# QFL- 0342 – Reatividade de Compostos Orgânicos

## *4. Adição Eliminação*

Prof. Dr. Daniel Nopper Silva Rodrigues

# Tópicos da Aula

A) Literatura recomendada.

B) Princípios.
- a) Compostos carboxílicos.
- b) Reação.
- c) Mecanismo geral.
  - Grupo de partida.
- d) Reatividade relativa.
- e) O grupo de partida sob a ótica do $pK_A$.

C) Hidrólise.
- a) Mecanismo.
  - Meio ácido.
  - Meio Alcalino.
- b) Saponificação.

# Tópicos da Aula

D) Esterificação
- a) Mecanismo.
  - - Catálise ácida.
- b) A partir de cloretos de ácido.
- c) Trans-esterificação.

E) Preparação de Cloretos de ácido.

F) Preparação de Anidridos

G) Formação de amida
- a) Reações.
- b) Mecanismo.

# Tópicos da Aula

H) Ácido carboxílico
   a) Formação via de nitrilas.
   b) Descarboxilação.

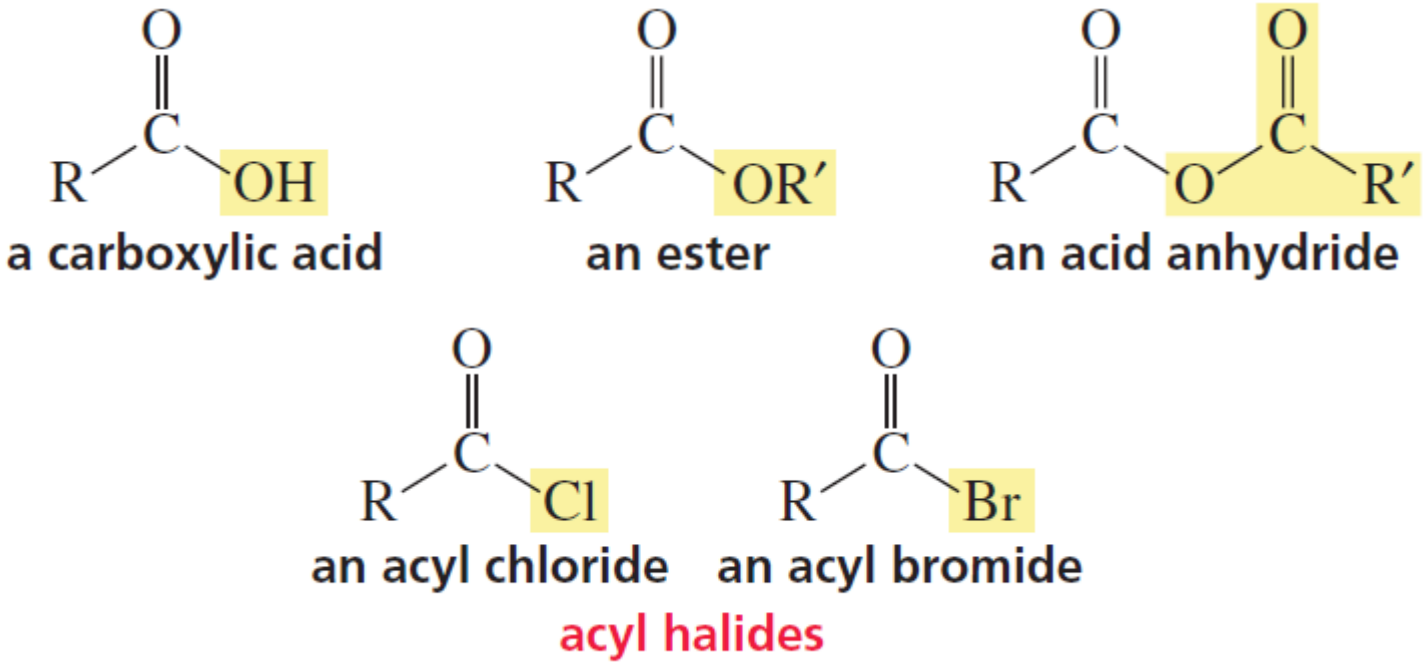
I) Resumo.

# Literatura recomendada

- *Organic Chemistry:* J. Clayden, N. Greeves, S. Warren, P. Wothers. (**Capítulos XII**)
- *Organic Chemistry:* P. Bruice : (**Capítulo XVII**)
- *Organic Chemistry:* J. McMurray : (**Capítulo XX e XXI**)

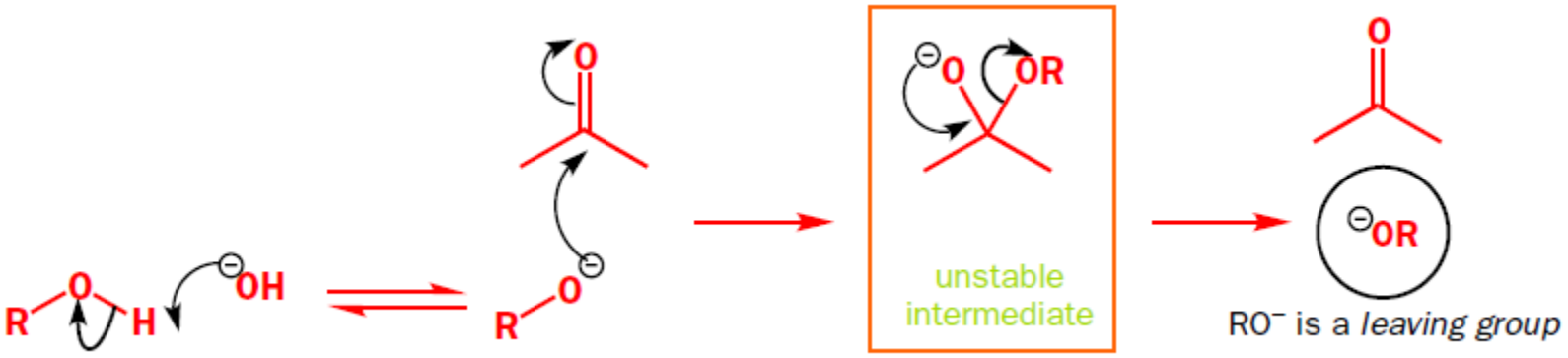
# Princípios

## Compostos carboxílicos



# Princípios

## A reação



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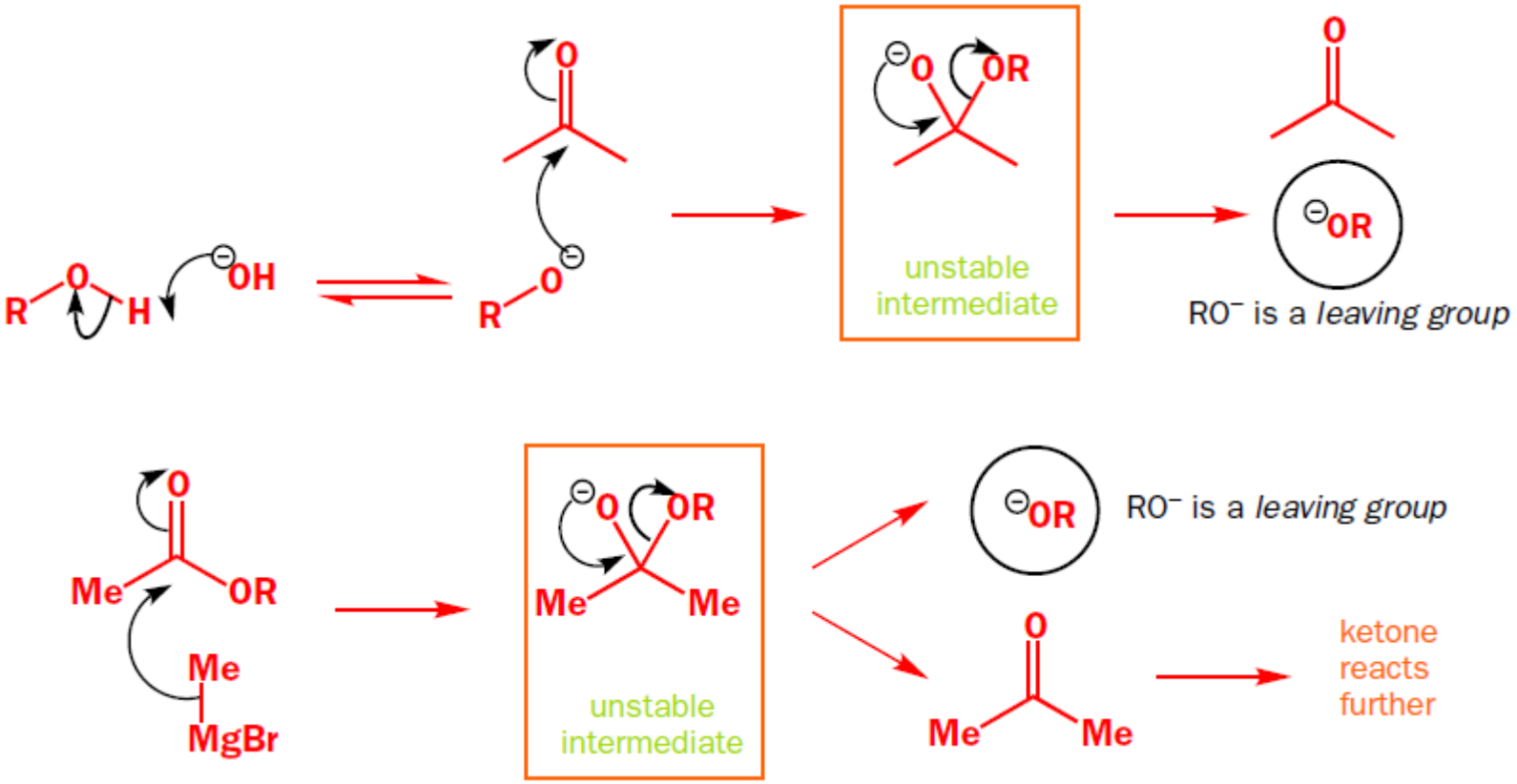

# Princípios

## Mecanismo geral

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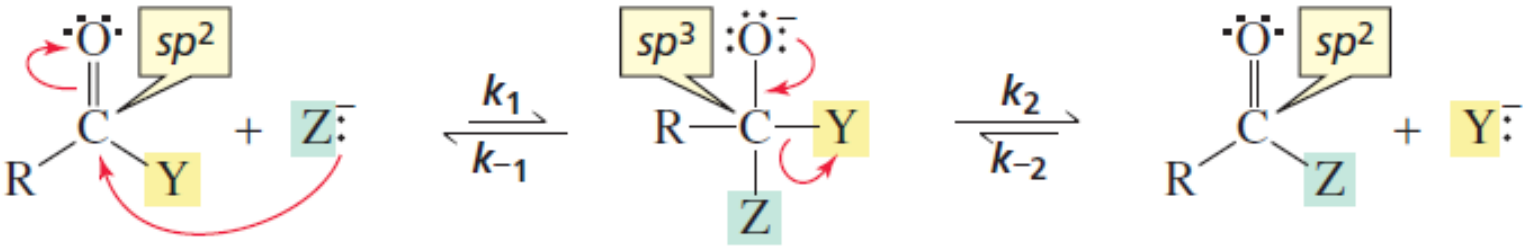
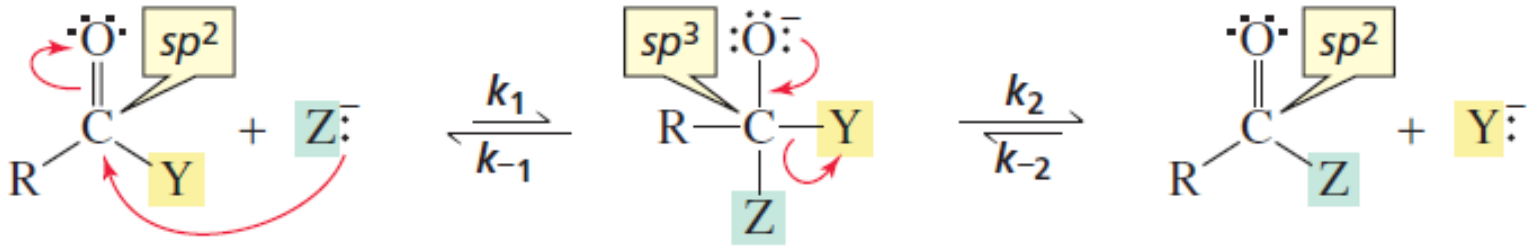
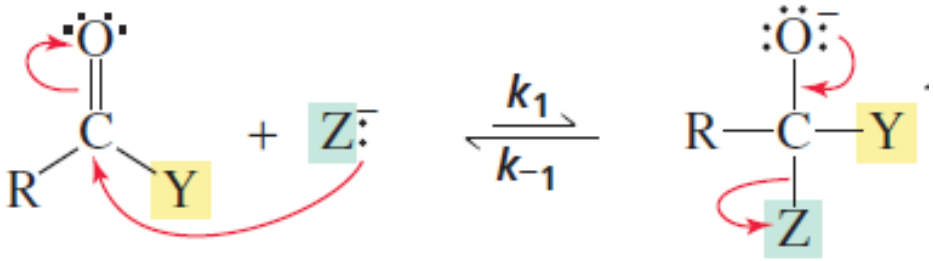



a tetrahedral intermediate

# Princípios

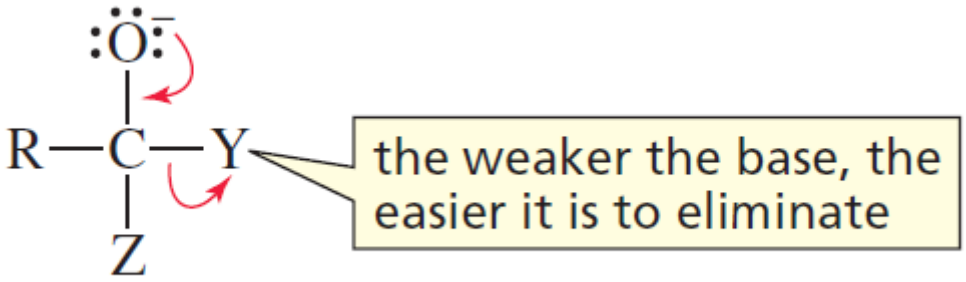
## Mecanismo geral



## O Grupo de partida

*Grupos de partida são os grupos que, ao serem removidos do intermediário tetraédrico recuperam a carbonila levando ao produto mais estável possível.*



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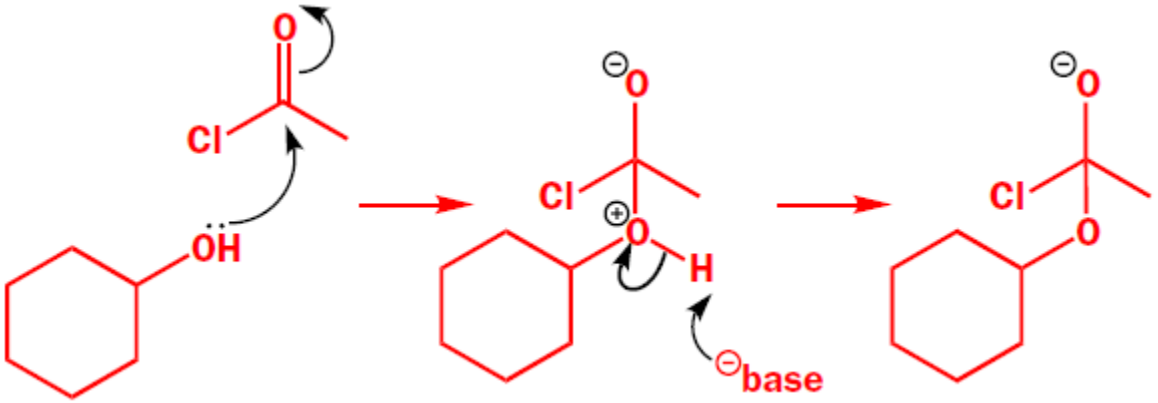

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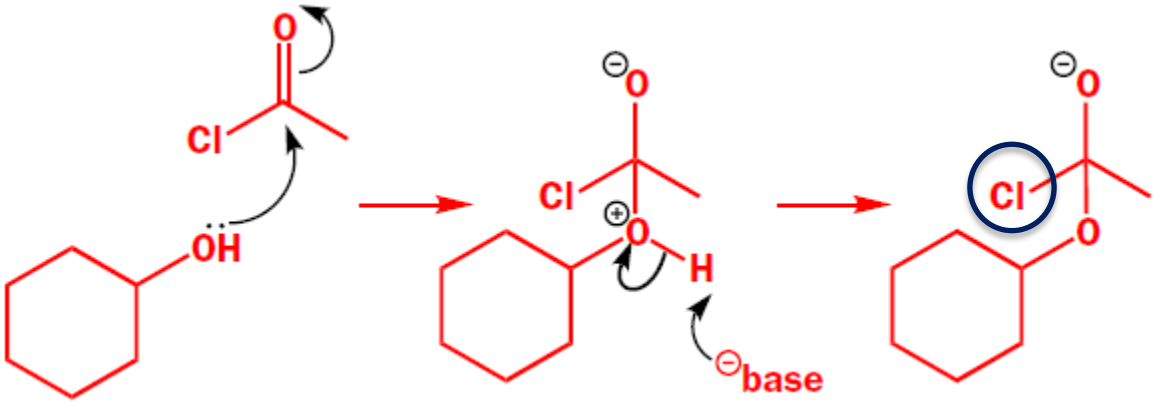

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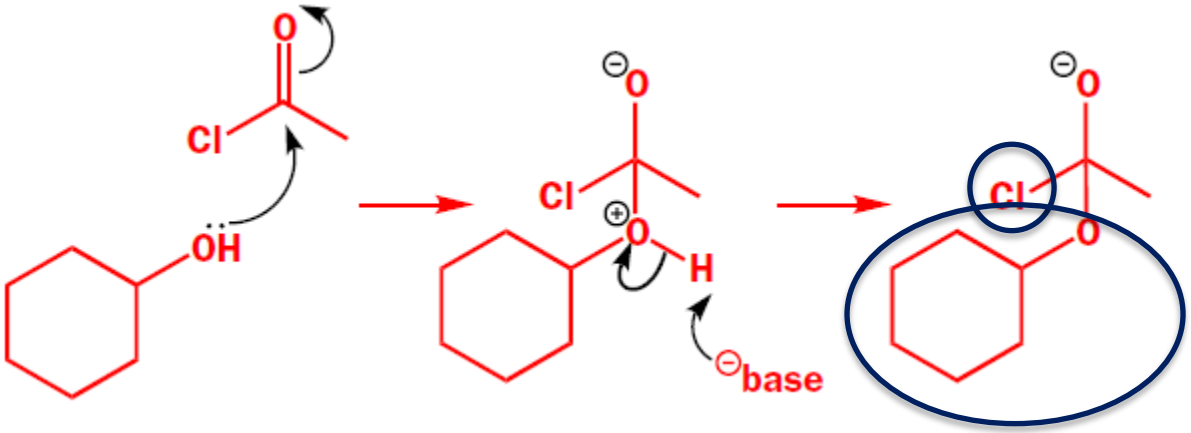

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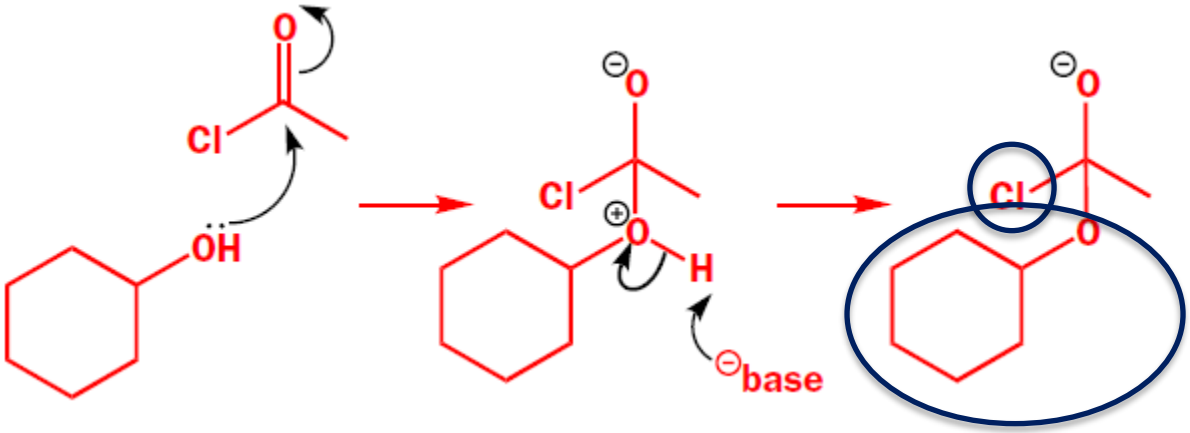


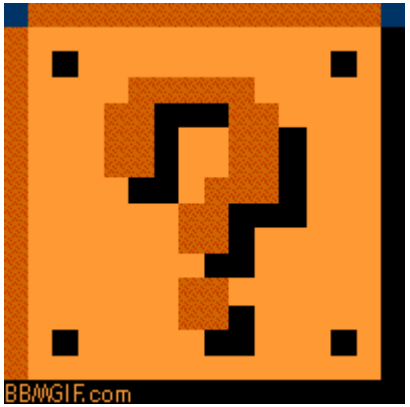

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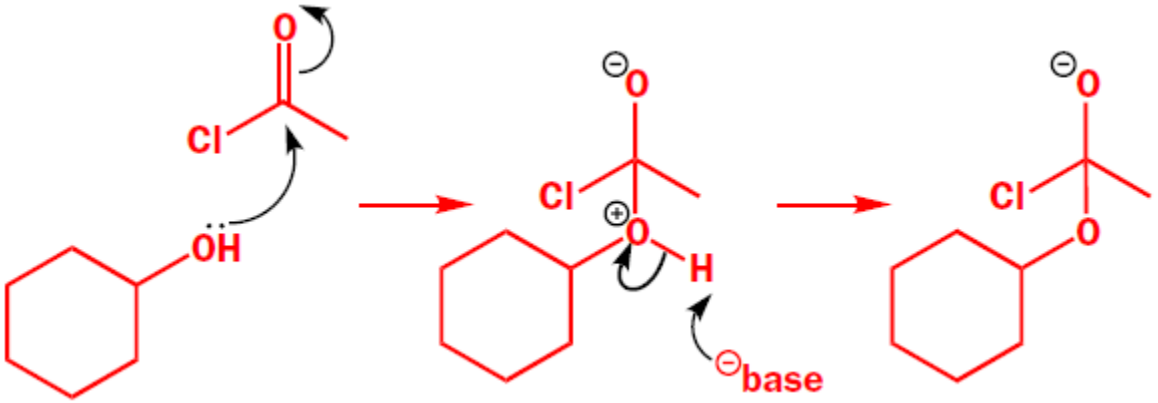


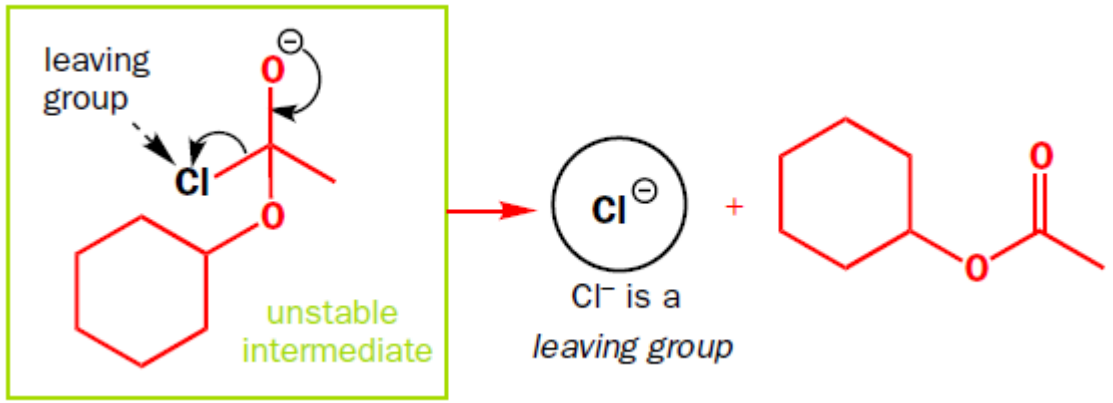

# Princípios

## Reatividade relativa

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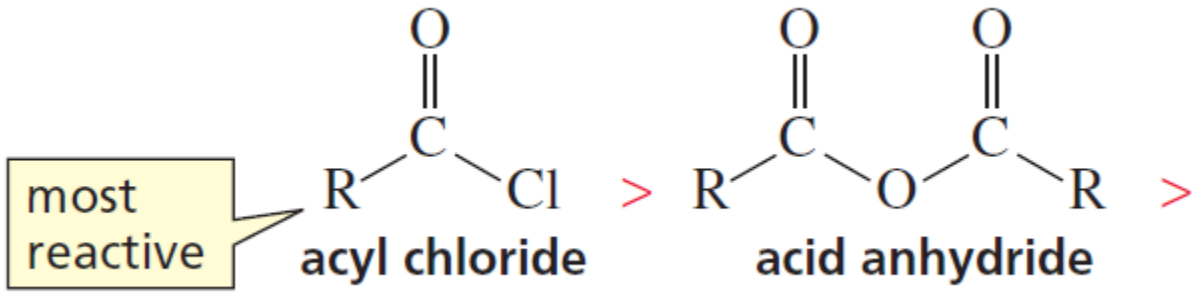

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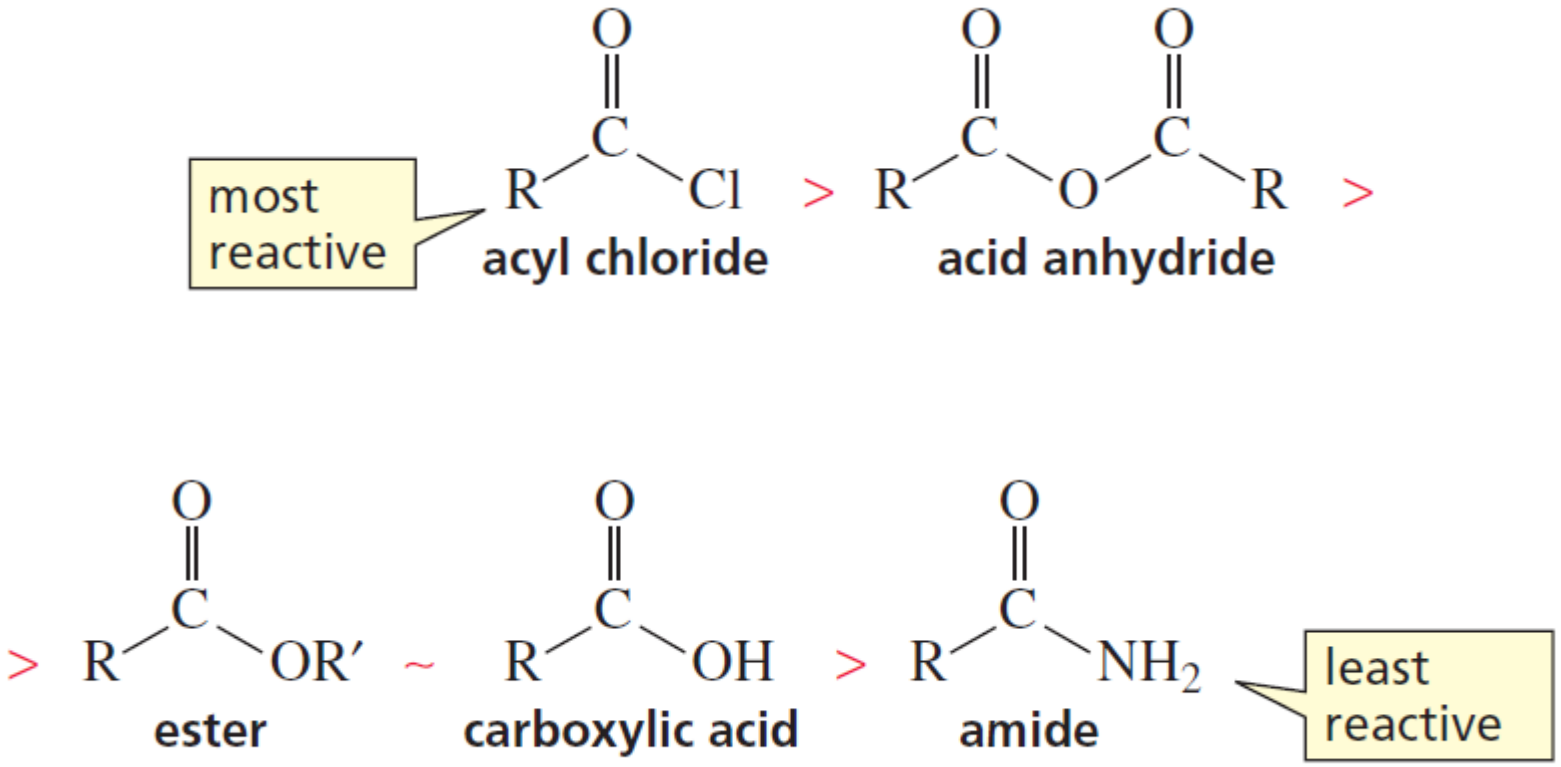

# Princípios

## Grupo de partida sob a ótica do $pK_A$

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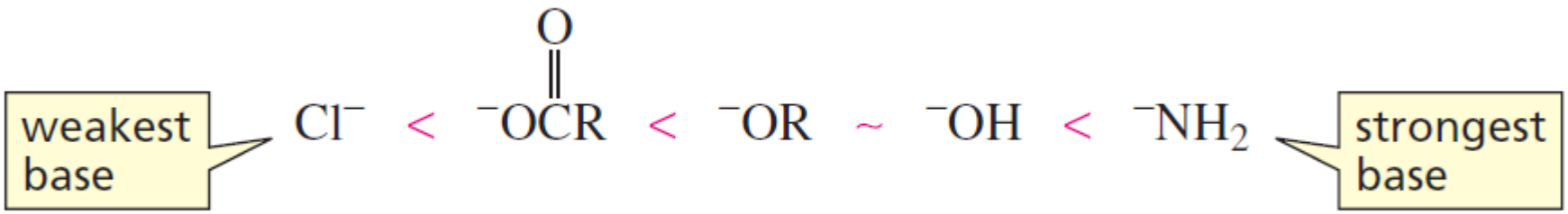

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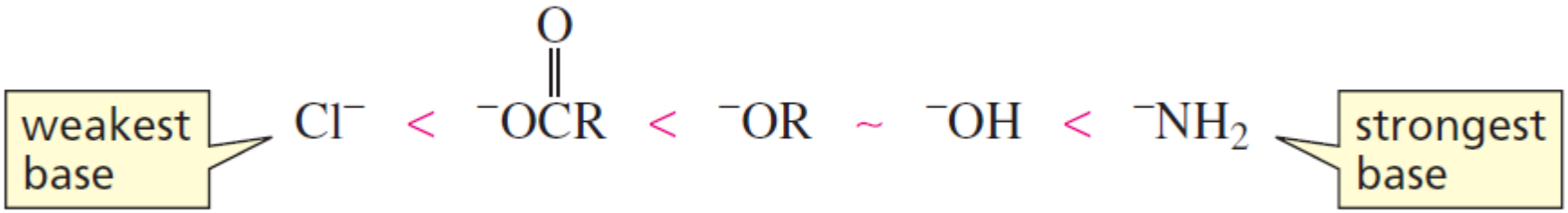


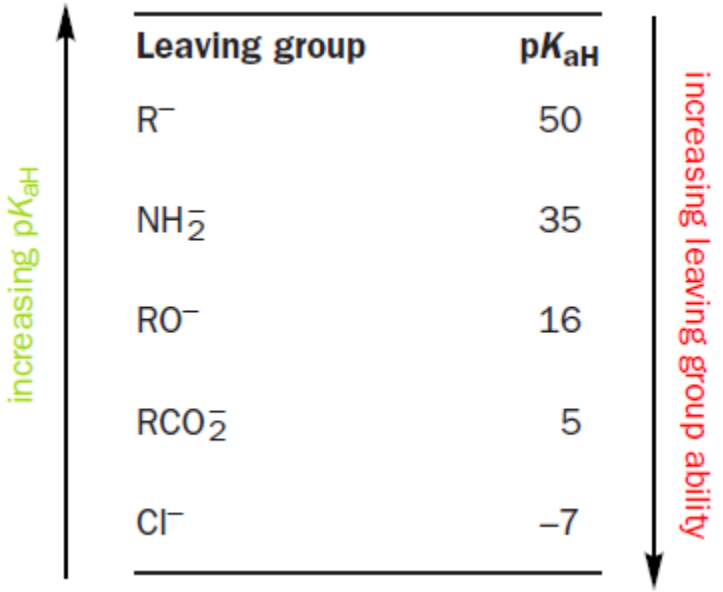

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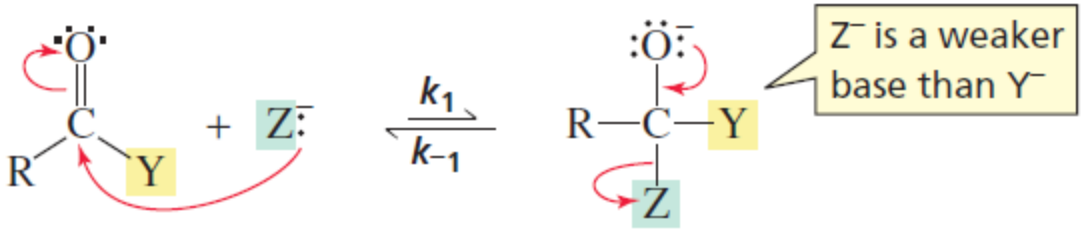

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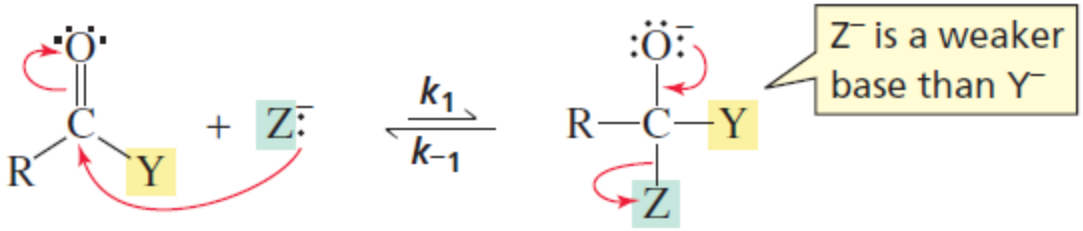


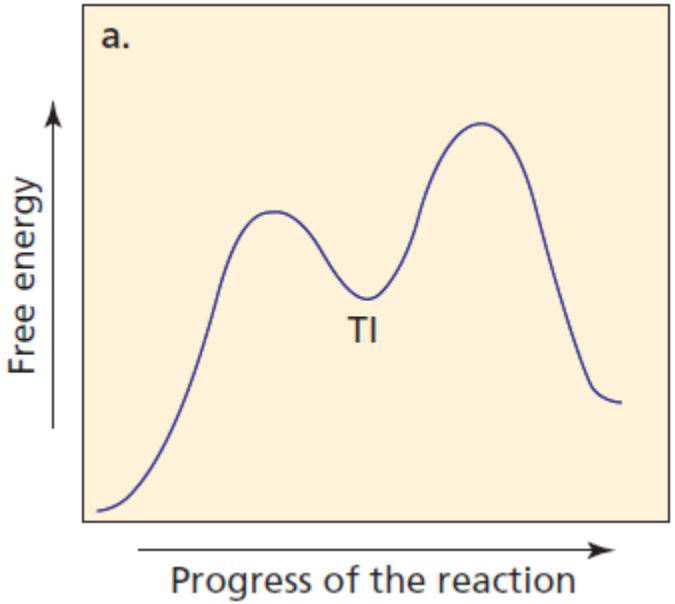

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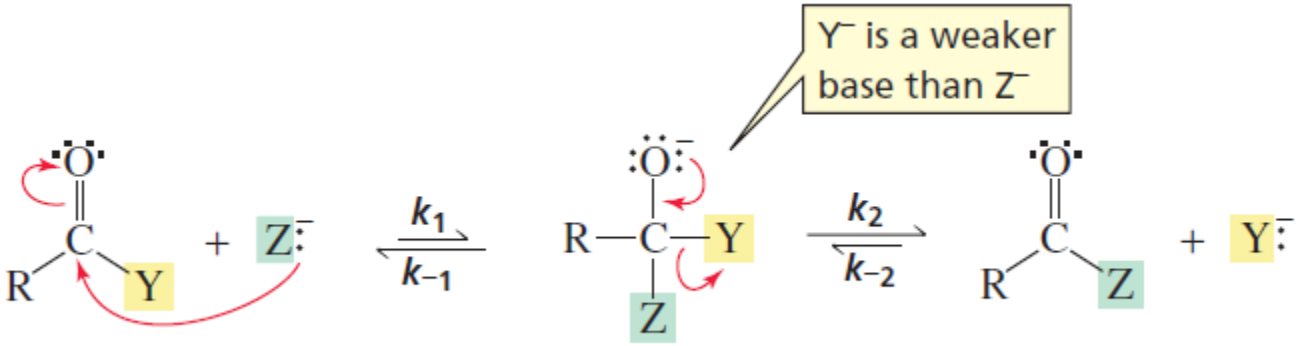

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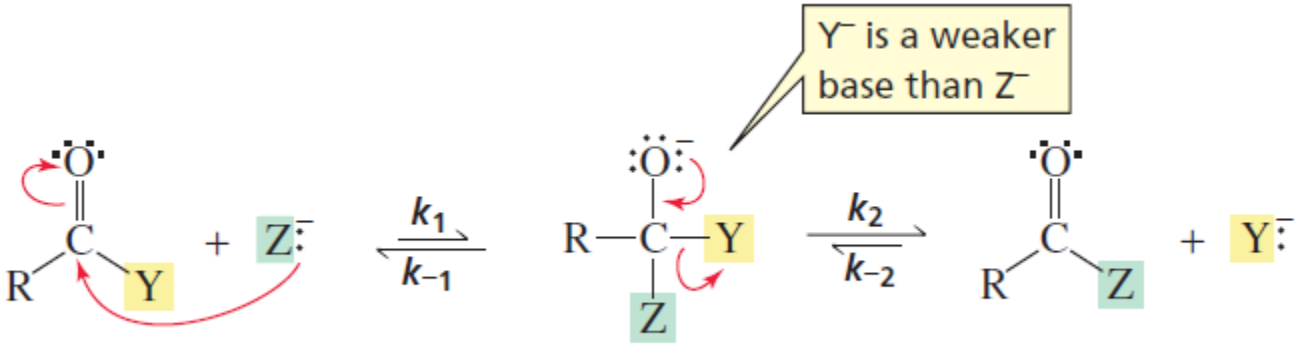


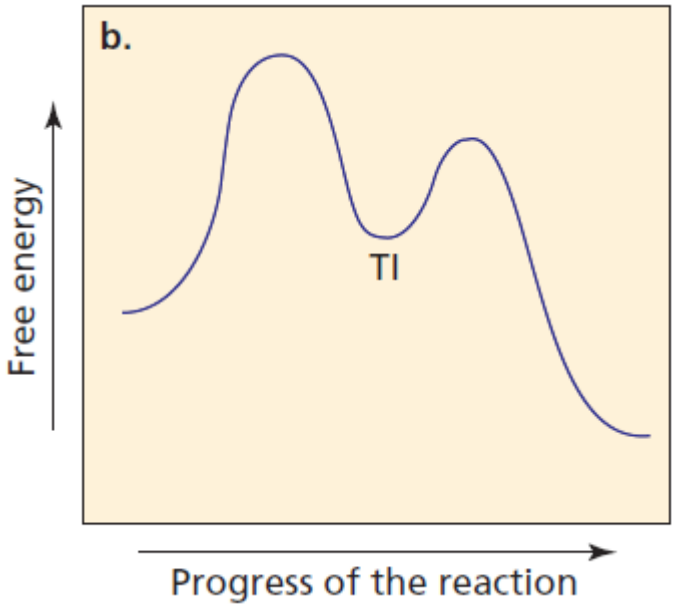

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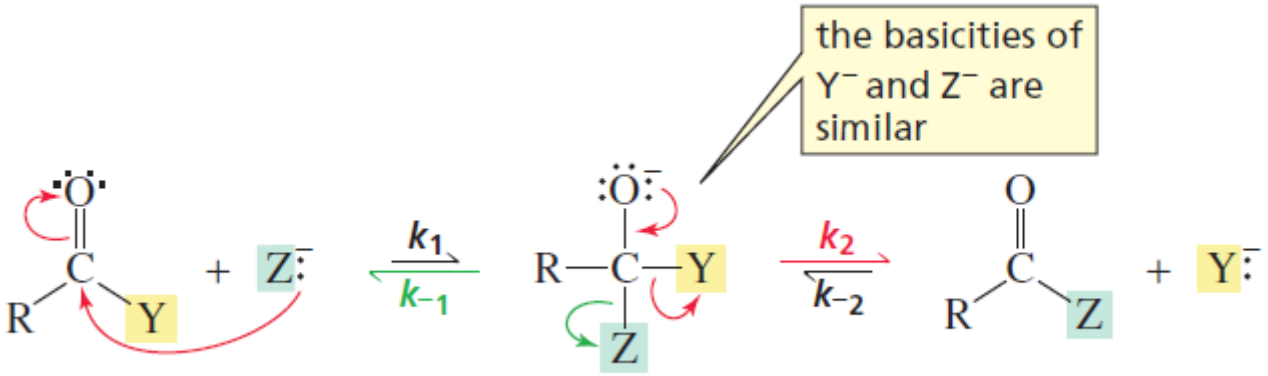

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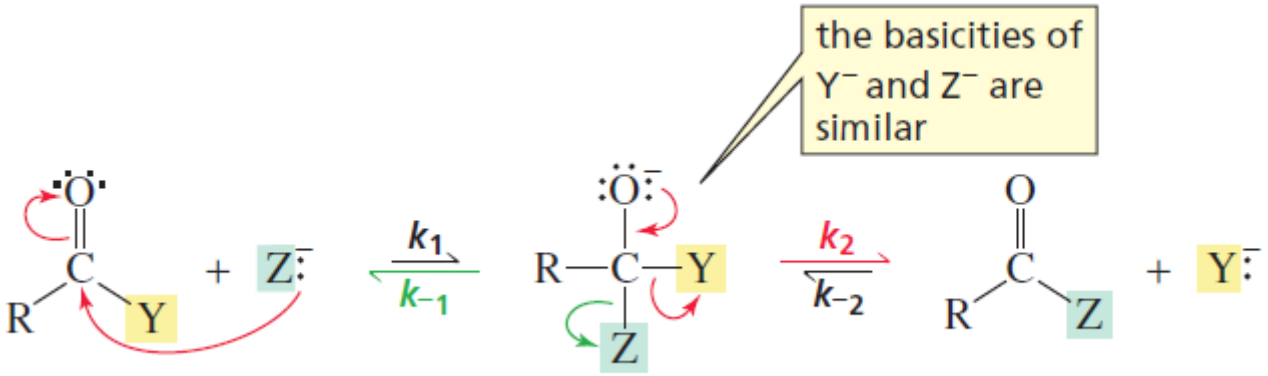


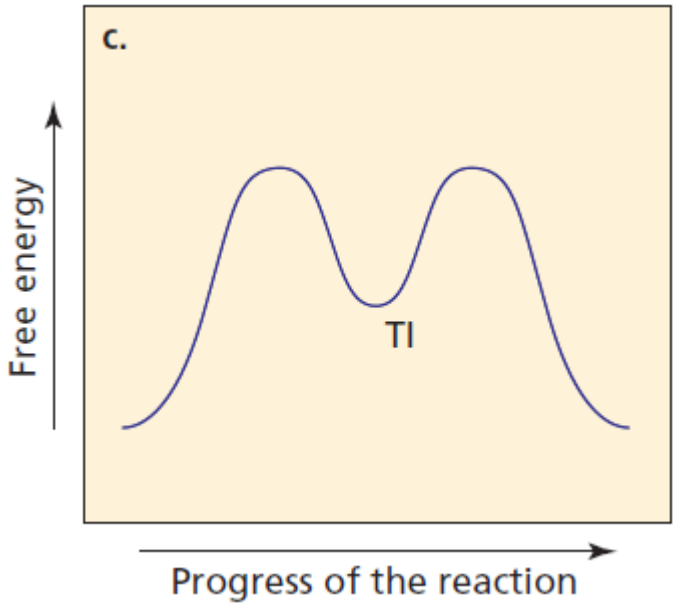

# Hidrólise

## Mecanismo

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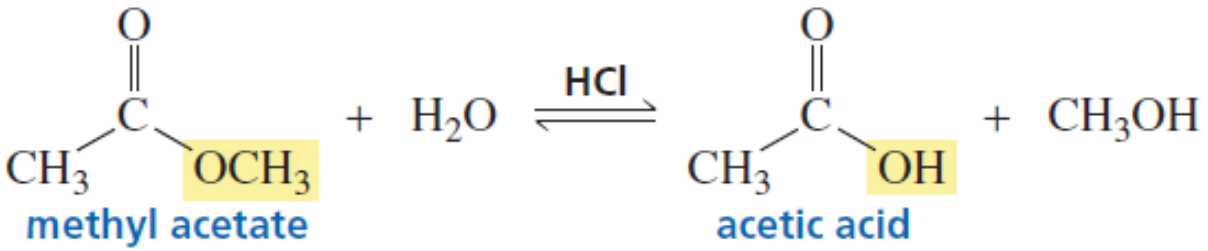

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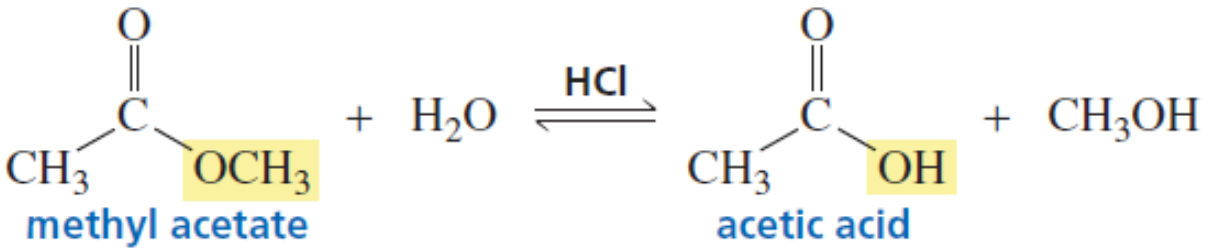
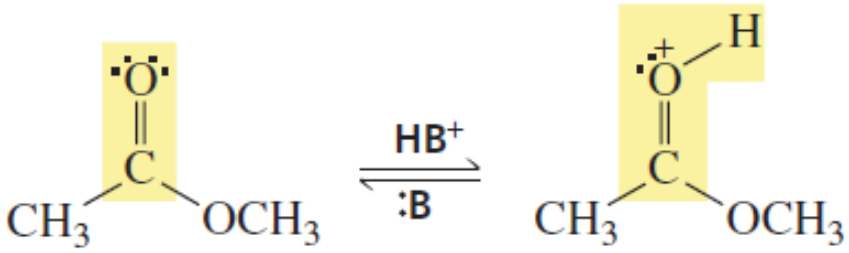
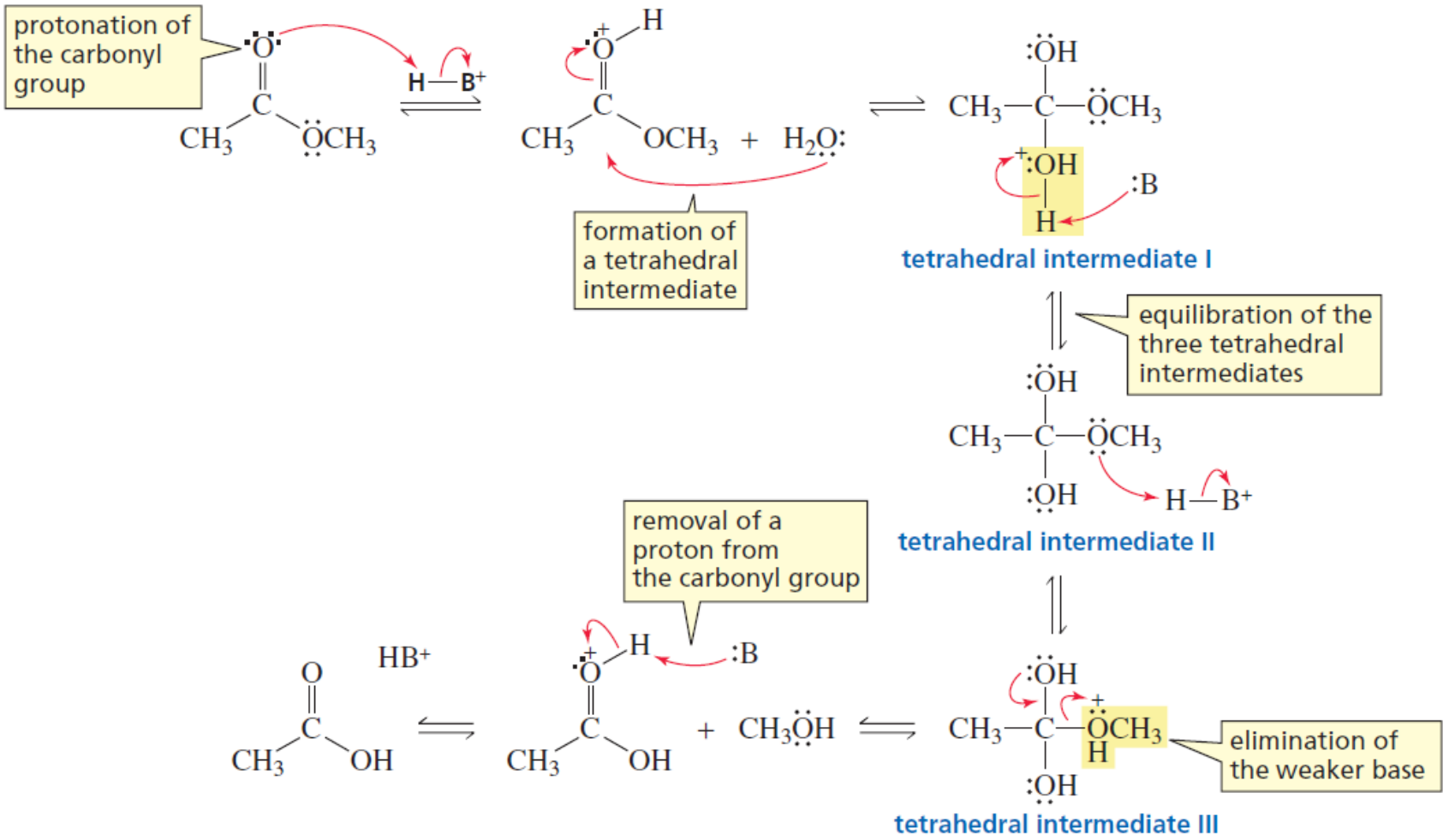


# Hidrólise

## Meio ácido



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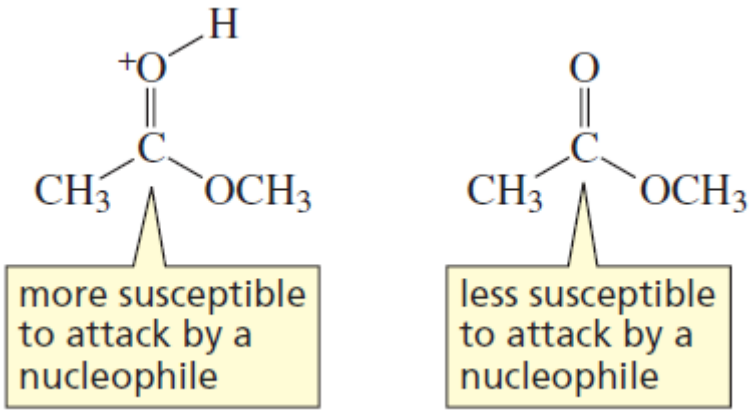

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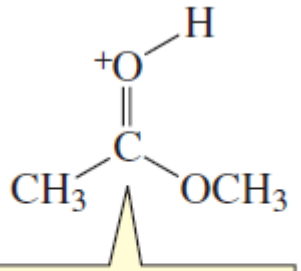
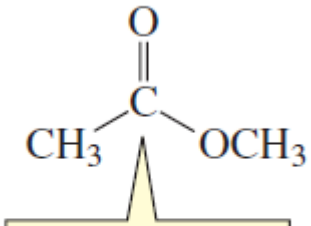



more susceptible to attack by a nucleophile

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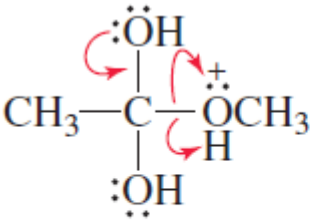
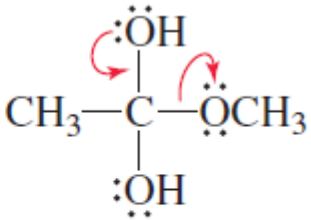


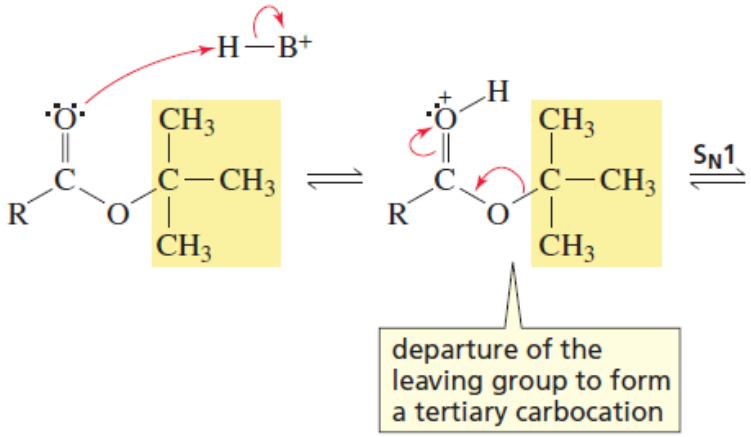

tetrahedral intermediate in acid-catalyzed ester hydrolysis




tetrahedral intermediate in uncatalyzed ester hydrolysis

# Hidrólise

## Meio ácido



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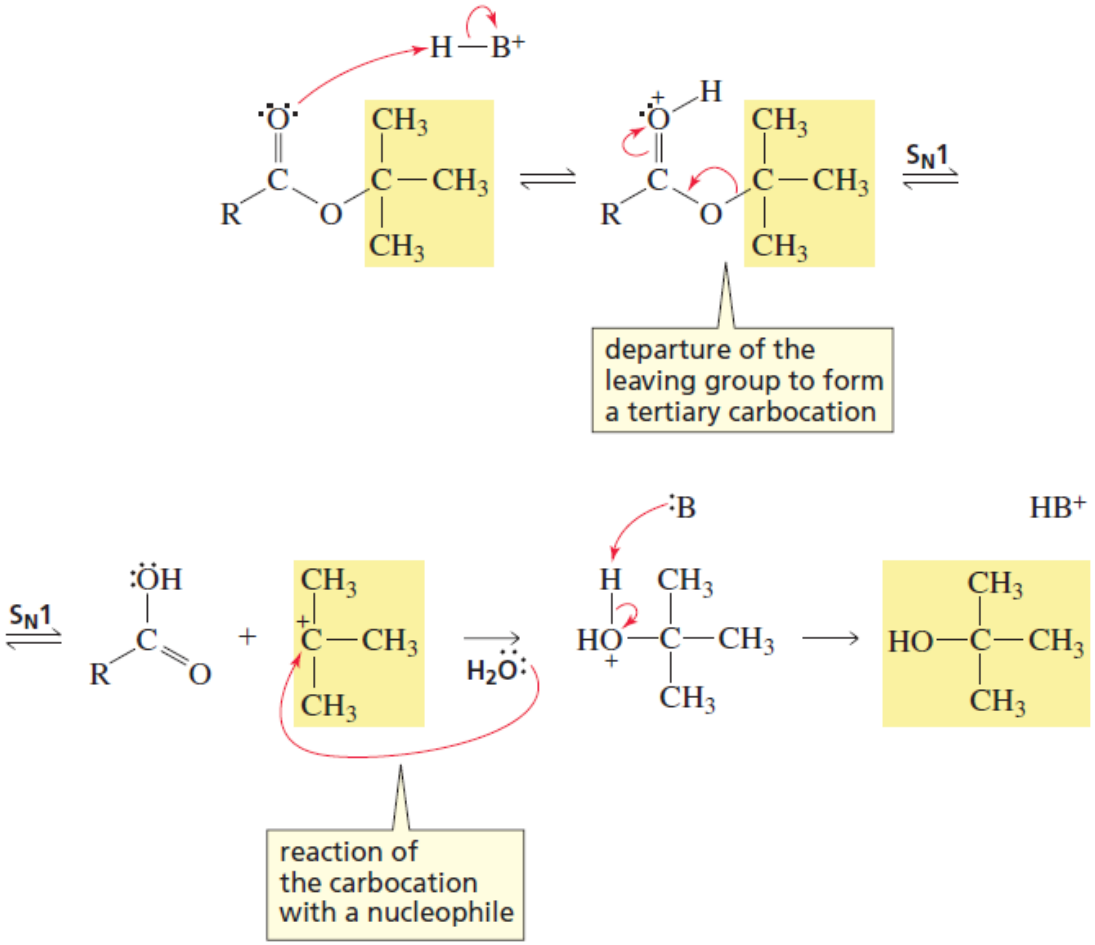

# Hidrólise

## Meio Alcalino

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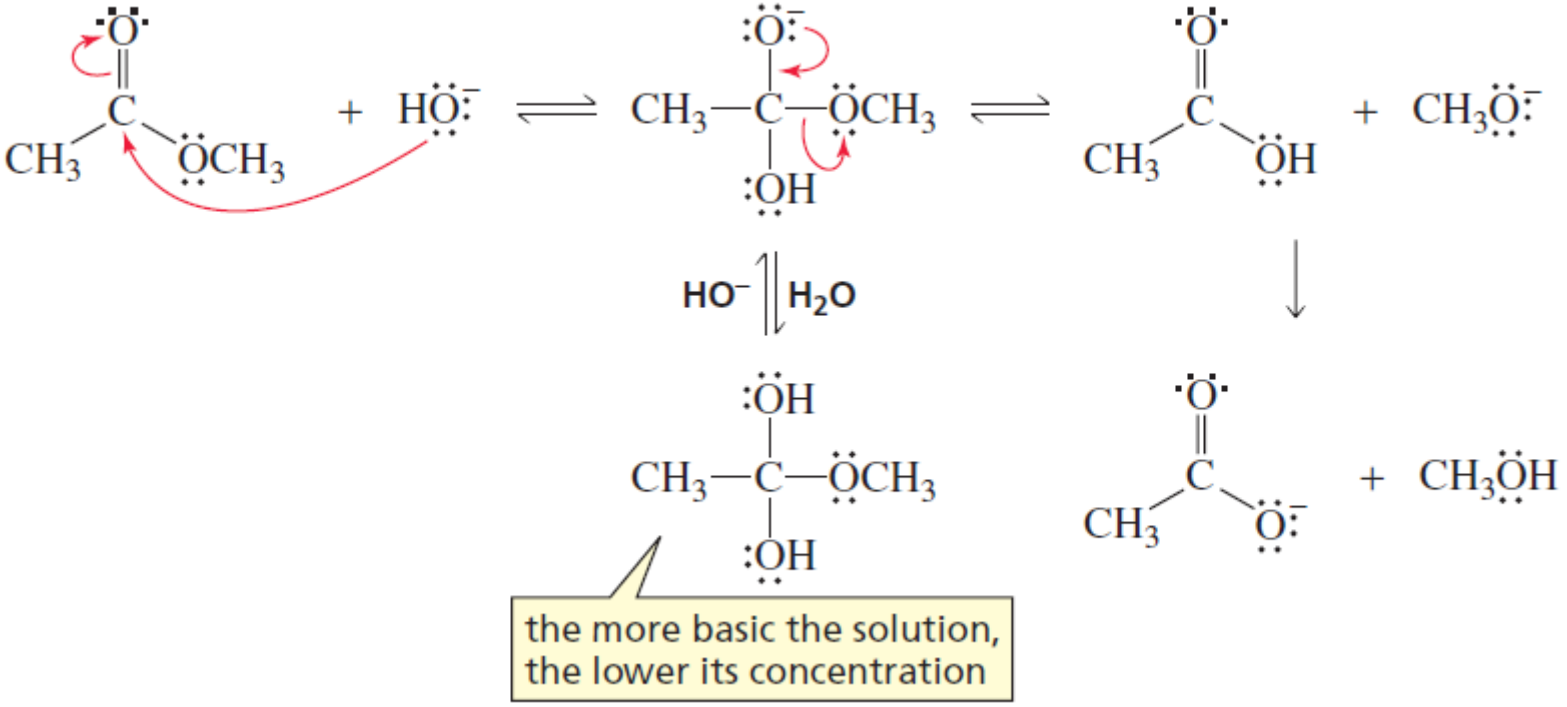

# Hidrólise

## Saponificação

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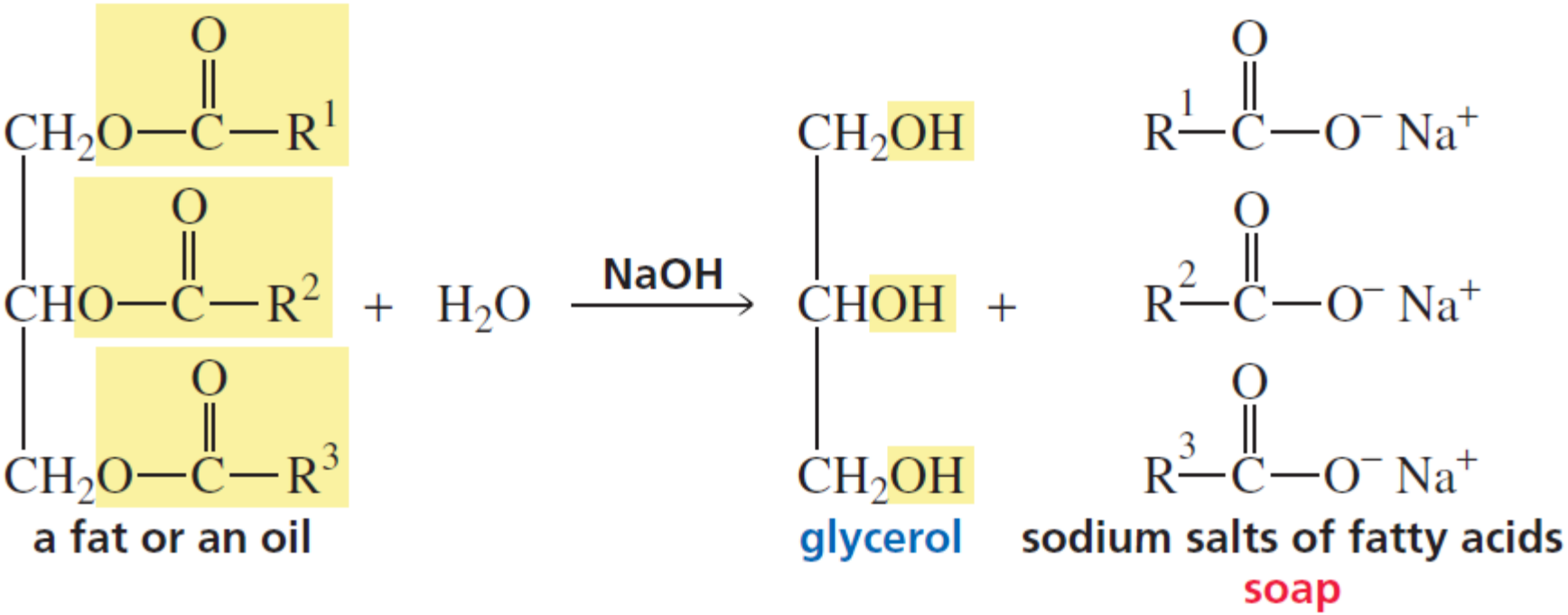

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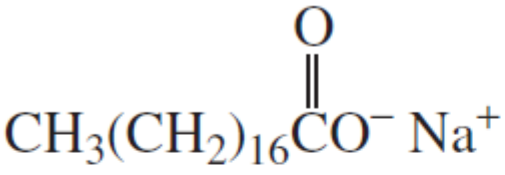
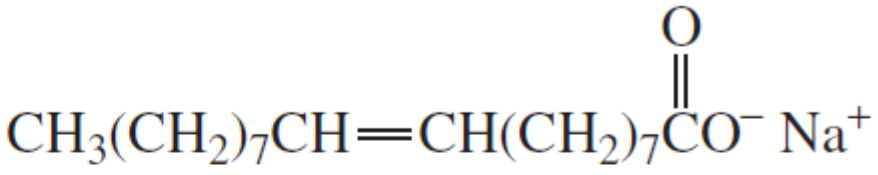
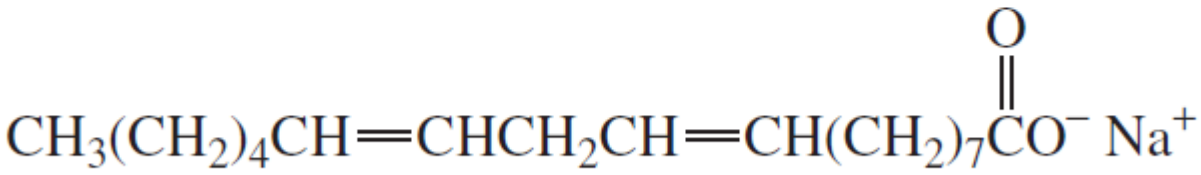



sodium stearate




sodium oleate




sodium linoleate

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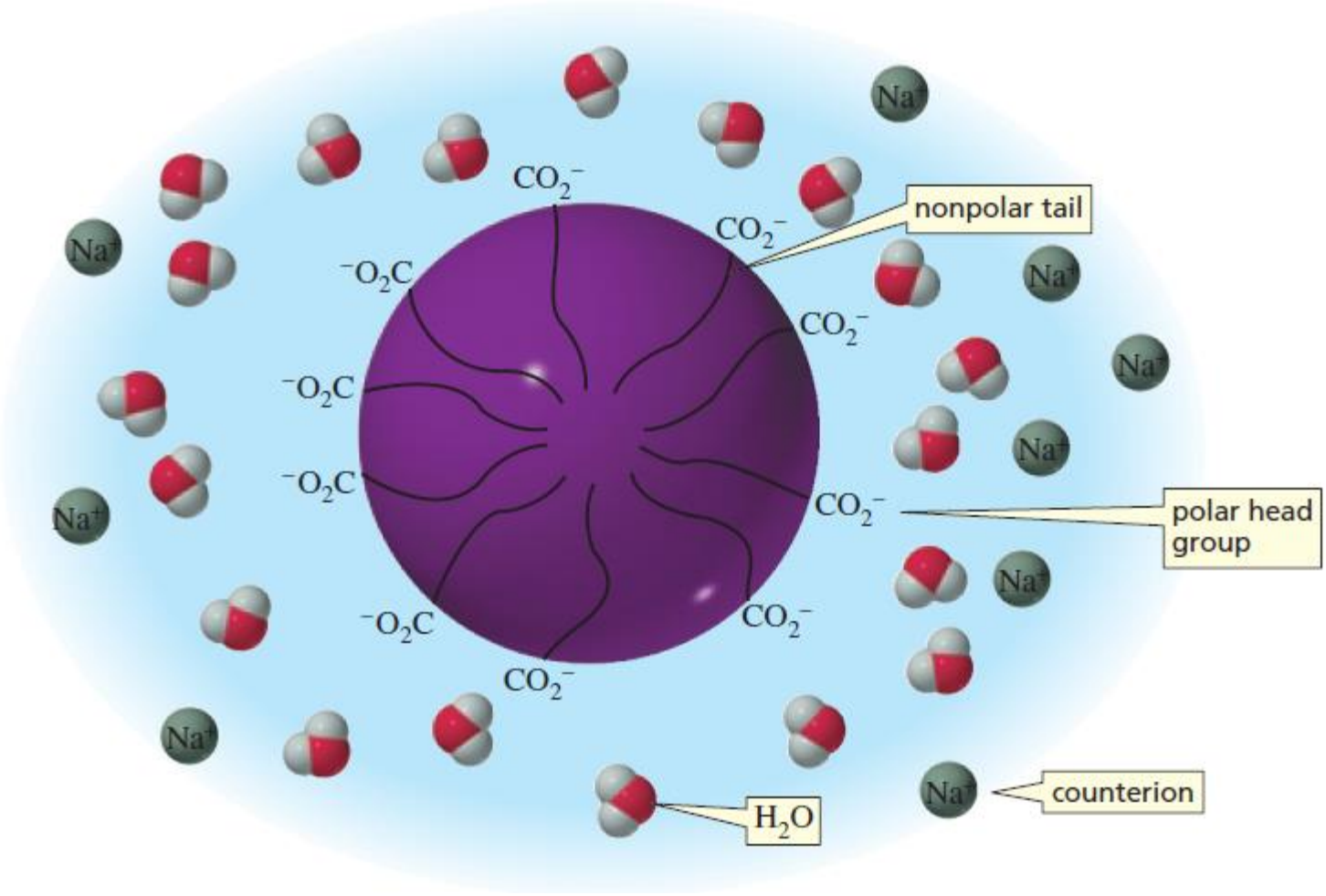

# Esterificação

## Mecanismo

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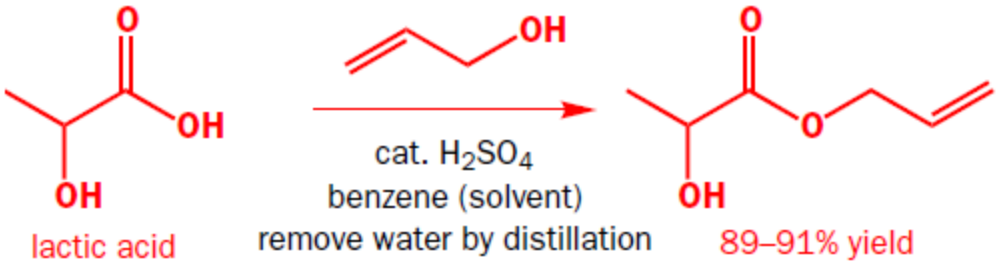

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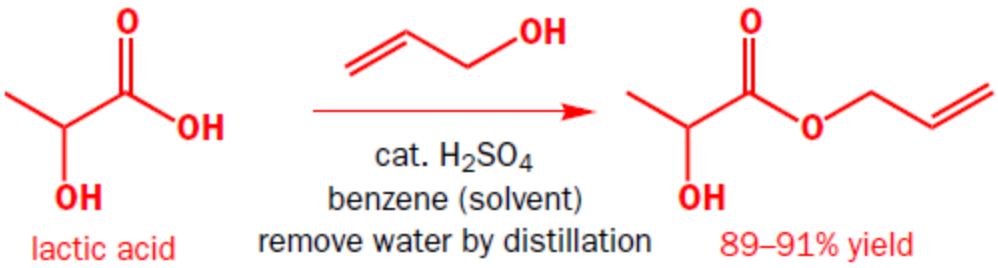


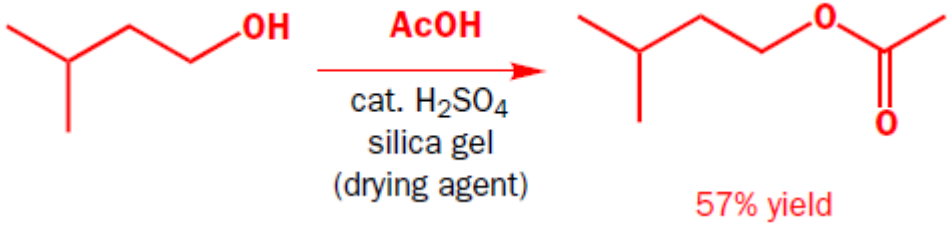

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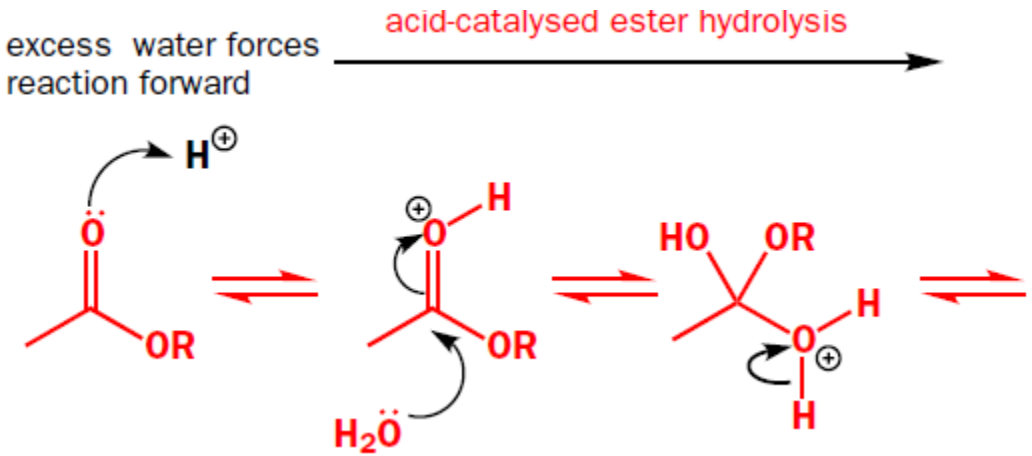

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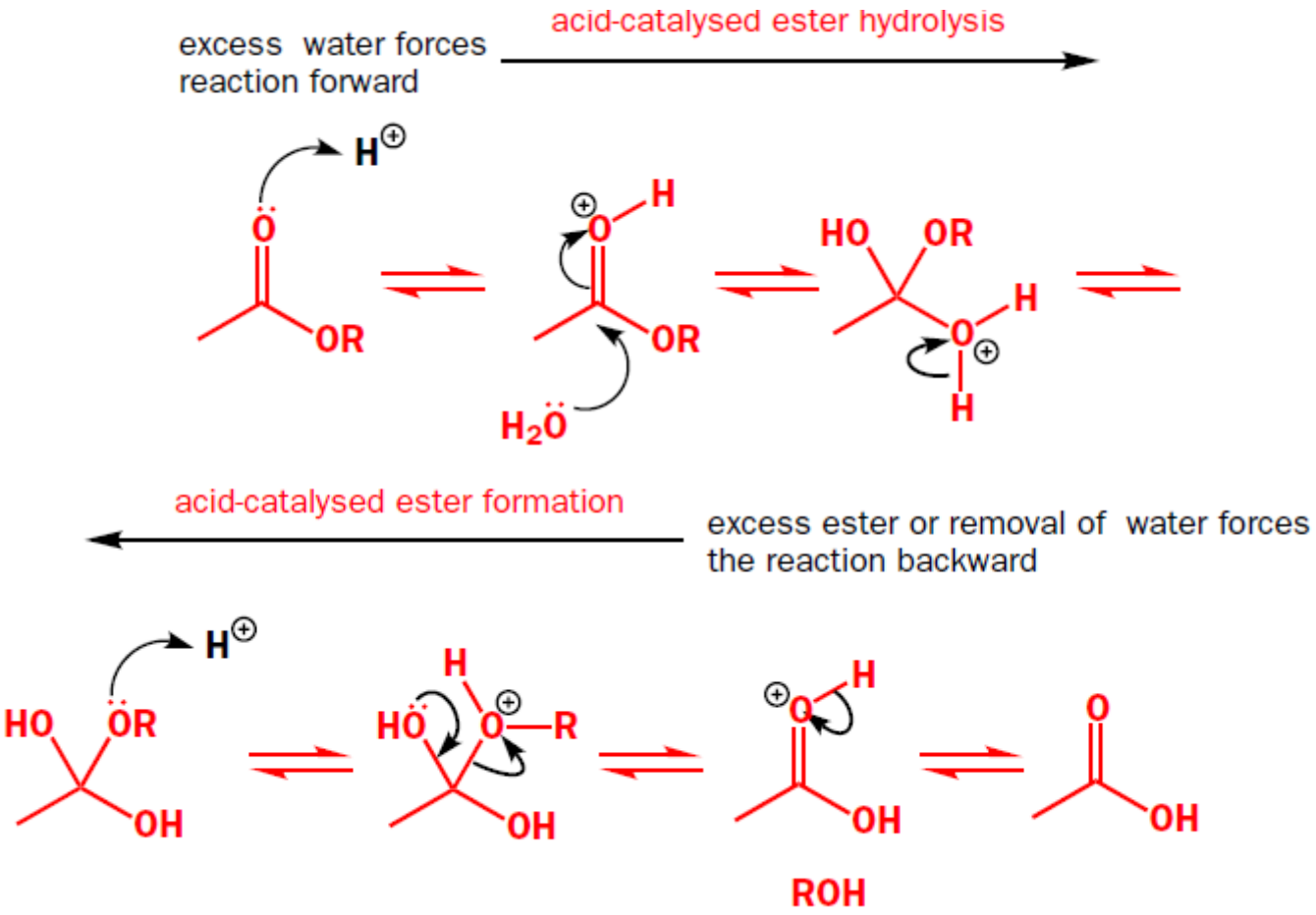

# Esterificação

## A partir de cloretos de ácido

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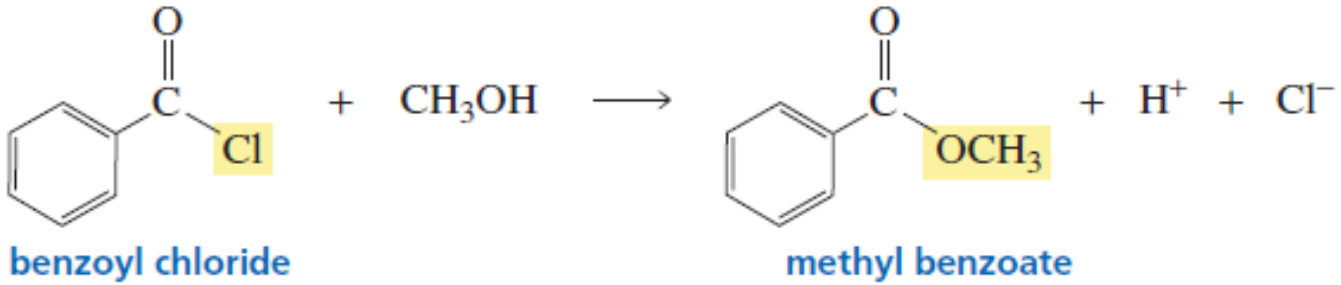
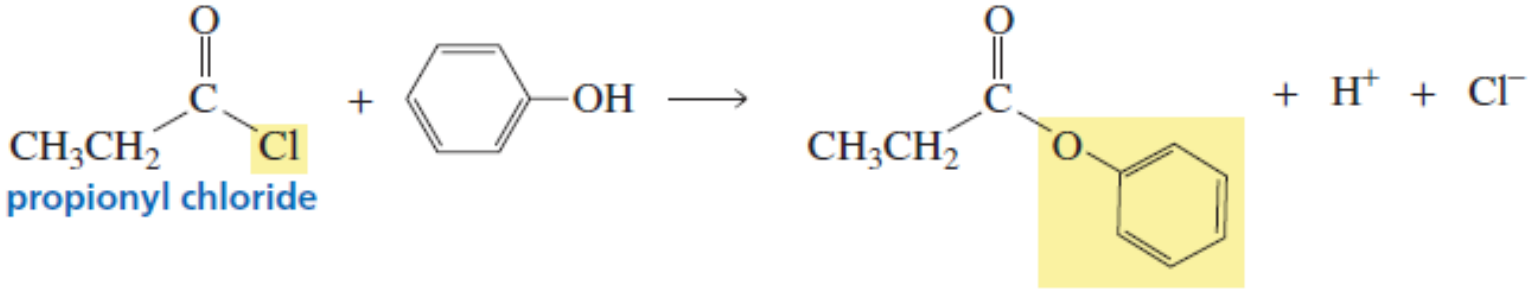



benzoyl chloride

methyl benzoate

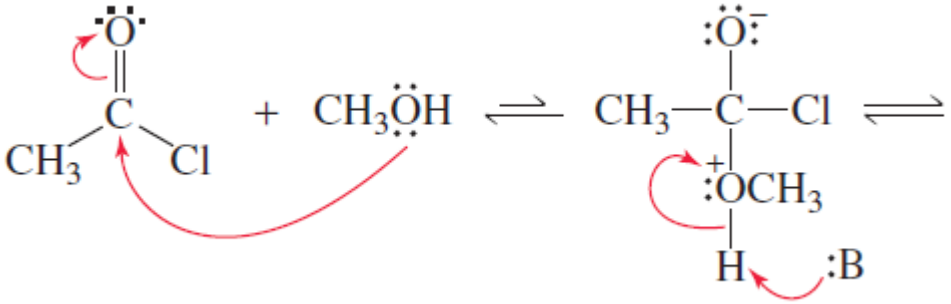



propionyl chloride

phenyl propionate

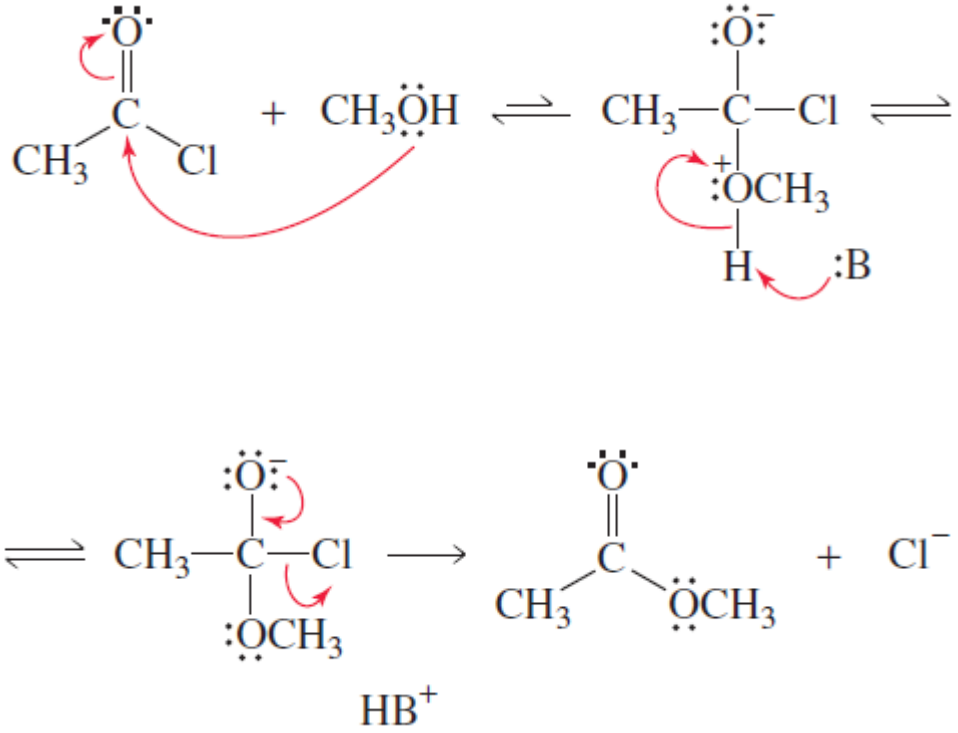
# Esterificação

## A partir de cloretos de ácido



# Esterificação

## A partir de cloretos de ácido



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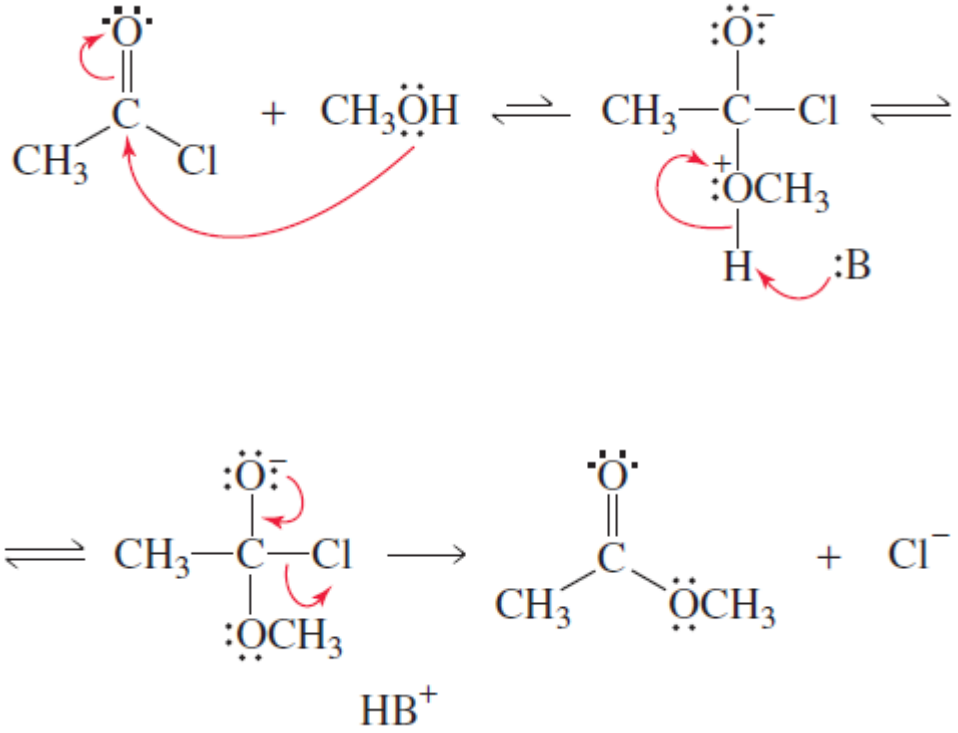

# Esterificação

## Catálise nucleofílica

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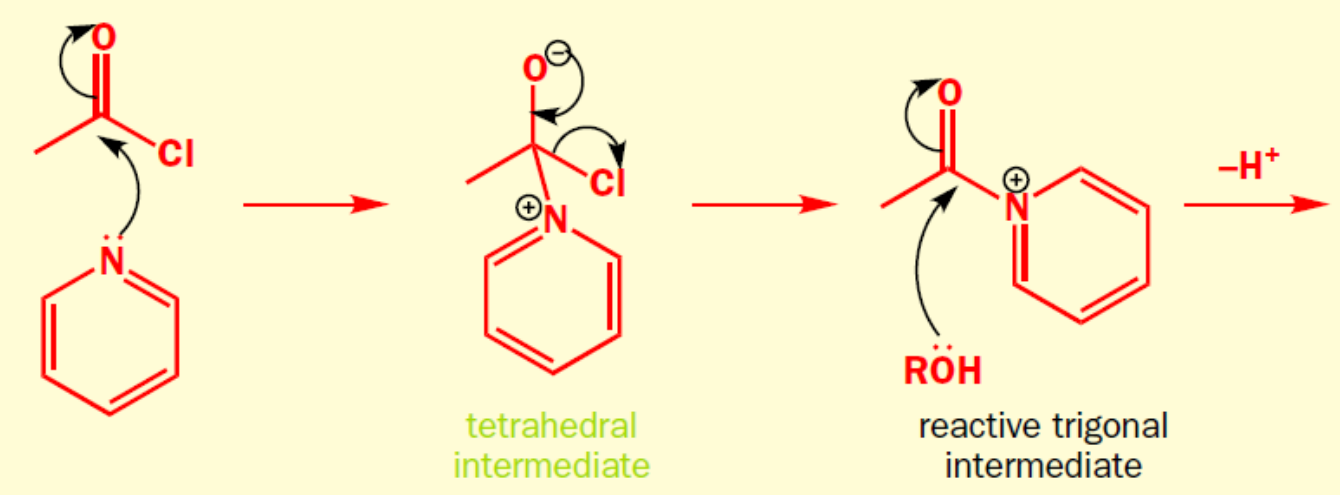
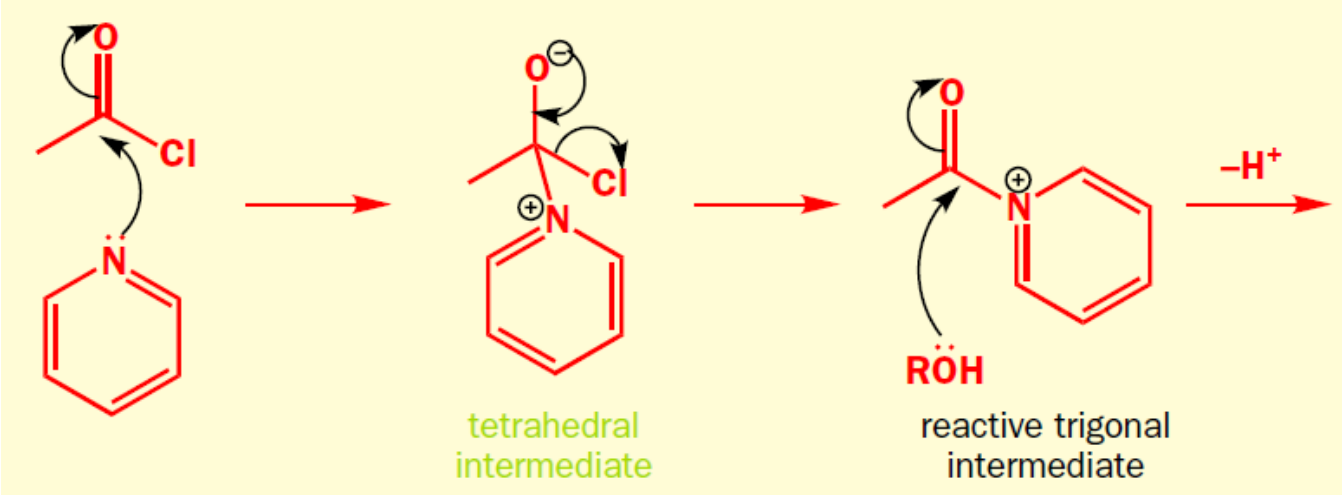
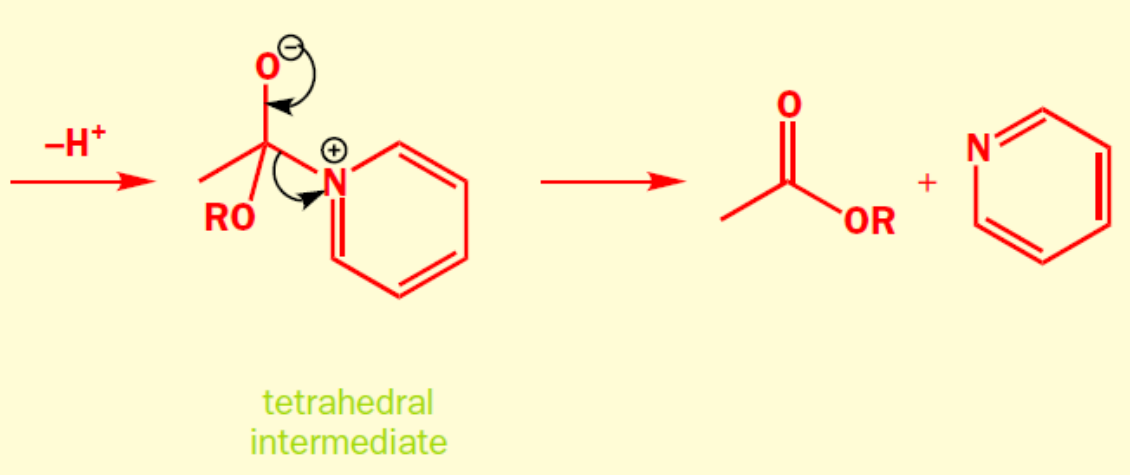


# Esterificação

## Catálise nucleofílica



# Esterificação

## Transesterificação

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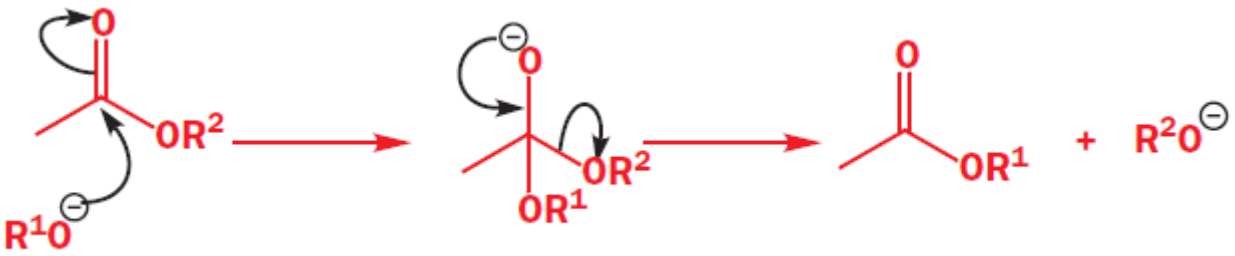

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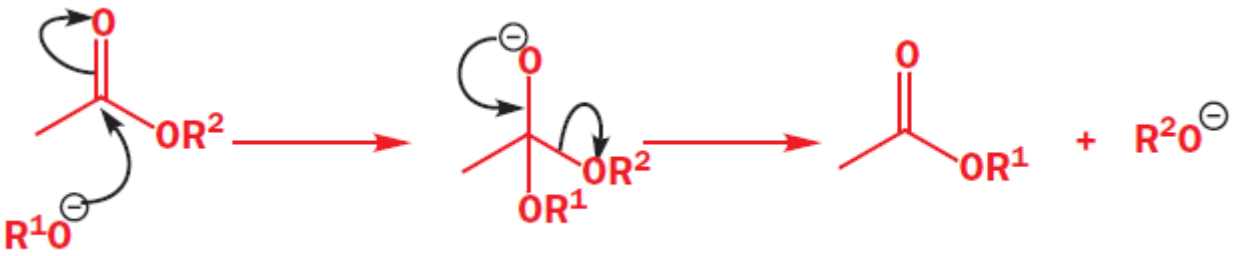
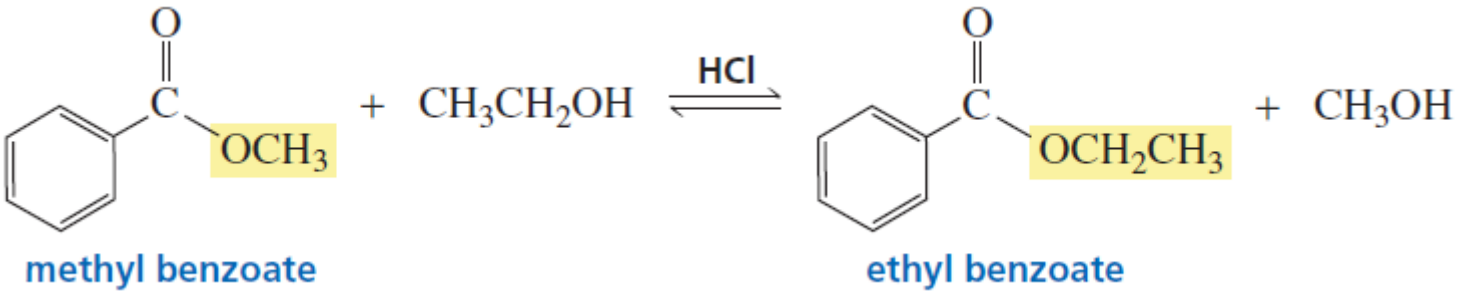


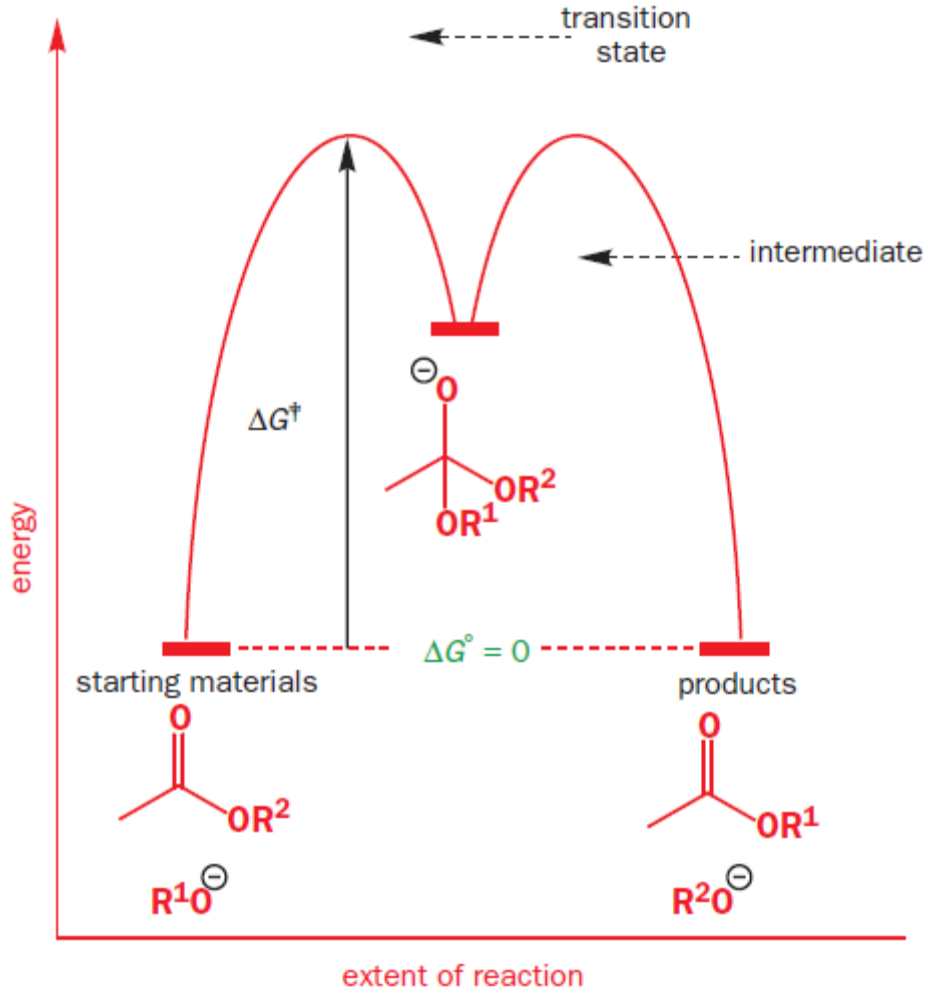




methyl benzoate

ethyl benzoate

# Esterificação

## Transesterificação



# Preparação de haletos de acila

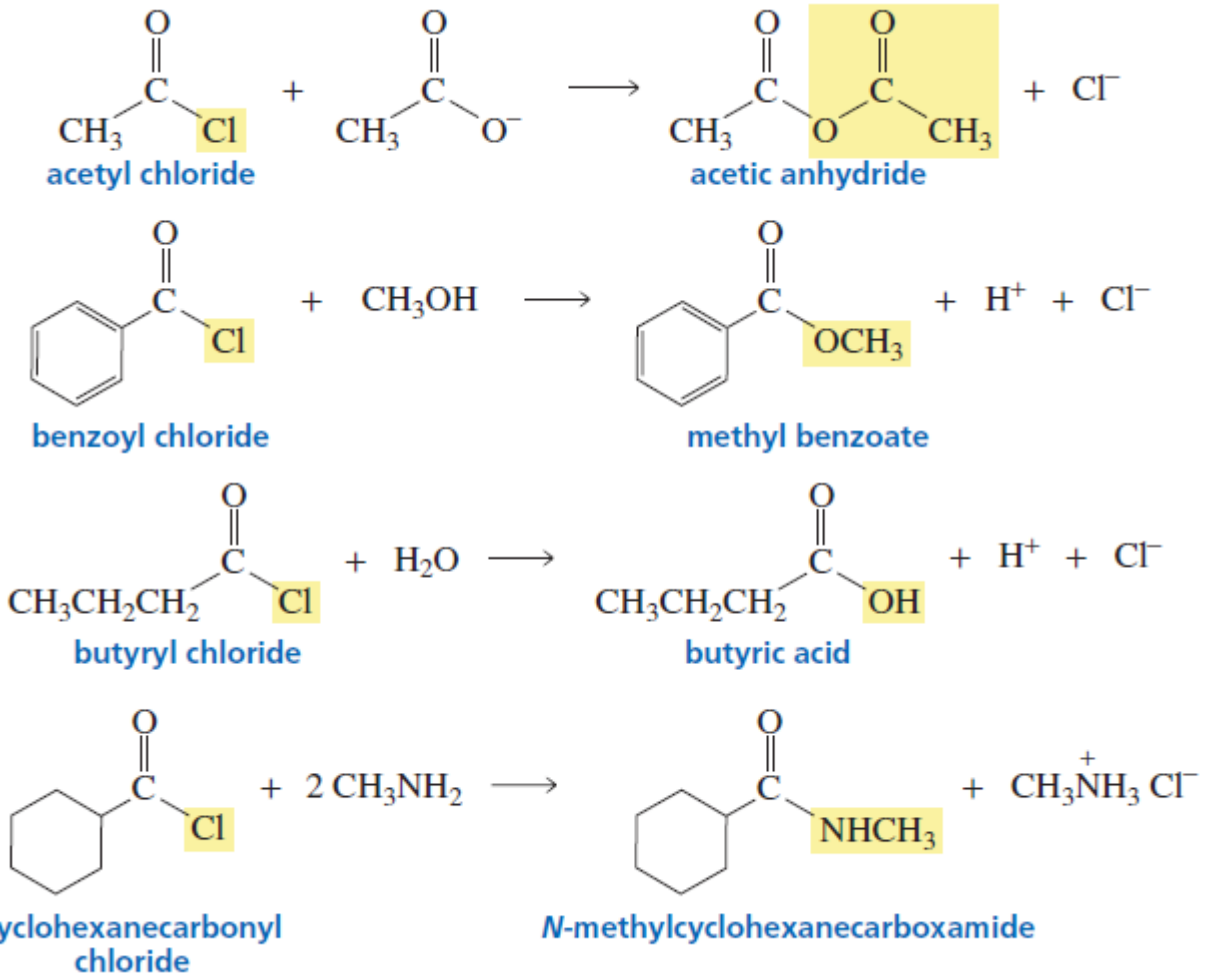
## Reatividade

# Preparação de haletos de acila



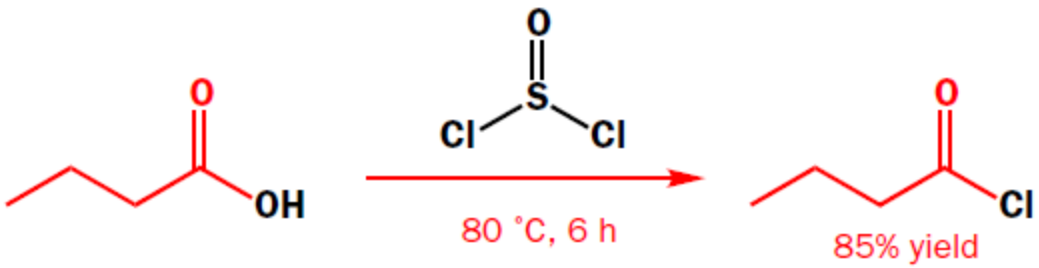


## Reatividade



# Preparação de haletos de acila

## Via $SOCl_2$



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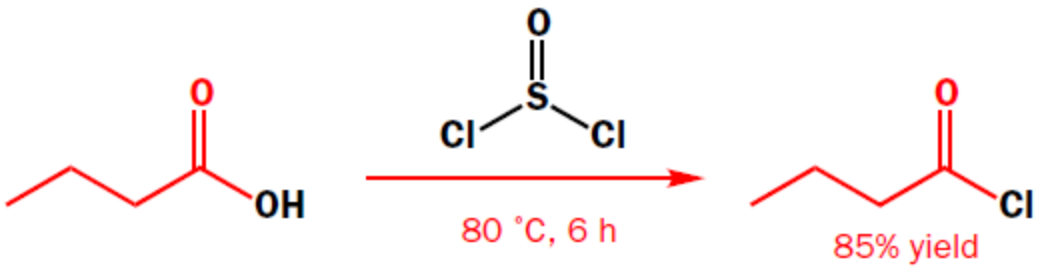


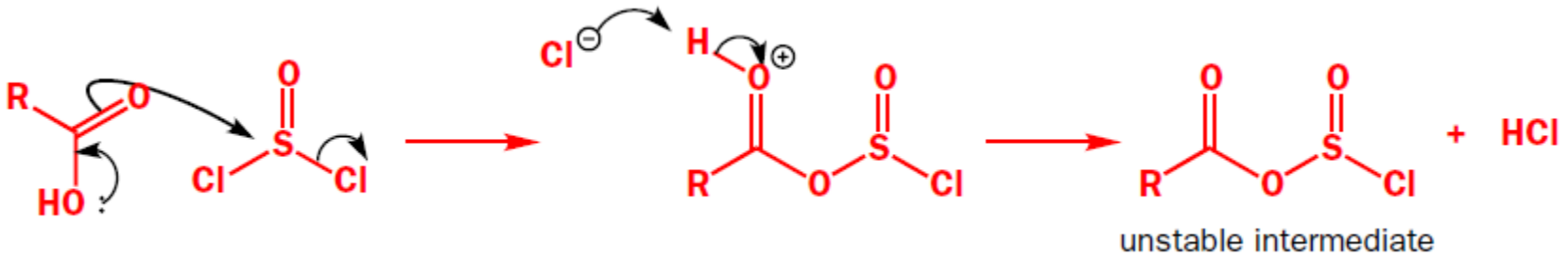

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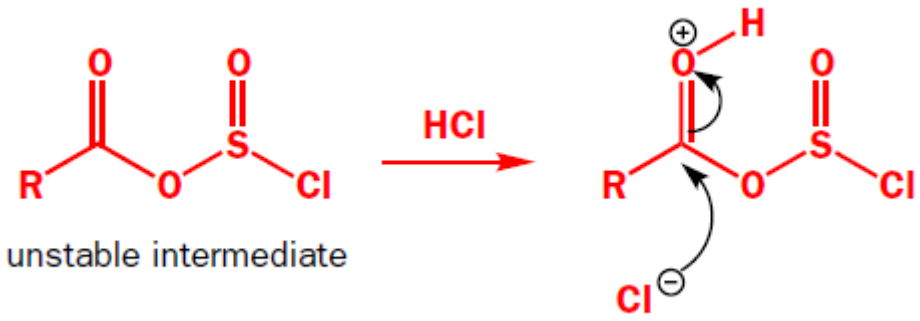

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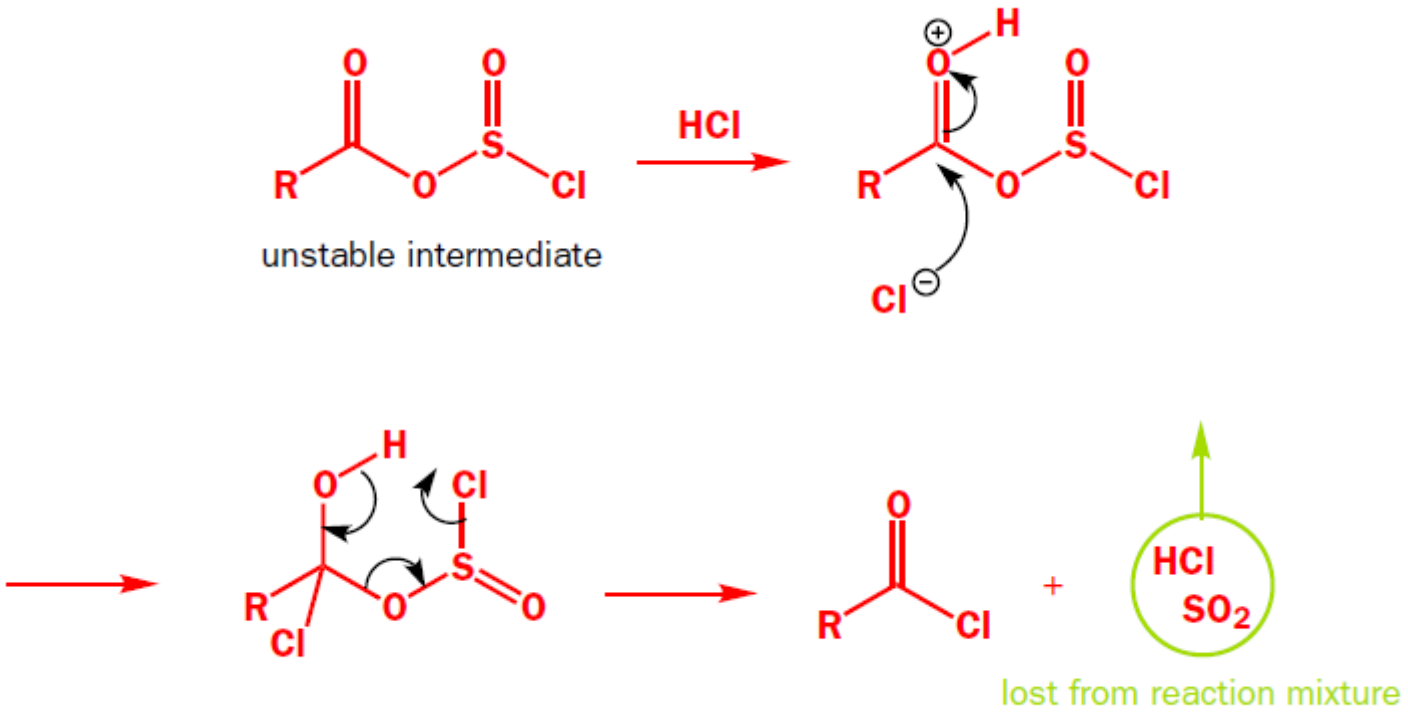
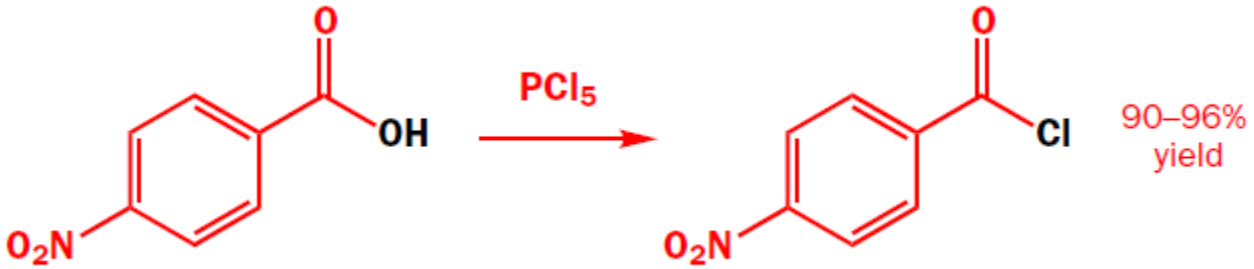


# Preparação de haletos de acila

## Via $PCl_5$

acid chlorides are made from carboxylic acids with phosphorus pentachloride



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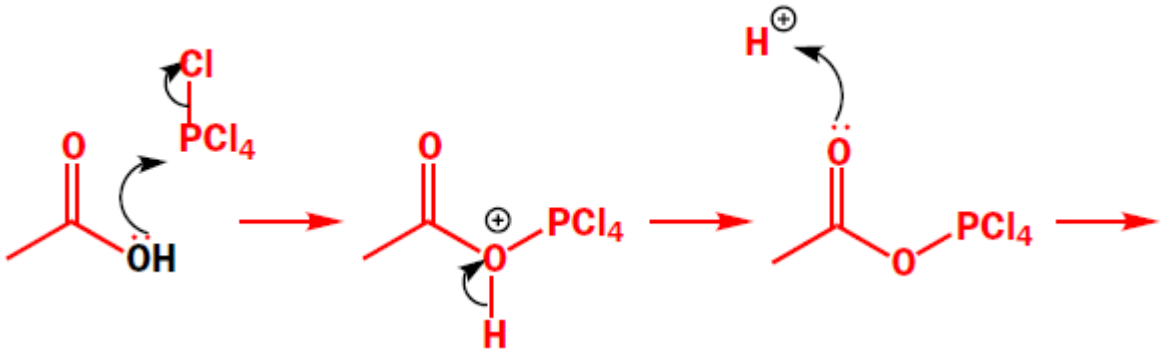
## Via $PCl_5$



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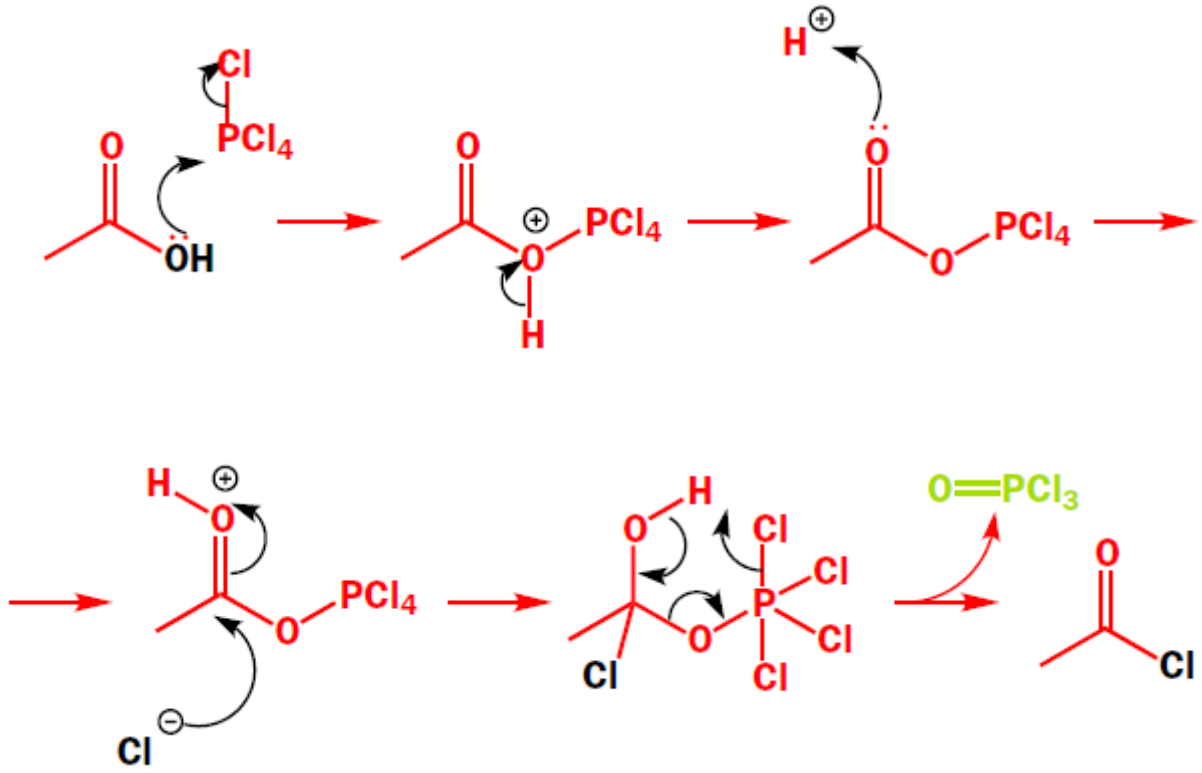

# Preparação de anidridos

## A partir de haletos de acila

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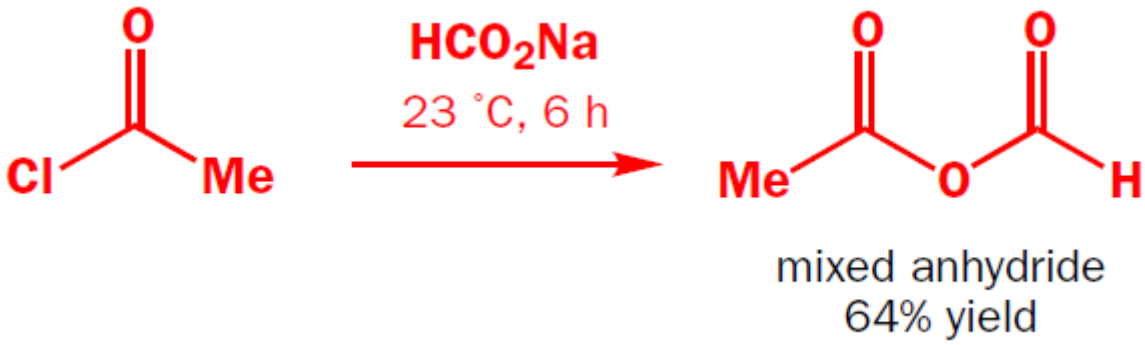

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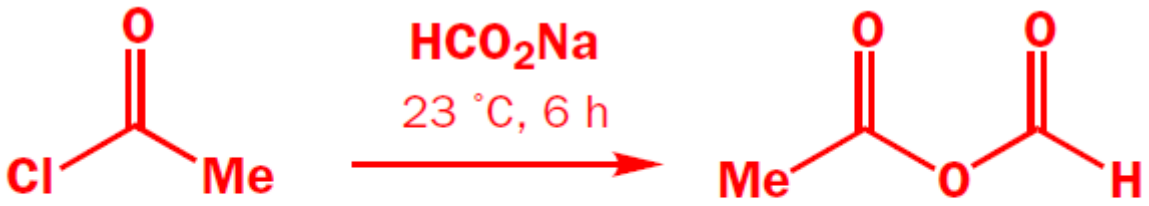
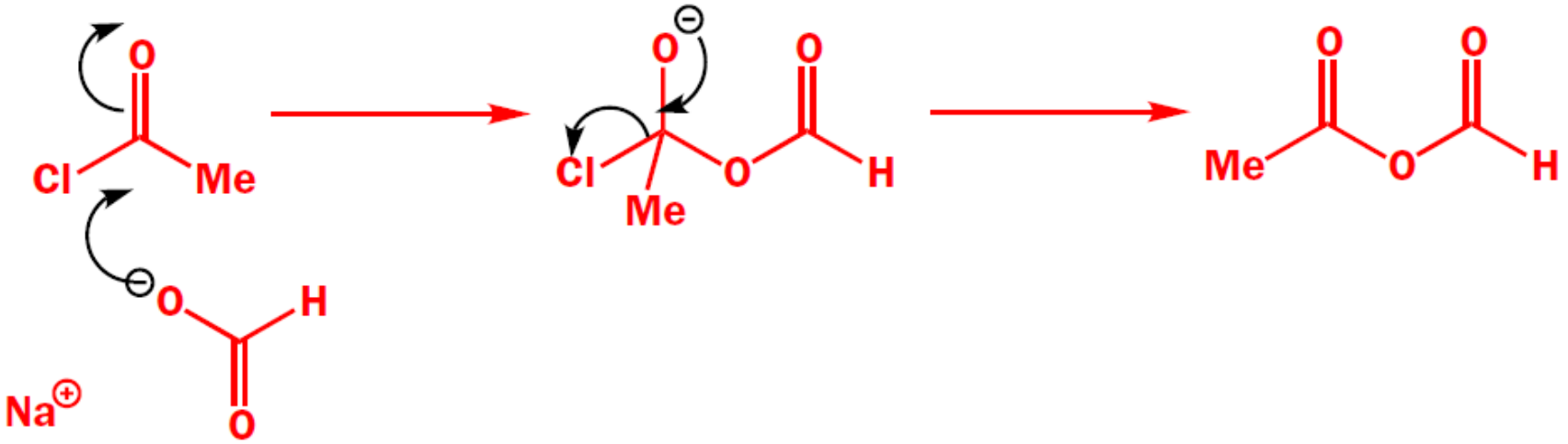
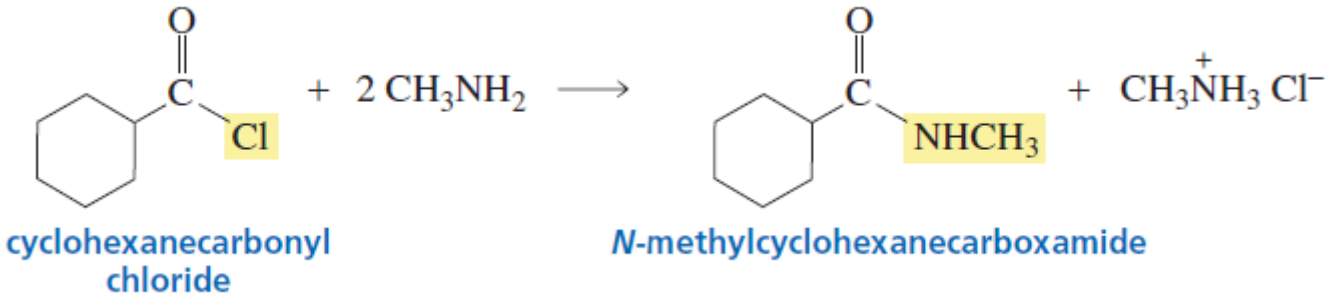



mixed anhydride
64% yield



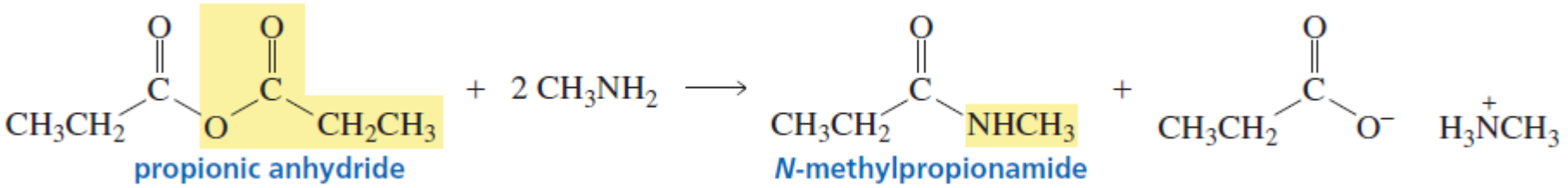
# Formação de Amidas

## A partir de haletos de acila




cyclohexanecarbonyl chloride

*N*-methylcyclohexanecarboxamide



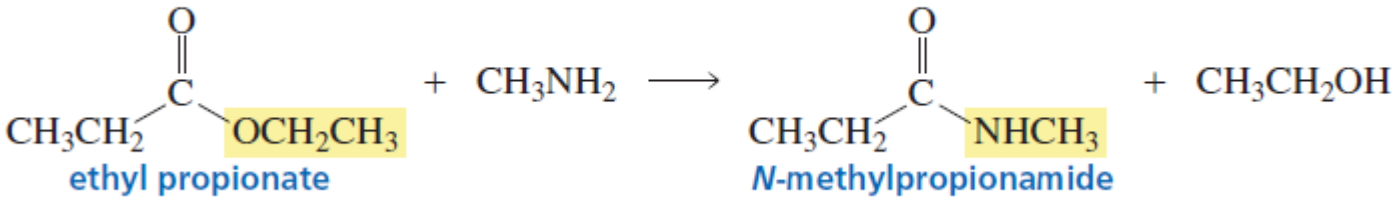

propionic anhydride

*N*-methylpropionamide

# Formação de Amidas

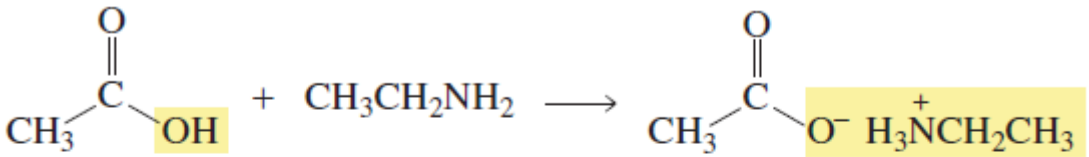
## A partir de haletos de acila

an aminolysis reaction

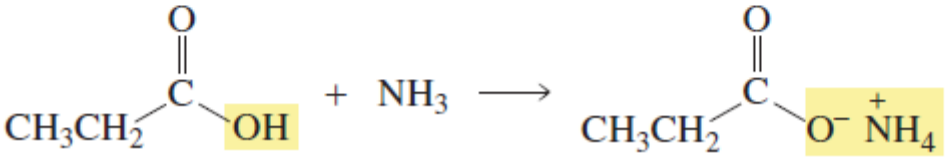



ethyl propionate

*N*-methylpropionamide




an ammonium carboxylate salt



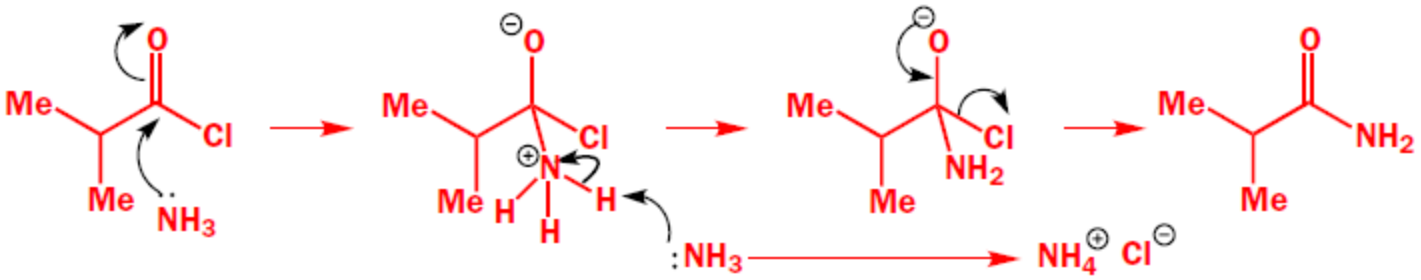
# Formação de Amidas

## Mecanismo

# Formação de Amidas

## Mecanismo

*São necessários 2 equivalentes de aminas para cada carboxila.*



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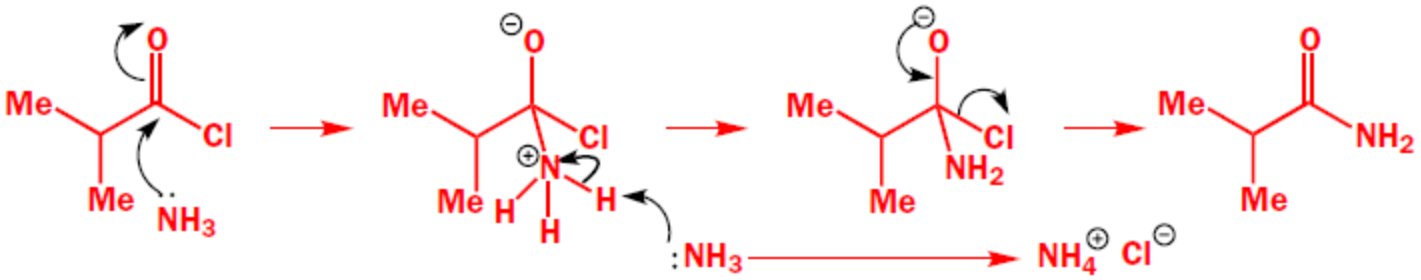


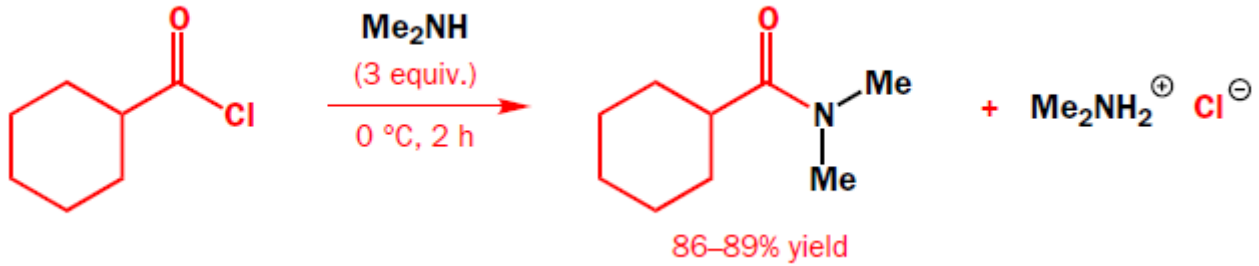

# Formação de Amidas

## Mecanismo

*Não se produz amidas a partir de ácidos carboxílicos em meio alcalino.*

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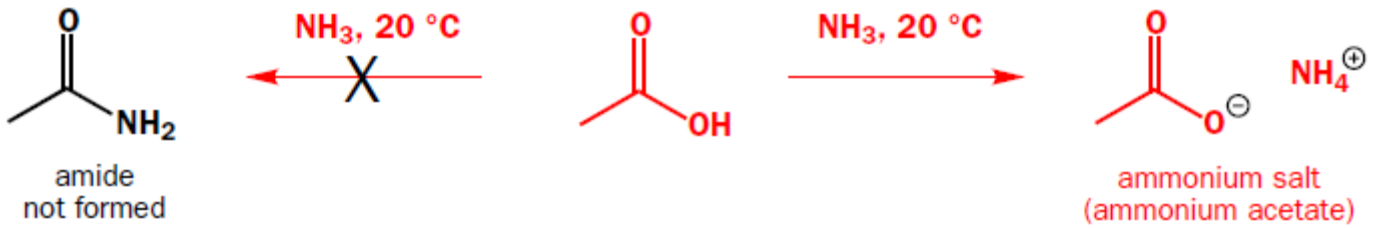

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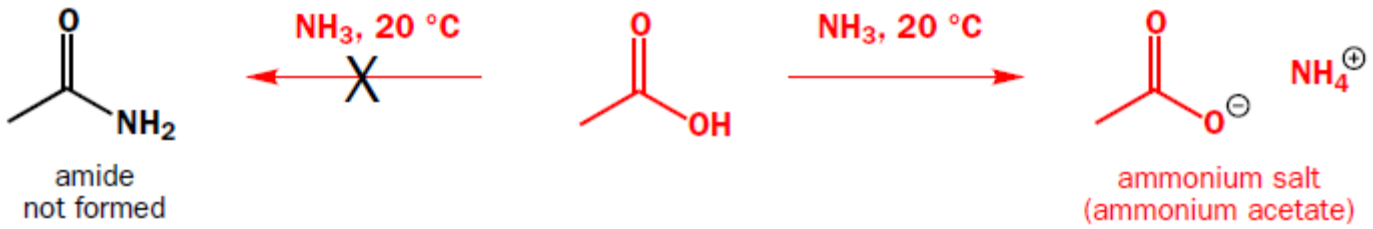


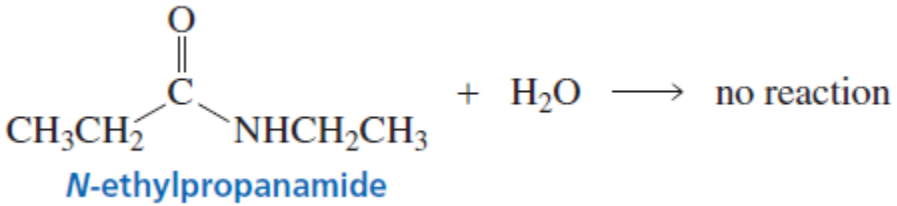

# Formação de Amidas

## Mecanismo

*Porém, é possível hidrolisar amidas em meio ácido.*

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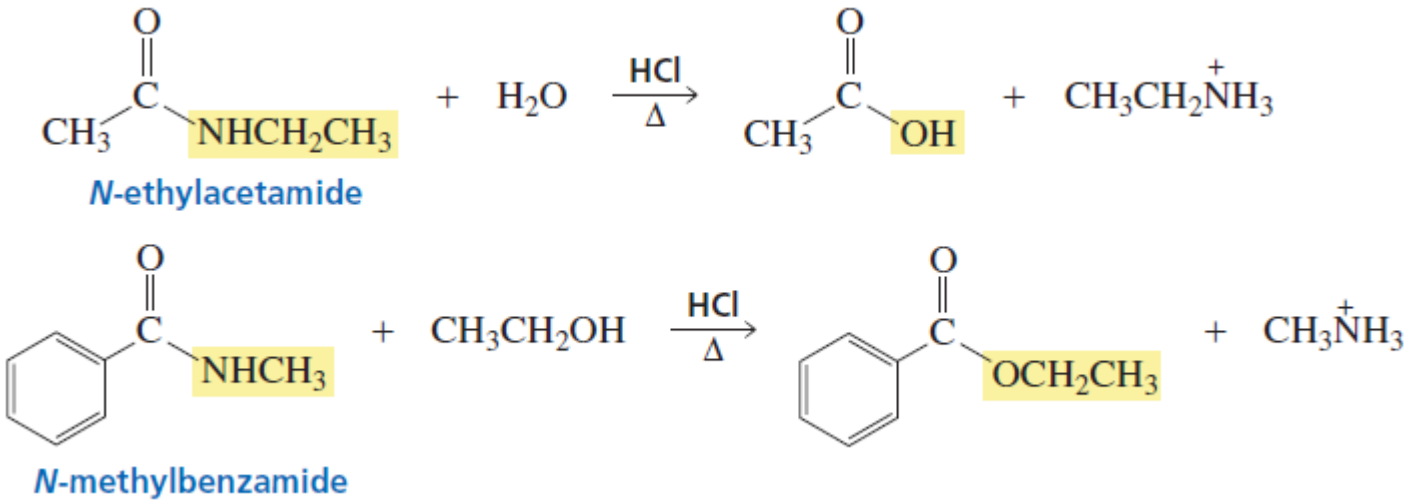
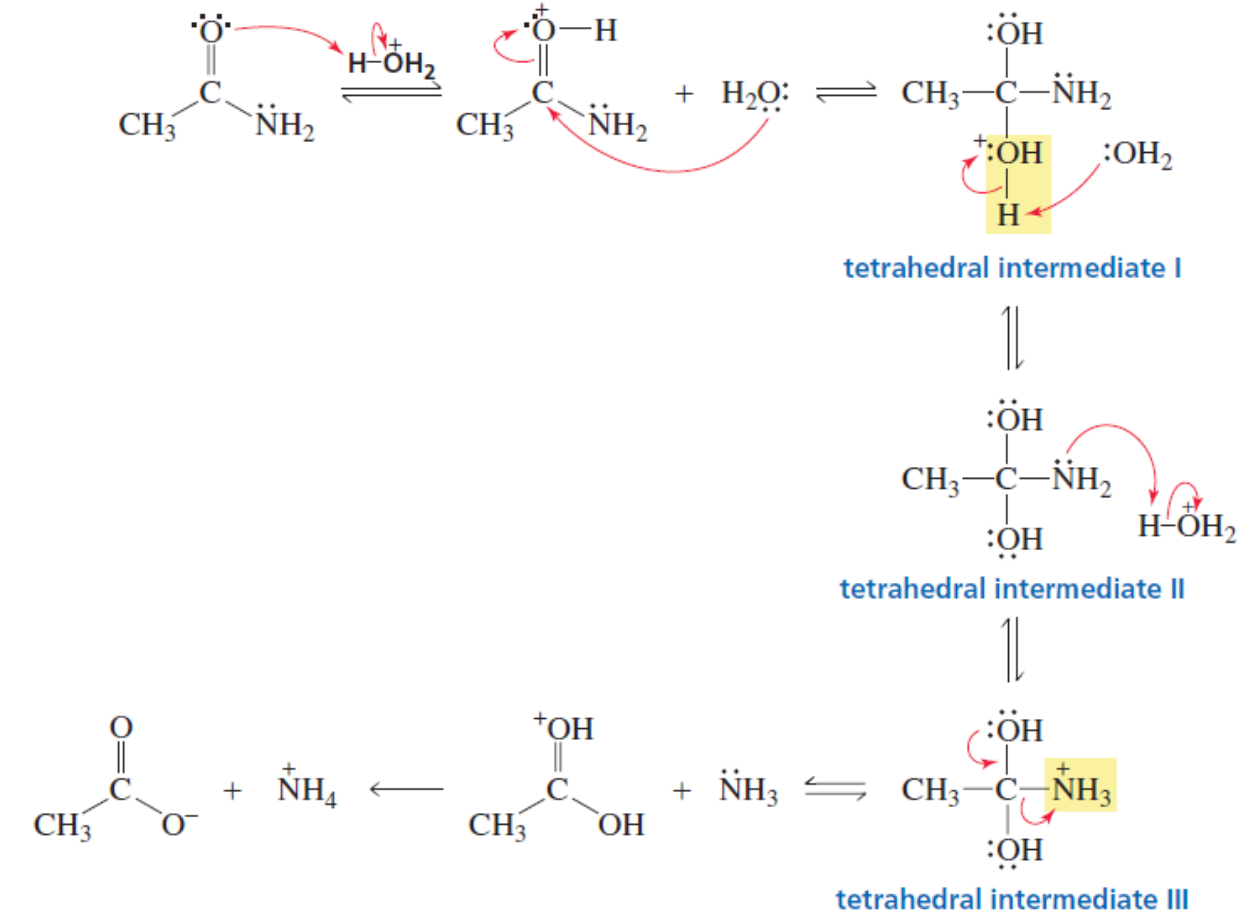


# Formação de Amidas

## Mecanismo

mechanism for acid-catalyzed hydrolysis of an amide



# Ácidos carboxílicos

## Via nitrilas

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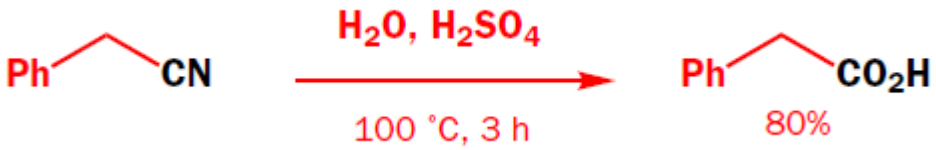

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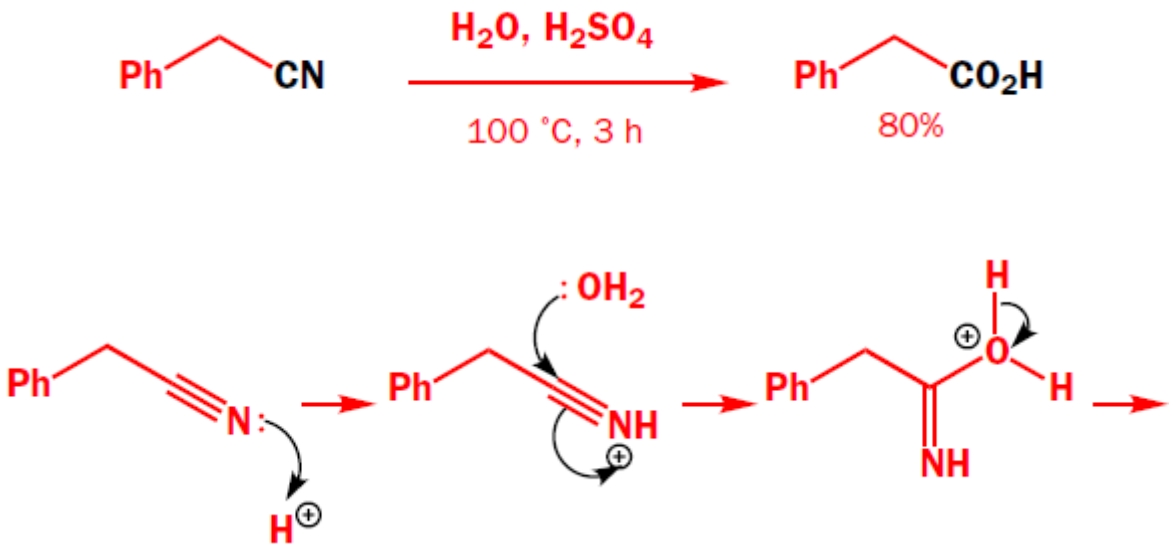

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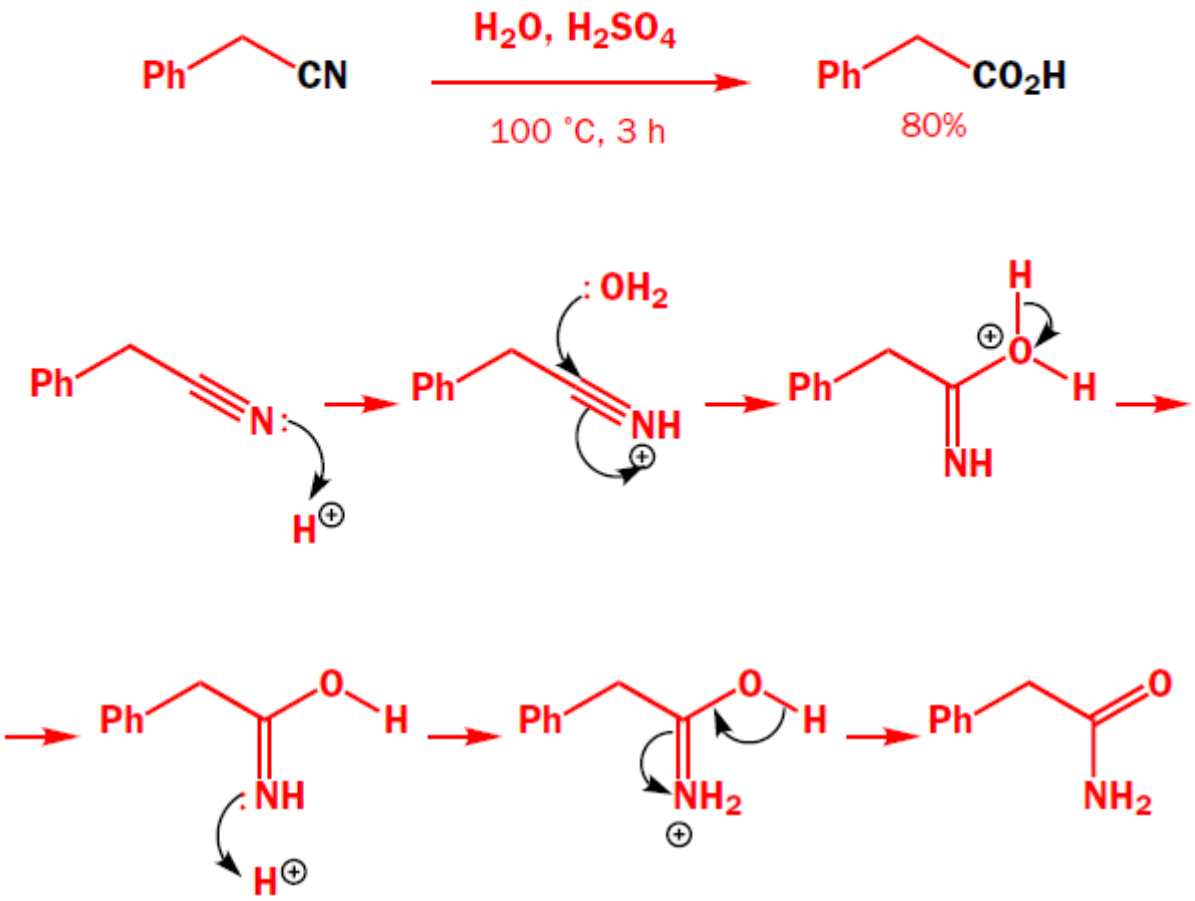
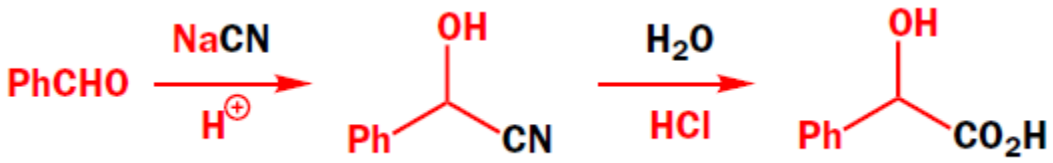


# Ácidos carboxílicos

## Via nitrilas

synthesis of mandelic acid from benzaldehyde




mandelic acid
50–52% yield

# Ácidos carboxílicos

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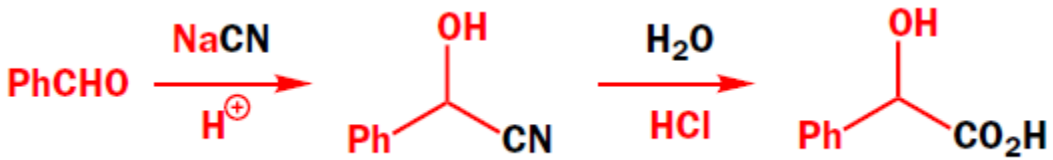
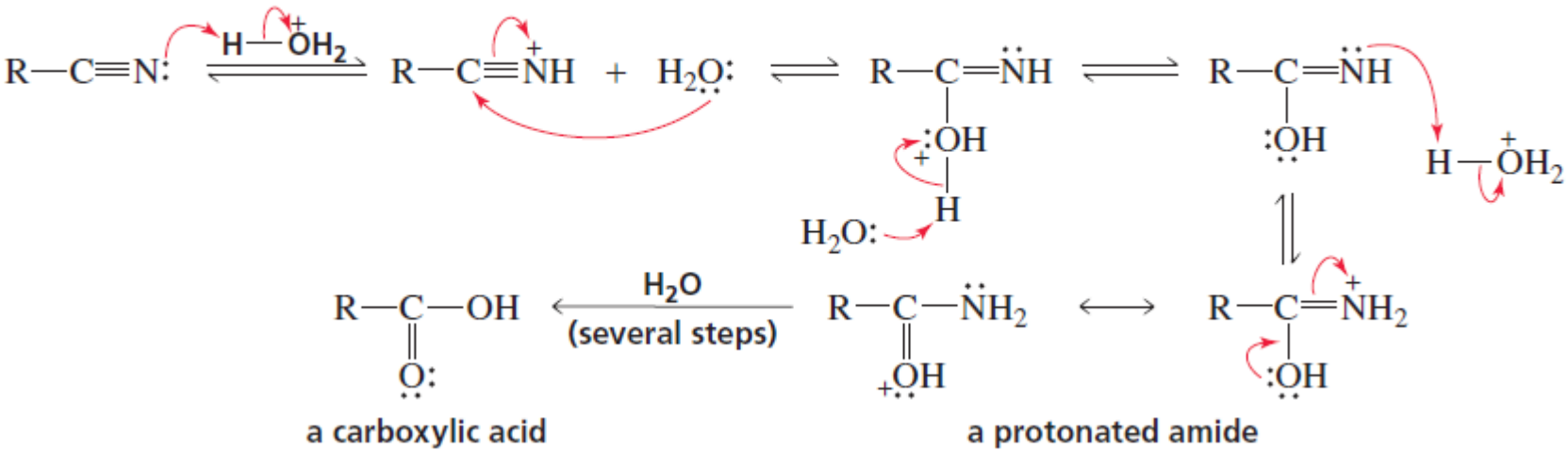



mandelic acid
50–52% yield

**mechanism for acid-catalyzed hydrolysis of a nitrile**



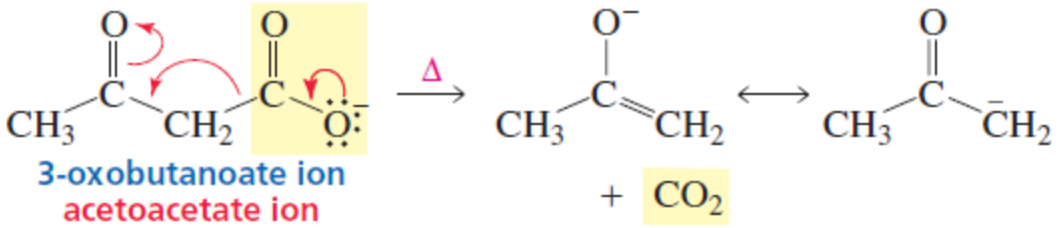

a carboxylic acid

a protonated amide

# Ácidos carboxílicos

## Descarboxilações

removing $CO_2$ from an $\alpha$-carbon



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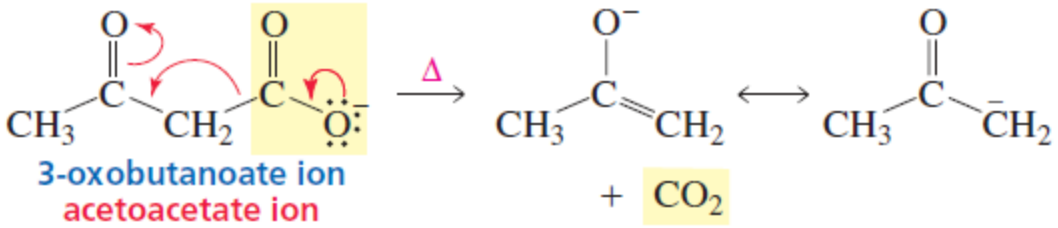


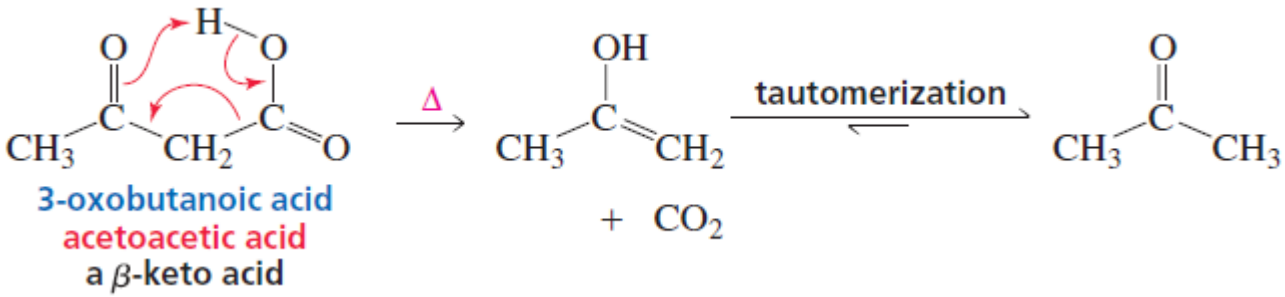

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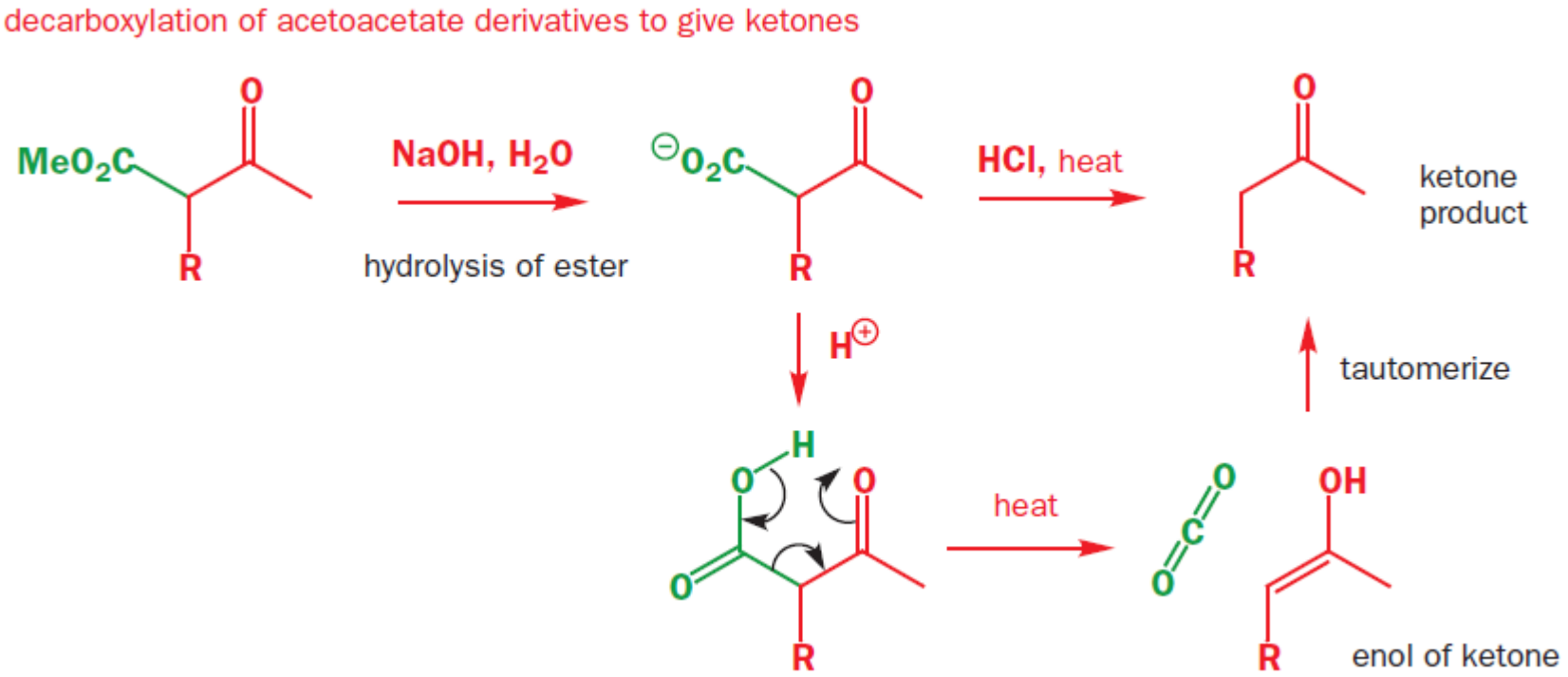
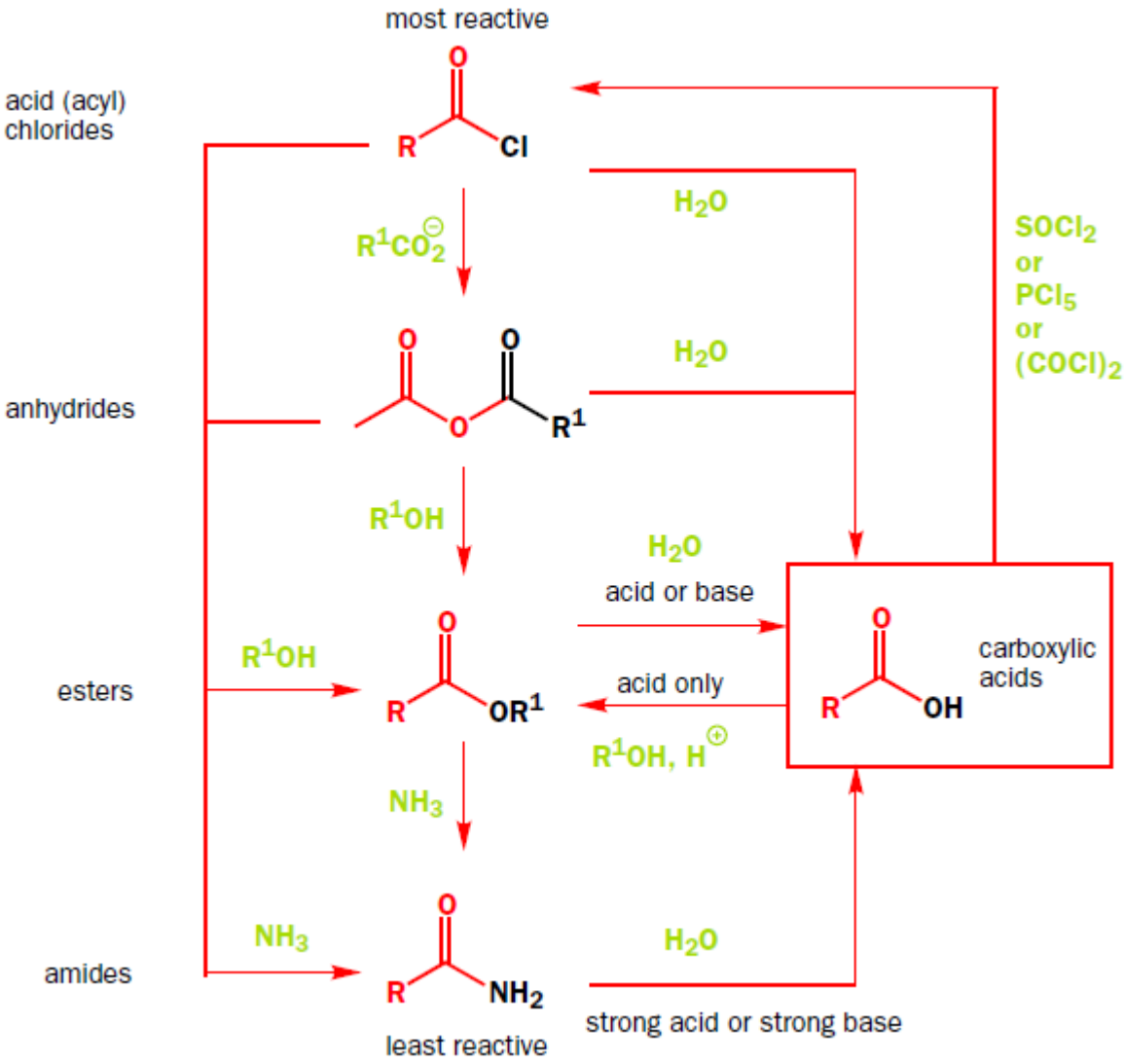
## Descarboxilações



# Resumo


most reactive
acid (acyl) chlorides
R
Cl
$R^1CO_2^{\ominus}$
$H_2O$
$SOCl_2$ or $PCl_5$ or $(COCl)_2$
anhydrides
$R^1$
$H_2O$
$R^1OH$
$H_2O$
acid or base
esters
$R^1OH$
$OR^1$
acid only
$R^1OH, H^{\oplus}$
carboxylic acids
OH
$NH_3$
amides
$NH_3$
$NH_2$
$H_2O$
strong acid or strong base
least reactive