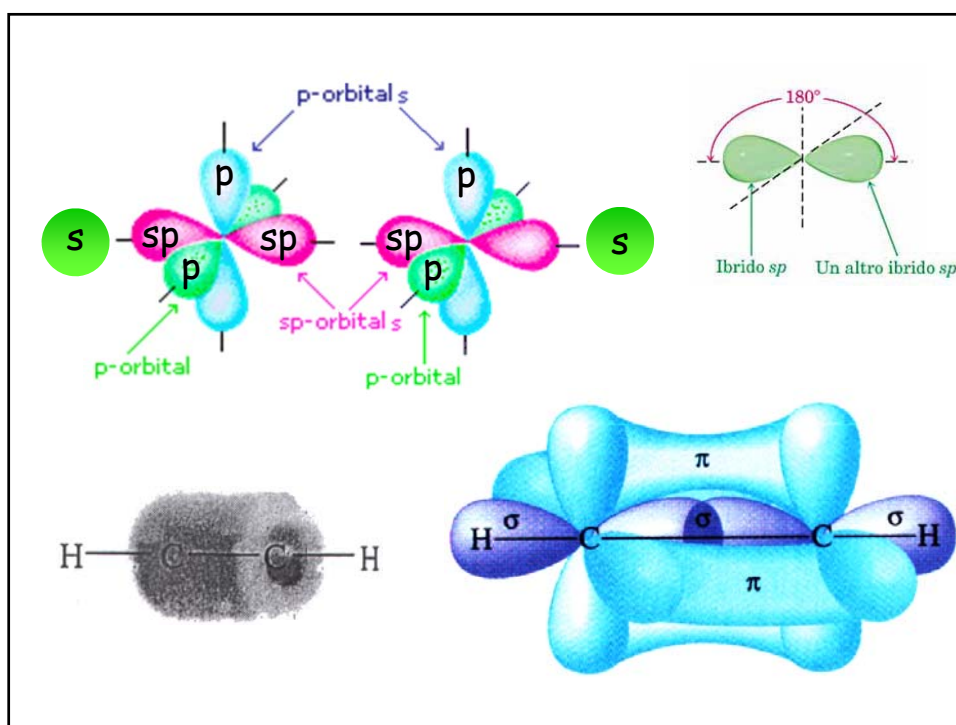
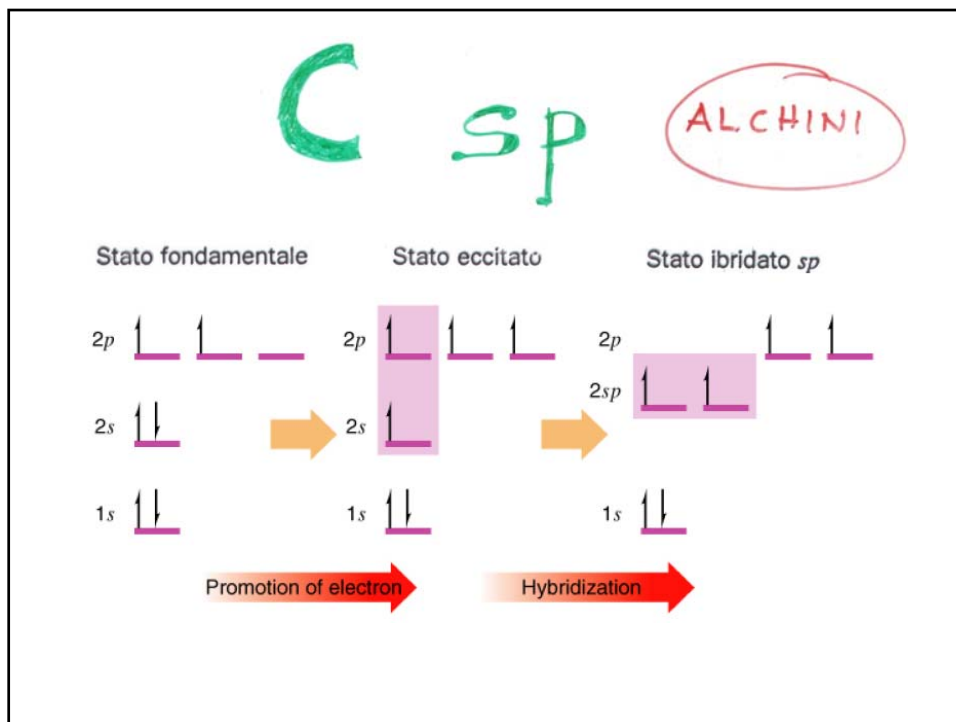
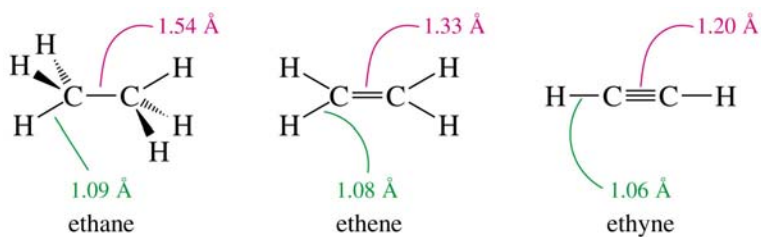






Forza dei legami multipli C-C

legame	tipo	Lunghezza Å	Energia		Molecola misurata
			kcal	kJ	
C-C	sp^3-sp^3	1.54	83	347	CH_3CH_3
C=C	sp^2-sp^2	1.34	146	611	$CH_2=CH_2$
C≡C	$sp-sp$	1.20	200	837	$HC\equiv CH$

alcheni π 63 kcal/mol

alchini 2nd π 54 kcal/mol

carattere s

più corto

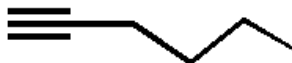
Legami σ tipici hanno energie di circa 80-120 kcal/mole

Legami π tipici hanno energie di circa 50-60 kcal/mole

Come per gli alcheni, gli alchini interni sostituiti sono più stabili di quelli esterni



More stable

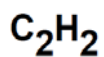


NOMENCLATURA

IUPAC:

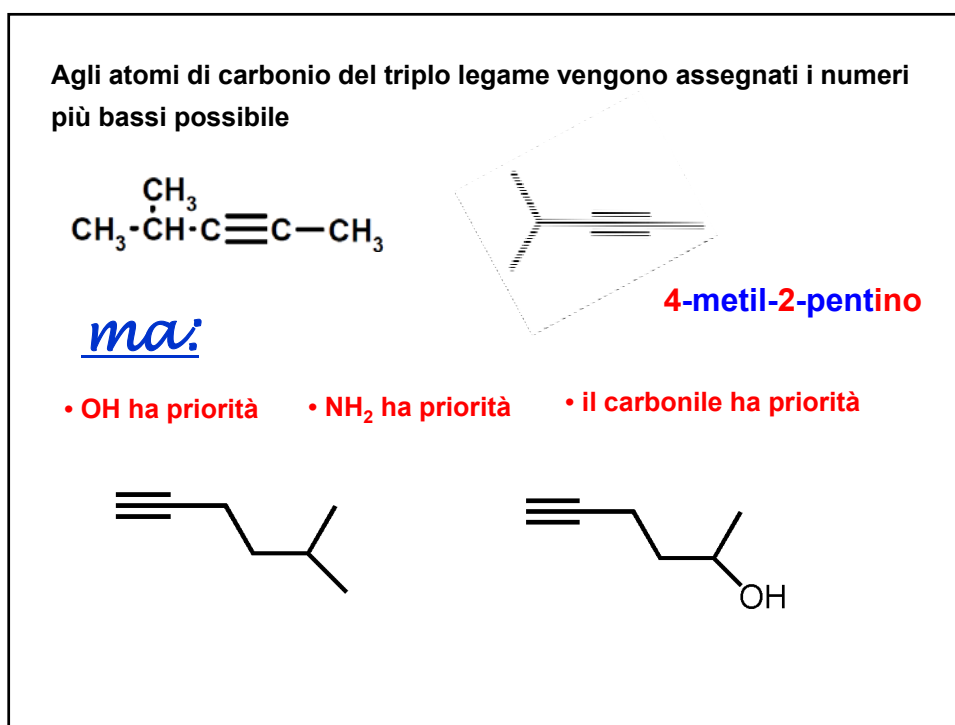
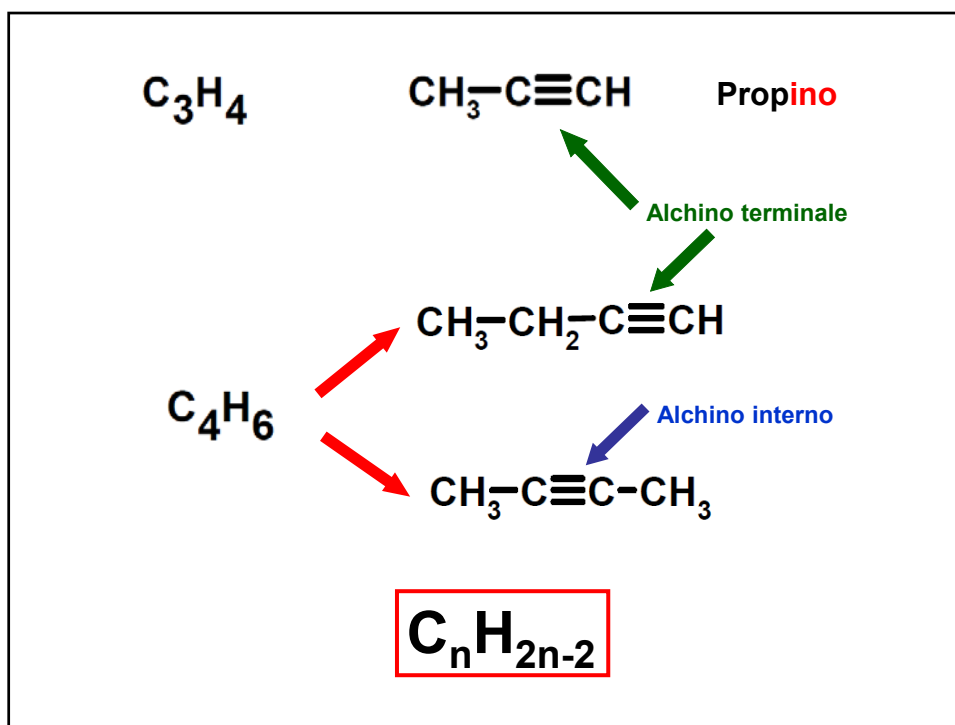
alcano → alchino

alchile → alchilinile

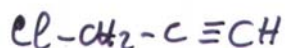
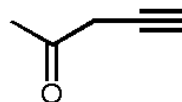
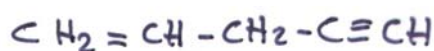
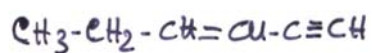
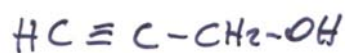
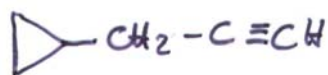


Etino (acetilene)





Se nella catena principale ci sono legami doppi e tripli, la catena va numerata in modo da dare ai legami multipli i numeri più bassi possibile. A *parità di numerazione*, il numero più basso spetta al *doppio legame*.



Nome		pf (°C)	pe (°C, 1 atm)	Densità d ²⁰ (g mL ⁻¹)
Metano		-182	-161,5	
Etano		-183	-88,6	
Elene	CH ₂ =CH ₂	-169	-104	0,384 [#]
Etino	HC≡CH	-80,8	-84,0 ⁷⁶⁰ _(sub)	
Propano		-188	-42,1	
Propene	CH ₃ CH=CH ₂	-185	-47	0,514
Propino	CH ₃ C≡CH	-101,51	-23,2	
Butano		-138	-0,5	
1-Butene	CH ₃ CH ₂ CH=CH ₂	-185	-6,3	0,595
(Z)-2-Butene	CH ₃ CH=CHCH ₃ (cis)	-139	3,7	0,621
(E)-2-Butene	CH ₃ CH=CHCH ₃ (trans)	-106	0,9	0,604
1-Butino	CH ₃ CH ₂ ≡CH	-125,7	8,1	
2-Butino	CH ₃ C≡CCH ₃	-32,3	27	

Nome	Formula	pf (°C)	pe (°C)	Densità d_4^{20} (g ml ⁻¹)
Etino	HC≡CH	-80,8	-84,0 ⁷⁶⁰ _(sub)	
Propino	CH ₃ C≡CH	-101,51	-23,2	
1-Butino	CH ₃ CH ₂ ≡CH	-125,7	8,1	
2-Butino	CH ₃ C≡CCH ₃	-32,3	27	0,68
1-Pentino	CH ₃ (CH ₂) ₂ C≡CH	-90	39,3	0,68
2-Pentino	CH ₃ CH ₂ C≡CCH ₃	-101	55,5	0,71
1-Esino	CH ₃ (CH ₂) ₃ C≡CH	-132	71	0,71
2-Esino	CH ₃ (CH ₂) ₂ C≡CCH ₃	-88	84	0,73
3-Esino	CH ₃ CH ₂ C≡CCH ₂ CH ₃	-101	81,8	0,72

THE LONGEST CA INDEX NAME (1,578 characters)

CAS Registry Number: 86417-45-0

C₆₀₁ H₆₇₈ Br₂ Cl₁₈ N₆₆ O₁₈₄ P₁₈

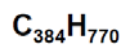
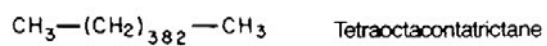
Adenosine, [(dimethylethyl)benzoyl](tetrahydromethoxypyranil)adenyl-yl-(3'→5')-(dimethylphenyl)(tetrahydromethoxypyranil)uridylyl-(3'→5')-(dimethylphenyl)(tetrahydromethoxypyranil)uridylyl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[[[(dimethylethyl)phenyl]acetyl](tetrahydromethoxypyranil)guanylyl-(3'→5')-[[[(dimethylethyl)phenyl]acetyl](tetrahydromethoxypyranil)guanylyl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)adenyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-(dimethylphenyl)(tetrahydromethoxypyranil)uridylyl-(3'→5')-(dimethylphenyl)(tetrahydromethoxypyranil)uridylyl-(3'→5')-[[[(dimethylethyl)phenyl]acetyl](tetrahydromethoxypyranil)guanylyl-(3'→5')-(dimethylphenyl)(tetrahydromethoxypyranil)uridylyl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)adenyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[(dimethylethyl)benzoyl](tetrahydromethoxypyranil)cytidyl-yl-(3'→5')-[(dimethylethyl)benzoyl](methoxymethylene)-, octadecakis(2-chlorophenyl) ester, 5'-[2-(dibromomethyl)benzoate] (9CI)

C₆₀₁H₆₇₈Br₂Cl₁₈N₆₆O₁₈₄P₁₈

Synthesized yeast
alanine tRNA

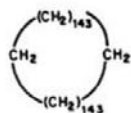
(1983)

THE LONGEST ALIPHATIC CHAIN (384 carbons)



CA 102:185585k (1985)

THE LARGEST SINGLE-RING PARENT (288 carbons)

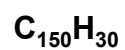
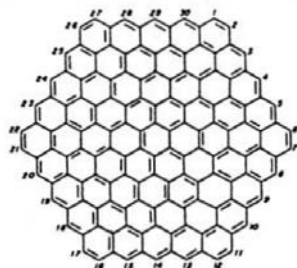


Cyclooctacontadictane



CA 89:179585g (1978)

THE LARGEST RING SYSTEM (61 rings)



CA 102:112511y (1985)

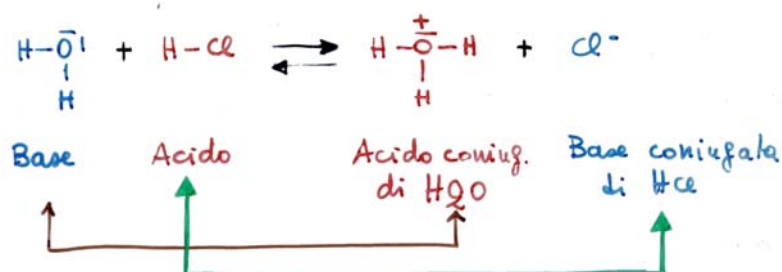
Acidità e Basicità

delle molecole organiche

① Brønsted - Lowry

Acido: sostanza in grado di **donare un protone**

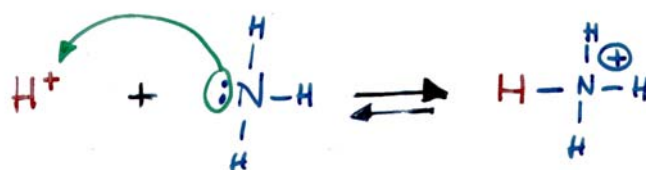
Base: sostanza in grado di **accettare un protone**



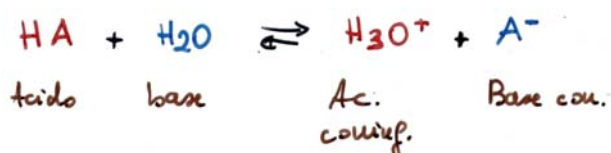
② Lewis

Acido: accetta una coppia di e^-

Base: dona una coppia di e^-



ACIDO:



$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \text{ cost.}$$

$$K_A = K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \text{ mol L}^{-1}$$

$$\text{p}K_a = -\log K_a$$



$$K_b = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

$$K_B = K' [H_2O] = \frac{[HA][OH^-]}{[A^-]} \text{ mol L}^{-1}$$

$$pK_b = -\log K_b$$

$$K_a \times K_B = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w = 10^{-14}$$

$$pK_a + pK_b = 14$$



Acido debole

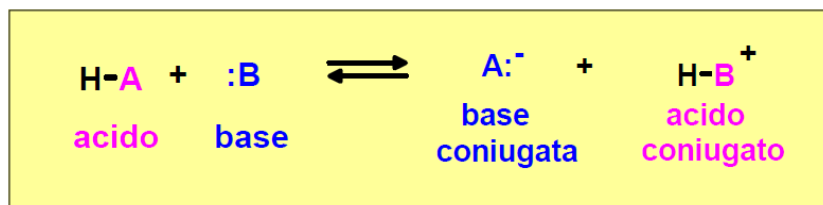
Base debole

Base forte

Acido forte

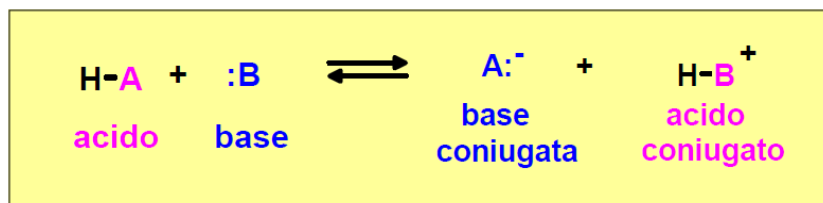


$$pK_b = 14 - 4.7 = 9.3$$



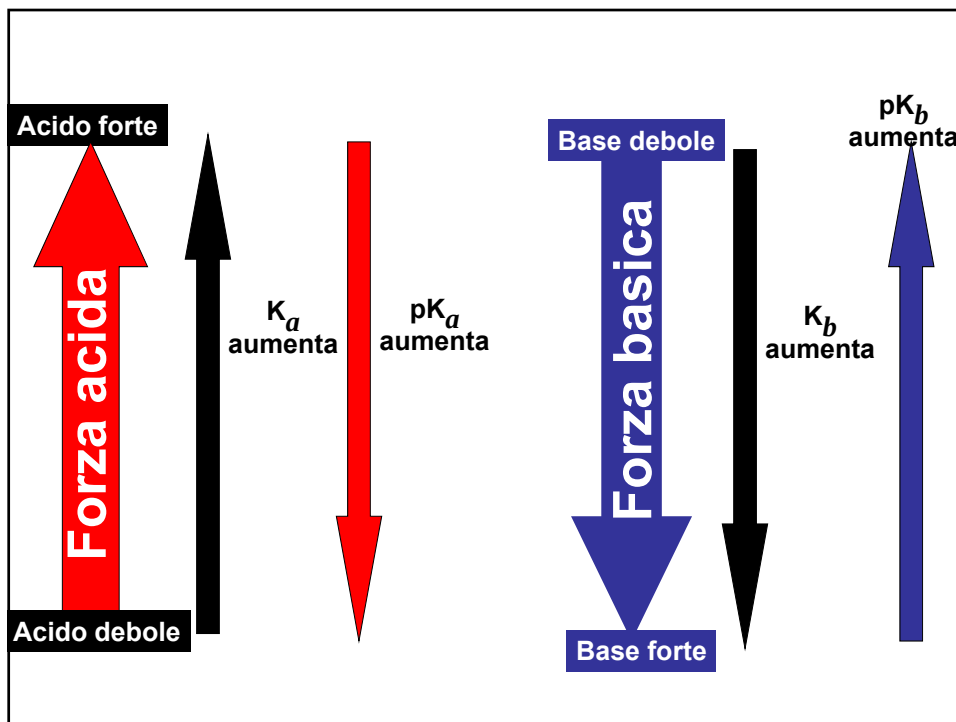
forte  debole

debole  forte



forte  debole

debole  forte



STRUTTURA e FORZA DI UN ACIDO

①. ELETTRONEGATIVITA' DELL'ATOMO A CUI È LEGATO L'IDROGENO ACIDO

→ legame X-H più polare

EN maggiore $\Rightarrow$ elettroni di legame tenuti più saldamente
 $\Rightarrow$ eliminazione del protone più facile

C N O F

—————→

EN

$$X-H \rightarrow \ddot{X}^{\ominus} + H^+$$

R_3C-H

R_2-N-H

$R-O-H$

$F-H$

Forza acida maggiore →

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

2. DIMENSIONE DELL'ATOMO A CUI È LEGATO L'IDROGENO ACIDO

Un atomo più grande difonde meglio la carica negativa $\Rightarrow$ maggiore stabilizzazione della base coniugata $\rightarrow$ Acido più forte

Forza legame HX	VI	VII	EN aumenta	DIMENSIONE AUMENTA	ACIDITA' AUMENTA	<u>pK_a</u>
	O	F				3.45
	S	Cl				-7
	Se	Br				-9
		I				-9.5

3. IBRIDAZIONE

C sp^3 sp^2 sp

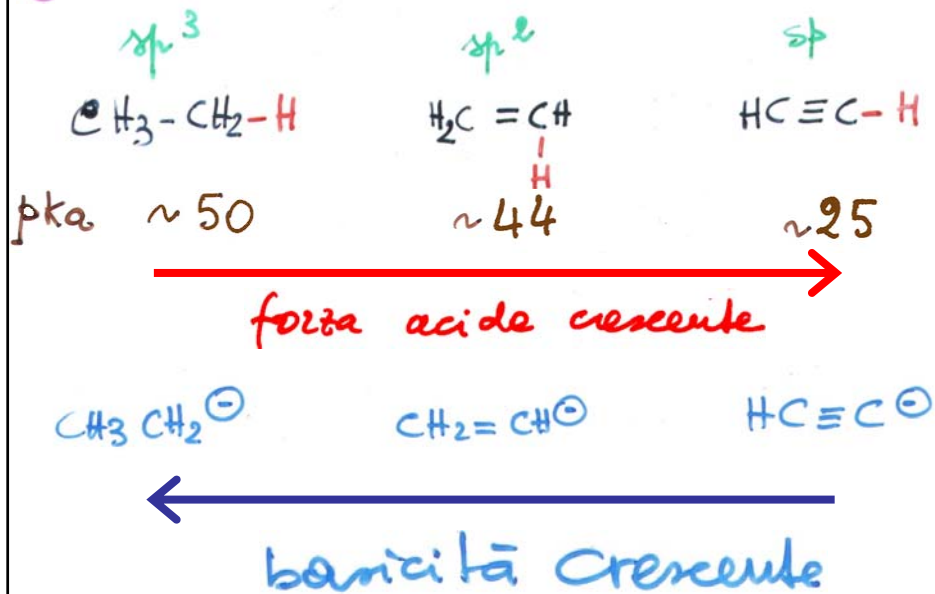
aumenta il carattere "s" dell'orbit. ibrido

e^- più vicini al nucleo $\Rightarrow$ EN maggiore

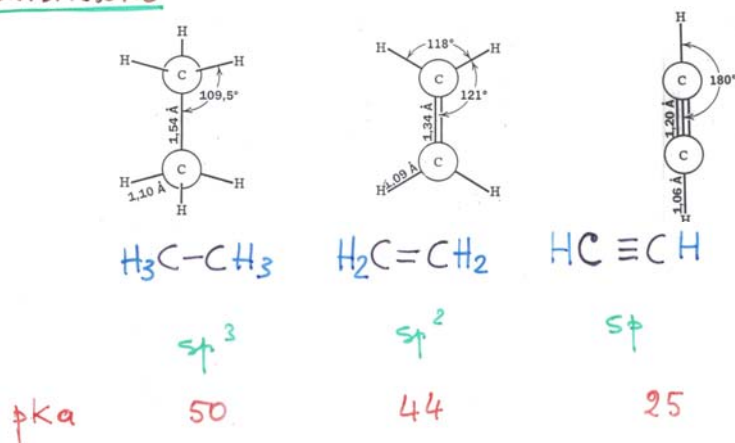
aumento di polarità del legame C-H

forza acide crescente

3. IBRIDAZIONE



3. IBRIDAZIONE

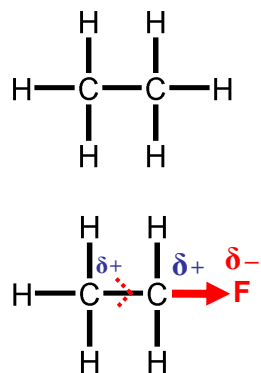


gli alchini terminali sono acidi.

$H_2O: pK_a 15.7$

$ROH: pK_a \sim 15-18$

4. Effetto induttivo



l'effetto induttivo si
trasmette attraverso lo
spazio e attraverso i
legami

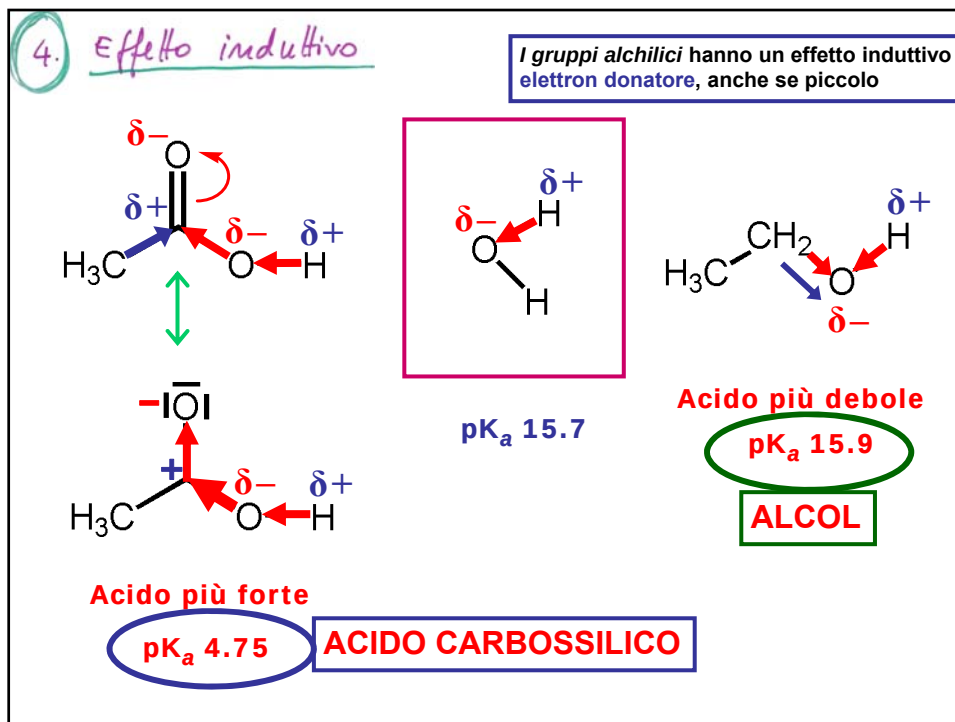
EFFETTO INDUTTIVO

+I

SOSTITUENTI ELETTRON DONATORI

-I

SOSTITUENTI ELETTRON ATTRATTORI



Gruppi elettron **attrattori** aumentano l'acidità $\downarrow$ pK_a

L'effetto induttivo si trasmette attraverso lo spazio

Compound	pK_a	Compound	pK_a
	4.81		4.05
	2.86		4.52

Gruppi elettron **attrattori** aumentano l'acidità ↓ pK_a

L'effetto induttivo dipende anche dall'elettronegatività dell'atomo

	Derivative	pK_a
		4.75
		2.59
		2.85
		2.90
		3.12

EN aumenta ↑

-I

Acidità aumenta ↑

pK_a ↓

Gruppi elettron **attrattori** aumentano l'acidità ↓ pK_a

L'effetto induttivo è ADDITIVO

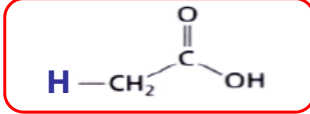
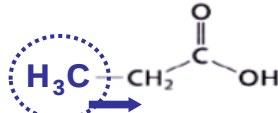
	Derivative	pK_a
		4.75
		2.85
		1.48
		0.70

-I

Red arrows indicate the inductive effect from the chlorine atoms towards the carboxyl group.

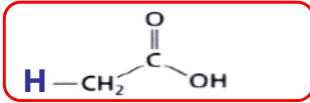
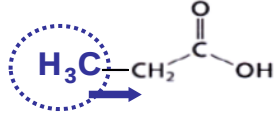
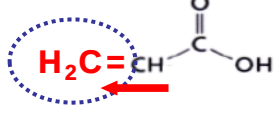
Gruppi elettron **donatori** diminuiscono l'acidità $\uparrow$ pK_a

I gruppi alchilici hanno un effetto induttivo elettron donatore, anche se piccolo

	<i>Derivative</i>	<i>pK_a</i>
		4.75
+ I		4.87

Gruppi elettron **attrattori** aumentano l'acidità $\downarrow$ pK_a
 Gruppi elettron **donatori** diminuiscono l'acidità $\uparrow$ pK_a

L'effetto induttivo dipende anche dall'ibridazione dell'atomo

	<i>Derivative</i>	<i>pK_a</i>
		4.75
+ I		4.87
- I		4.35

Gruppi elettron **attrattori** aumentano l'acidità ↓ pK_a
 Gruppi elettron **donatori** diminuiscono l'acidità ↑

	Composto	pK_a	
	H ₂ O	15,7	
+ I	CH ₃ OH	15,5	
	CH ₃ CH ₂ OH	15,9	1 gruppo alchilico
	(CH ₃) ₂ CHOH	17,1	2 gruppi alchilici
	(CH ₃) ₃ COH	18	3 gruppi alchilici
- I	ClCH ₂ CH ₂ OH	14,3	1 Cl in β
	CF ₃ CH ₂ OH	12,4	3 F in β
	CF ₃ CH ₂ CH ₂ OH	14,6	3 F in γ
	CF ₃ CH ₂ CH ₂ CH ₂ OH	15,4	3 F in δ

EFFETTO MESOMERICO

effetto mesomero / coniugativo / di risonanza

Riguarda quei sostituenti che possono provocare una *delocalizzazione elettronica* a causa della risonanza, **modificando così la densità elettronica**.

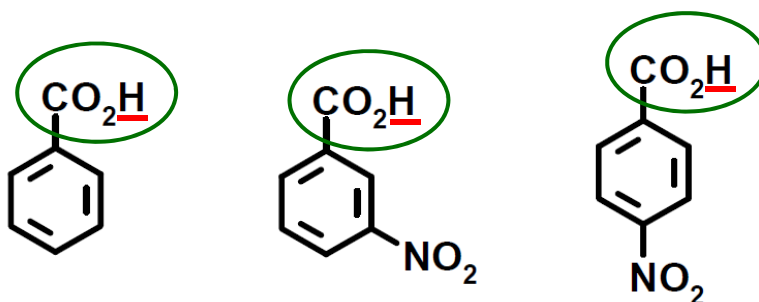
+R

SOSTITUENTI ELETTRON DONATORI

-R

SOSTITUENTI ELETTRON ATTRATTORI

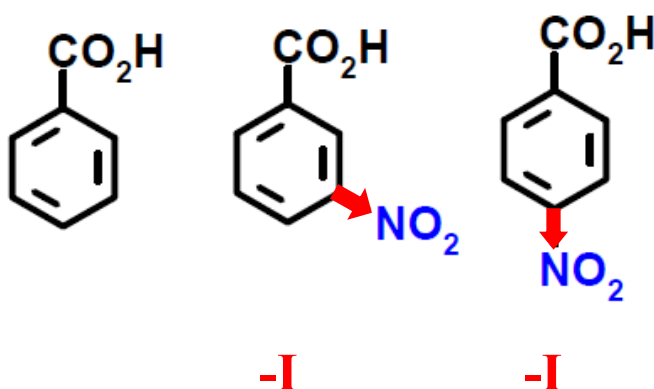
L'effetto coniugativo si **aggiunge** all'effetto induttivo



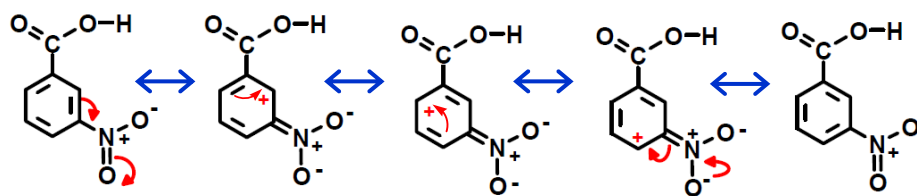
1. l'idrogeno acido è lo stesso

2. legato allo stesso gruppo funzionale

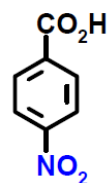
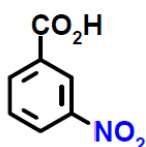
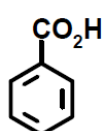
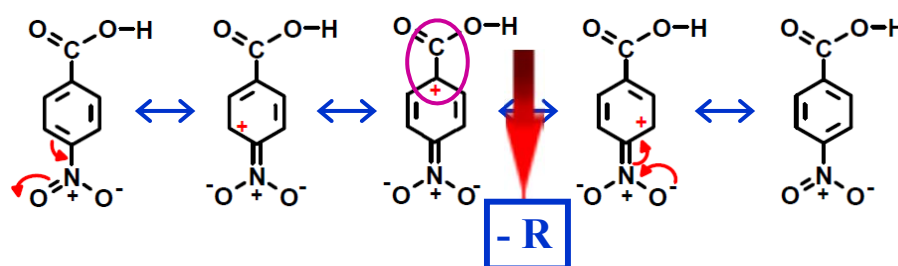
EFFETTO INDUTTIVO



EFFETTO MESOMERICO



La risonanza non interessa mai il carbossile $R = 0$



-I



-I, -R

pKa

4.2

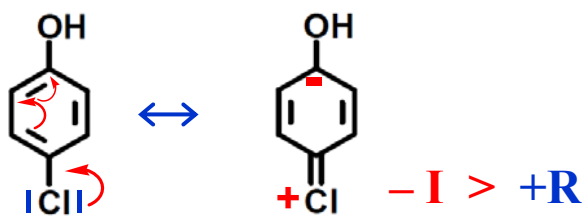
3.5

3.4

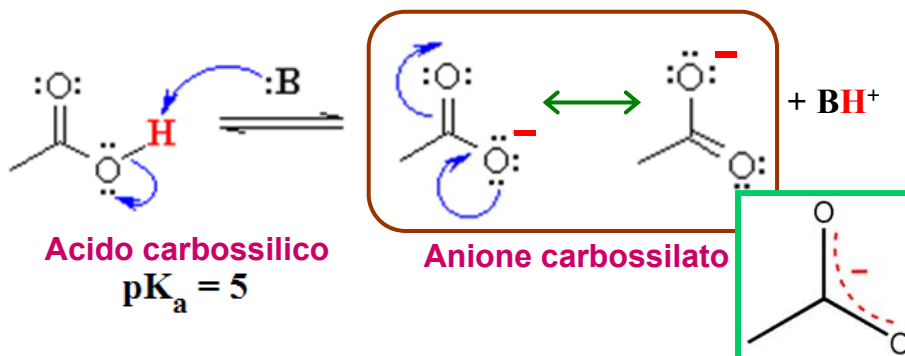
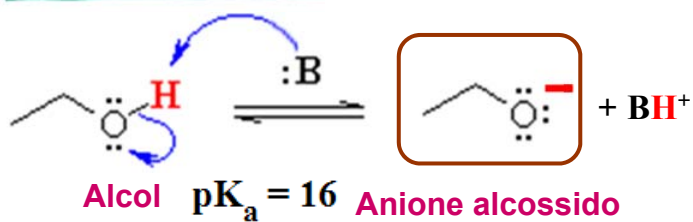
quando l'atomo responsabile dell'effetto -I,+R è **azoto** o **ossigeno**

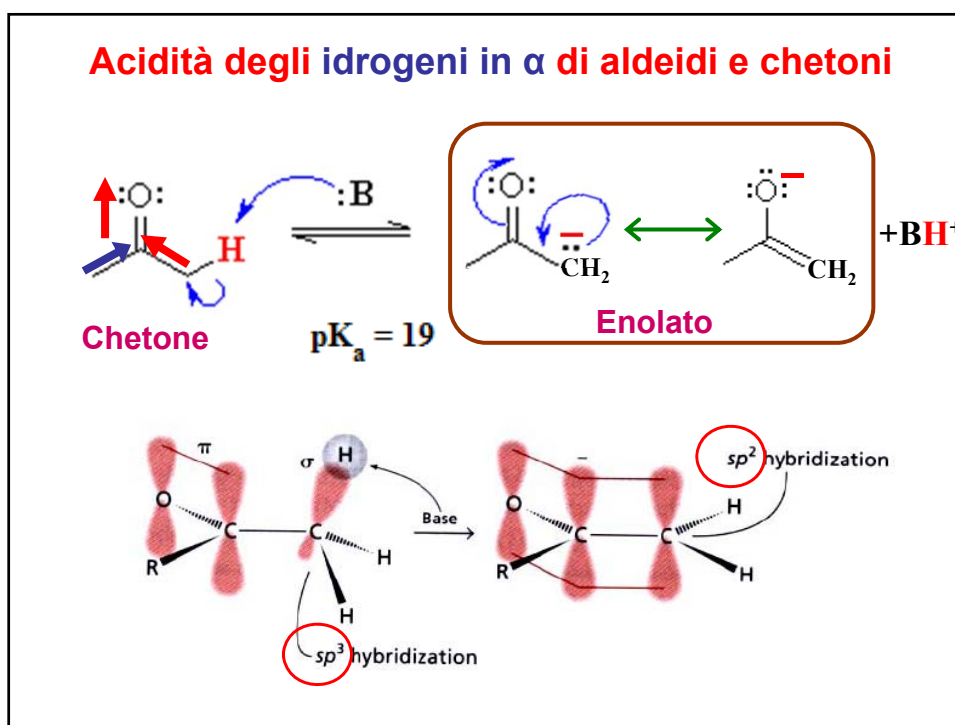
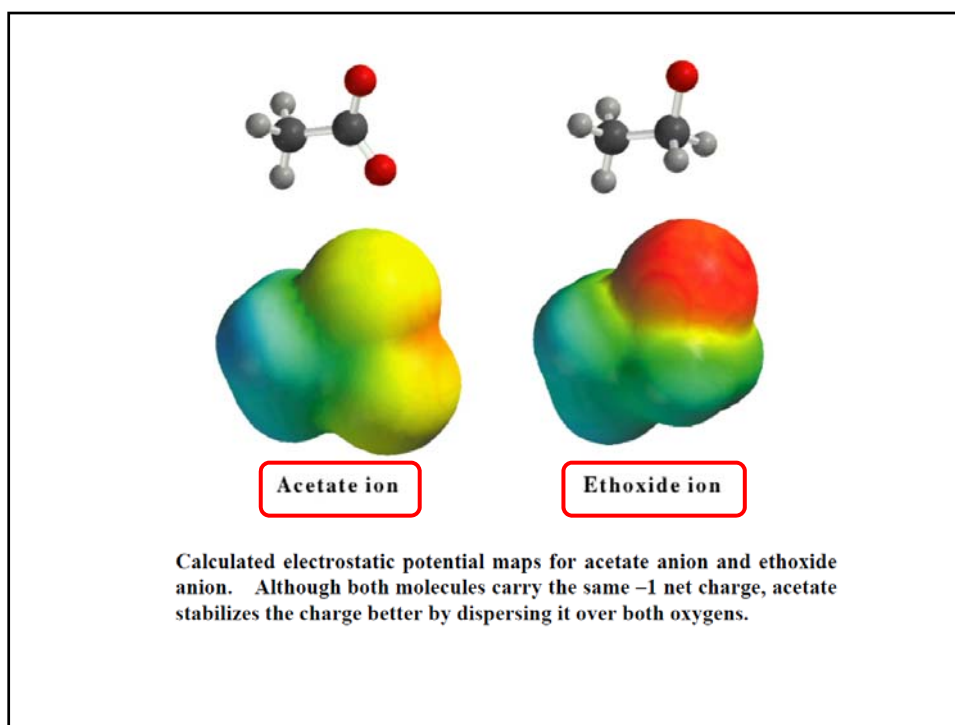


quando l'atomo responsabile dell'effetto -I,+R è un **alogeno**

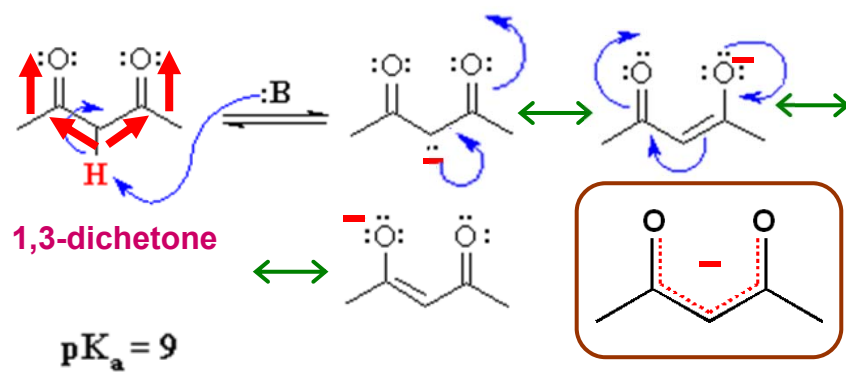
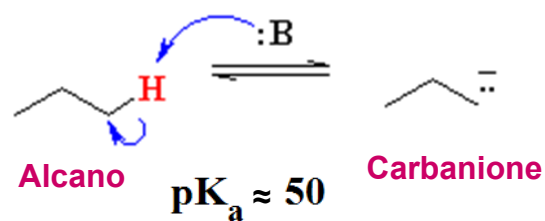
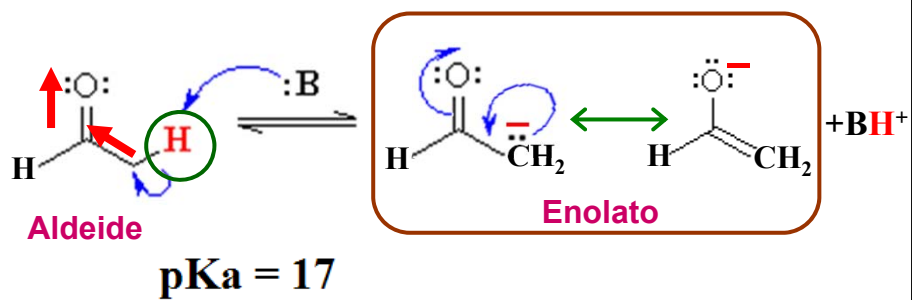


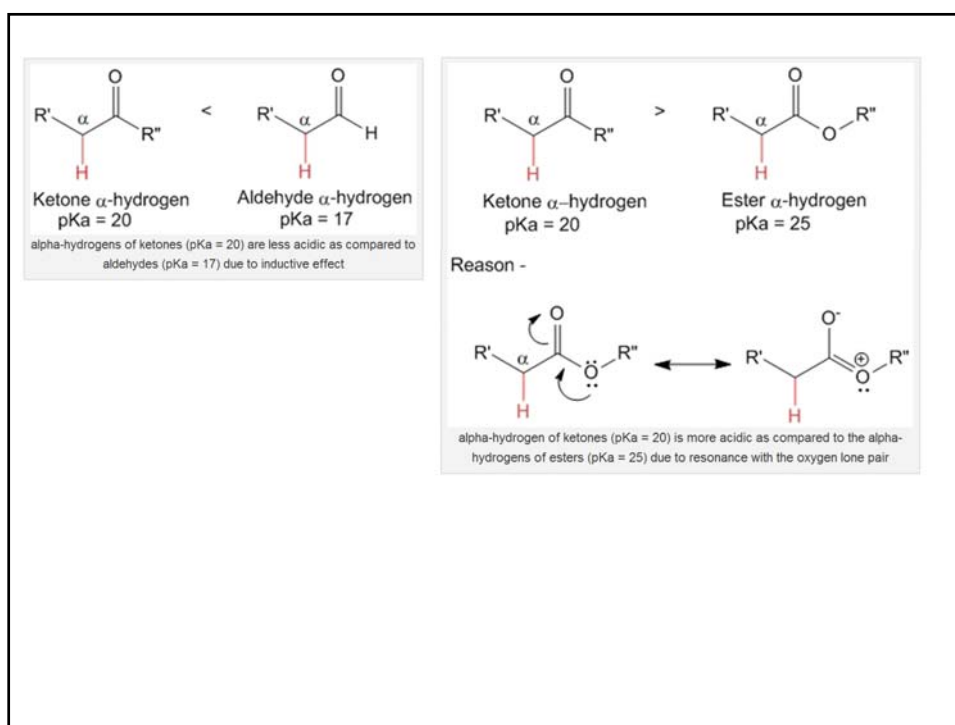
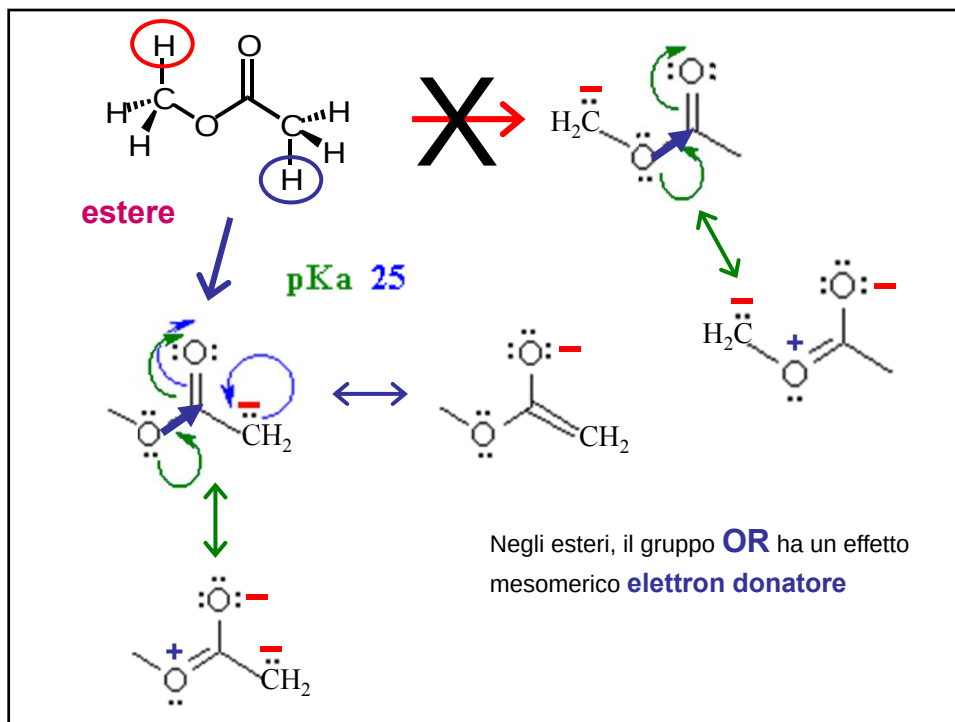
5. Risonanze

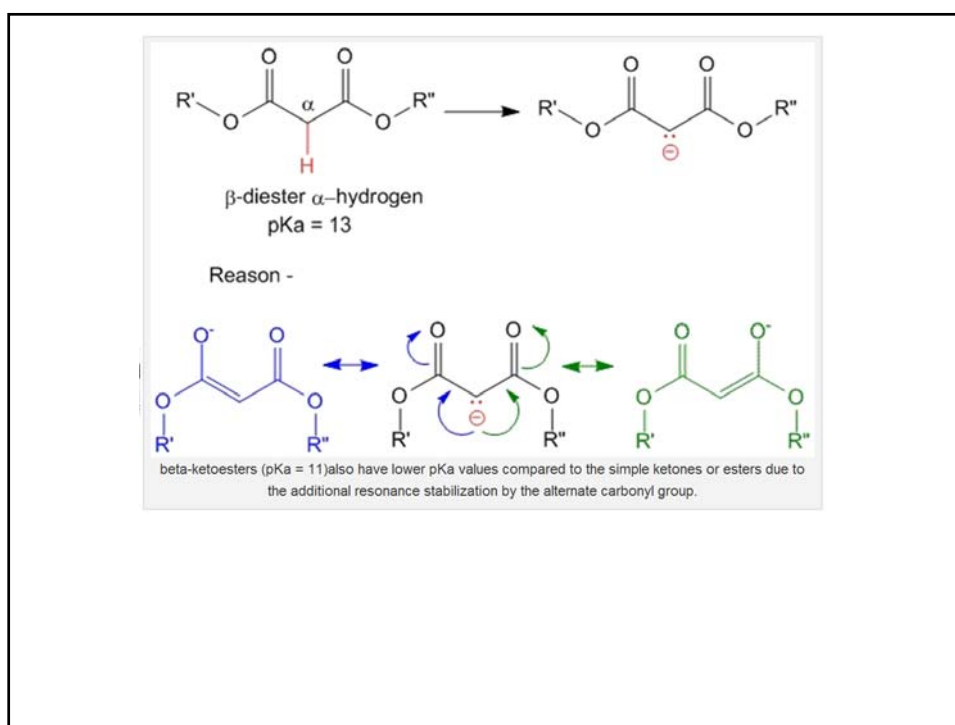
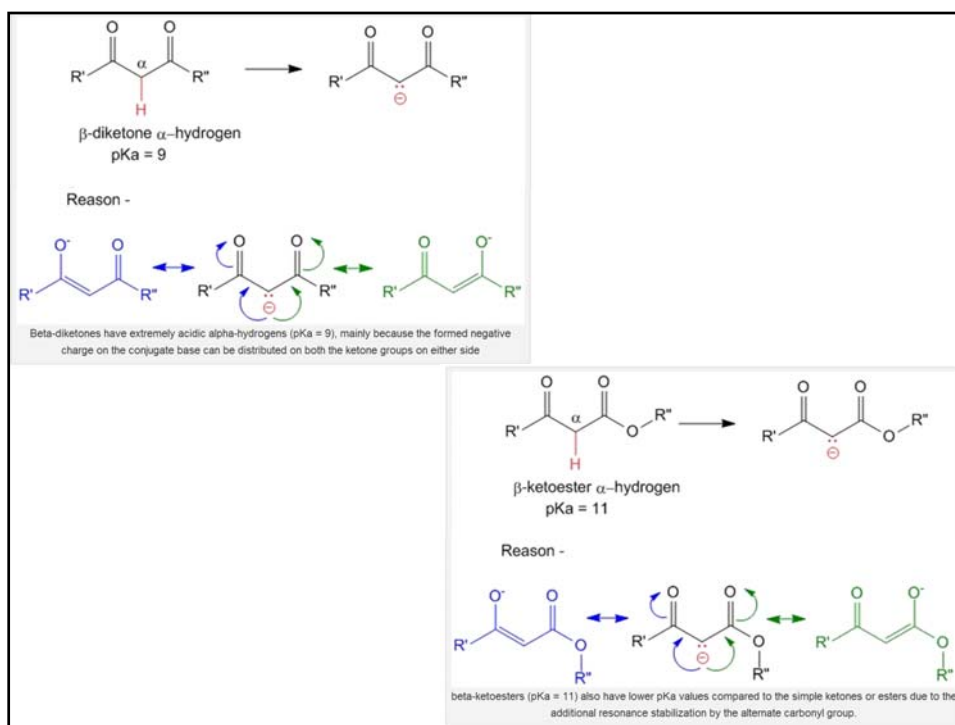


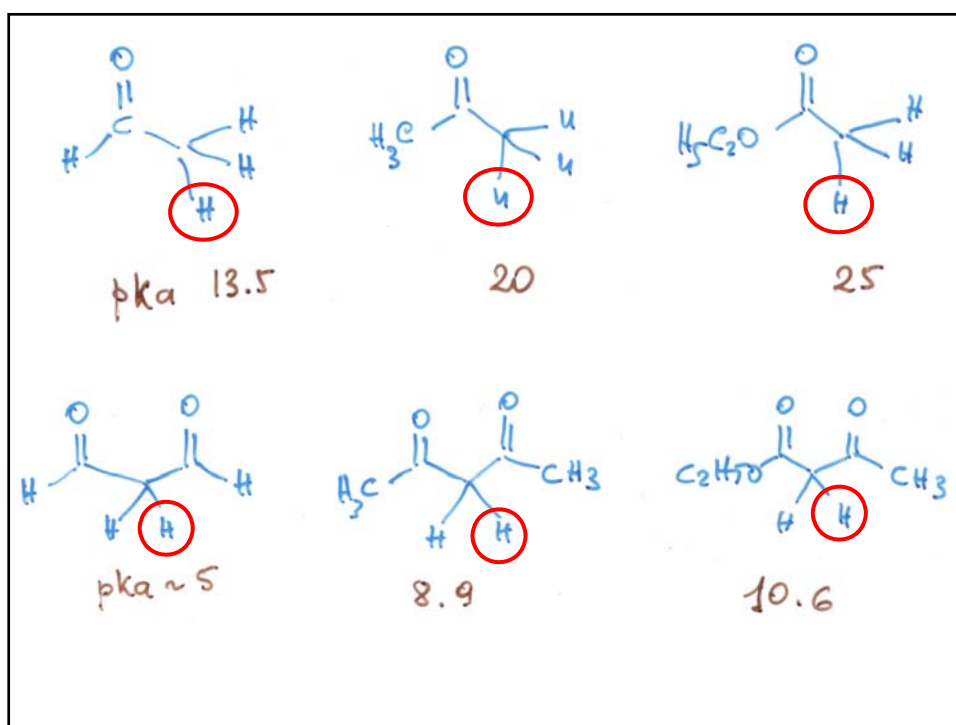
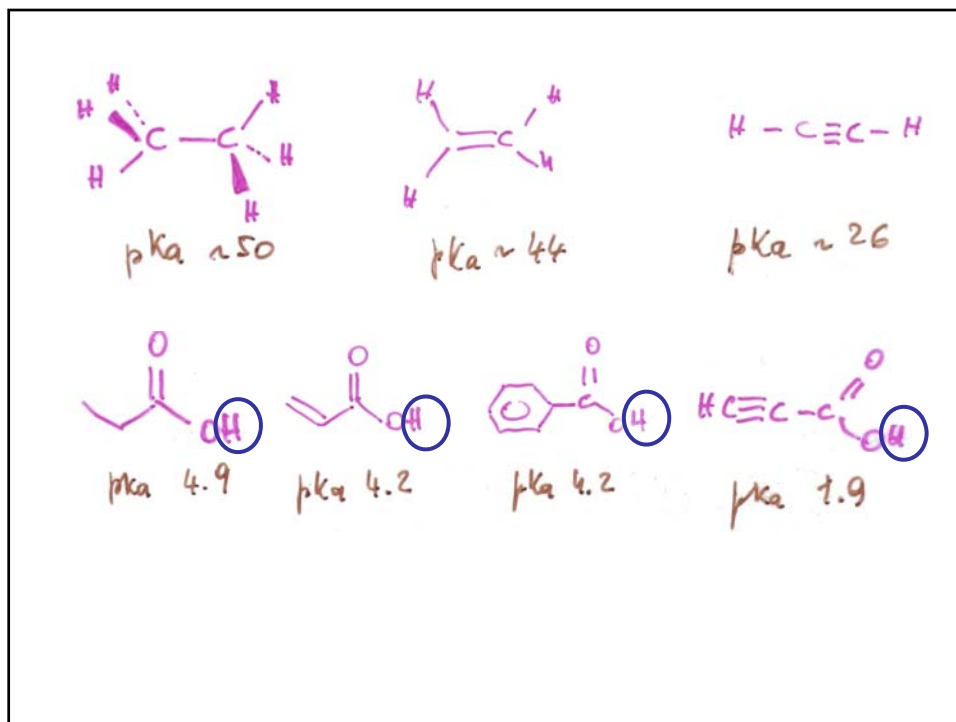


Acidità degli idrogeni in α di aldeidi e chetoni

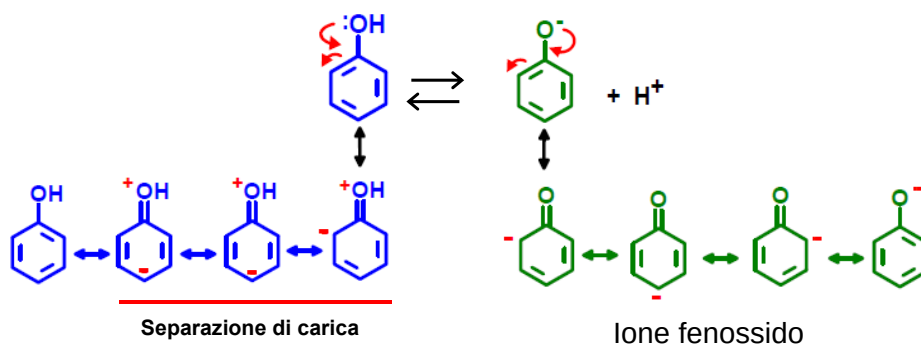




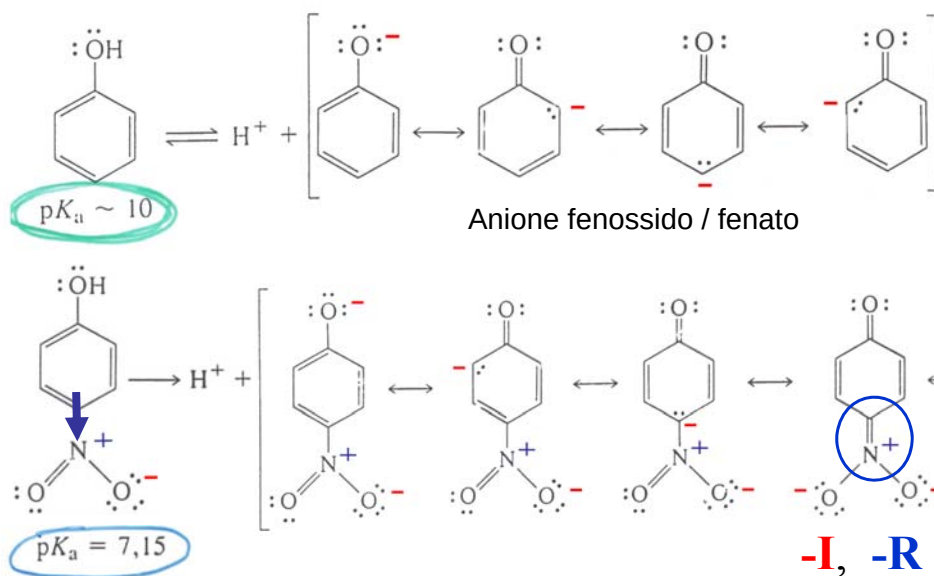


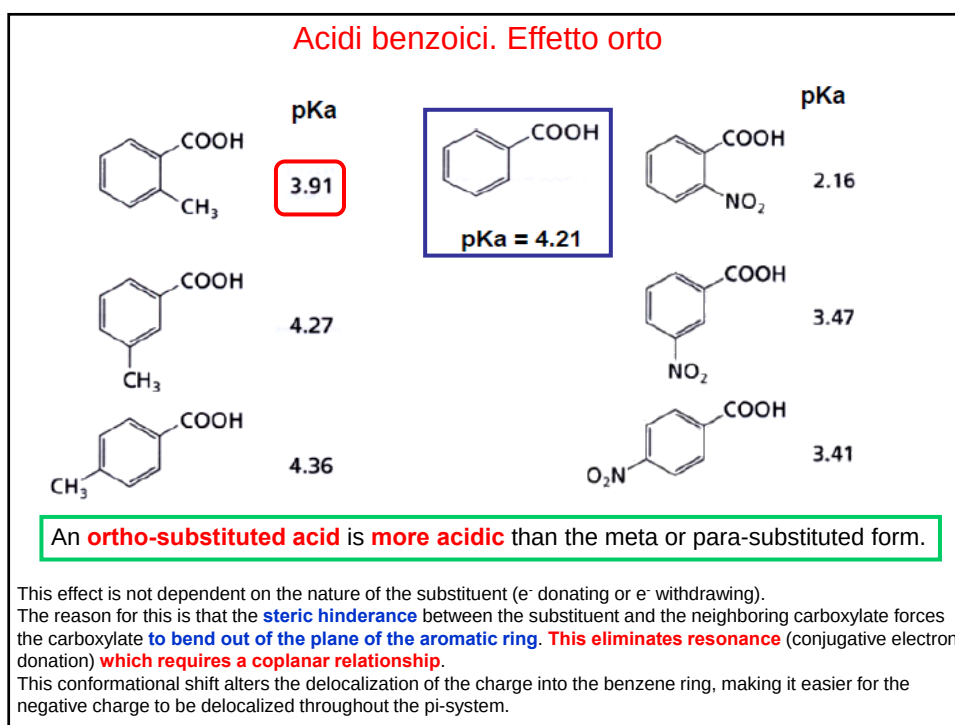
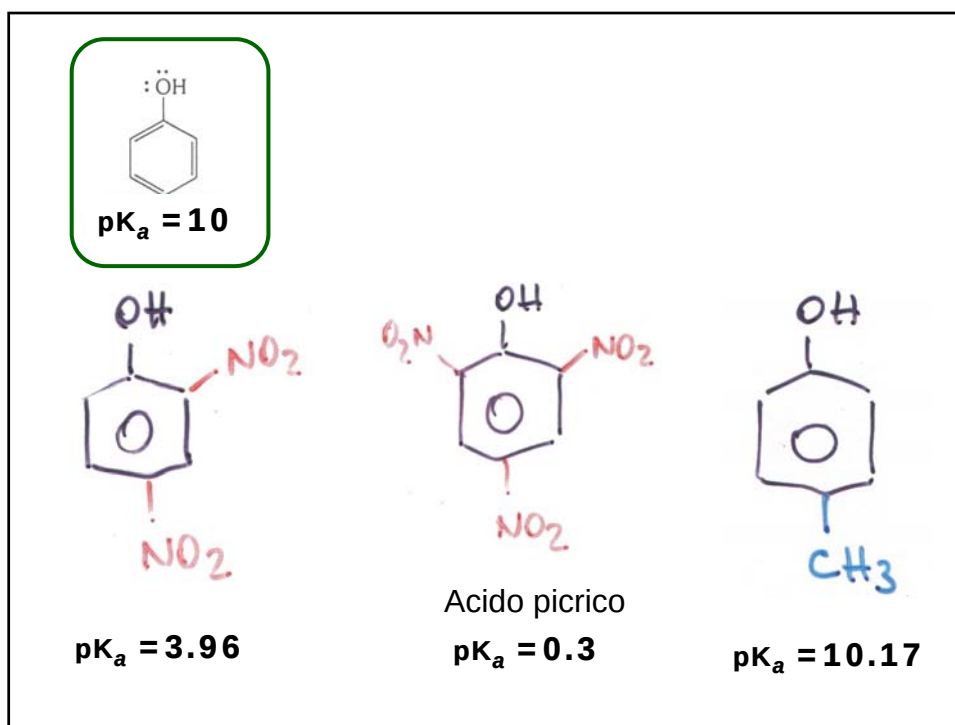


ACIDITÀ DEI FENOLI

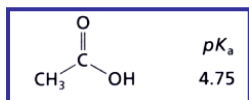


ACIDITÀ DEI FENOLI



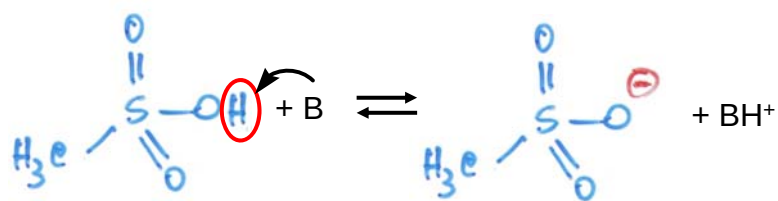


Acidi dicarbossilici

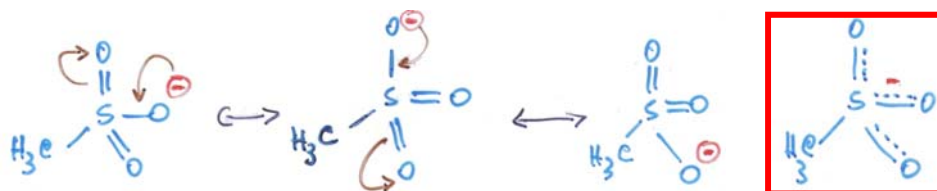


Compound	Name	pK_1	pK_2
	Oxalic acid	1.23	4.19
	Malonic acid	2.83	5.69
	Succinic acid	4.16	5.61
	Glutaric acid	4.34	5.41
	Adipic acid	4.43	5.41

Gli acidi solfonici

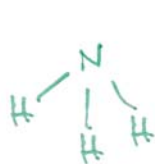


acido metansolfonico

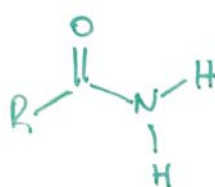


$pK_a = -2$

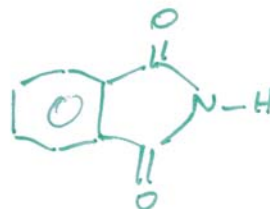
Acidi contenenti gruppi NH



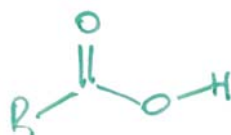
pKa 33



pKa 17

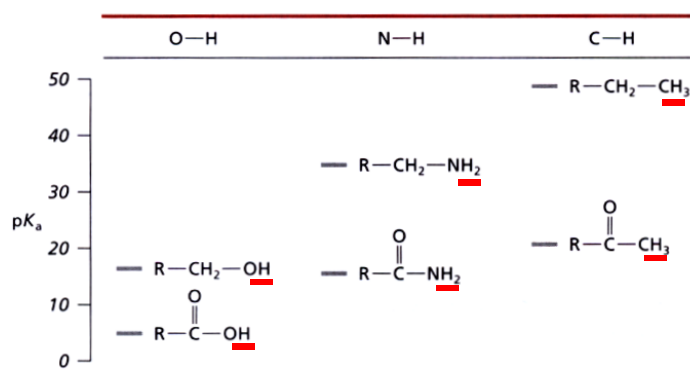


pKa 8.3



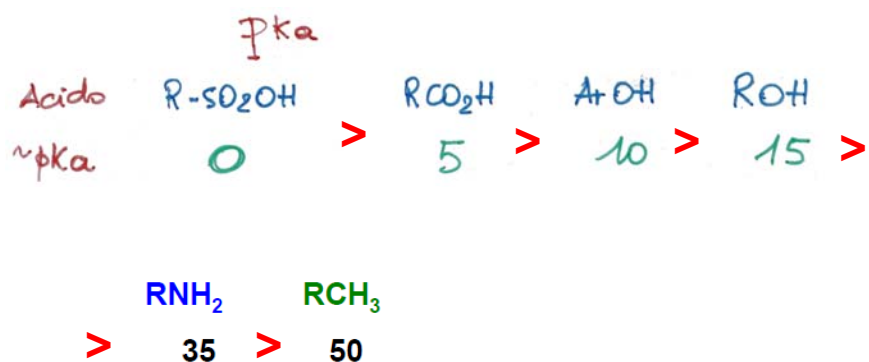
pKa 5 EN

C	N	O
2.5	3.04	3.44



Valori del pK_a di vari acidi carbossilici e di altri acidi

Composto	pK_a	Composto	pK_a
Acidi alcanoici		Acidi benzoici	
CH_3COOH	4,74	$\text{C}_6\text{H}_5\text{COOH}$	4,19
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	4,9	$4\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$	4,36
ClCH_2COOH	2,86	$4\text{-ClC}_6\text{H}_4\text{COOH}$	3,98
$\text{CH}_3\text{CH}_2\text{CHClCOOH}$	2,8	Altri acidi	
$\text{CH}_3\text{CHClCH}_2\text{COOH}$	4,1	H_3PO_4	2,15 (pK_a primario)
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$	4,5	HNO_3	-1,3
Cl_2CHCOOH	1,26	HCl	-2,2
Cl_3CCOOH	0,64	H_2SO_4	-5,2 (pK_a primario)
F_3CCOOH	0,23	H_2O	15,7
Acidi dioici		CH_3OH	15,5
$\text{HOOCCH}_2\text{COOH}$	1,23; 4,19		
$\text{HOOCCH}_2\text{CH}_2\text{COOH}$	2,83; 5,69		
$\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$	4,16; 5,61		
$\text{HOOC(CH}_2)_4\text{COOH}$	4,43; 5,41		



carboxylic acid	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	pKa 5
nitro	CH_3-NO_2	9
amide	$\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	15
aldehyde	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	17
ketone	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	20
ester	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$	25
nitrile	CH_3-CN	25
amide	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}(\text{CH}_3)_2$	30
alkane	CH_3-CH_3	~50

BASICITA'

base: {

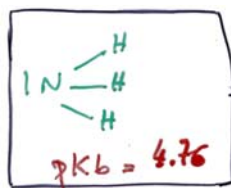
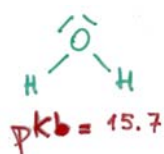
- accetta un protone
- dona un doppietto di e^-

→ { più accessibili sono gli elettroni,
più forte è la base

→ { più è stabile l'acido coniugato
più forte è la base

A) effetto del doppio non condiviso:

- Il doppio e^- non condiviso è più facilmente accessibile se è su un elemento meno elettronegativo.



10^{10} volte
più basica
nell'acqua



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Effetti che diminuiscono la densità elettronica
nell'azoto:

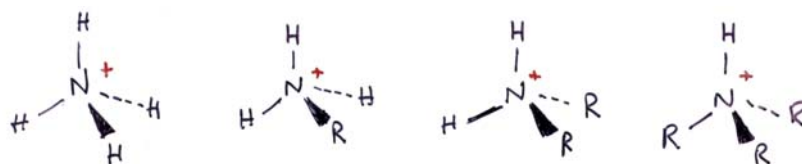
- l'azoto è legato a un gruppo e^- attrattore
- il doppio è in un orbitale π o π^2
- il doppio è coniugato con un gruppo e^- attrattore
- il doppio è coinvolto nel mantenere l'aromaticità della molecola

il doppio è meno disponibile per la
protonazione $\Rightarrow$ l'anilina è una base
più debole.

R	pK _b		
	RNH ₂	R ₂ NH	R ₃ N
Me	3.4	3.2	4.2
Et	3.3	3.0	3.2
n-Pr	3.3	3.0	3.7
n-Bu	3.3	2.7	4.1
H			4.8

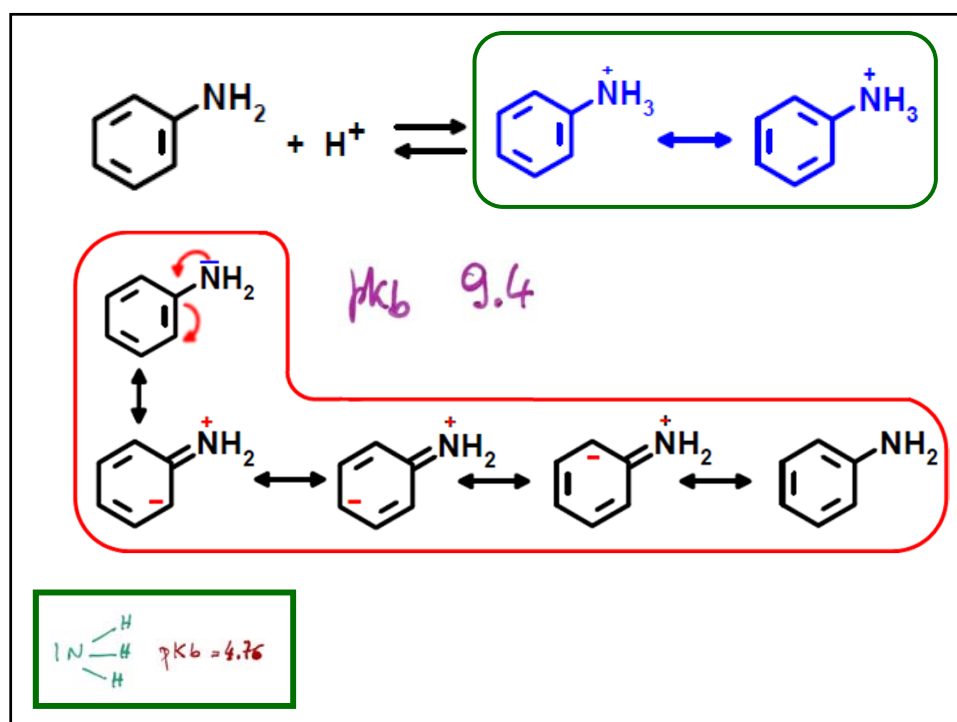
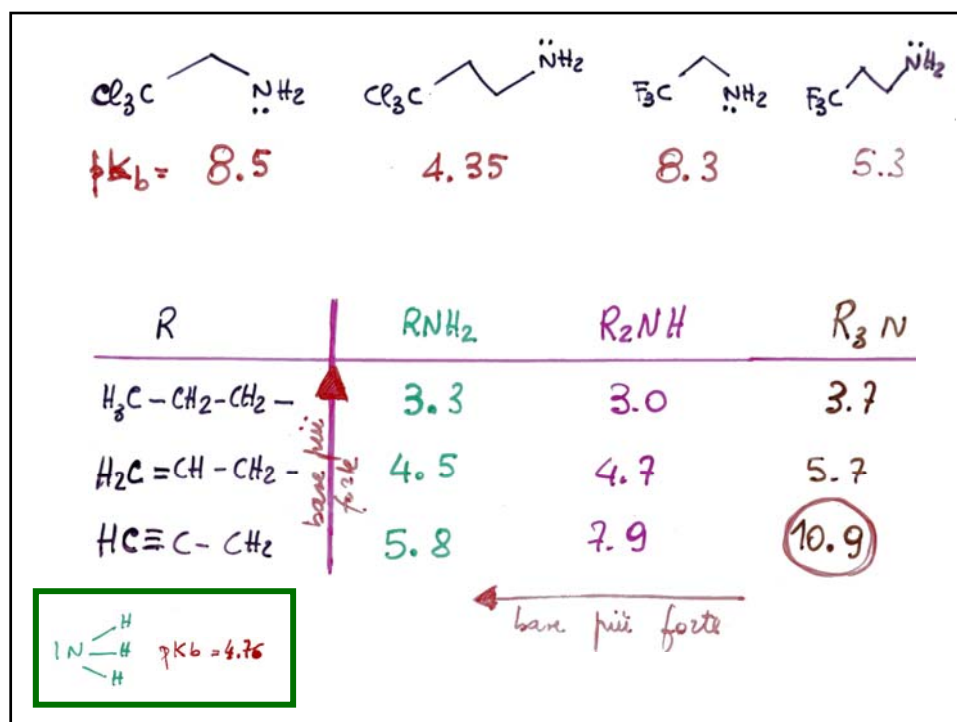
NH₃

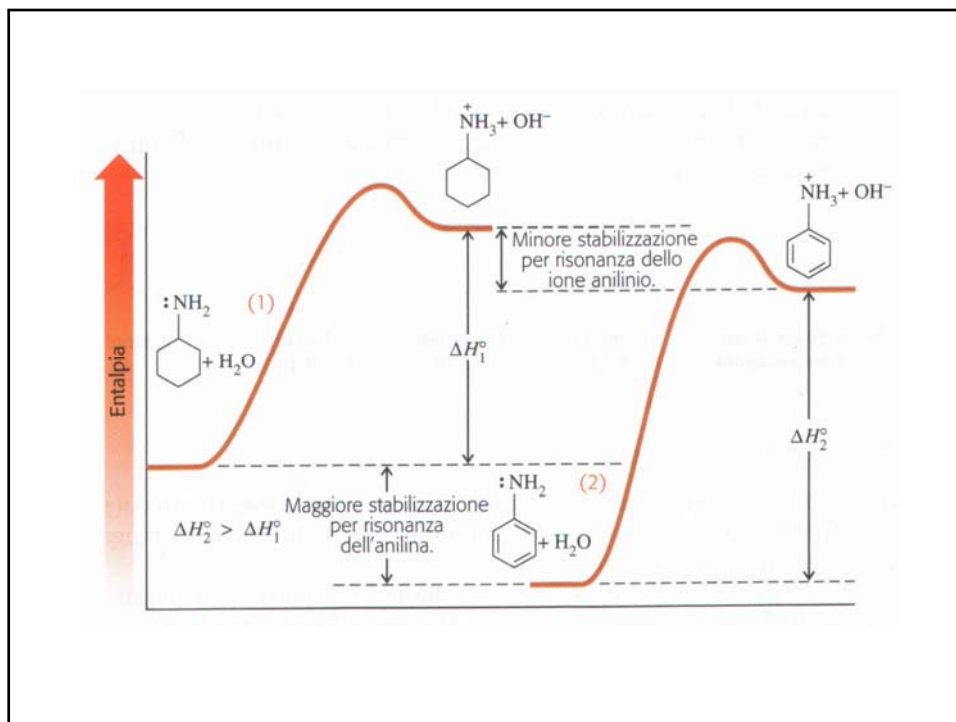
③ STABILIZZAZIONE DELL'ACIDO CONIUGATO



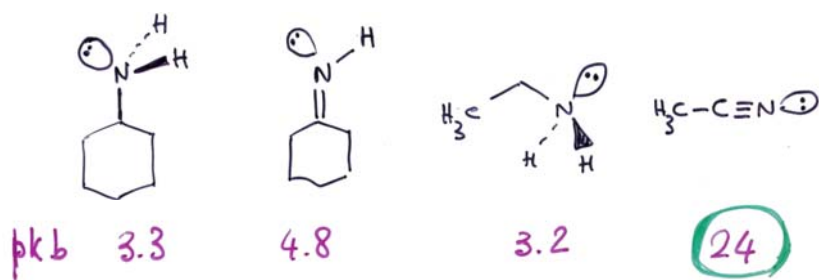
→ stabilizz. della carica $\oplus$ da parte del gruppo alchilico

← stabilizz. della carica $\oplus$ dal legame a idrogeno con il solvente $\Rightarrow$ maggior leg. a H $\Rightarrow$ maggior stabilizz.





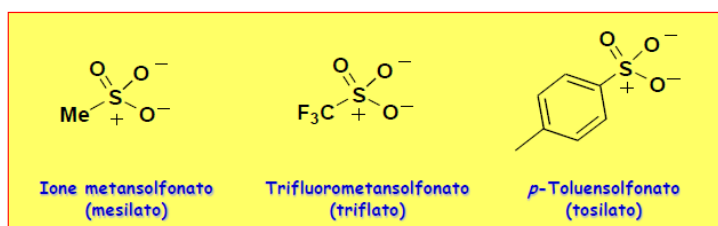
				sp^3
pK_b	2.8	2.89	3.02	
				sp^2
	Piridina	Pirimidina	Pirrolo	
pK_b	8.77	11.3	13.6	9.5
	$pK_b = 4.75$			



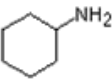
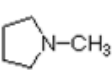
Come fare di un OH^- un buon gruppo uscente?

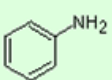
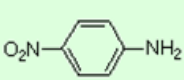
Lo si trasforma nel corrispondente

ESTERE SOLFONICO

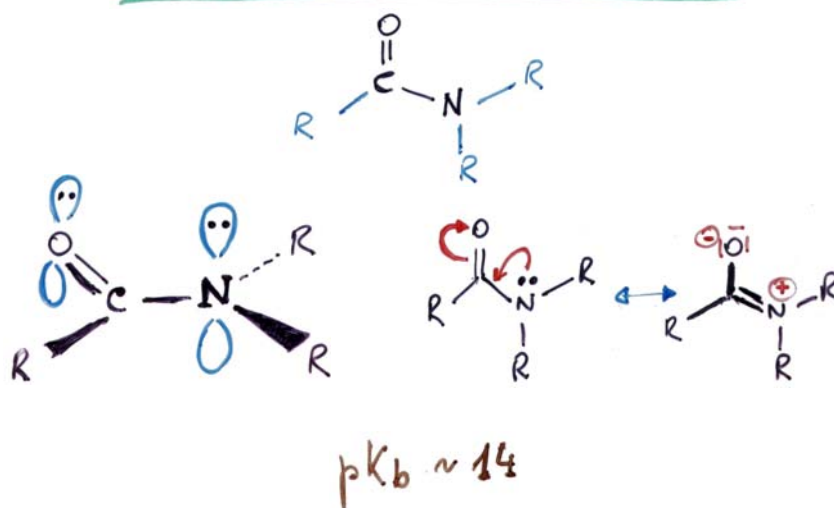


Miglior gruppo uscente: $\text{I}^- > \text{RSO}_3^- > \text{Br}^- > \text{Cl}^- \gg \text{RCOO}^-$

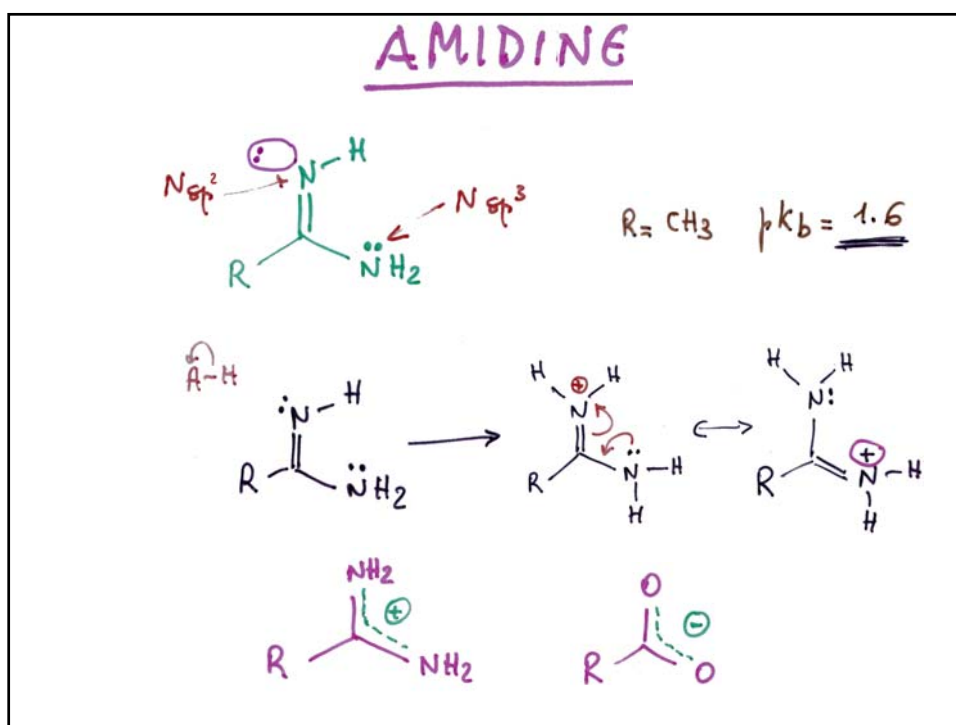
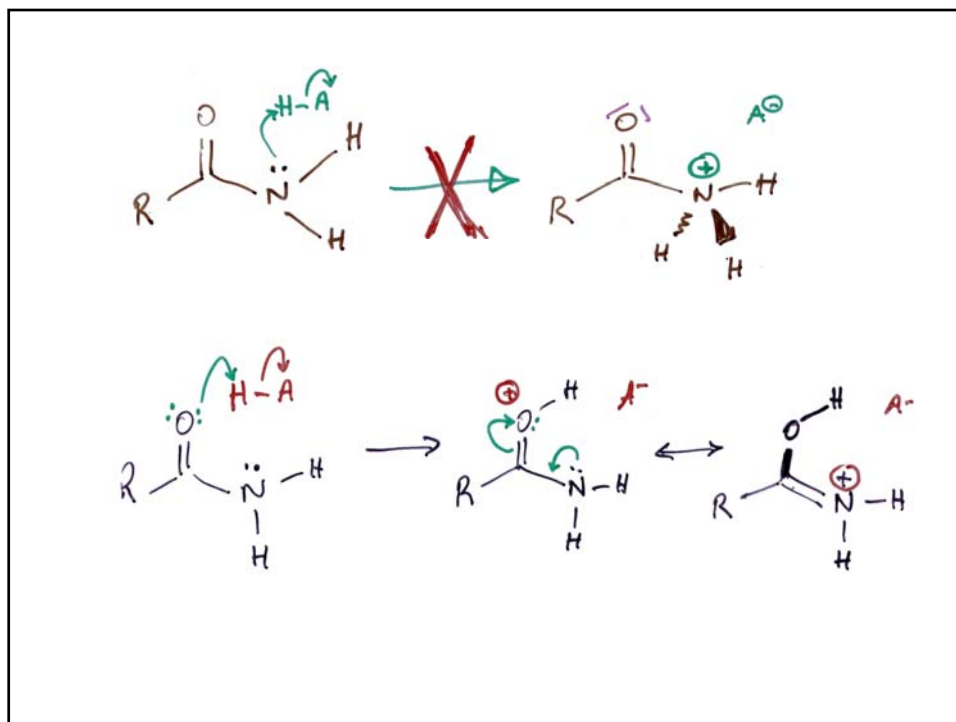
Compound				NH_3
pK_b	3	3.3	3.3	4.7

Compound						$\text{CH}_3\text{C}\equiv\text{N}$
pK_b	8.8	9.4	13	14	15	24

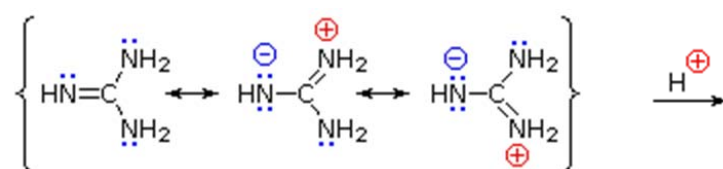
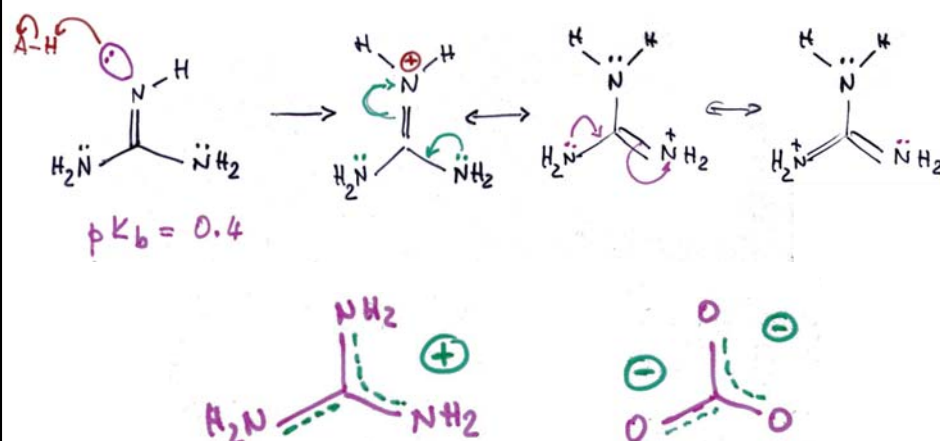
IL GRUPPO AMMIDICO



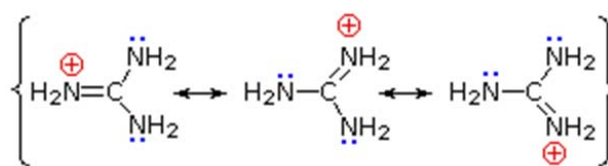
Le **ammidi** sono **basi debolissime** e manifestano un comportamento **debolmente acido**



GUANIDINE



guanidine base
small stabilization



guanidinium conjugate acid
large stabilization

Numero di ossidazione

Per numero di ossidazione si intende

IL NUMERO DI ELETTRONI CEDUTI O ACQUISTATI IN MANIERA TOTALE O
PARZIALE DA UN ATOMO PER LA FORMAZIONE DI UN LEGAME CHIMICO

o, in altre parole, gli elettroni di valenza di un atomo impegnati in un legame chimico.

LA CARICA CHE L'ATOMO ASSUMEREBBE SE GLI ELETTRONI DI LEGAME
FOSSERO ASSEGNATI ALL'ELEMENTO PIÙ ELETTRONEGATIVO

Determinazione del numero di ossidazione

