SAPIENZA
UNIVERSITÀ DI ROMA

Corso di Laurea Magistrale in Ingegneria Biomedica

Complementi di Chimica e Biochimica per le Tecnologie Biomediche

Derivati degli acidi carbossilici

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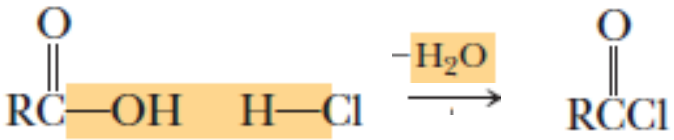
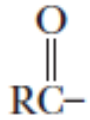
DIPARTIMENTO DI
SCIENZE DI BASE E APPLICATE PER L'INGEGNERIA

Cloruri acilici: definizione e struttura





Gruppo acile: gruppo funzionale del tipo RCO, con R alifatico o aromatico

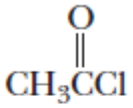
Cloruro acilico (o cloruro acido): composto contenente un gruppo acile legato a un cloruro

Cloruri acilici: nomenclatura

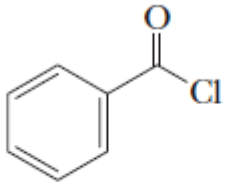
Cloruro + di + nome della catena + *ile*

oppure

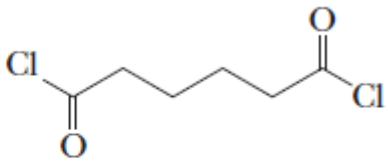
Nome della catena + *il +* cloruro



Ethanoyl chloride
(Acetyl chloride)



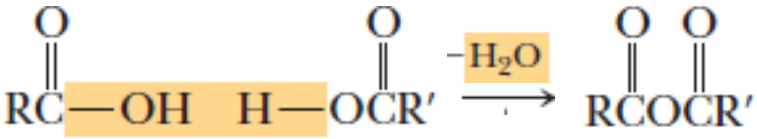
Benzoyl chloride



Hexanedioyl chloride
(Adipoyl dichloride)

Per il resto valgono tutte le regole di nomenclatura già viste per gli acidi carbossilici

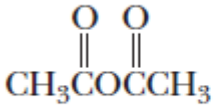
Anidridi: definizione e struttura



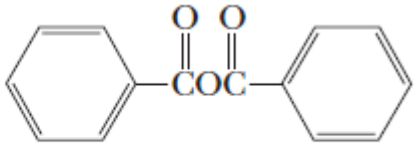
Anidride acida: composto contenente due gruppi acili legati a un atomo di ossigeno

Anidridi: nomenclatura

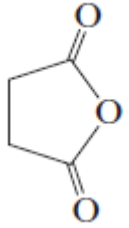
Anidride + nome della catena + *oica (ica)*



Acetic anhydride



Benzoic anhydride

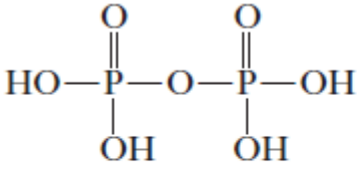


Succinic anhydride

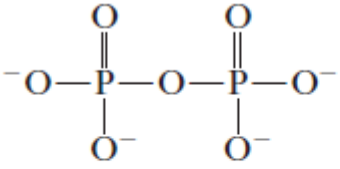
In pratica, nel nome dell'acido precursore si sostituisce «acido» con «anidride»
Per il resto valgono tutte le regole di nomenclatura già viste per gli acidi carbossilici

Anidridi fosforiche

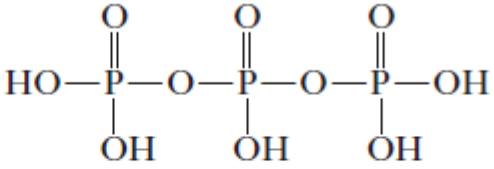
Anidride fosforica: composto contenente due gruppi fosforici legati a un atomo di ossigeno



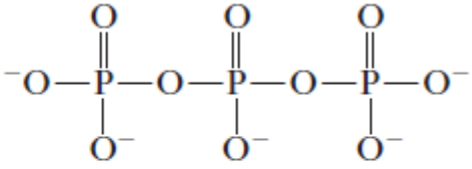
Diphosphoric acid
(Pyrophosphoric acid)



Diphosphate ion
(Pyrophosphate ion)

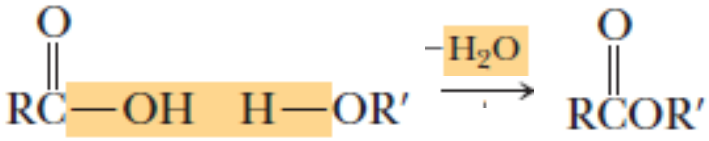


Triphosphoric acid



Triphosphate ion

Esteri: definizione e struttura



Estere: composto contenente un gruppo acile legato a un gruppo –OR o –OAr

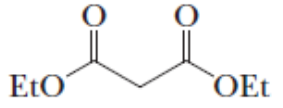
Esteri: nomenclatura

Nome della catena dell'acido precursore + *oato* + di + nome della catena R'

oppure

Nome della catena R' + *il* + nome della catena dell'acido precursore + *ato*

Ethyl ethanoate (Ethyl acetate)

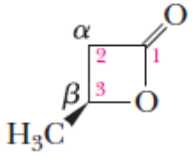


Diethyl propanedioate (Diethyl malonate)

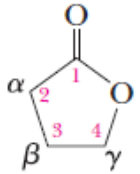
Esteri ciclici: lattoni

Nome della catena dell'acido precursore + *olattone*

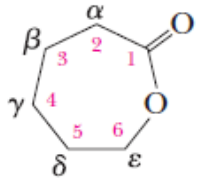
- La posizione dell'ossigeno è indicata con un numero o una lettera greca



(*S*)-3-Butanolactone ((*S*)-β-Butyrolactone)



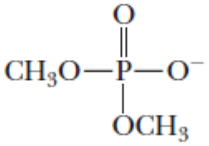
4-Butanolactone (γ-Butyrolactone)



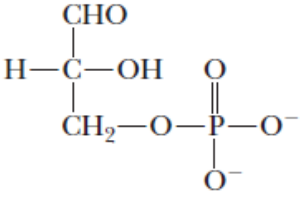
6-Hexanolactone (ε-Caprolactone)

Esteri fosforici

Estere fosforico: estere formato a partire dall'acido fosforico per introduzione di 1, 2 o 3 catene alchiliche/ariliche sui gruppi -OH



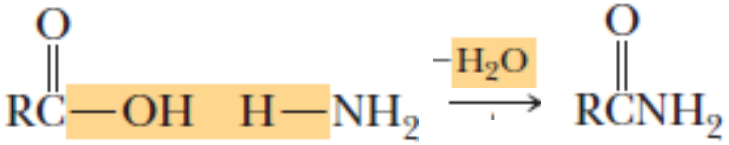
Dimethyl phosphate



Glyceraldehyde 3-phosphate

Per il resto valgono tutte le regole di nomenclatura già viste per gli acidi carbossilici

Ammidi: definizione e struttura

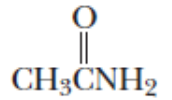


Ammide: composto contenente un gruppo acile legato a un atomo di N

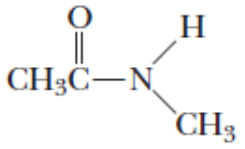
Ammidi: nomenclatura

Nome della catena dell'acido precursore + ammide

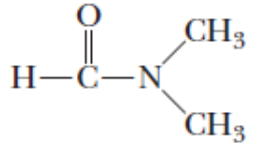
- Se N è legato a gruppi alchilici/arilici, questi si nominano e se ne indica la posizione con *N*



Acetamide
(a 1° amide)



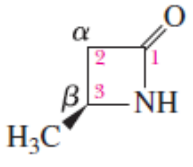
***N*-Methylacetamide**
(a 2° amide)



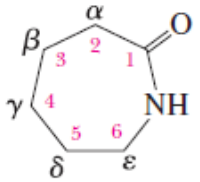
***N*,*N*-Dimethyl-formamide (DMF)**
(a 3° amide)

Ammidi cicliche: lattami

Nome della catena dell'acido precursore + *olattame*



(*S*)-3-Butanolactam
((*S*)-β-Butyrolactam)



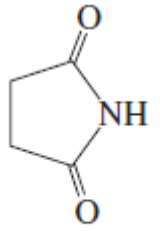
6-Hexanolactam
(ε-Caprolactam)

Per il resto valgono tutte le regole di nomenclatura già viste per gli acidi carbossilici

Immidi: definizione, struttura e nomenclatura

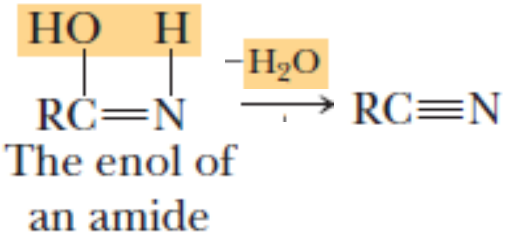
Immide: composto contenente due gruppi acili legati a un atomo di N

Nome della catena dell'acido precursore + immide

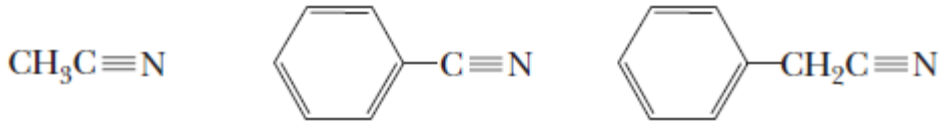


Succinimide

Nitrili: definizione, struttura e nomenclatura



Nitrile: composto contenente un gruppo ciano (-CN) legato a un atomo di C



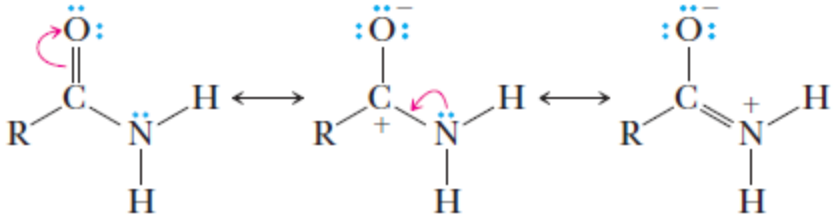
Ethanenitrile (Acetonitrile) **Benzonitrile** **Phenylethanenitrile (Phenylacetonitrile)**

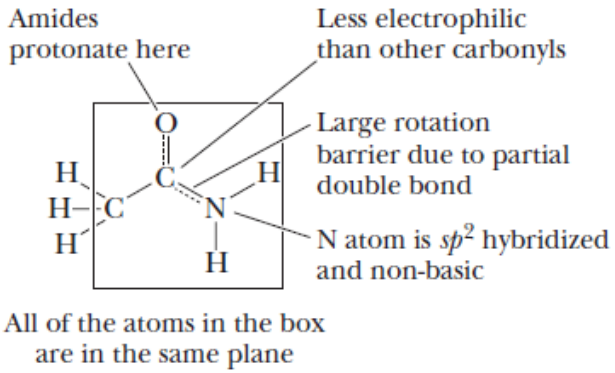
Nomenclatura IUPAC: nome alcano precursore + nitrile

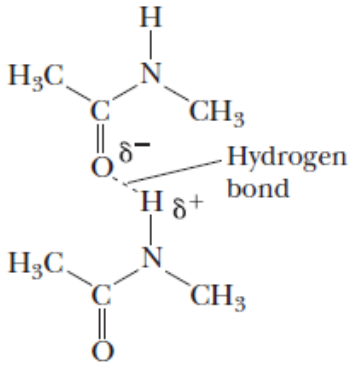
Nomenclatura comune: nome catena acido precursore + nitrile

Per il resto valgono tutte le regole di nomenclatura già viste per gli acidi carbossilici

Il legame ammidico

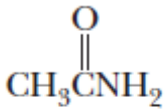




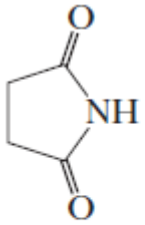


- Il legame ammidico ha parziale carattere di doppio legame
- N è trigonale planare e sp^2
- Il doppietto elettronico parzialmente delocalizzato non può interagire con acidi di Lewis
- C ha parziale carica positiva inferiore rispetto al normale C carbonilico (meno sensibile ad attacco nucleofilo)

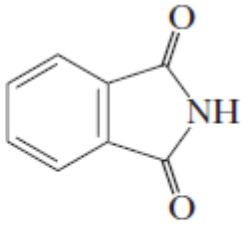
Acidità di ammidi e immidi



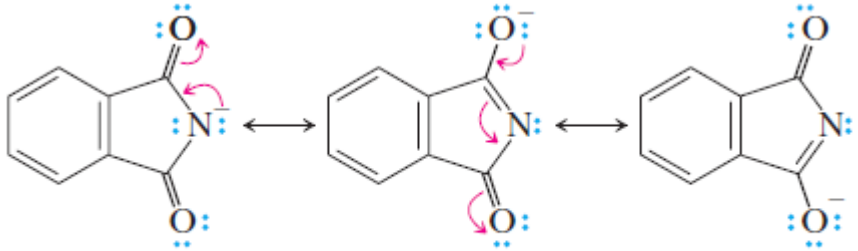
Acetamide
pK_a 15–17



Succinimide
pK_a 9.7



Phthalimide
pK_a 8.3

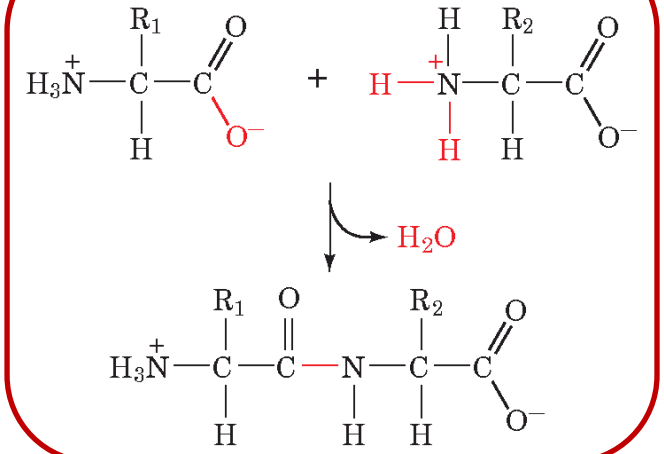


A resonance-stabilized anion

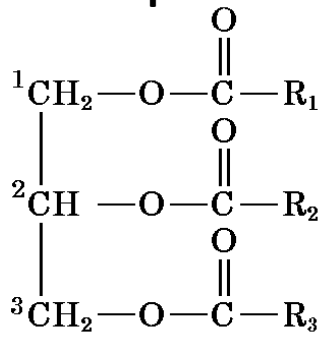
Le immidi sono più acide delle ammidi perché gli anioni corrispondenti sono stabilizzati per risonanza

Derivati degli acidi carbossilici in natura e in chimica farmaceutica

Proteine

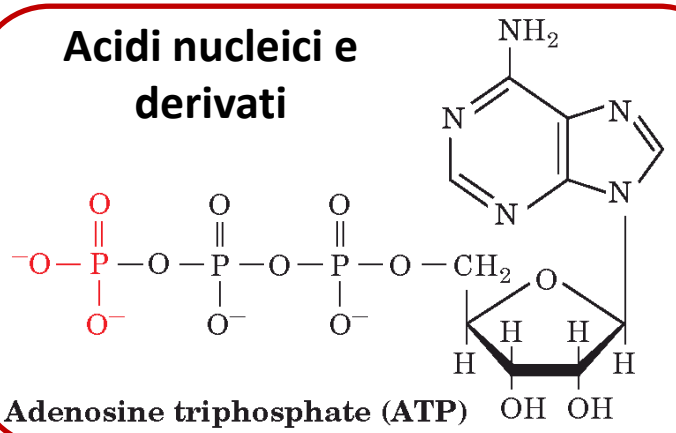


Lipidi



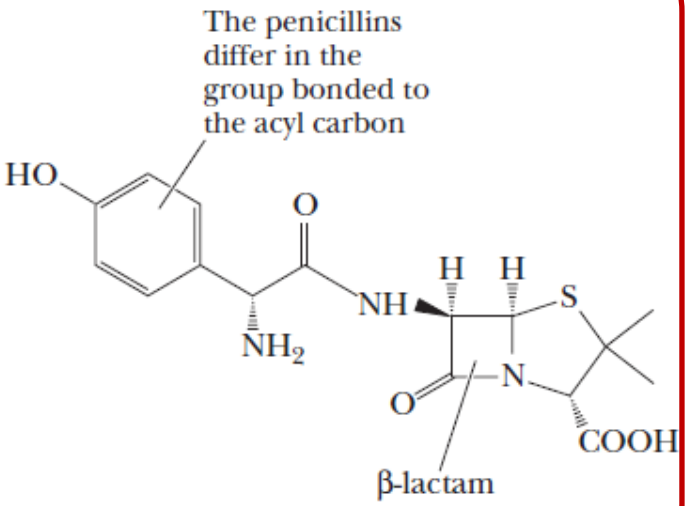
Triacilglicerolo

Acidi nucleici e derivati



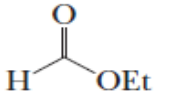
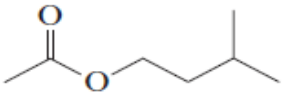
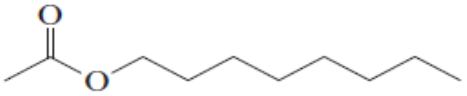
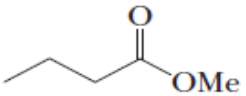
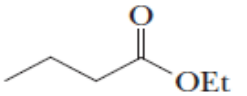
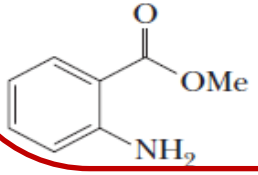
Adenosine triphosphate (ATP)

Farmaci



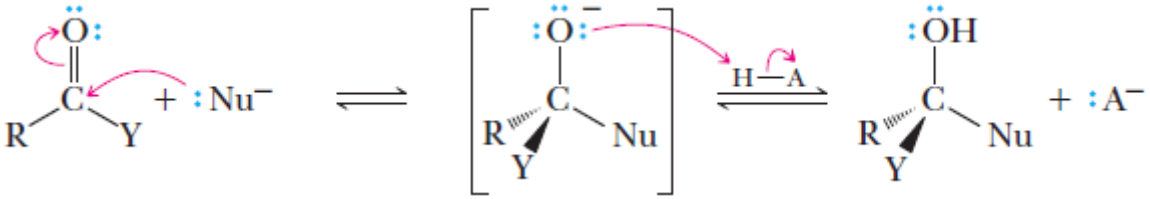
Amoxicillin
(a β-lactam antibiotic)

Aromi

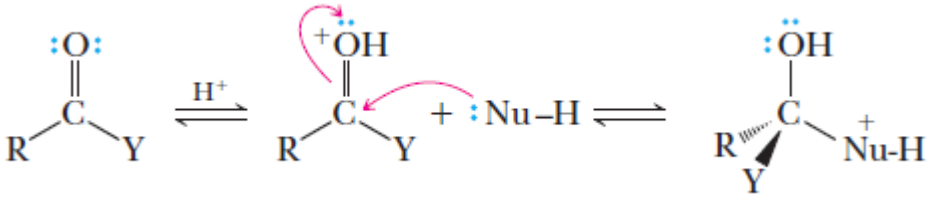
Structure	Name	Flavor
	Ethyl formate	Rum
	(3-Methyl)butyl acetate (Isopentyl acetate)	Banana
	Octyl acetate	Orange
	Methyl butanoate	Apple
	Ethyl butanoate	Pineapple
	Methyl 2-aminobenzoate (Methyl anthranilate)	Grape

Addizione nucleofila acilica

In ambiente basico

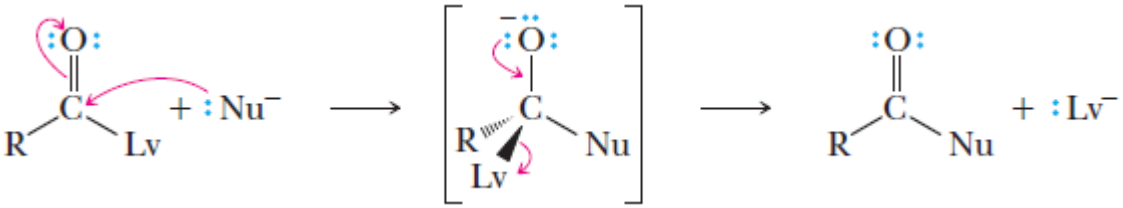


In ambiente acido

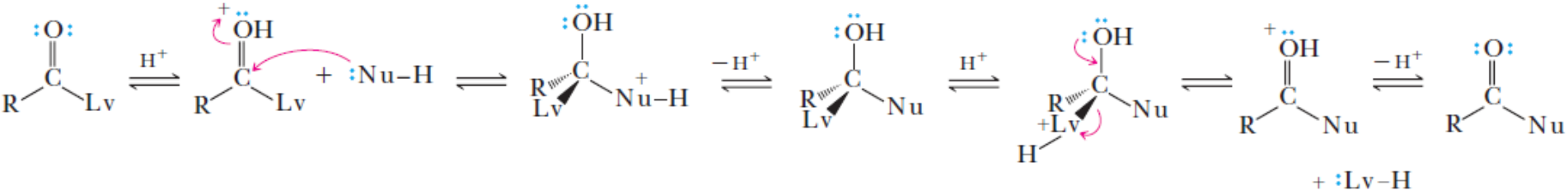


Sostituzione nucleofila acilica

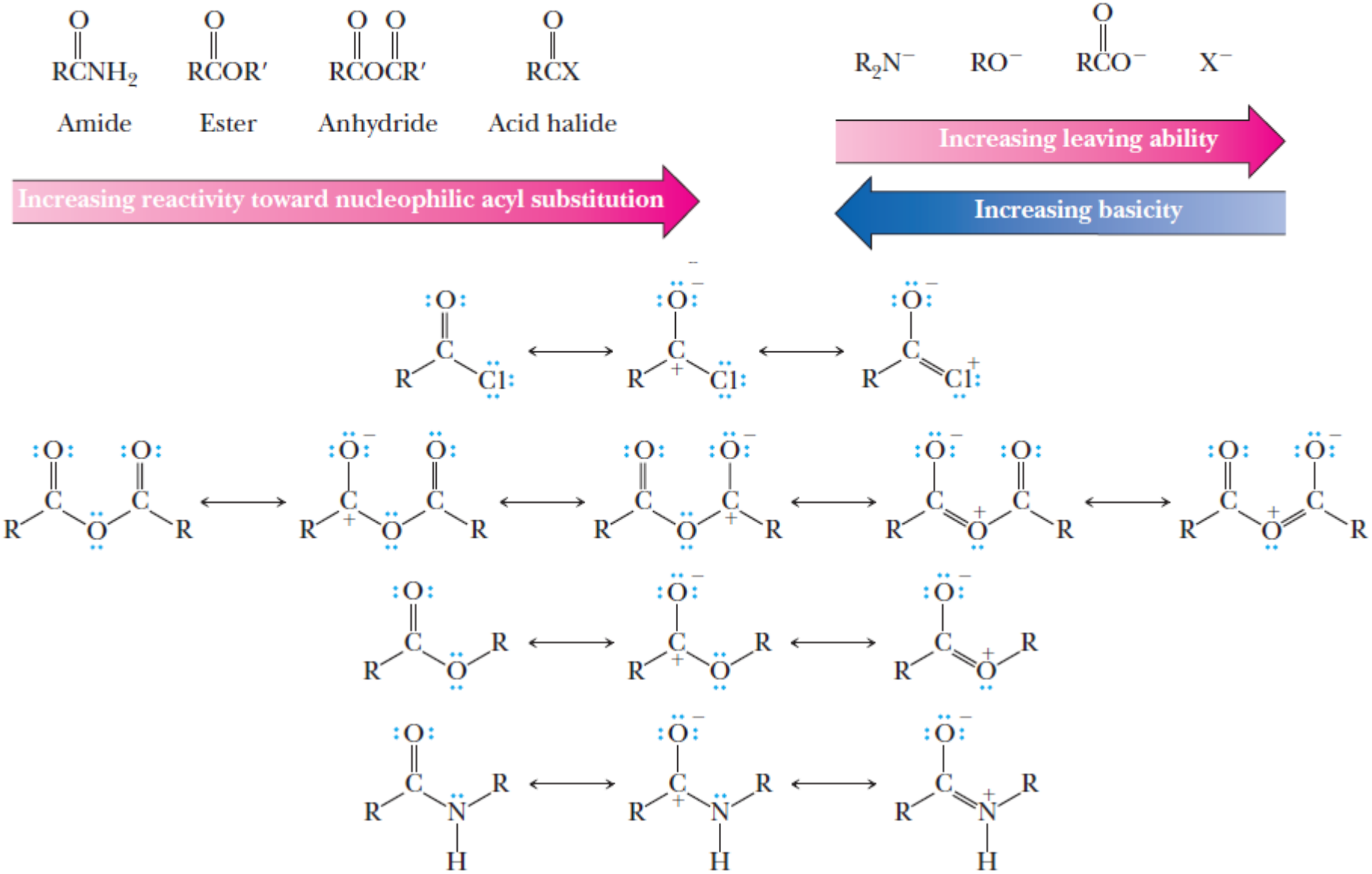
In ambiente basico



In ambiente acido



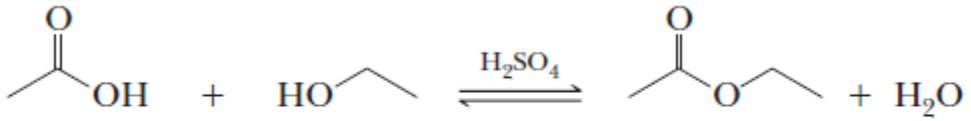
Reattività relativa



I composti più reattivi sono quelli contenenti il miglior gruppo uscente e meno stabilizzati per risonanza

Esterificazione di Fisher

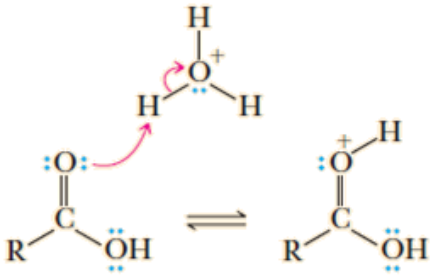
Reazione di formazione di un estere a partire da acido carbossilico e alcol portati a riflusso in presenza di un catalizzatore acido (es. HCl, H_2SO_4)



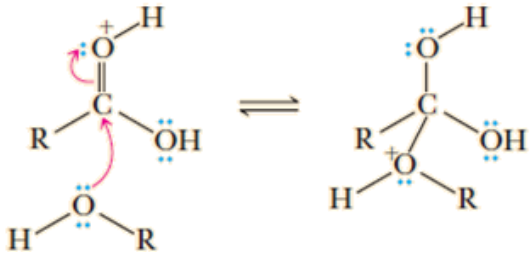
Ethanoic acid (Acetic acid) + **Ethanol (Ethyl alcohol)** ⇌ **Ethyl ethanoate (Ethyl acetate)** + H_2O

Reazione reversibile

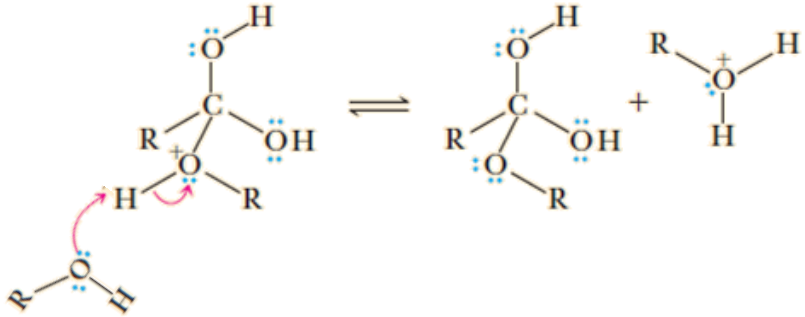
1° Stadio



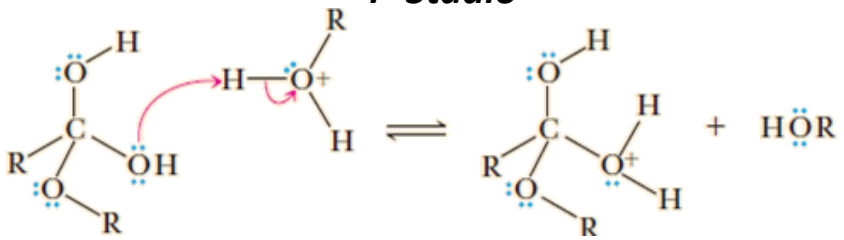
2° Stadio



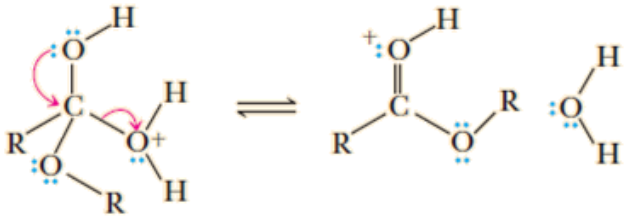
3° Stadio



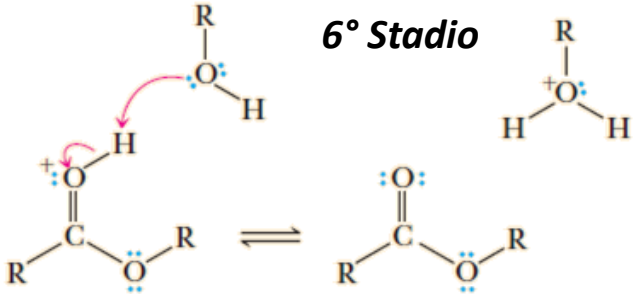
4° Stadio



5° Stadio



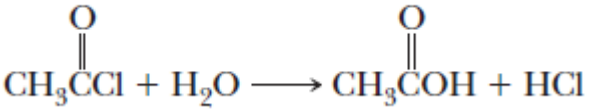
6° Stadio



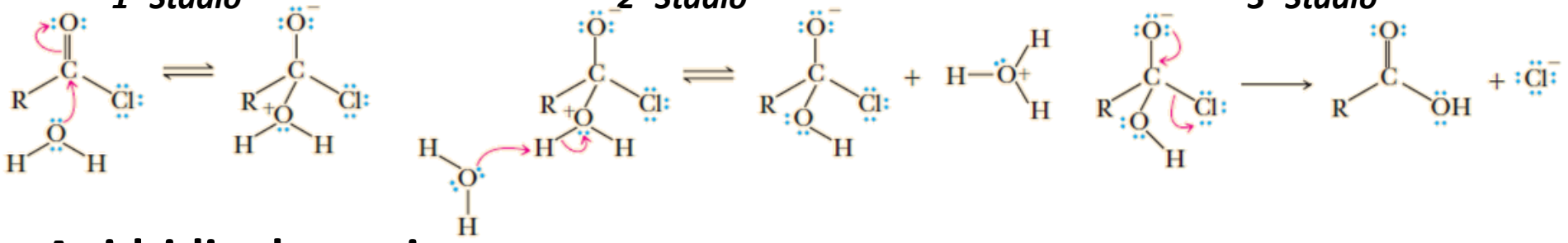
Idrolisi

Reazione di formazione di un acido carbossilico a partire da un suo derivato

Cloruri acilici

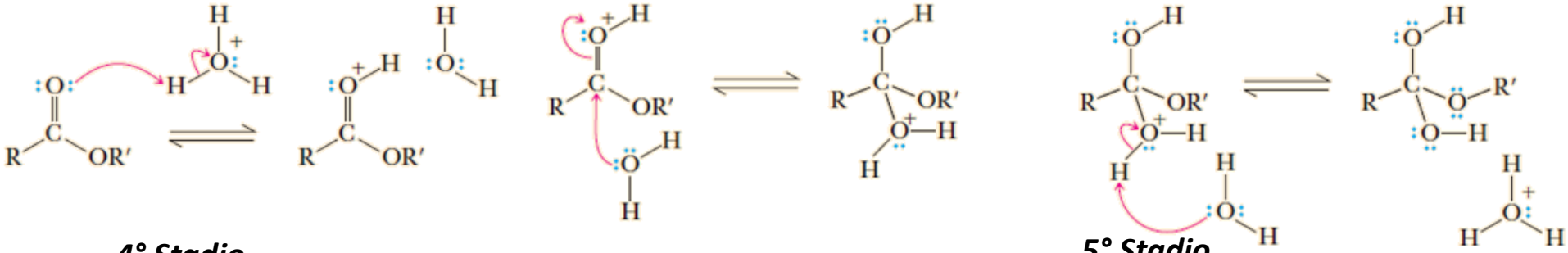


1° Stadio *2° Stadio* *3° Stadio*



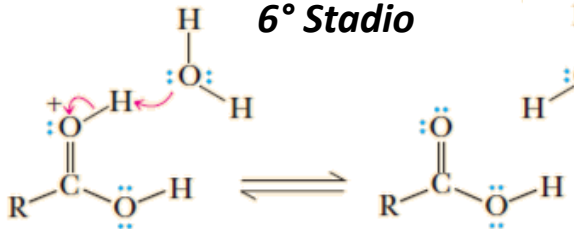
Anidridi ed esteri – catalisi acida

1° Stadio *2° Stadio* *3° Stadio*



4° Stadio *5° Stadio*

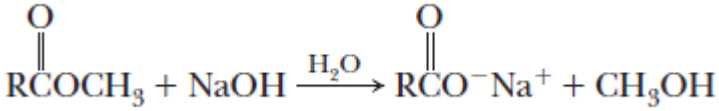
6° Stadio



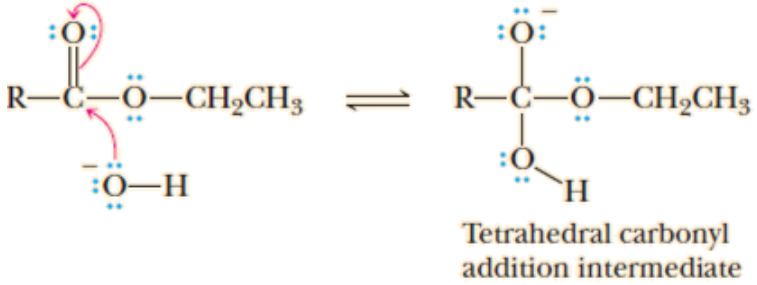
Idrolisi

Reazione di formazione di un acido carbossilico a partire da un suo derivato

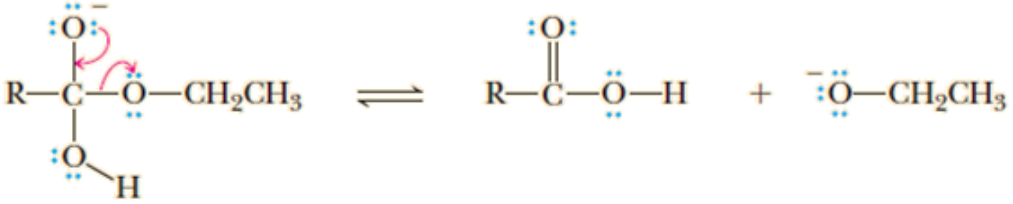
Esteri – catalisi basica: reazione di saponificazione



1° Stadio



2° Stadio

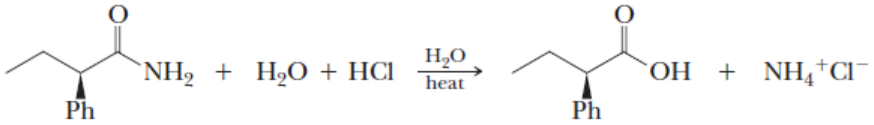


3° Stadio

- Acido catalitico, base stechiometrica
- Idrolisi acido-catalizzata reversibile, base-catalizzata irreversibile

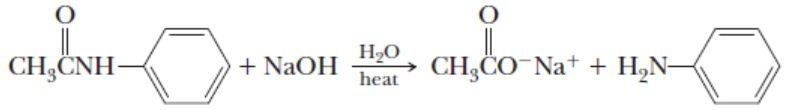
Idrolisi

Ammidi



(*R*)-2-Phenylbutanamide

(*R*)-2-Phenylbutanoic acid



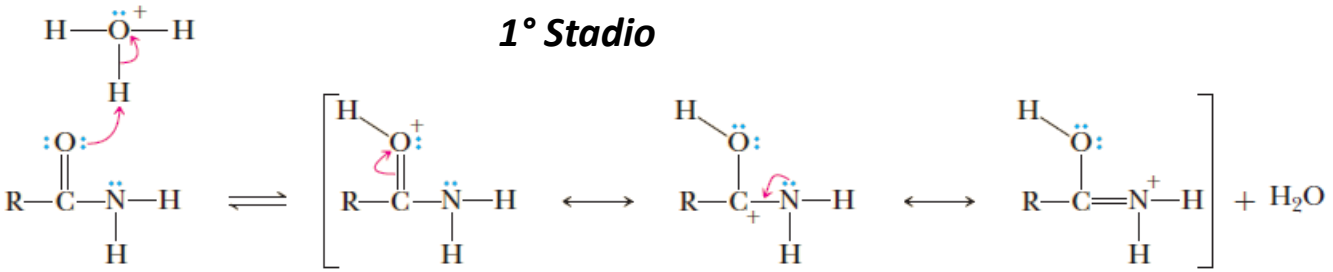
N-Phenylethanamide (*N*-Phenylacetamide, Acetanilide)

Sodium acetate

Aniline

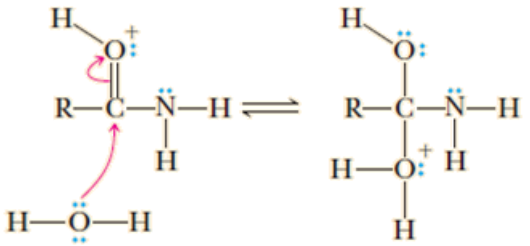
Catalisi acida

1° Stadio

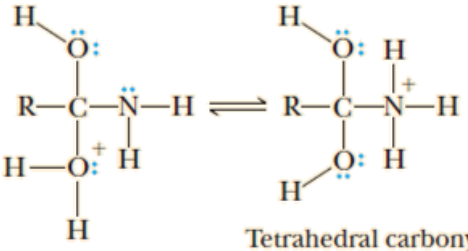


Cation stabilized by resonance delocalization

2° Stadio

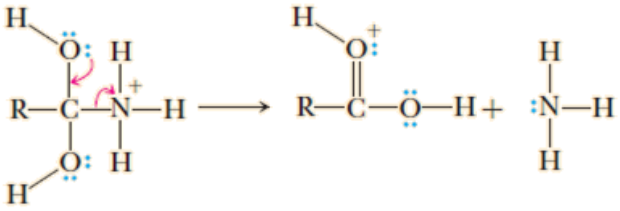


3° Stadio

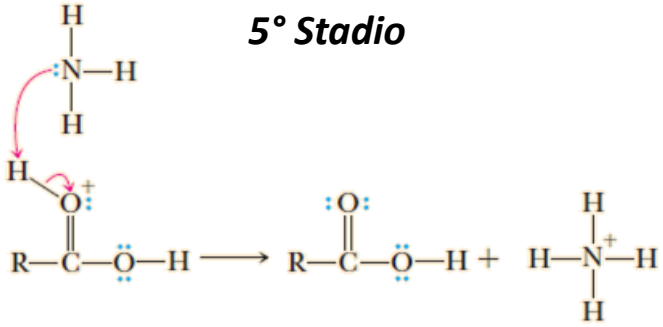


Tetrahedral carbonyl addition intermediate

4° Stadio

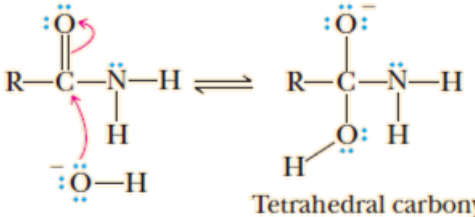


5° Stadio



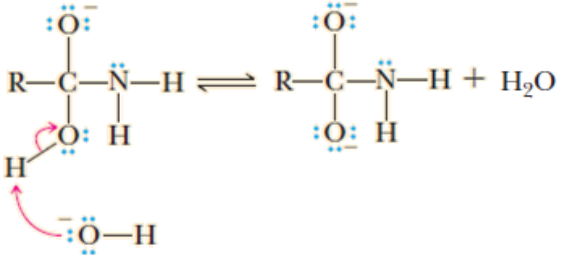
Catalisi basica

1° Stadio

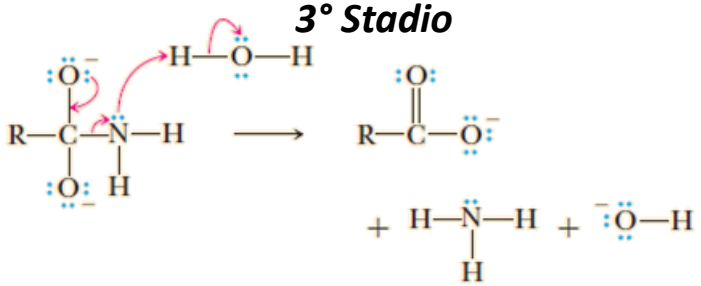


Tetrahedral carbonyl addition intermediate

2° Stadio



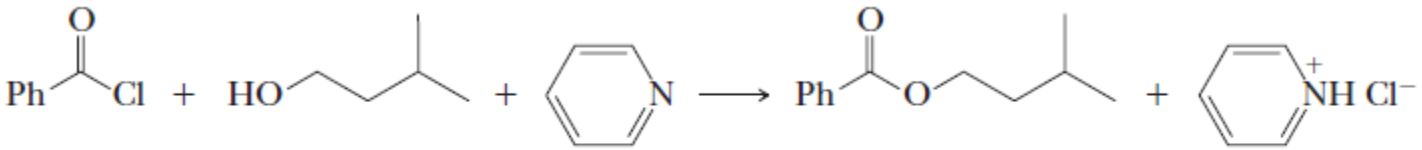
3° Stadio



Reazione con alcol

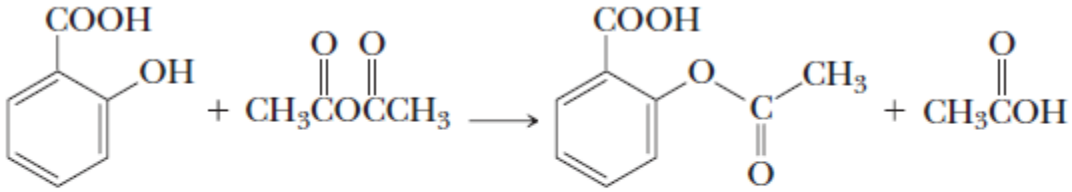
Reazione di formazione di un estere a partire da un derivato di un acido carbossilico

Cloruri acilici



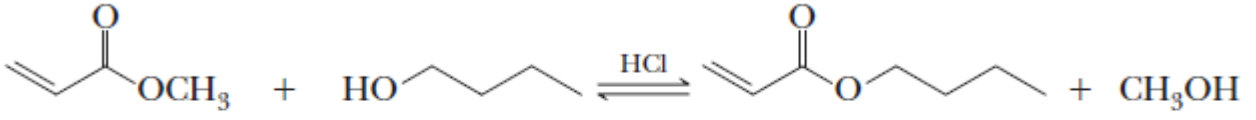
Benzoyl chloride + 3-Methyl-1-butanol (Isoamyl alcohol) + Pyridine → 3-Methylbutyl benzoate (Isoamyl benzoate) + Pyridinium chloride

Anidridi



2-Hydroxybenzoic acid (Salicylic acid) + Acetic anhydride → Acetylsalicylic acid (Aspirin) + Acetic acid

Esteri



Methyl propenoate (Methyl acrylate) (bp 81°C) + 1-Butanol (bp 117°C) ⇌ (HCl) Butyl propenoate (Butyl acrylate) (bp 147°C) + Methanol (bp 65°C)

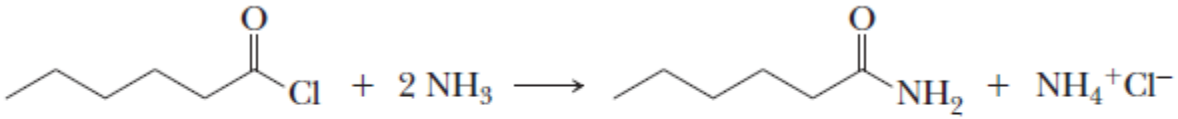
Transesterificazione

Le ammidi <u>non</u> reagiscono con gli alcoli

Reazione con ammoniaca e ammine

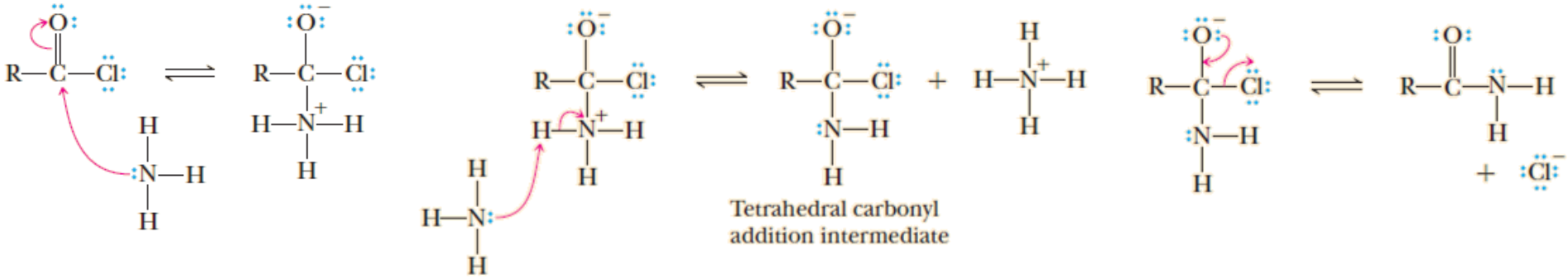
Reazione di formazione di un'ammide a partire da un derivato di un acido carbossilico

Cloruri acilici

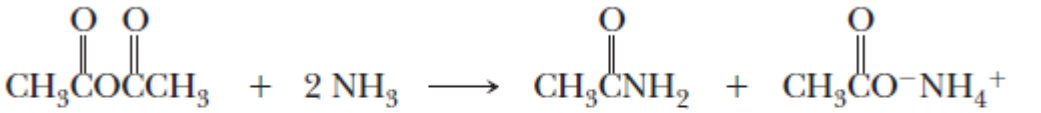


Hexanoyl chloride — Ammonia — Hexanamide — Ammonium chloride

1° Stadio ***2° Stadio*** ***3° Stadio***

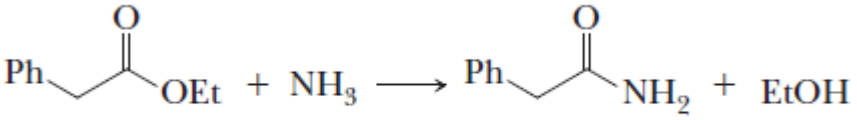


Anidridi



Acetic anhydride — Ammonia — Ethanamide (Acetamide) — Ammonium acetate

Esteri

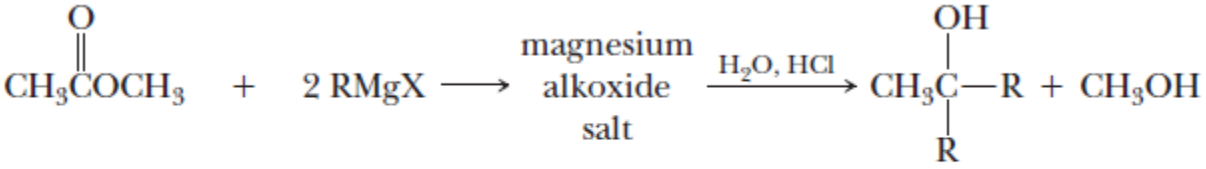


Ethyl phenylacetate — Phenylacetamide — Ethanol

Le ammidi <u>non</u> reagiscono con ammoniaca e ammine

Reazione di esteri con reattivi di Grignard

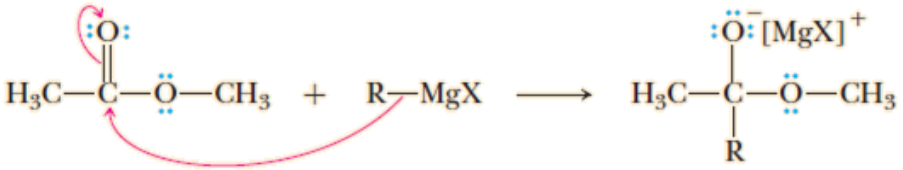
Reazione di formazione di un alcol a partire da un estere



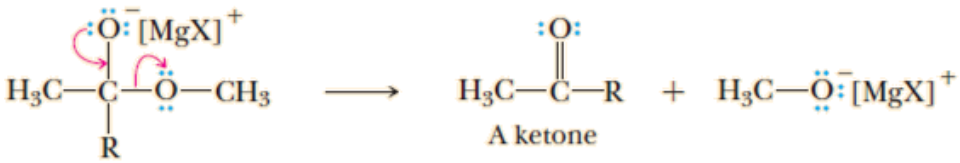
An ester of any acid other than formic acid

A 3° alcohol

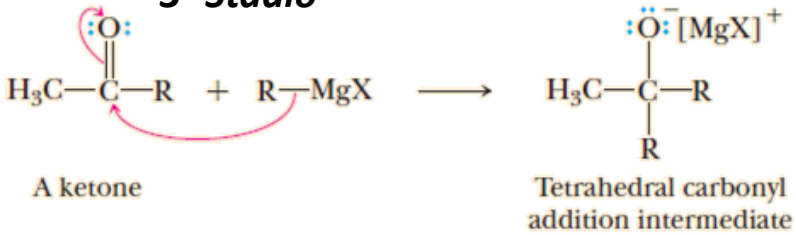
1° Stadio



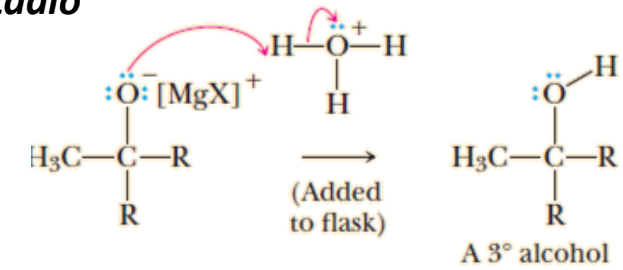
2° Stadio



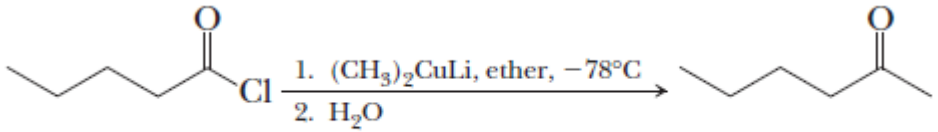
3° Stadio



4° Stadio



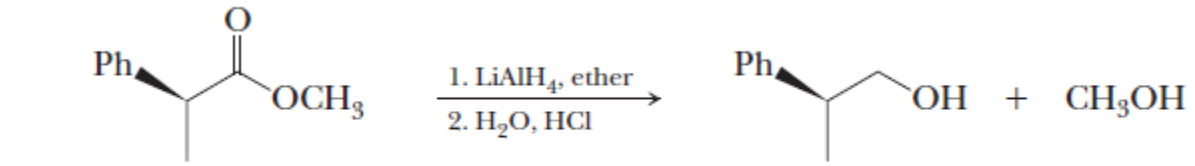
N.B. Per ottenere il chetone bisogna utilizzare un organocuprato



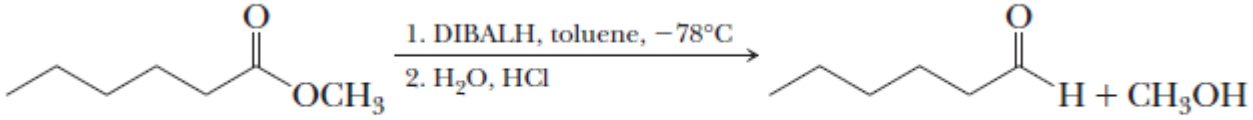
Pentanoyl chloride **2-Hexanone**

Riduzione

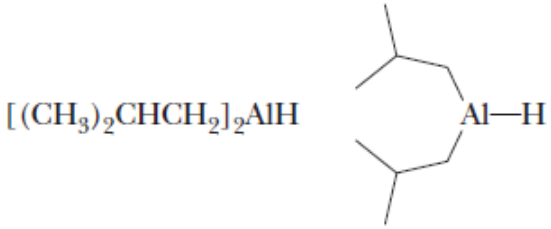
Esteri



Methyl(*S*)-2-phenylpropanoate (*S*)-2-Phenyl-1-propanol Methanol

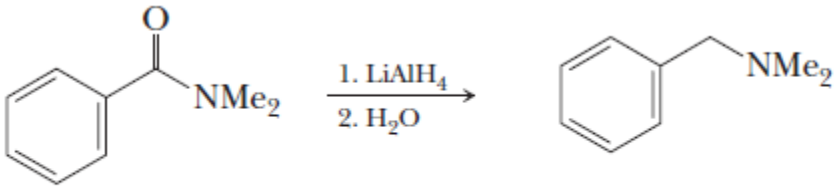


Methyl hexanoate Hexanal



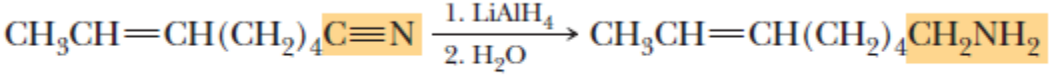
Diisobutylaluminum hydride (DIBALH)

Ammidi



N,*N*-Dimethylbenzamide *N*,*N*-Dimethylbenzylamine

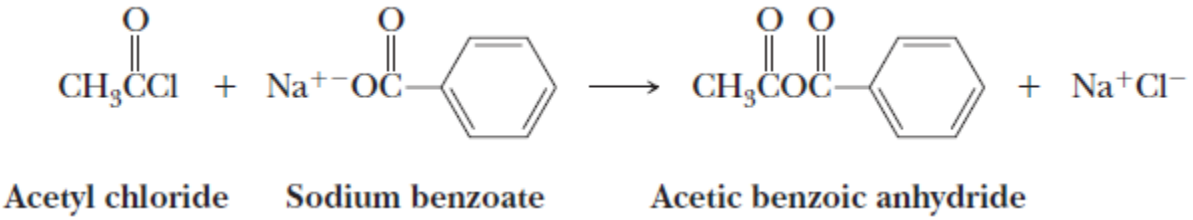
Nitrili



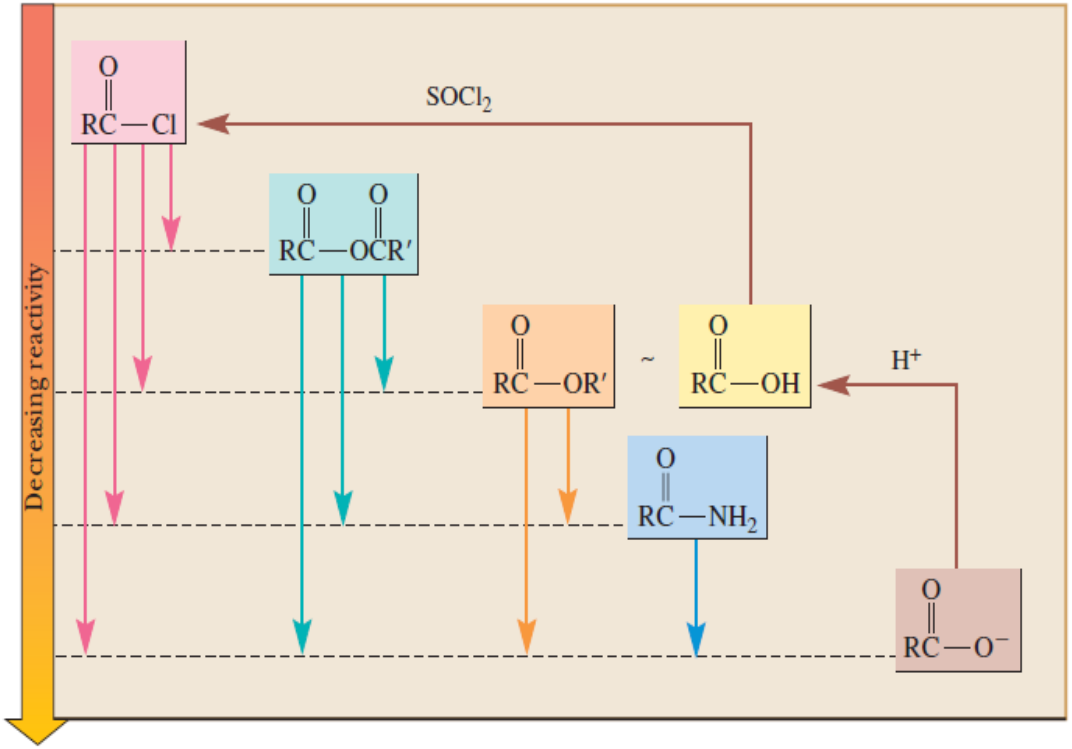
6-Octenenitrile 6-Octen-1-amine

Reazione tra cloruri acilici e carbossilati

Reazione di formazione di un'anidride mista

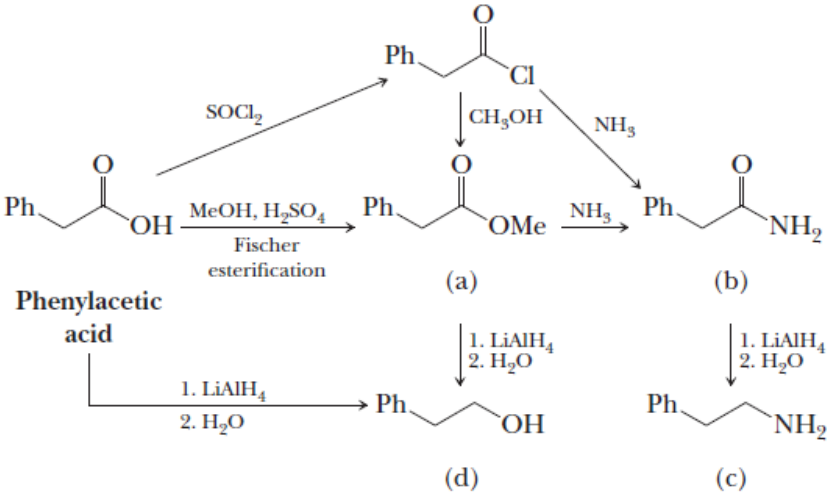


Interconversione di gruppi funzionali



Esempio

Conversione dell'acido fenilacetico



Esercizi riassuntivi

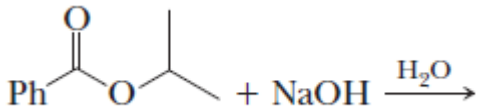
Esercizio

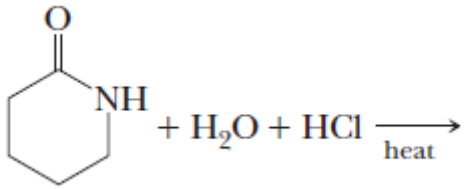
Scrivere le formule di struttura dei seguenti composti:

a) 3-metilbutanoato di metile **b)** 3-ossobutanoato di etile **c)** esandiammide **d)** anidride fenilacetica

Esercizio

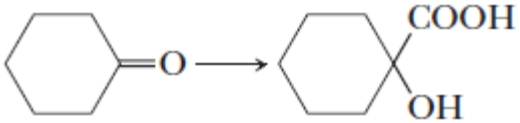
Completare e bilanciare le seguenti reazioni di idrolisi, mostrando tutti i prodotti che si formano



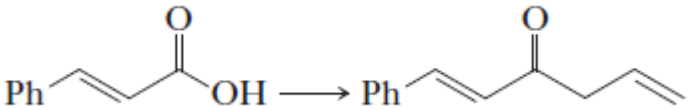


Esercizio

Mostrare come effettuare le seguenti conversioni



Suggerimento: effettuare più stadi ed utilizzare in uno degli stadi l'idrolisi di un gruppo ciano



Suggerimento: effettuare più stadi

Esercizio

Completare le seguenti reazioni