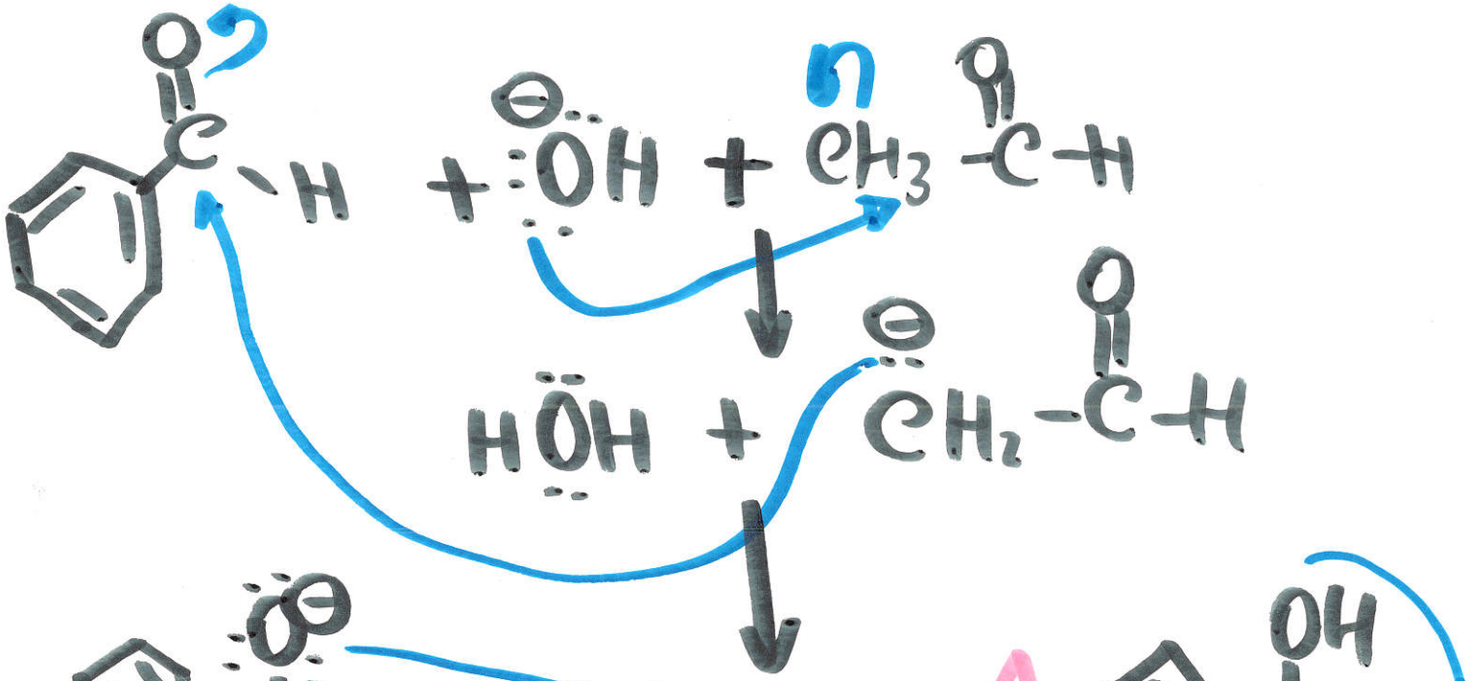
BENZALDEIDE

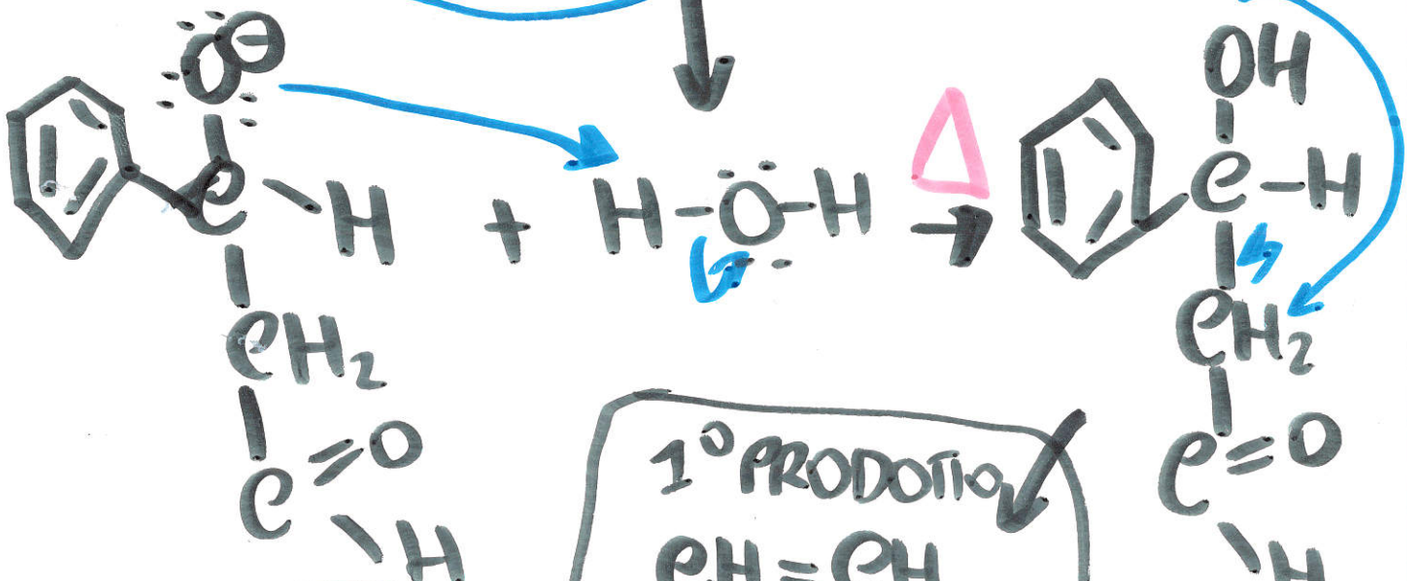


FORMALDEIDE

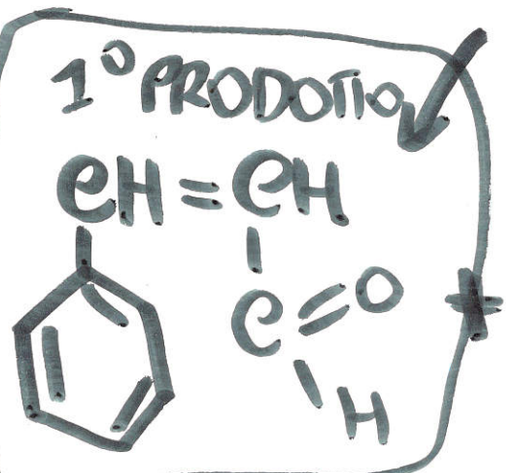


2,2 DIMETIL PROPANALE

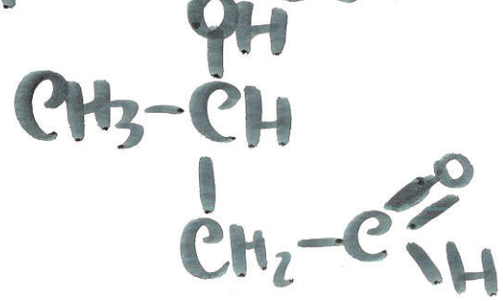




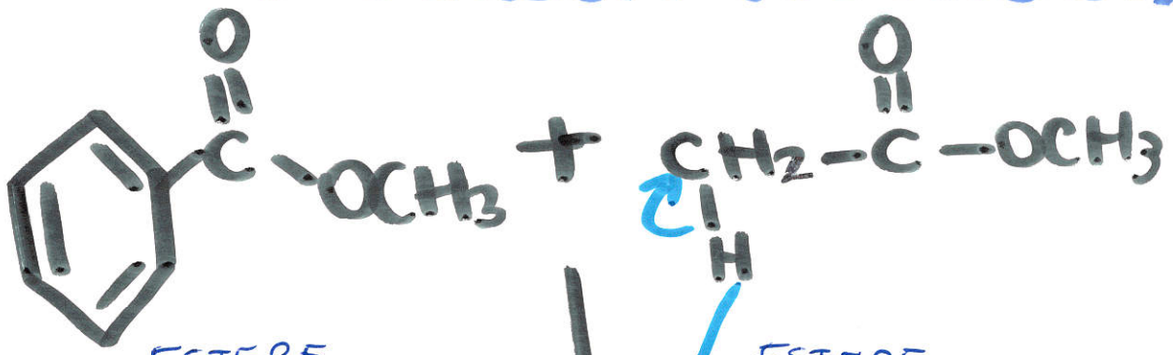
1° PRODOTTO



+ 2° PRODOTTO



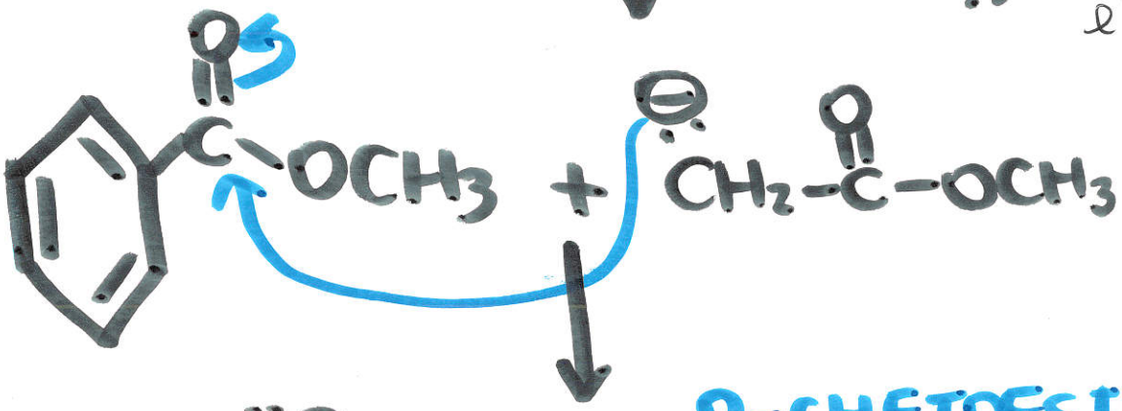
COND. di CLAISEN INCROCIATA

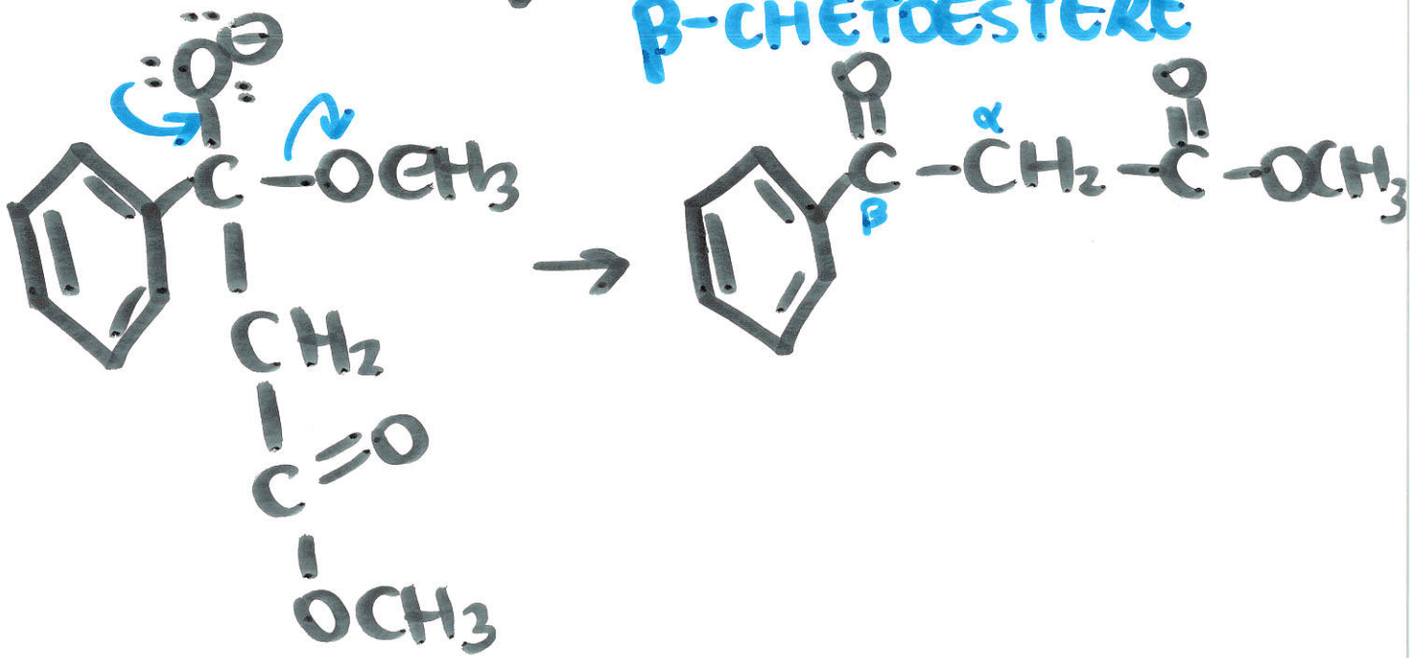


ESTERE
non enolizzabile
non ha H sul C α

ESTERE
Enolizzabile

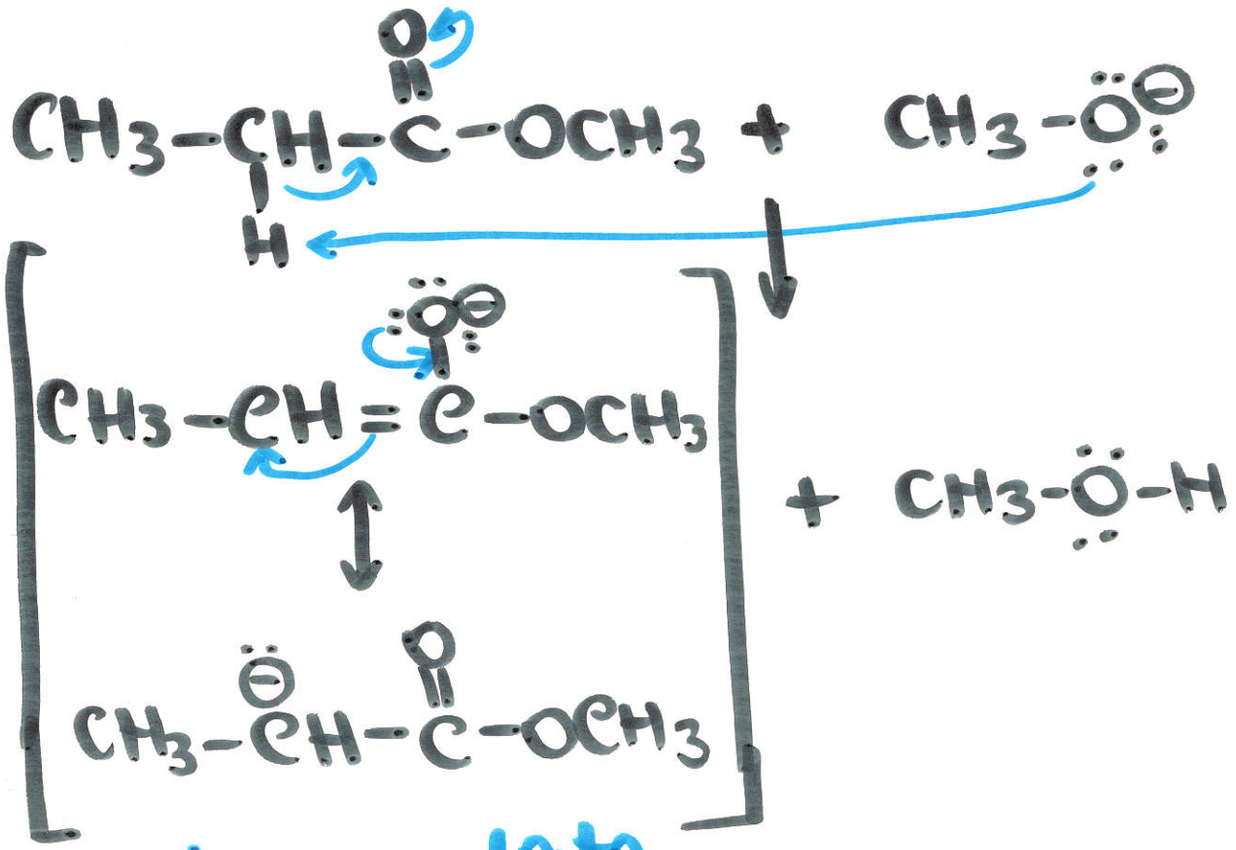
base adatta a DEPROTONARE l'ESTERE



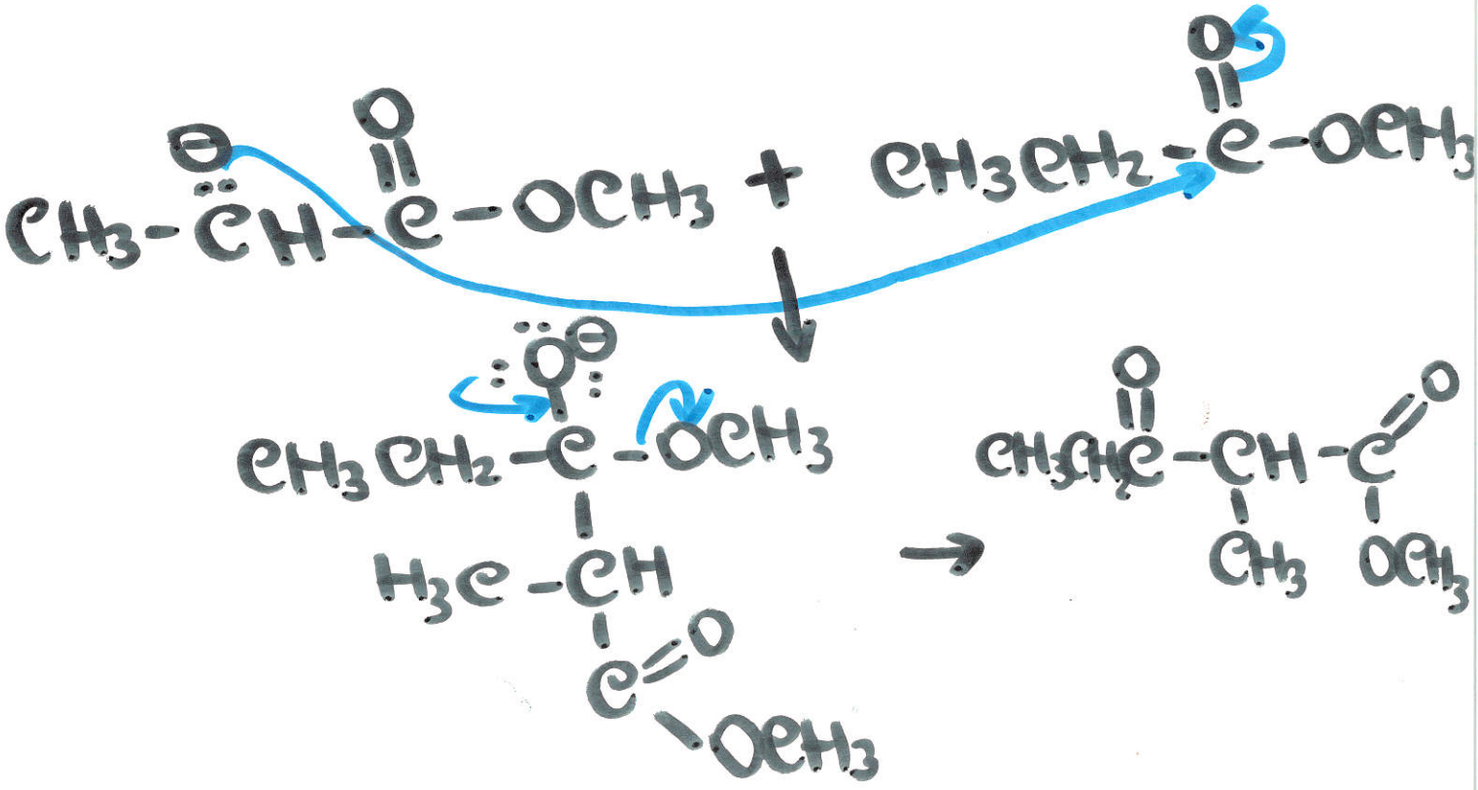


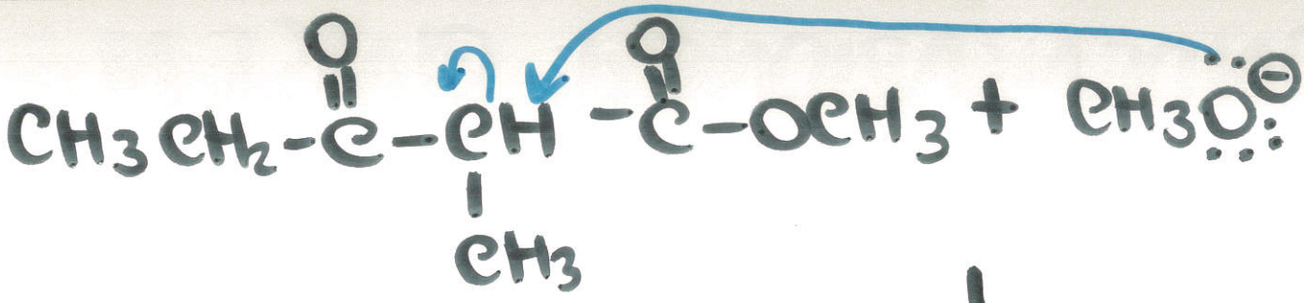
β-CHETOESTERE

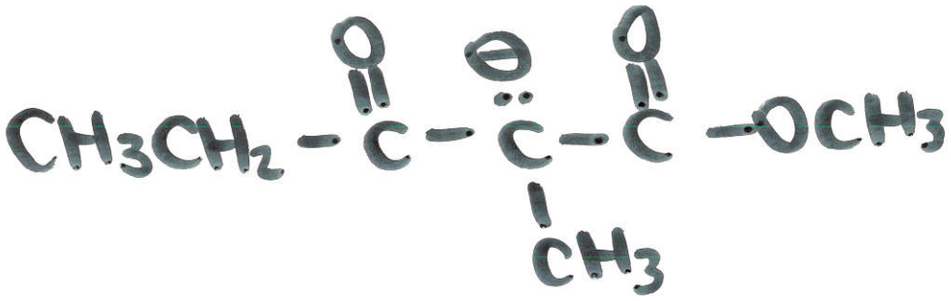
CONDENSAZIONE di CLAISEN



anione enolato

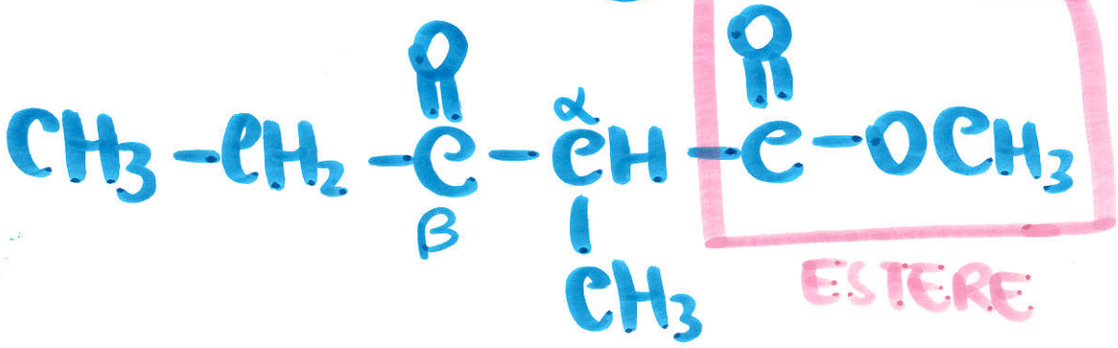






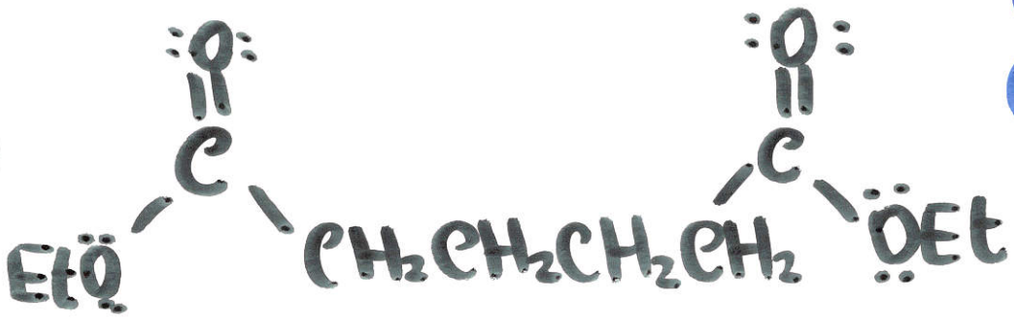
Anione enolato

β-CHETOESTERE

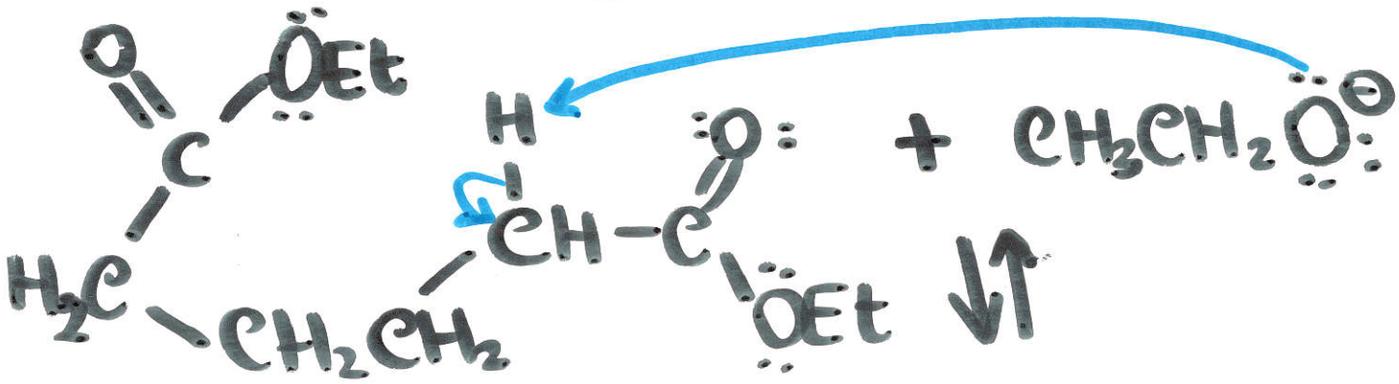


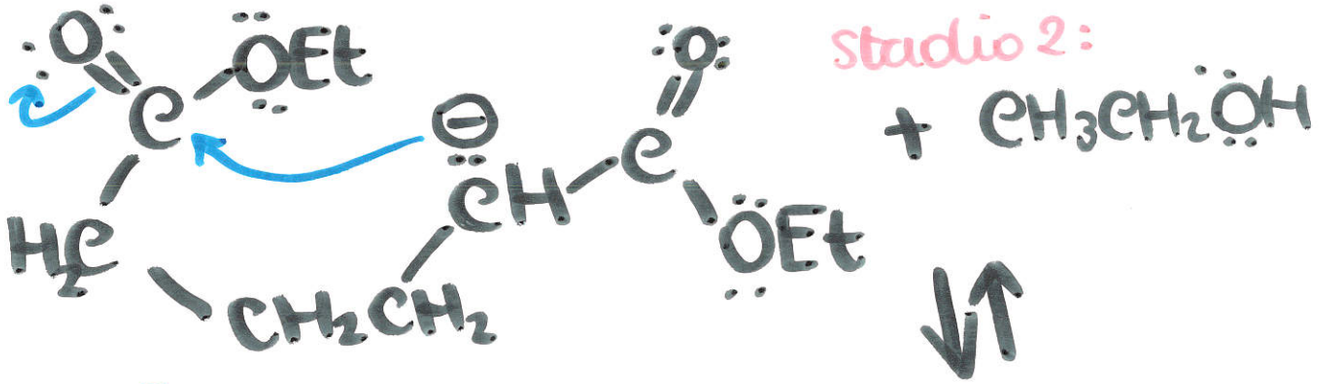
CONDENSAZ. di DIECKMAN

(CLAISEN INTRAMOLECOLARE)



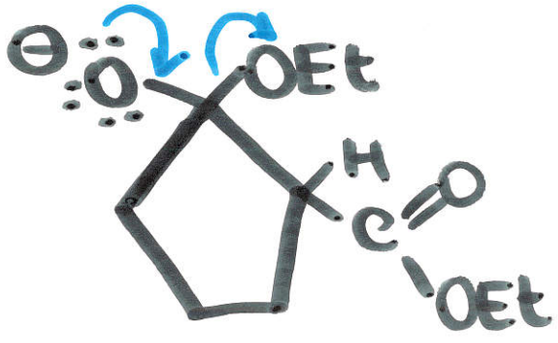
stadio 1:



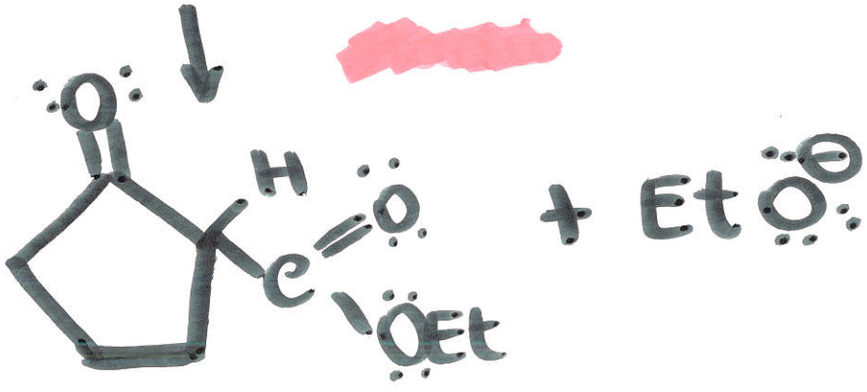


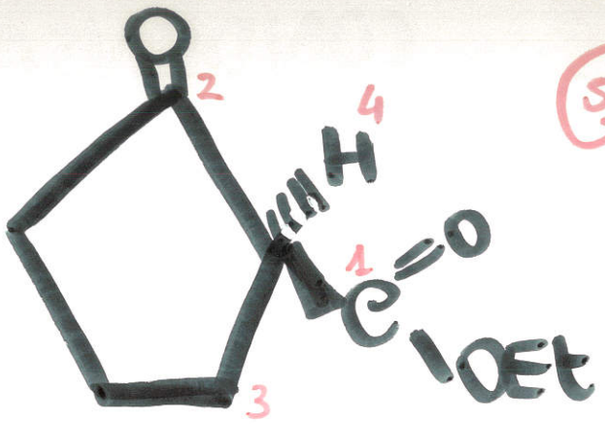
stadio 2:

stadio 3:



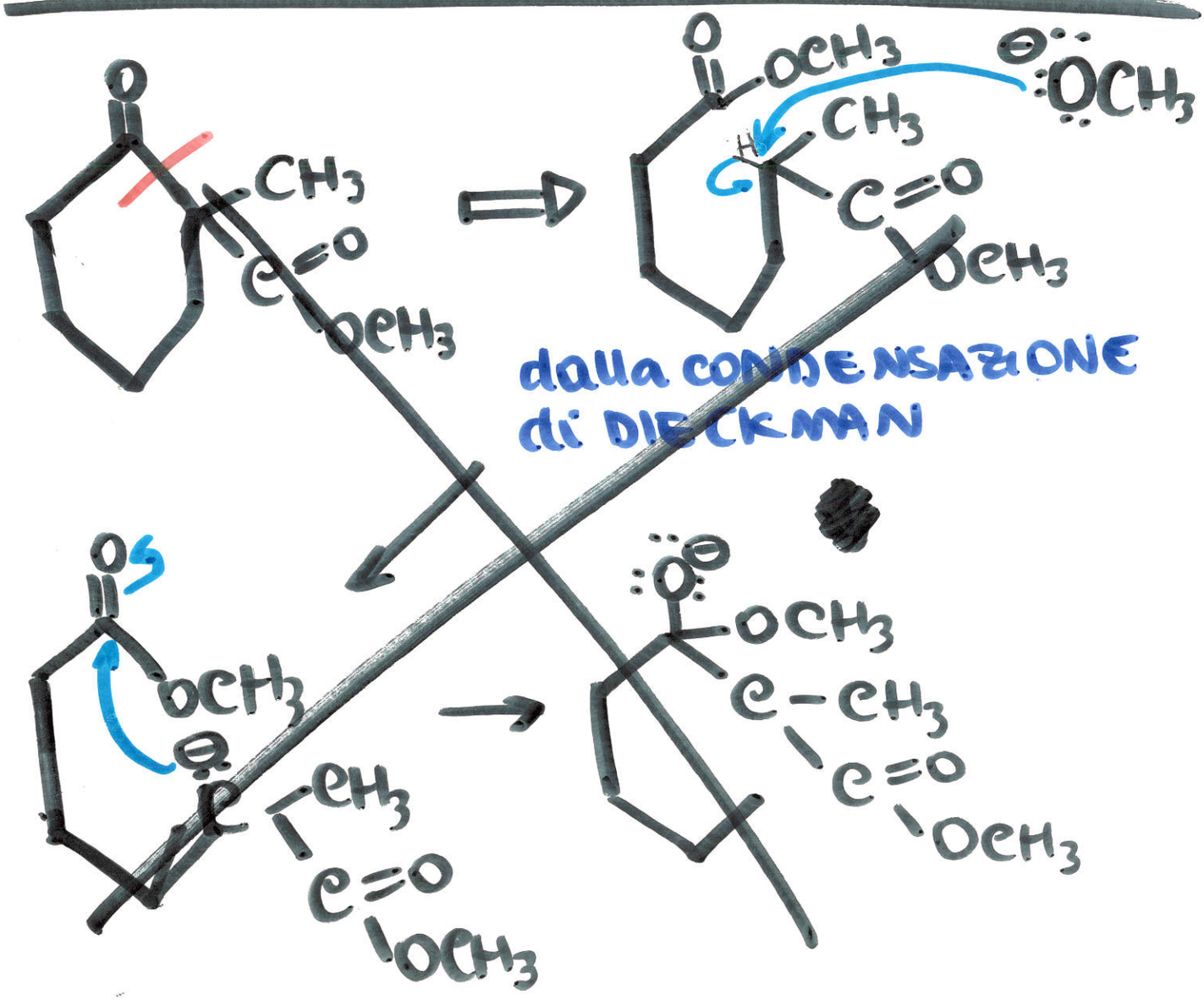
addotto TETRAEDRICO





(S)

ENANTIOMEROS



RETROSINTESI (CONDENSAZIONE di DIECKMAN)