Módulo 1 – Química Orgânica

4. Propriedades físicas e reatividade dos principais grupos funcionais

Propriedades físicas e reatividade das moléculas biológicas (aspetos fundamentais)

Álcoois, caráter anfotérico, álcoois primários, secundários e terciários.
Aldeídos e cetonas
Ácidos carboxílicos
Compostos aromáticos
Aminas

ÁLCOOIS: Propriedades físicas

Álcoois mono-hidroxilados	P.fusão (ºC)	P.eb. (ºC) (1 atm)	dens (g mL^{-1})
Metanol	-97	64.7	0.792
Etanol	-117	78.3	0.789
Propanol	-126	97.2	0.804
Isopropanol	-88	82.3	0.786
1-Butanol	-90	117.7	0.810
2-Metil-1-propanol (isobutílico)	-108	108.0	0.802
2-Butanol (sec-butílico)	-114	99.5	0.808
2-Metil-2-propanol (t-butílico)	25	82.5	0.789
Diois e tri**ó**is			
Etanodiol (etilenoglicol) *	-12.6	197	1.113
1,2-Propanodiol (propilenoglicol)	59	187	1.040
1,2,3-Propanotriol (glicerol)	18	290	1.261
*usado como líquido anticongelante			

R – OH

Álcoois primários não ramificados são líquidos até C12

ÁLCOOIS:

Influência das ligações intermoleculares nas propriedades físicas

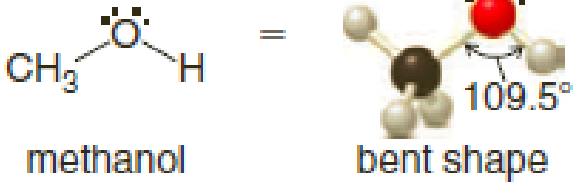
	Ponto de ebulição (ºC), 1 atm
CH_3CH_3	-88.5
$CH_3—O—CH_3$ *	-24
CH_3CH_2OH *	78.3
CH_3CH_2Cl	13.1
CH_3CHO	20.8
CH_3CH_2Br	38.4
CH_3CH_2I	72.3

isómeros

*C_2H_6O

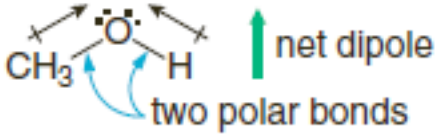
Nos álcoois há polarização das ligações C-O-H:

R – OH

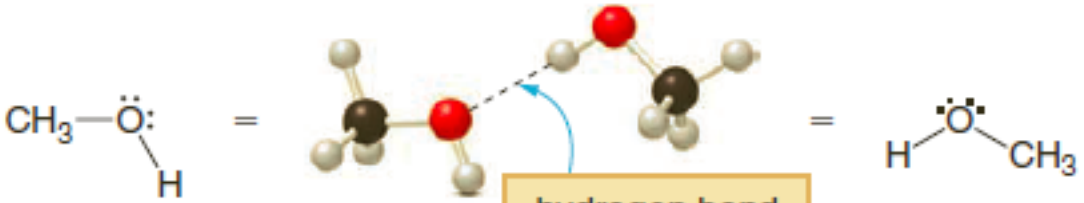


methanol — bent shape

An alcohol has a net dipole.



Alcohols exhibit intermolecular hydrogen bonding.



- Alcohols have higher boiling points and melting points than hydrocarbons of comparable size and shape.

$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2OH$ ← stronger intermolecular forces higher boiling point and melting point
butane	1-propanol
melting point: −138 °C boiling point: −0.5 °C	melting point: −127 °C boiling point: 97 °C

A solubilidade dos álcoois em água diminui com o tamanho da cadeia:

- Alcohols are soluble in organic solvents.
- Low molecular weight alcohols (those having less than six carbons) are soluble in water.
- Higher molecular weight alcohols (those having six carbons or more) are not soluble in water.

Thus, both ethanol (CH_3CH_2OH) and 1-octanol [$CH_3(CH_2)_7OH$] are soluble in organic solvents, but ethanol is water soluble and 1-octanol is not.

CH_3CH_2OH

only 2 C's in the chain

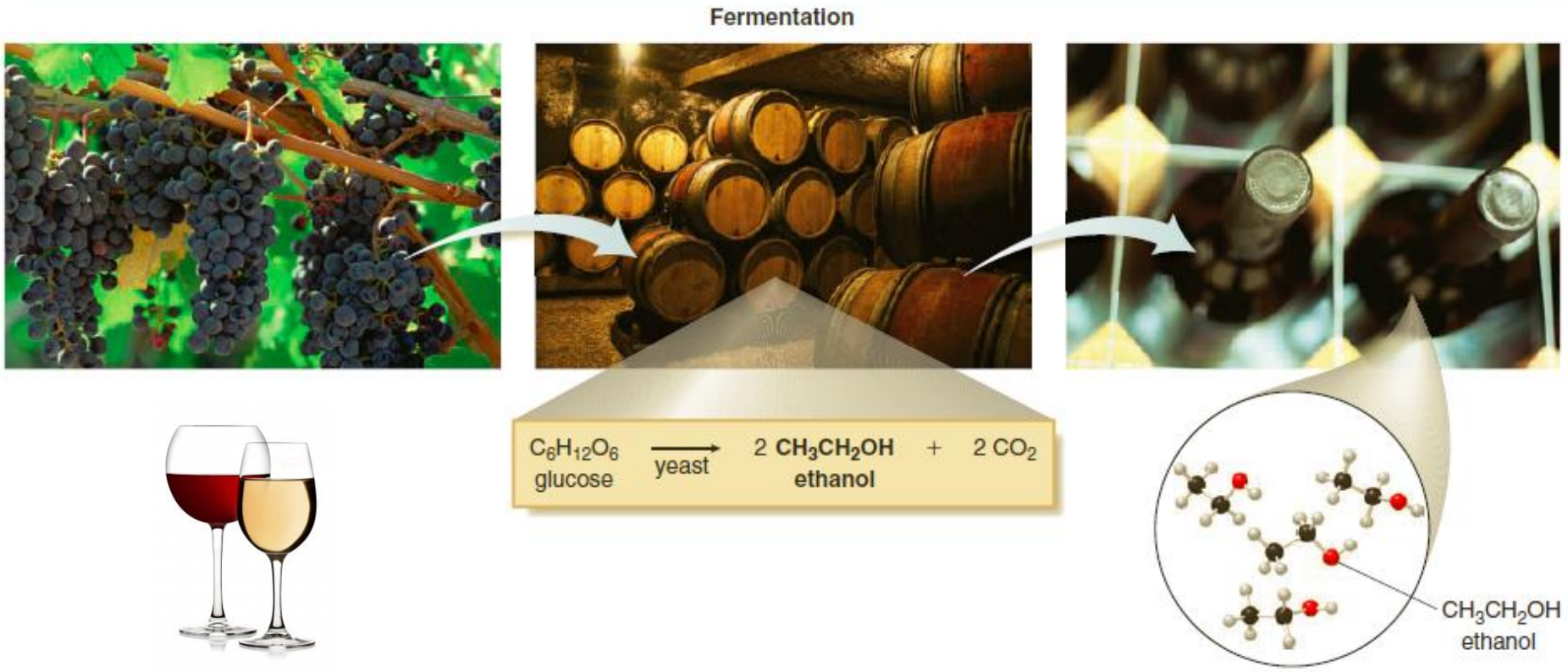
water soluble

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$

many nonpolar C–C and C–H bonds

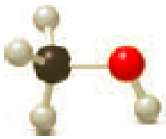
water insoluble

FIGURE 14.1 Ethanol—The Alcohol in Alcoholic Beverages



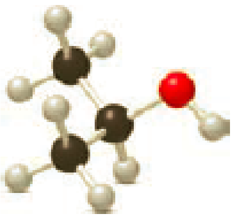
Ethanol is the alcohol in red wine, obtained by the fermentation of grapes. All alcoholic beverages are mixtures of ethanol and water in various proportions. Beer has 3–8% ethanol, wines have 10–14% ethanol, and other liquors have 35–90% ethanol.

FIGURE 14.2 Some Simple Alcohols



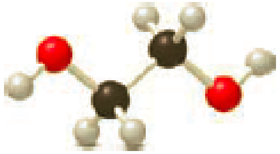
CH_3OH

- **Methanol (CH_3OH)** is a useful solvent and starting material for the synthesis of plastics. Methanol is extremely toxic because of the oxidation products formed when metabolized in the liver (Section 14.6A). Ingestion of as little as 15 mL (about half an ounce) causes blindness and 100 mL causes death.



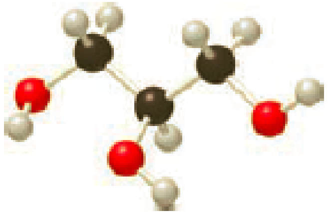
$(CH_3)_2CHOH$

- **2-Propanol [$(CH_3)_2CHOH$, isopropyl alcohol]** is the major component of rubbing alcohol. When rubbed on the skin it evaporates readily, producing a pleasant cooling sensation. 2-Propanol is used to clean skin before medical procedures and to sterilize medical instruments.



$HOCH_2CH_2OH$

- **Ethylene glycol ($HOCH_2CH_2OH$)** is the major component of antifreeze. It is sweet tasting but extremely toxic. Ethylene glycol is a starting material in the synthesis of synthetic fibers such as Dacron (Section 17.10).



$HOCH_2CHCH_2OH$ (with OH on the central C)

- **Glycerol [$(HOCH_2)_2CHOH$]** is a triol used in lotions, liquid soap, and shaving cream. Since it is sweet tasting and nontoxic, it is also an additive in candy and some prepared foods. Its three OH groups readily hydrogen bond to water, so it helps to retain moisture in these products.

ÁLCOOIS: reatividade

R – OH

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

-polarização das ligações C – O e O – H

-os pares de eletrões não partilhados do oxigénio são *básicos* e *nucleófilos*

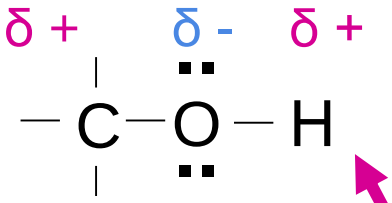
Reações:

-comportamento de ácido e de base
-desidratação (eliminação, formam **alcenos**)
-oxidação

Álcoois são substâncias anfotéricas:

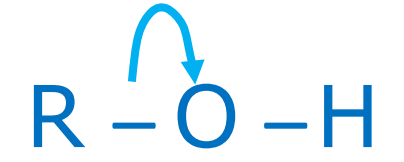
-rutura da ligação O-H, comportamento de ácido

-rutura da ligação C-OH, comportamento de base



ácido	Ka	
CH_3OH ($1^{ário}$)	$10^{-15.5}$	ácido mais forte
CH_3CH_2OH	$10^{-15.9}$	
$(CH_3)_3COH$ ($3^{ário}$)	10^{-18}	ácido mais fraco

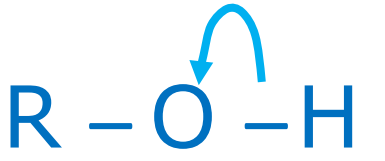
Ataque por ácidos e eletrófilos (caráter básico)



$R^+ + OH^-$

FORMAÇÃO DE CARBOCATIÃO

Ataque por bases (caráter ácido)



$RO^- + H^+$

Comportamento de ácido (O–H)

-Ocorre por ação de uma base

-A labilidade do hidrogénio funcional origina a formação de alcóxido ou alcoolato

álcool 1ário > álcool 2ário > álcool 3ário

Maior reatividade ← menor reatividade

Explicado pelo efeito indutor repulsivo dos substituintes alquilo

-O efeito indutor influência a força dos ácidos:

H_2O > R—OH > R—C≡C—H > H_2 > NH_3 > R—H

A base conjugada do álcool é o ião alcóxido

R^- > NH_2^- > R—C≡C$^-$ > RO^- > OH^-

bases fortes (bases conjugadas de ácidos fracos)

Comportamento de base (C–OH)

-Ocorre por ação de um ácido:

álcool 3ário > álcool 2ário > álcool 1ário

Maior reatividade **Menor reatividade**

-é explicada pela estabilidade do carbocatião formado:

carbocatião 3ário > carbocatião 2ário > carbocatião 1ário

Maior estabilidade **Menor estabilidade**

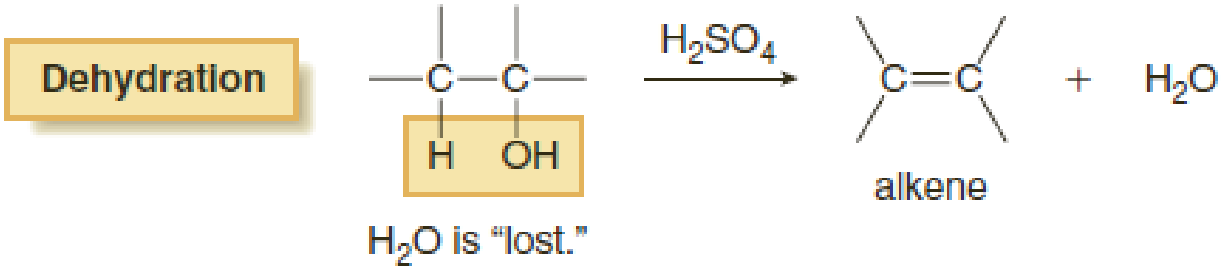
-O efeito indutor influência o comportamento como "bases" dos álcoois

Os substituintes **alquilo** estabilizam o carbocatião formado (por efeito indutor repulsivo)

Reações dos álcoois: Eliminação

-por desidratação, os alcoóis podem formar alcenos (em meio ácido, com aquecimento)

$$H_2CH - CH_2OH \rightarrow H_2C = CH_2 + H_2O$$



facilidade de desidratação

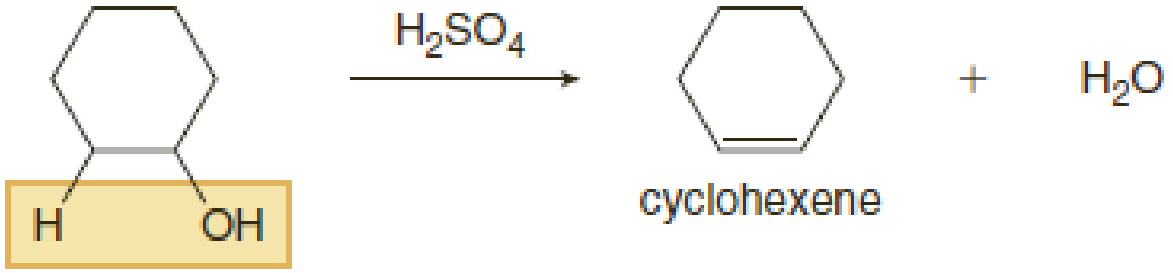
terciário > secundário > primário

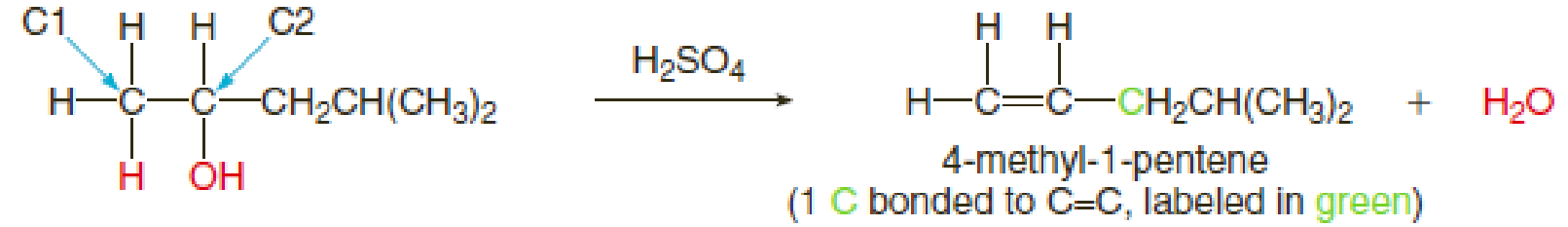
Estabilidade do carbocatião intermédio

terciário > secundário > primário

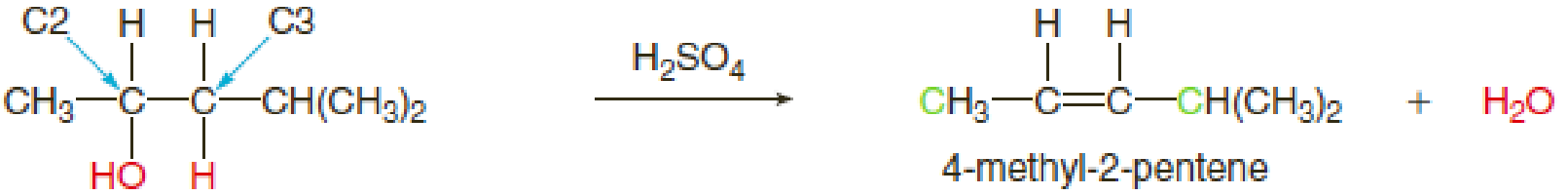
Regra de Zaitzev:

É o carbono menos hidrogenado que perde o H porque se forma um carbocatião mais estável





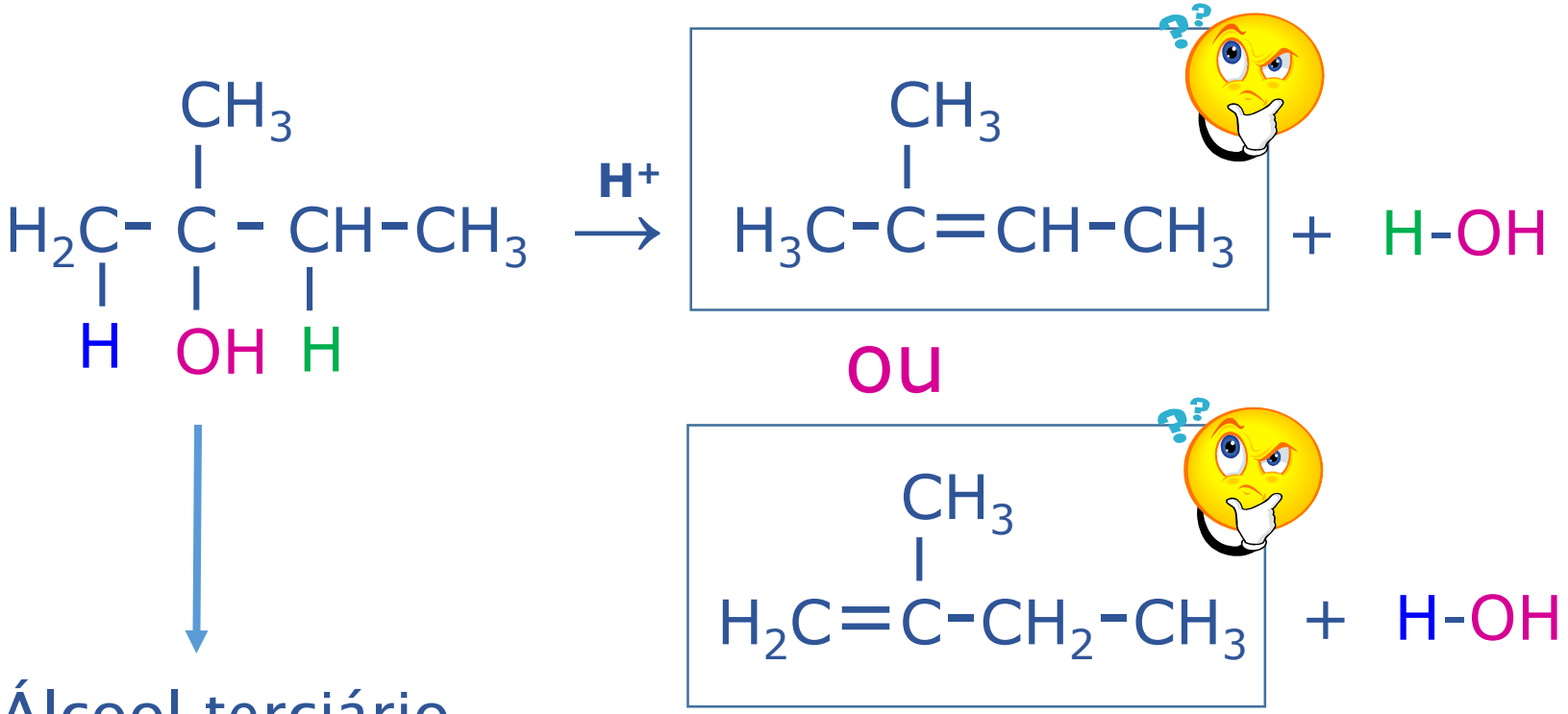
4-methyl-1-pentene
(1 C bonded to C=C, labeled in green)



4-methyl-2-pentene
(2 C's bonded to C=C, labeled in green)

major product

Ex: síntese do 2-metil-2-buteno a partir do 2-metil-2-butanol, por desidratação, em meio ácido

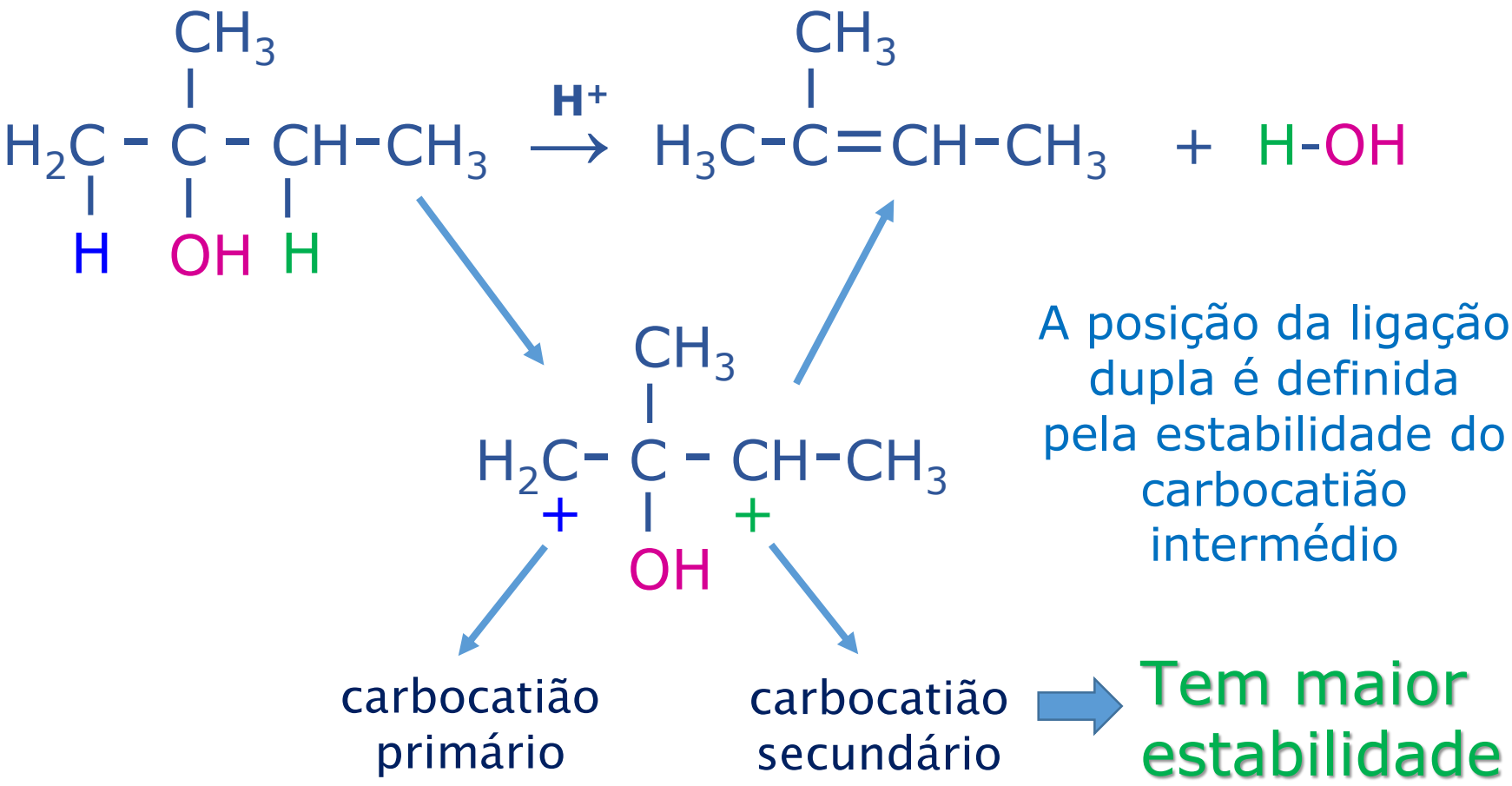


Álcool terciário

-sofre fácil desidratação

-a posição da dupla depende da estabilidade do carbocatião intermédio

A Regra de Zaitsev define a posição da dupla ligação formada:



A posição da ligação dupla é definida pela estabilidade do carbocatião intermédio

Ex: síntese do 2-metil-2-buteno a partir do 2-metil-2-butanol

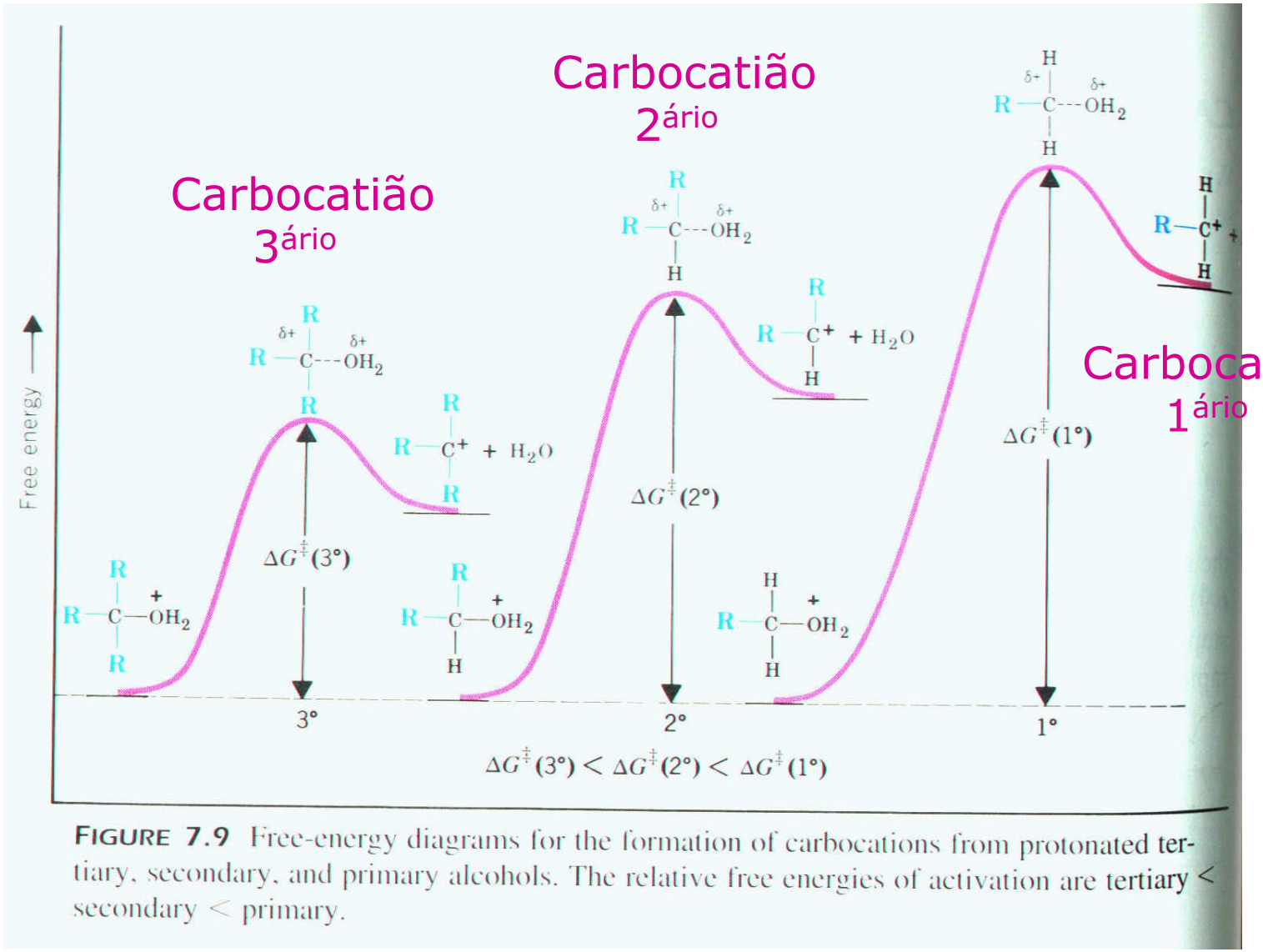
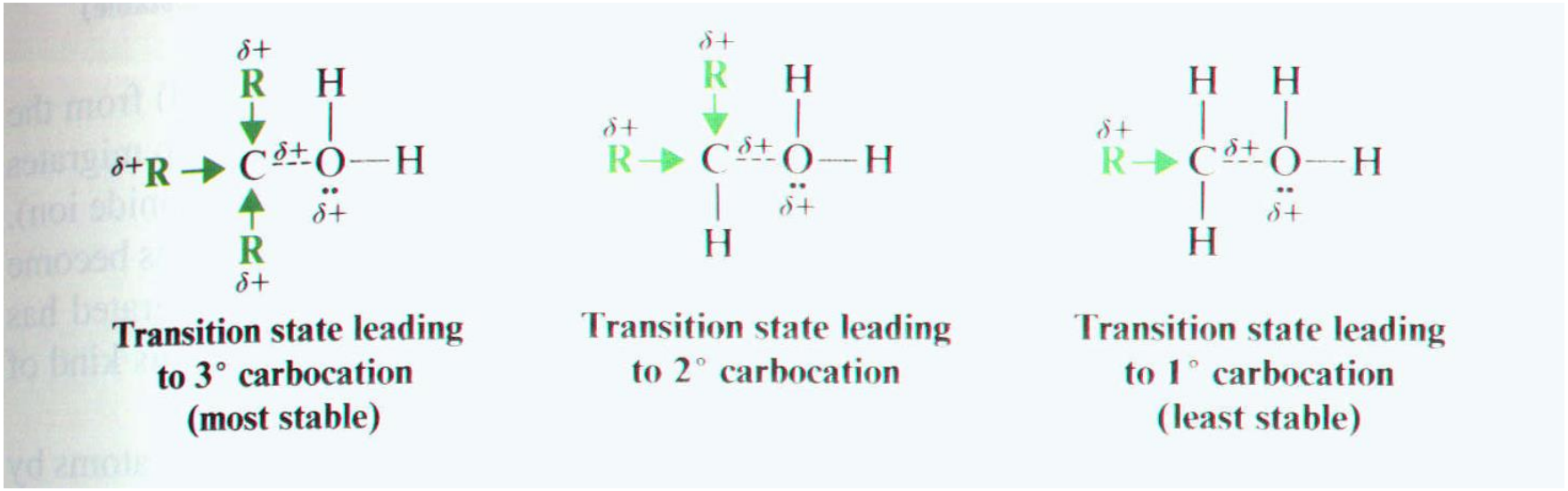


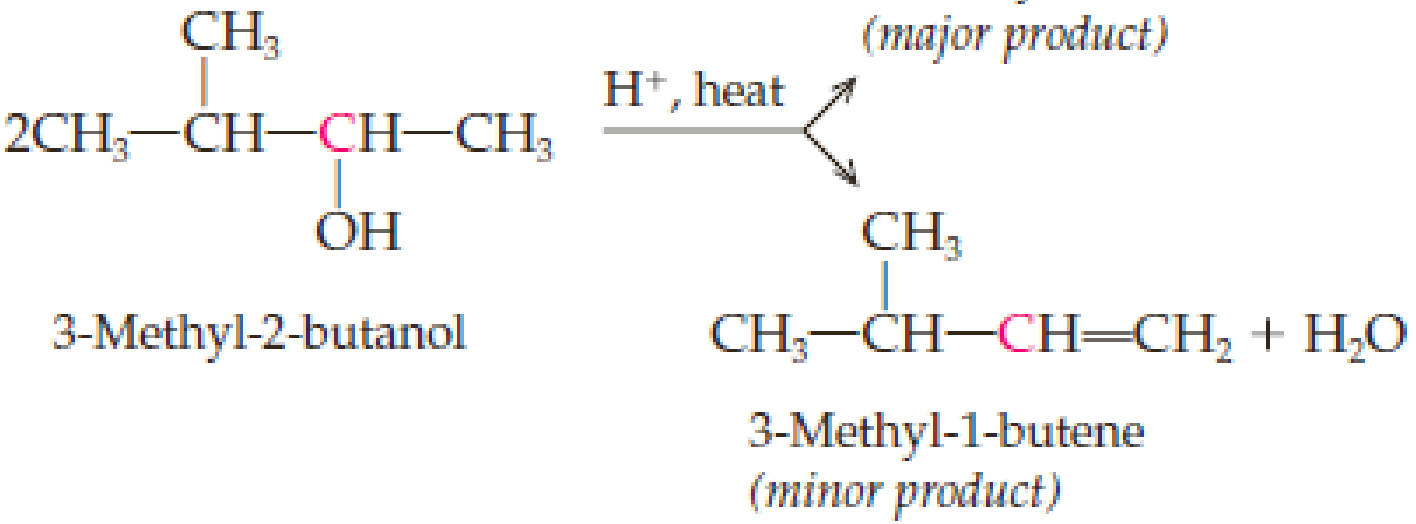
FIGURE 7.9 Free-energy diagrams for the formation of carbocations from protonated tertiary, secondary, and primary alcohols. The relative free energies of activation are tertiary < secondary < primary.



Carbocatião 3ário é mais estável

O efeito indutor repulsivo mais acentuado atenua a carga positiva do catião intermédio

Exercício:
Qual o composto formado a partir da desidratação do 3-metil-2-butanol?
Justifique.



Write an equation showing the dehydration of each of the following alcohols. If there are two possible alkene products, indicate which is the major product and which is the minor product.

a. CH_3CH_2OH

b. $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

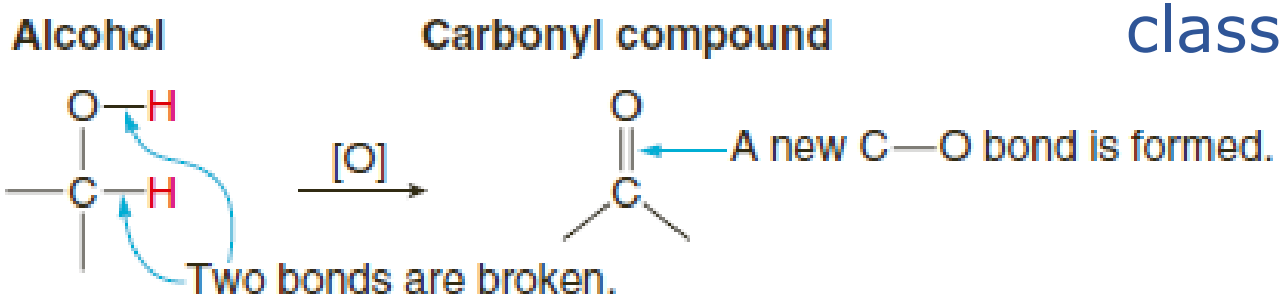
c. $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$

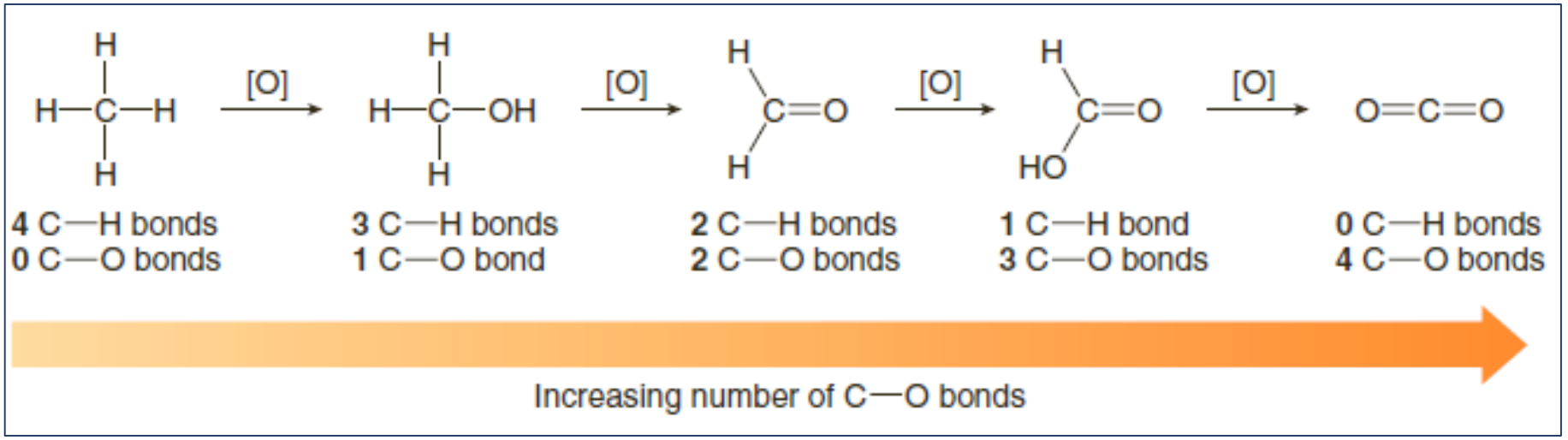
d. $CH_3\underset{\displaystyle OH}{\underset{|}{C}}\underset{\displaystyle CH_3}{\underset{|}{C}}H_3$

ÁLCOOIS: oxidação

Ganho de oxigénio
Perda de H

A reação de oxidação permite diferenciar as três classes de álcoois

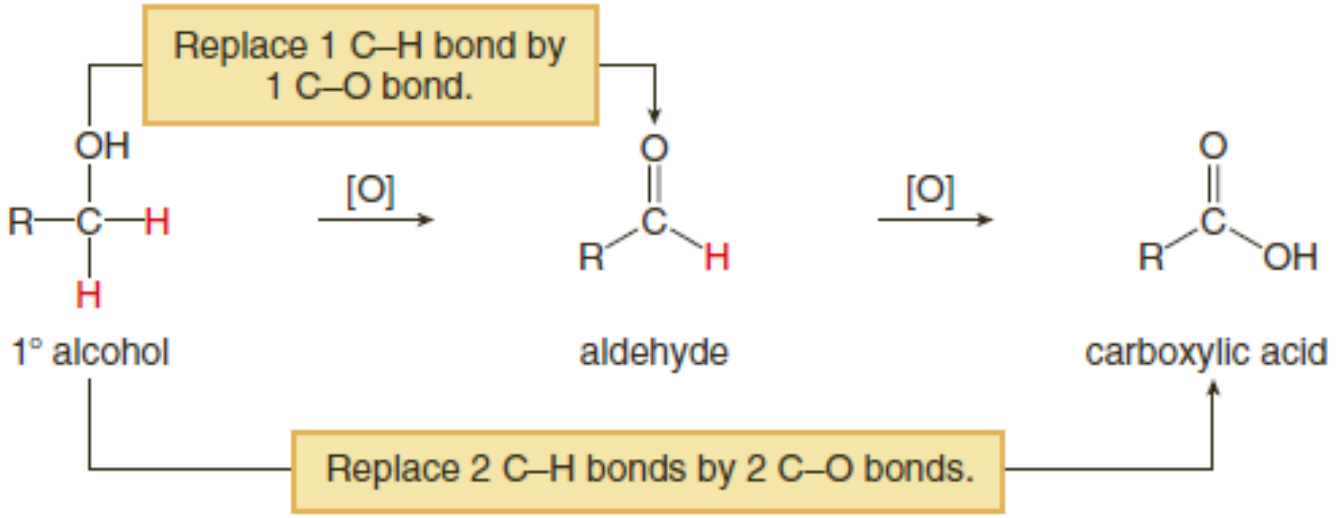




ÁLCOOIS primários:

Primário $\xrightarrow{ox}$ Aldeido $\xrightarrow{ox}$ Ácido

- Primary (1°) alcohols are first oxidized to aldehydes (RCHO), which are further oxidized to carboxylic acids (RCOOH) by replacing one and then two C—H bonds by C—O bonds.

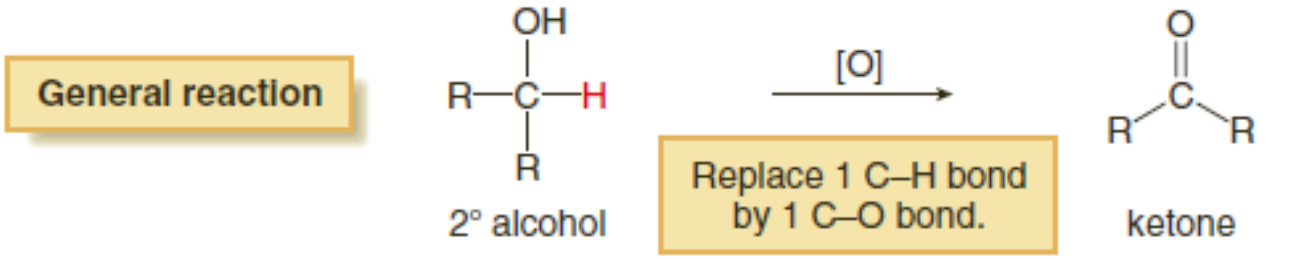


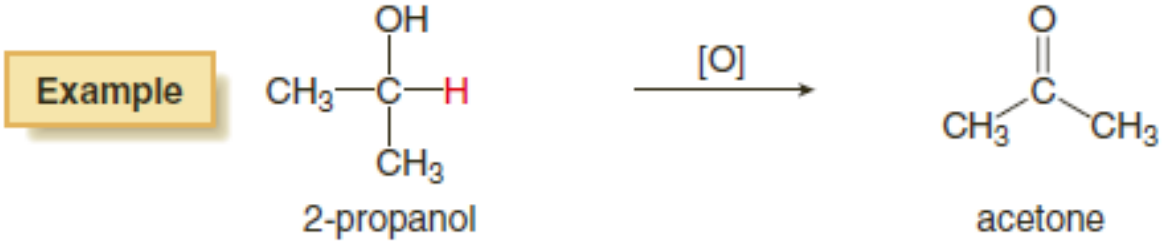
Álcoois primários são facilmente oxidados
Reação ocorre rapidamente em meio ácido na presença de agentes oxidantes fracos ($KMnO_4$, $K_2Cr_2O_7$, HNO_3)

ÁLCOOIS secundários:

Secundário $\xrightarrow{ox}$ Cetona $\xrightarrow{ox}$ 2 Ácidos

- Secondary (2°) alcohols are oxidized to ketones (R_2CO), by replacing one C—H bond by one C—O bond.

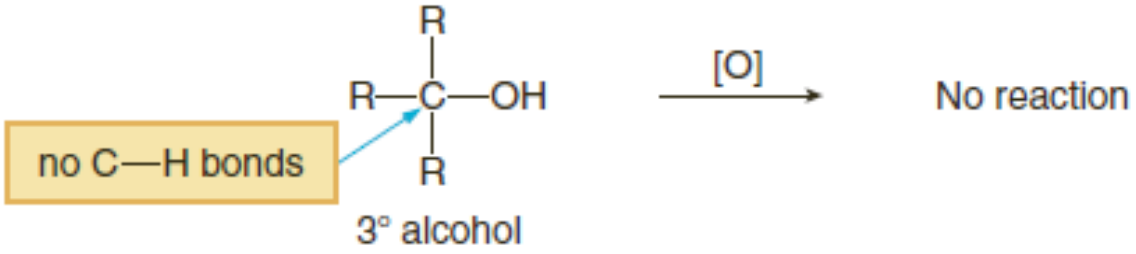




As cetonas não são facilmente oxidadas
A reação ocorre por ação de agentes oxidantes fortes em condições mais enérgicas, $KMnO_4$ a quente, H_2CrO_4, em meio ácido

ÁLCOOIS terciários:

- Tertiary 3° alcohols have no H atoms on the carbon with the OH group, so they are not oxidized.



Os álcoois terciários não se oxidam

➡ Sofrem desidratação em meio ácido formando alcenos

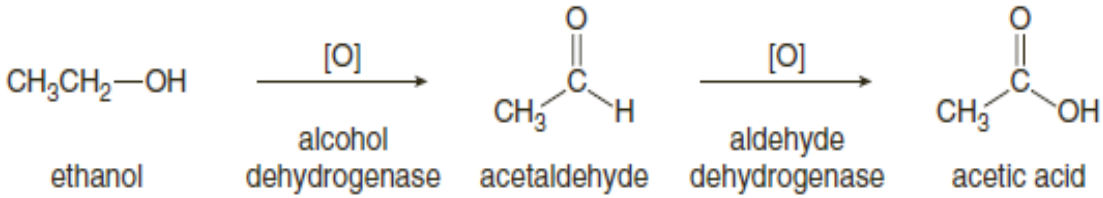
A química orgânica no nosso dia-a-dia

While alcohol use is socially acceptable, alcohol-related traffic fatalities are common with irresponsible alcohol consumption. In 2004, almost 40% of all fatalities in car crashes in the United States were alcohol-related.

14.6A THE METABOLISM OF ETHANOL

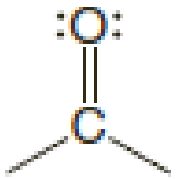
When ethanol is consumed, it is quickly absorbed in the stomach and small intestines and then rapidly transported in the bloodstream to other organs. Ethanol is metabolized in the liver, by a two-step oxidation sequence. The body does not use chromium reagents as oxidants. Instead, high molecular weight enzymes, alcohol dehydrogenase and aldehyde dehydrogenase, and a small molecule called a **coenzyme** carry out these oxidations.

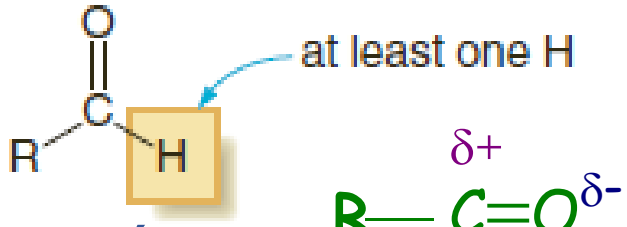
The products of the biological oxidation of ethanol are the same as the products formed in the laboratory. When ethanol (CH_3CH_2OH, a 1° alcohol) is ingested, it is oxidized in the liver first to CH_3CHO (acetaldehyde), and then to CH_3COOH (acetic acid).



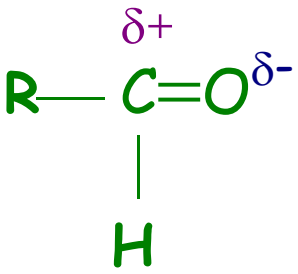
If more ethanol is ingested than can be metabolized in a given time period, the concentration of acetaldehyde accumulates. This toxic compound is responsible for the feelings associated with a hangover.

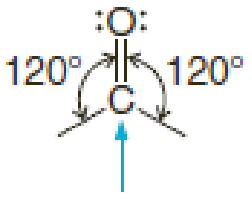
ALDEÍDOS e CETONAS
-compostos com o grupo carbonilo





aldeído





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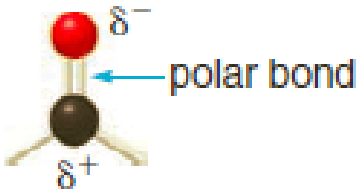
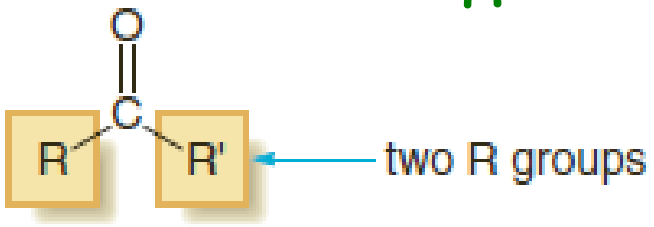
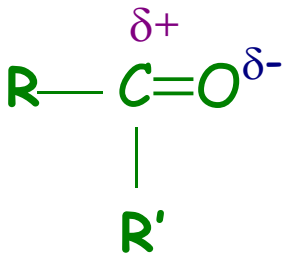
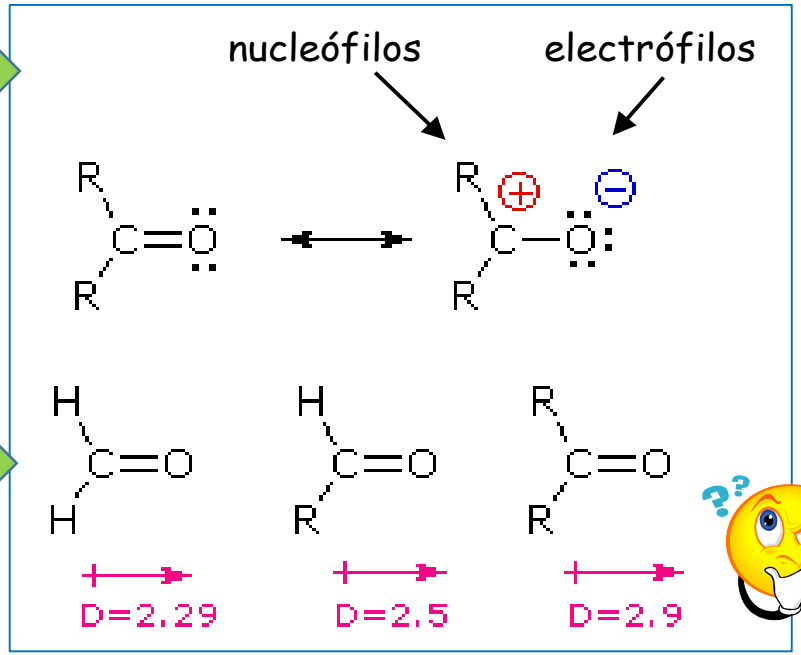




cetona



Polarização mais acentuada



Momento dipolar é explicado pelo efeito indutor

ALDEÍDOS e CETONAS: Propriedades físicas

Forças intermoleculares determinam características físicas: ponto de ebulição (BP) e solubilidade em água (S)

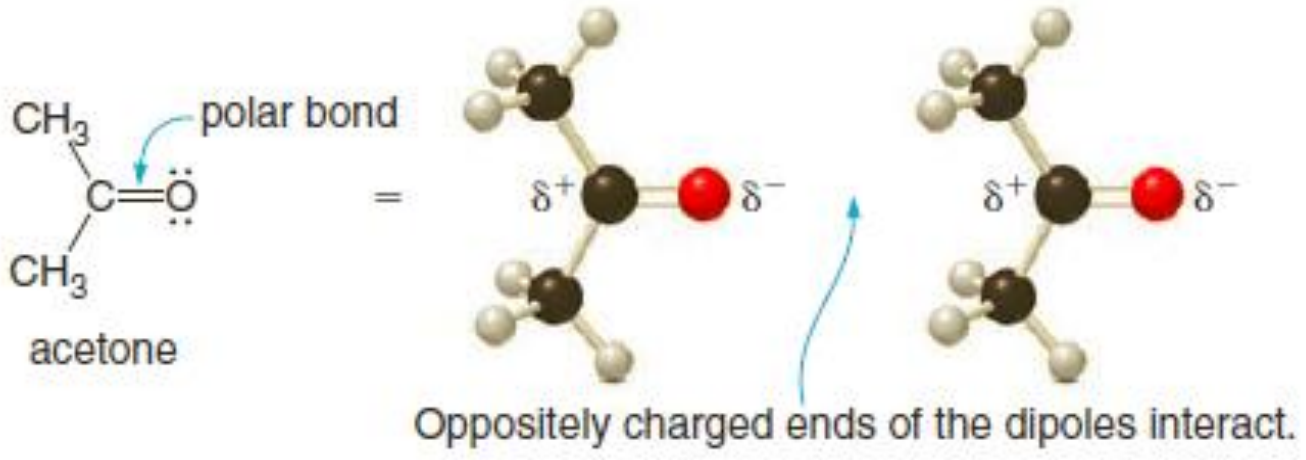
Composto	BP (°C)	S (g/100g água)
$(CH_3)_2C=CH_2$	7	0.04
$(CH_3)_2C=O$	58	Muito elevada
$CH_3CH_2CH_2CH=CH_2$	30	0.03
$CH_3CH_2CH_2CH=O$	76	7

- Low molecular weight aldehydes and ketones (those having less than six carbons) are soluble in both organic solvents and water.
- Higher molecular weight aldehydes and ketones (those having six carbons or more) are soluble in organic solvents, but insoluble in water.

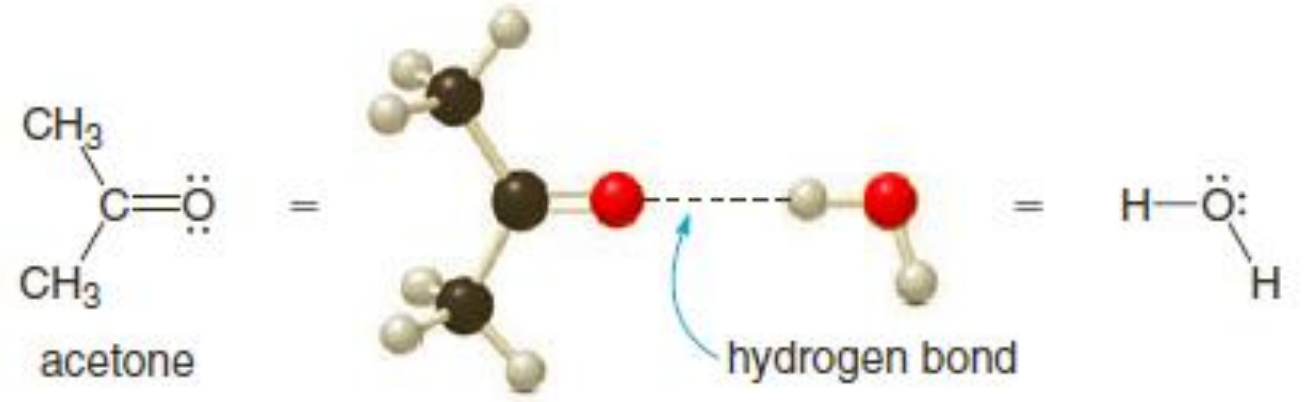
Dipolo permanente:

Forças intermoleculares

-dipolo-dipolo

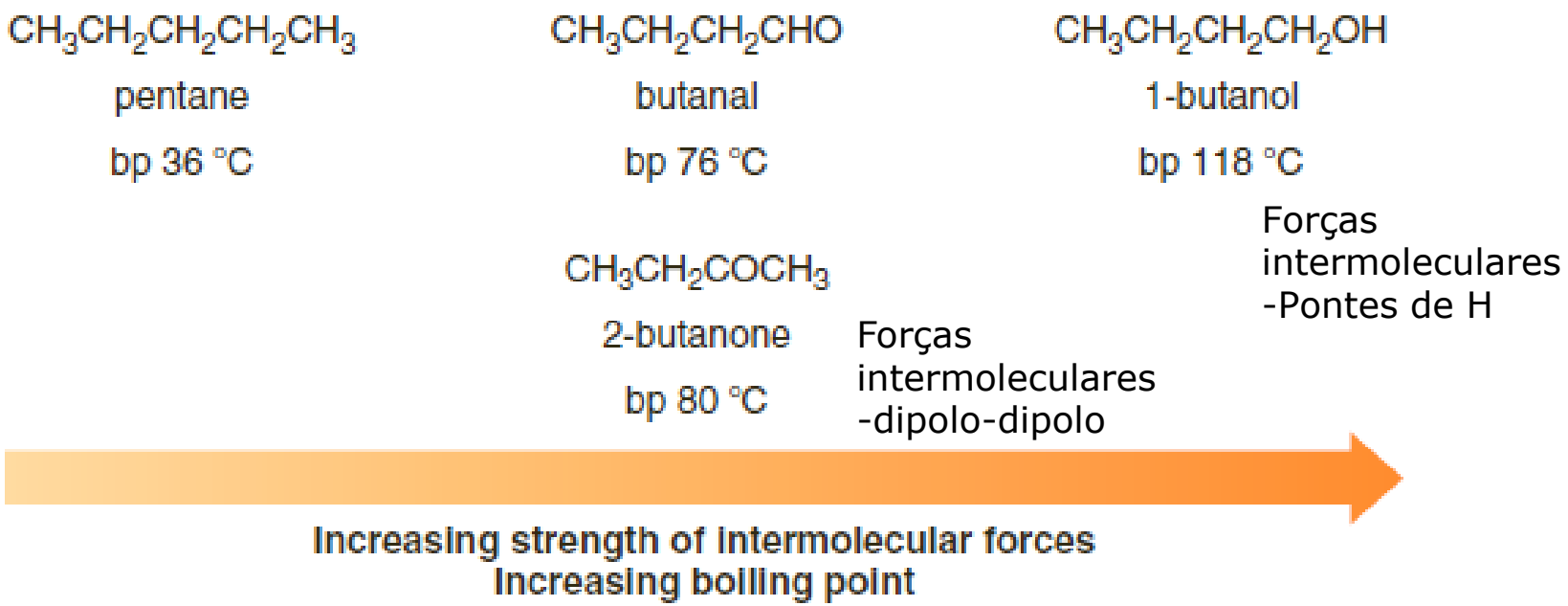


-Pontes de H



O ponto de ebulição (BP) de álcoois, aldeídos e cetonas é determinado pelas forças intermoleculares que se estabelecem entre as moléculas:

- Aldehydes and ketones have *higher* boiling points than hydrocarbons of comparable size.
- Aldehydes and ketones have *lower* boiling points than alcohols of comparable size.



ALDEÍDOS e CETONAS

A reatividade resulta de:

-polarização do grupo carbonilo com momento dipolar elevado

-ligação dupla C=O

-2 pares de e^- não ligantes

-possivel estabilização por ressonância

Sofre ataque eletrófilo, adição

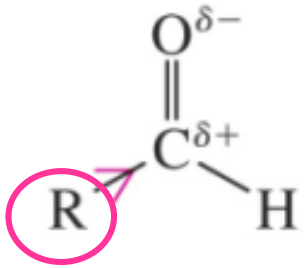
Causam ataque nucleófilo

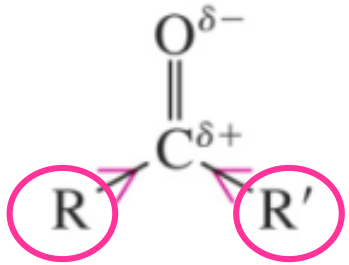
Reações:

Adição, Oxidação

ALDEIDOS e CETONAS

Nos aldeídos, o **carbono** do grupo carbonilo tem maior défice eletrónico, tornando o carbonilo mais reativo





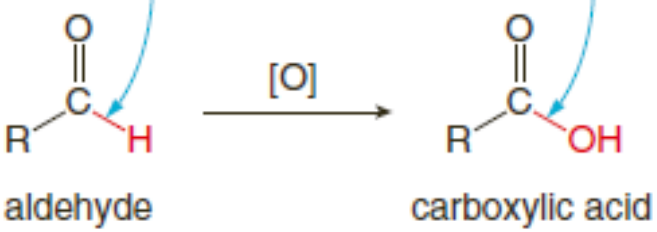
Este comportamento é influenciado pelo efeito indutor repulsivo atribuído aos substituintes alquilo

Reações de oxidação:

1. Aldehydes can be oxidized to carboxylic acids.

Oxidation

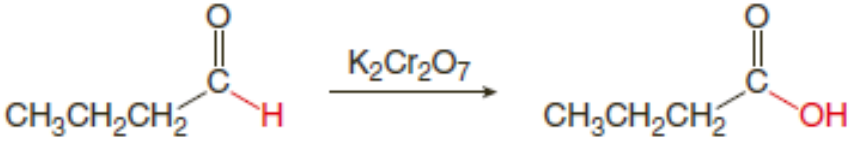
Replace 1 C—H bond by 1 C—O bond.



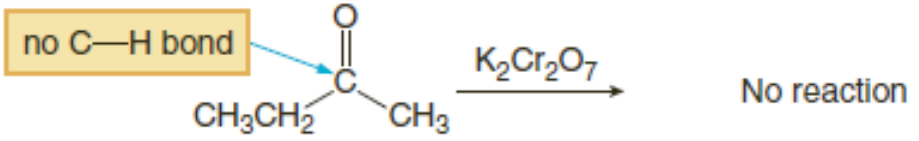
aldehyde carboxylic acid

Aldehydes are easily oxidized by oxygen in the air. When $CH_3CH_2CH_2CHO$ (butanal) stands at room temperature, it slowly develops the characteristic smell of its oxidation product, $CH_3CH_2CH_2COOH$ (butanoic acid), a compound that contributes to the distinctive odor of human sweat.

Examples



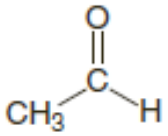
butanal butanoic acid

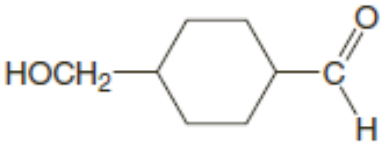


2-butanone No reaction

Oxidação dos aldeídos pelo Reagente de Tollens:

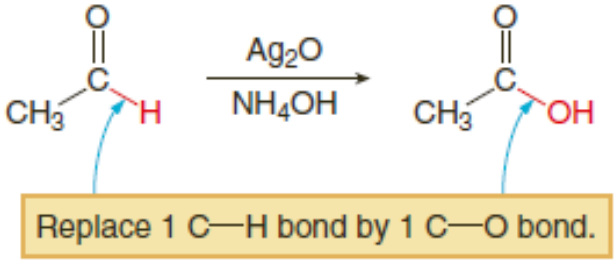
What product is formed when each compound is treated with Tollens reagent (Ag_2O, NH_4OH)?

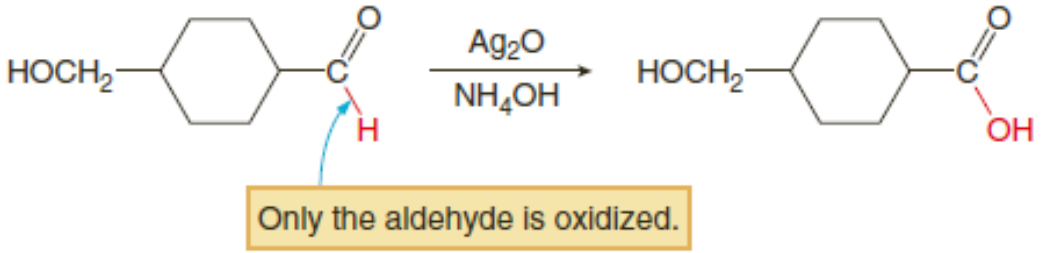
a. 

b. 

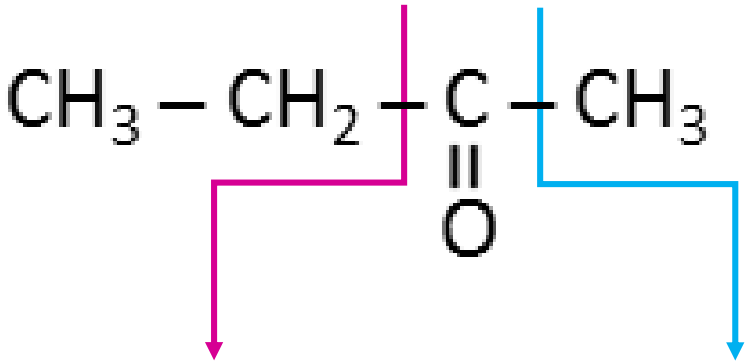
Only aldehydes (RCHO) react with Tollens reagent. Ketones and alcohols are inert to oxidation.

The aldehyde in both compounds is oxidized to RCO_2H, but the 1° alcohol in part (b) does not react with Tollens reagent.

a. 

b. 

Oxidação das cetonas:
-ocorre por agentes oxidants mais enérgicos
-ex:



Produtos formados:

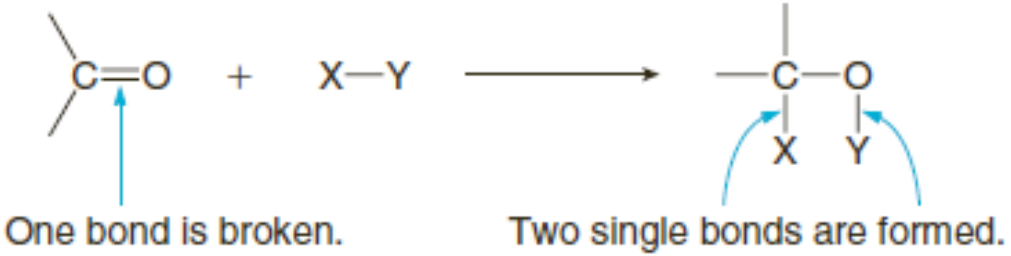
$CH_3 - COOH$ $\quad$ $CH_3 - CH_2 - COOH$

$CH_3 - COOH$ $\quad$ $COOH$

Reações de adição:

2. Aldehydes and ketones undergo addition reactions.

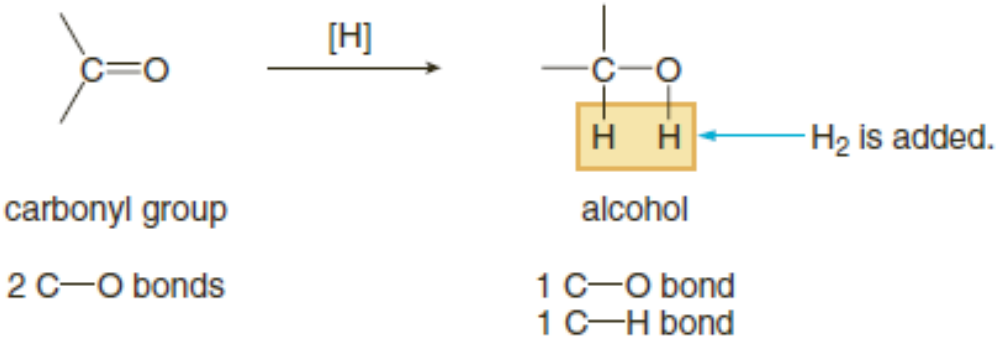
Addition



Redução:

Recall from Section 12.8 that to determine if an organic compound has been reduced, we compare the number of C—H and C—O bonds. **Reduction is the *opposite* of oxidation.**

Reduction

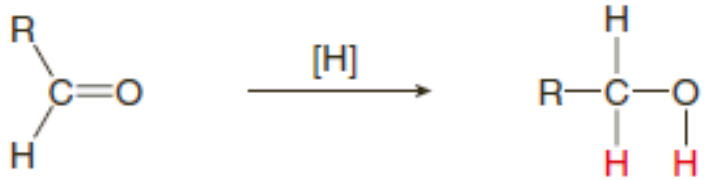


Redução é reação inversa da oxidação:

Primário $\underset{\text{red}}{\overset{\text{ox}}{\rightleftharpoons}}$ Aldeido $\xrightarrow{\text{ox}}$ Ácido

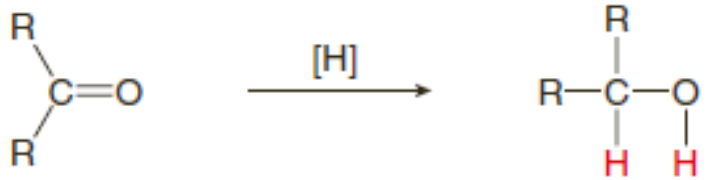
Secundário $\underset{\text{red}}{\overset{\text{ox}}{\rightleftharpoons}}$ Cetona $\xrightarrow{\text{ox}}$ 2 Ácidos

- Aldehydes (RCHO) are reduced to 1° alcohols (RCH_2OH).



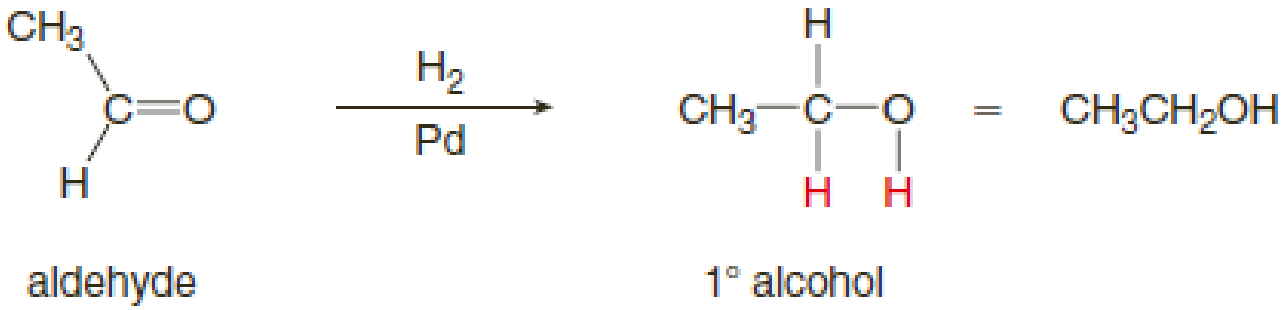
aldehyde 1° alcohol

- Ketones (RCOR) are reduced to 2° alcohols (R_2CHOH).

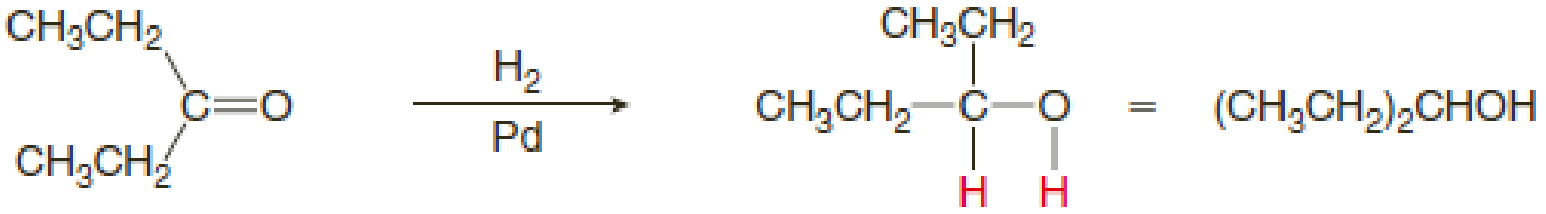


ketone 2° alcohol

A redução é reação inversa da oxidação:

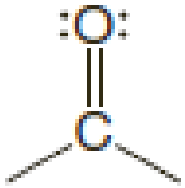


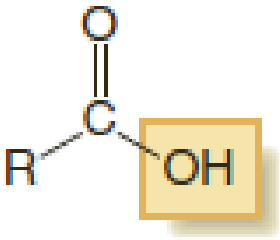
aldehyde 1° alcohol

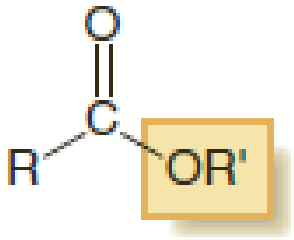


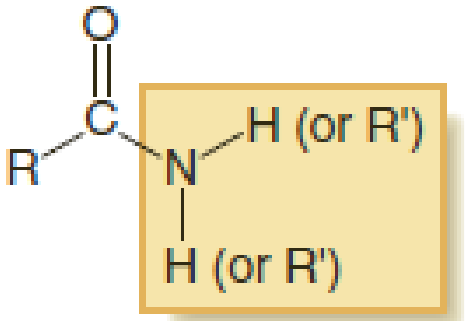
ketone 2° alcohol

Outros compostos com o grupo carbonilo ácidos carboxílicos, ésteres, amidas







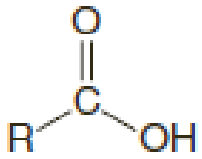


ácido carboxilico

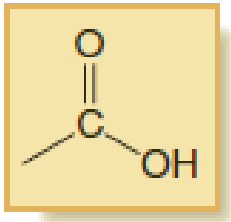
éster

amida

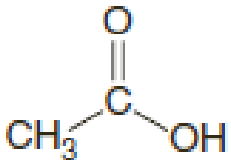
General structure



Ácido carboxilico

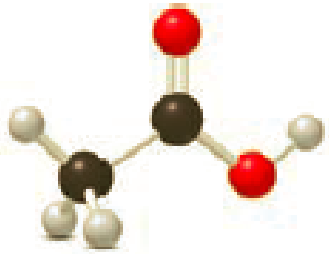


Grupo carboxilo



acetic acid

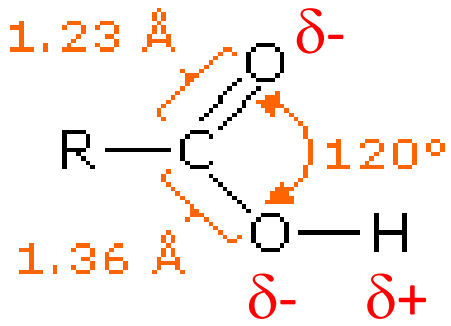
=



CH_3CO_2H

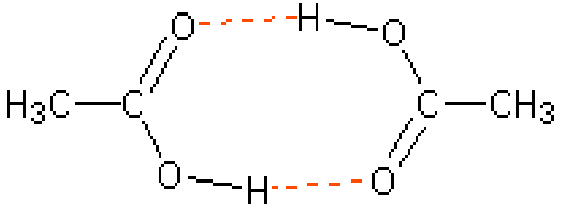
ÁCIDOS CARBOXíLICOS: Propriedades físicas

-Polarização da ligação O–H

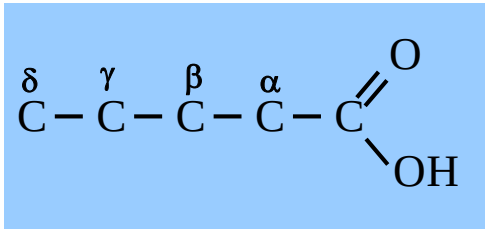


-Resultam do estabelecimento de forças atrativas pontes de hidrogénio e dipolo-dipolo entre moléculas

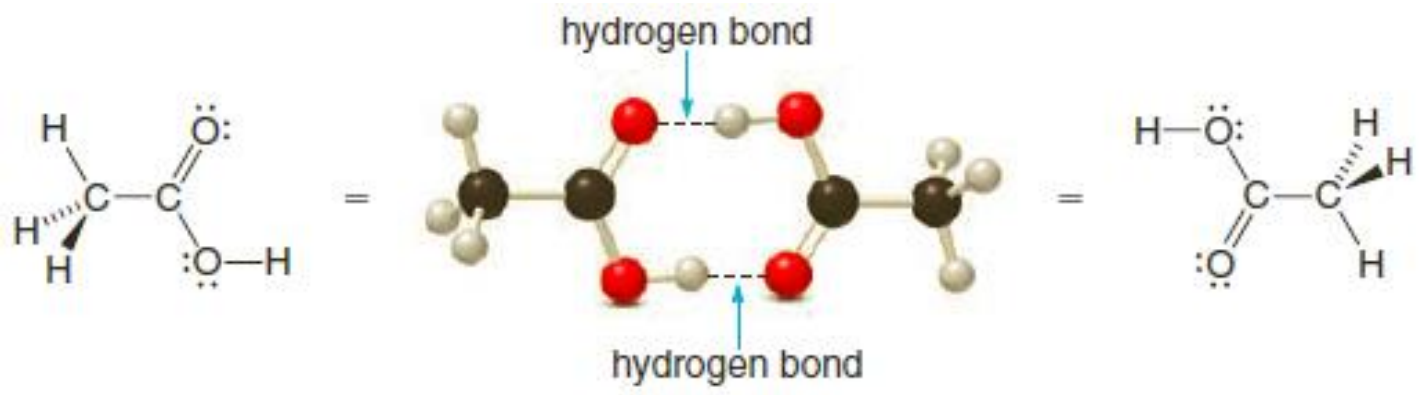
-Estas forças aumentam o ponto de ebulição e favorecem a solubilidade (ácidos carboxílicos têm ponto de ebulição elevado por estabelecerem 2 pontes H)



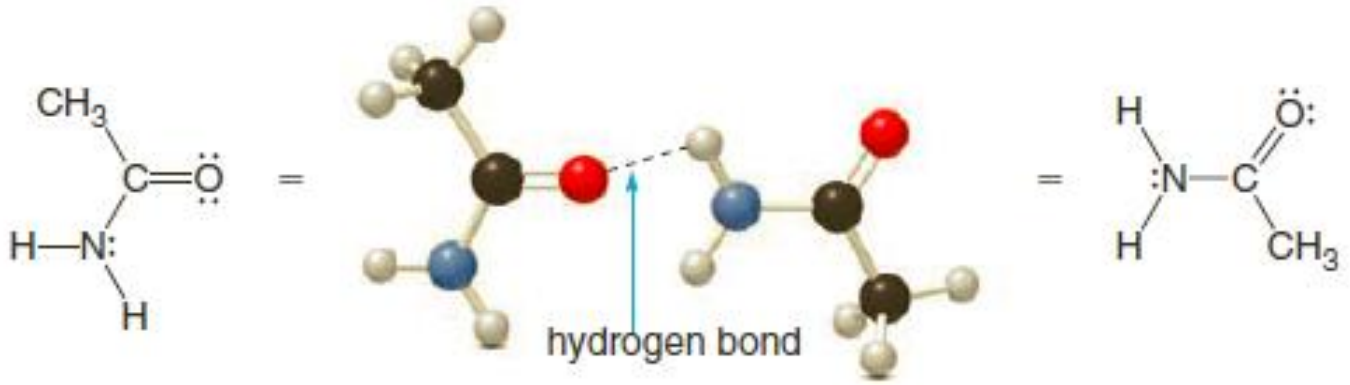
-As orgânicos de cadeia longa são moléculas dipolares
Ex: ácidos gordos constituintes dos lípidos, ácidos de cadeias longas, ac. palmitoleico e ac. palmítico



Formação de 2 pontes de hidrogénio entre 2 moléculas de ácido acético:



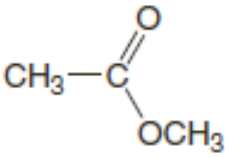
Formação de pontes de hidrogénio entre moléculas de CH_3CONH_2 (amida):



Consequências da formação de pontes de hidrogénio nos ácidos:

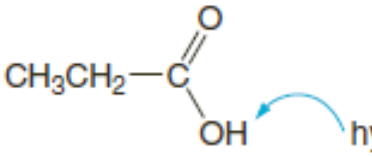
Ácidos vs ésteres:

- Carboxylic acids have stronger intermolecular forces than esters, giving them higher boiling points and melting points, when comparing compounds of similar size.



bp 58 °C

no hydrogen bonding possible

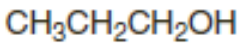


bp 141 °C

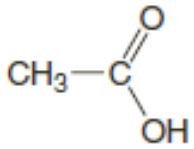
stronger intermolecular forces
higher boiling point

Ácidos vs álcoois:

- Carboxylic acids have higher boiling points and melting points than alcohols of comparable size.



1-propanol
bp 97 °C

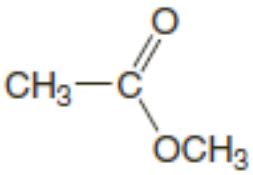


acetic acid
bp 118 °C

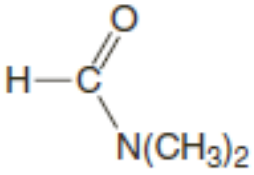
more hydrogen-bonding interactions possible
higher boiling point

Consequências da formação de pontes de hidrogénio nas amidas:

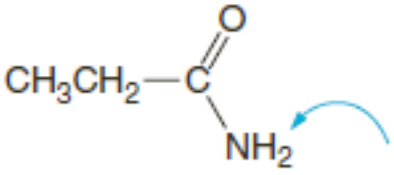
- Primary (1°) and 2° amides have higher boiling points and melting points than esters and 3° amides of comparable size.



ester
bp 58 °C



3° amide
bp 153 °C



hydrogen bonding possible

1° amide
bp 213 °C

strongest intermolecular forces
highest boiling point

A polarização da ligação O–H influencia as propriedades físicas: ponto de ebulição e a solubilidade

O ponto de ebulição aumenta regularmente com o tamanho da cadeia carbonada (o ponto de fusão não aumenta regularmente)

	Melting Point	Boiling Point
HCO_2H	8.4 ºC	101 ºC
CH_3CO_2H	16.6 ºC	118 ºC
$CH_3CH_2CO_2H$	-20.8 ºC	141 ºC
$CH_3(CH_2)_2CO_2H$	-5.5 ºC	164 ºC
$CH_3(CH_2)_3CO_2H$	-34.5 ºC	186 ºC
$CH_3(CH_2)_4CO_2H$	-4.0 ºC	205 ºC
$CH_3(CH_2)_5CO_2H$	-7.5 ºC	223 ºC
$CH_3(CH_2)_6CO_2H$	16.3 ºC	239 ºC
$CH_3(CH_2)_7CO_2H$	12.0 ºC	253 ºC

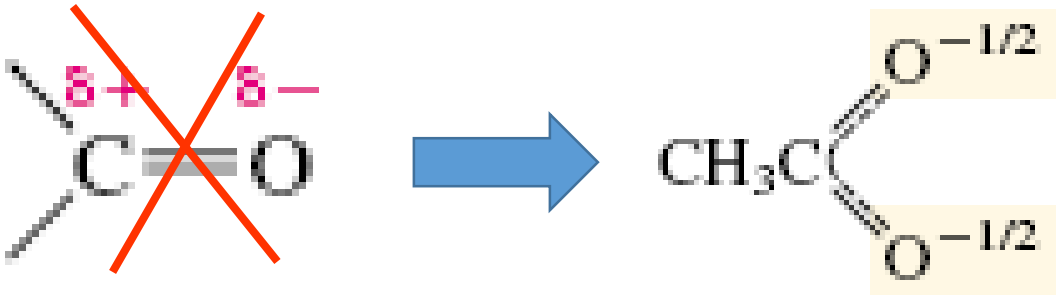
Diminuição da solubilidade em agua

-ligações duplas *cis* causam abaixamento do ponto de fusão

ÁCIDOS CARBOXÍLICOS:
reatividade do COOH

-não ocorre ataque nucleófilo à ligação dupla

Devido à estabilização por ressonância, não há polarização acentuada do grupo carbonilo (como se verifica em aldeídos e cetonas):

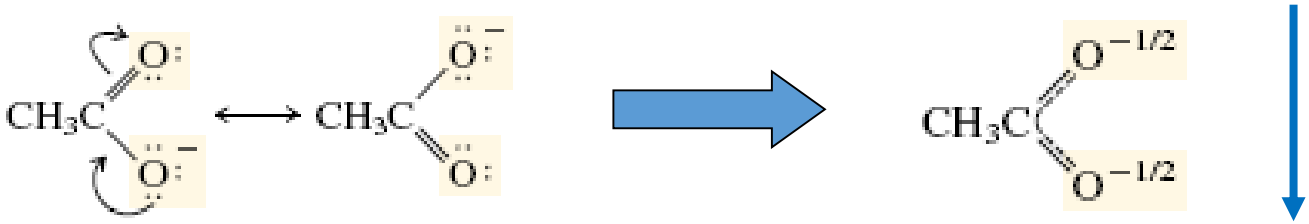


-Caráter ácido mais acentuado em ácidos que em álcoois

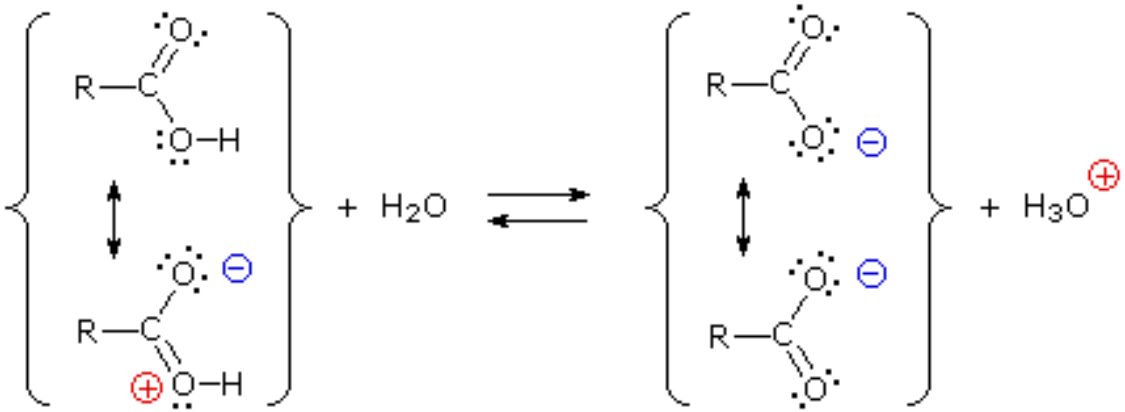
Ex: Etanol Ka=10^{-16}, Ácido acético Ka=$10^{-4.74}$

Ácidos orgânicos são (ácidos) mais fortes que álcoois

-Estabilização por ressonância do ião carboxilato favorece a forma iónica, pelo que se dissociam facilmente (maior caráter ácido):



- É o fator de maior importância para explicar a elevada acidez dos ácidos carboxílicos
- Compete com o efeito indutor



ÁCIDOS CARBOXÍLICOS:
Influencia do efeito indutor na acidez

- A influencia do efeito indutor é maior quanto menor a distância ao grupo carbonilo

- Substituintes eletronegativos aumentam a acidez por efeito indutor atrativo (F > Cl > Br > I)

	pK_a		pK_a		pK_a
HCO_2H	3.75	$BrCH_2COOH$	2.90	$ClCH_2CH_2CH_2CO_2H$	4.53
CH_3COOH	4.74	ICH_2COOH	3.10	$CH_3CHClCH_2CO_2H$	4.05
FCH_2COOH	2.65	Cl_3CCOOH	0.77	$CH_3CH_2CHClCO_2H$	2.89
$ClCH_2COOH$	2.85	$CH_3CH_2CH_2CO_2H$	4.82		

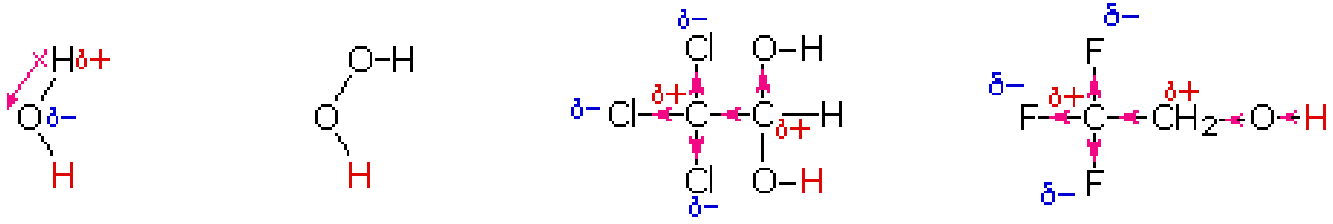
ÁCIDOS CARBOXÍLICOS: O grupo carbonilo tem caráter eletrófilo que favorece a acidez mas sofre influência da restante composição:

Álcoois e ácidos

Influência da natureza do substituinte: atrativos e repulsivos

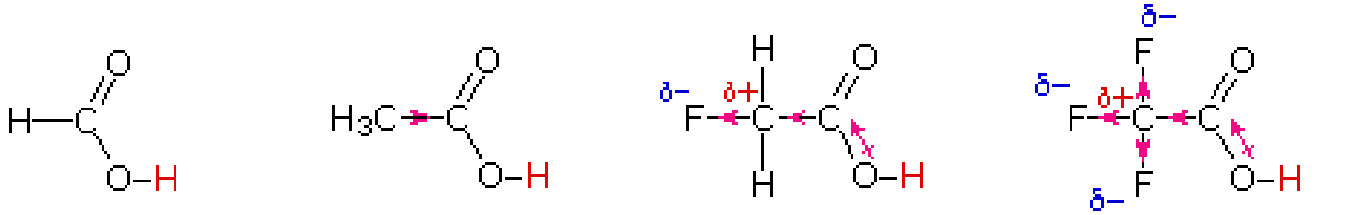
Influência da distância dos substituintes

1.



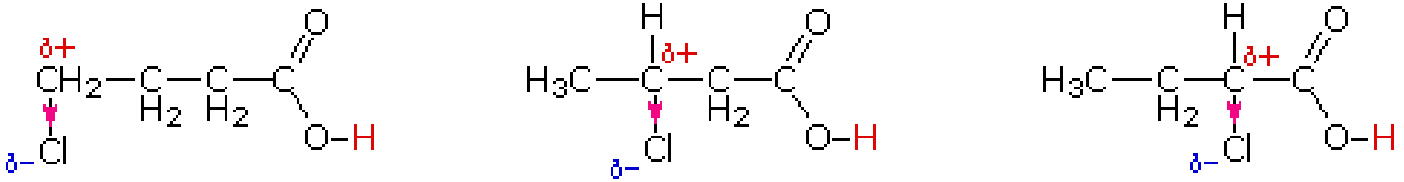
pK_a	15.7	11.6	10.0	12.2

2.



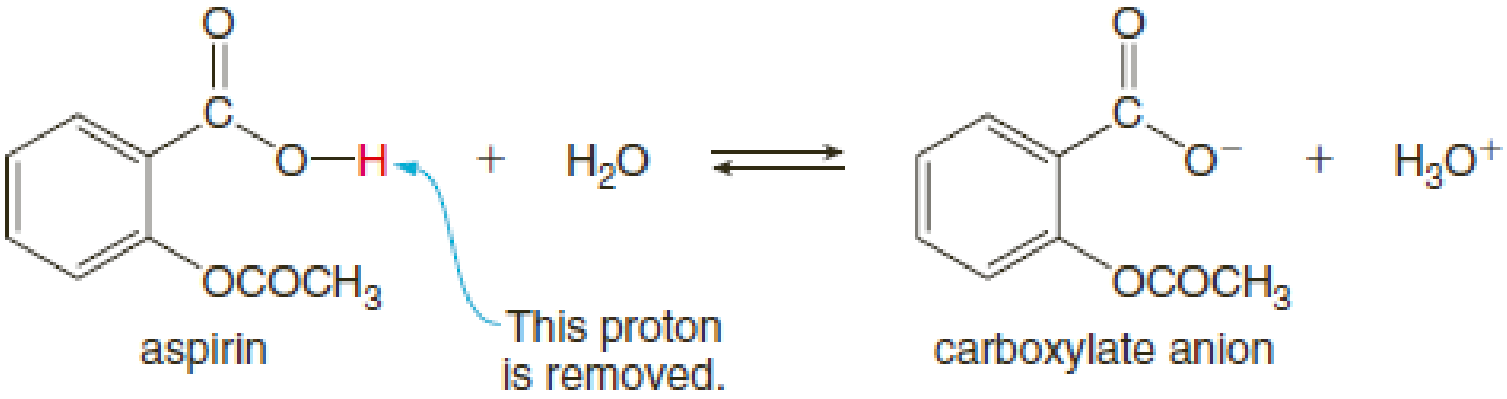
pK_a	3.75	4.74	2.65	0.0

3.



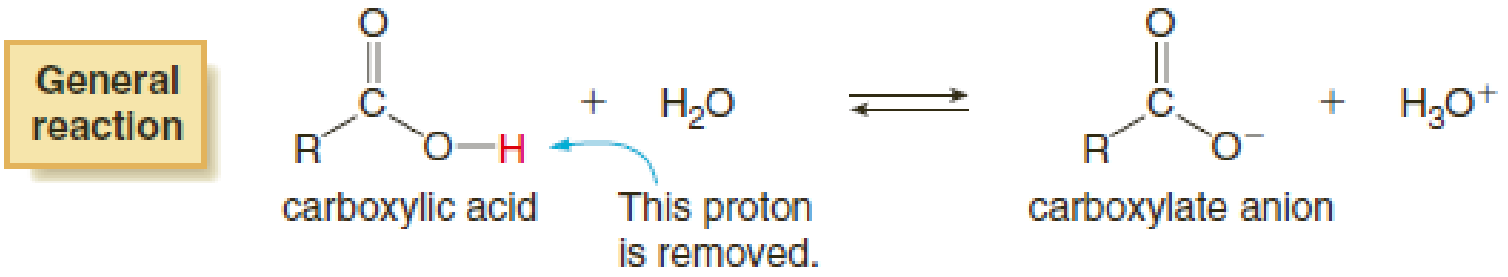
pK_a	4.53	4.05	2.89

Exemplo:
Consequências do caráter ácido

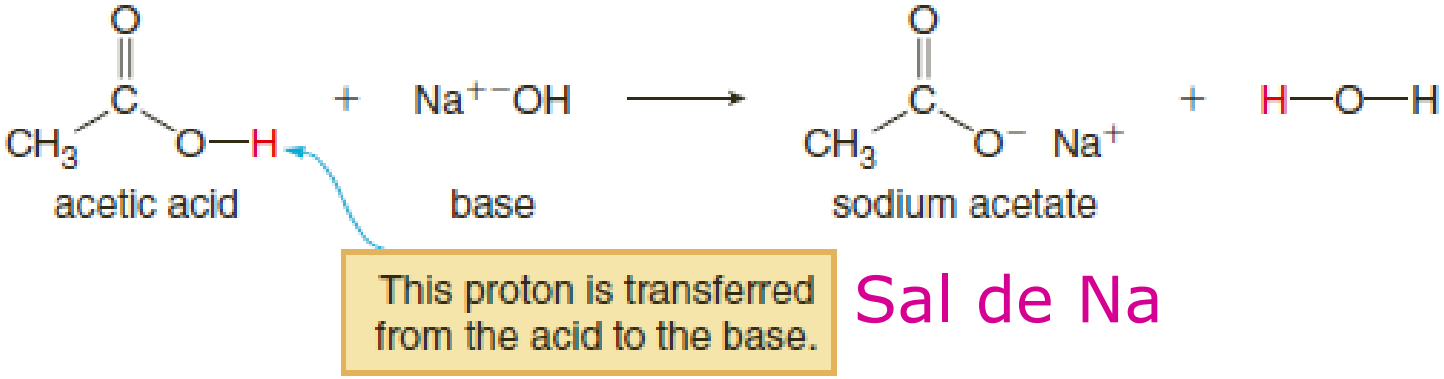


Why is this acid–base reaction important? **To be active, aspirin must cross a cell membrane, and to do so, it must be neutral, not ionic.** This means that aspirin crosses a cell membrane and is absorbed by the body in its neutral form in the stomach. Whether aspirin is present as its acid or its conjugate base is thus very important in determining whether it can enter a cell and act as a pain reliever and anti-inflammatory agent.

Consequências do caráter ácido:
Formação de sais por reação com bases:



Reação com NaOH



Sal de Na

Reação com KOH

$CH_3\text{-}COOH + KOH \rightarrow CH_3\text{-}COOK + H_2O$

Sal de K

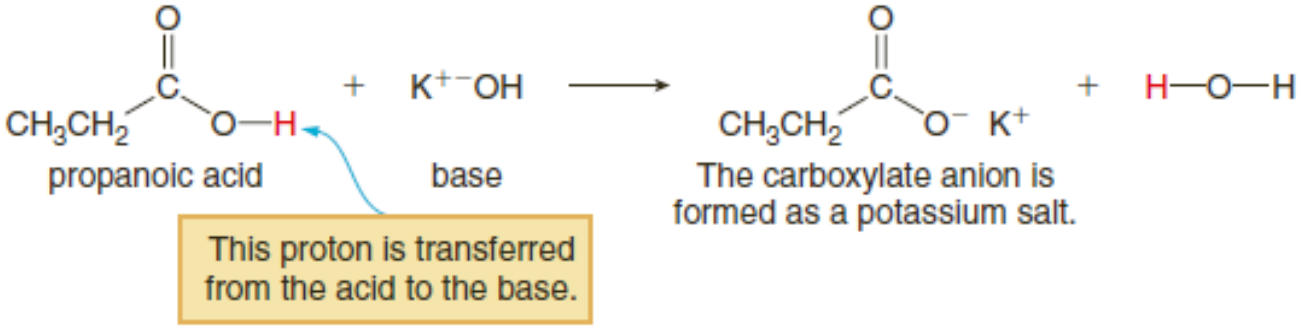
Exemplo:

What products are formed when propanoic acid (CH_3CH_2COOH) reacts with potassium hydroxide (KOH)?

ANALYSIS In any acid–base reaction with a carboxylic acid:

- Remove a proton from the carboxyl group (COOH) and form the carboxylate anion ($RCOO^-$).
- Add a proton to the base. If the base has a –1 charge to begin with, it becomes a neutral product when a proton (H^+) is added to it.
- Balance the charge of the carboxylate anion by drawing it as a salt with a metal cation.

SOLUTION

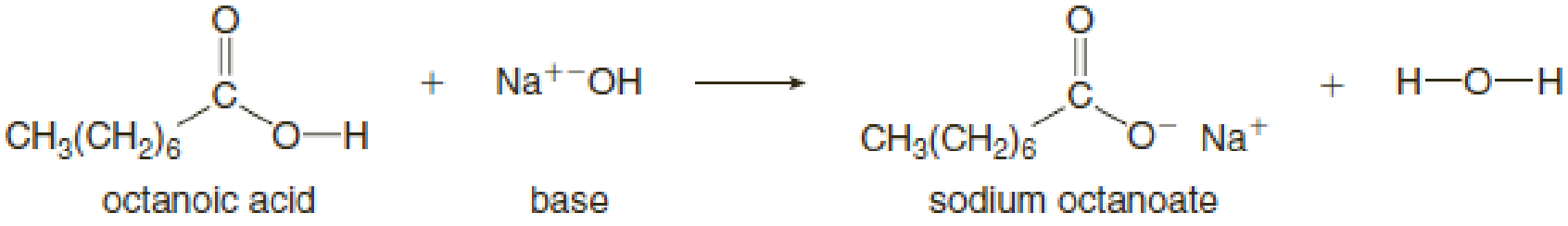


Thus, CH_3CH_2COOH loses a proton to form $CH_3CH_2COO^-$, which is present in solution as its potassium salt, $CH_3CH_2COO^-\,K^+$. Hydroxide (^-OH) gains a proton to form H_2O.

Os **sais** de ácidos gordos de cadeia curta formados com catiões monovalentes são solúveis em água, ionizando-se:

$$CH_3\text{-}COOK \rightarrow CH_3\text{-}COO^- + K^+$$

Ácidos carboxílicos de cadeia superior a 5C são insolúveis em água mas os sais resultantes, formados com catiões monovalentes, são solúveis em água, formando iões:



octanoic acid — base — sodium octanoate

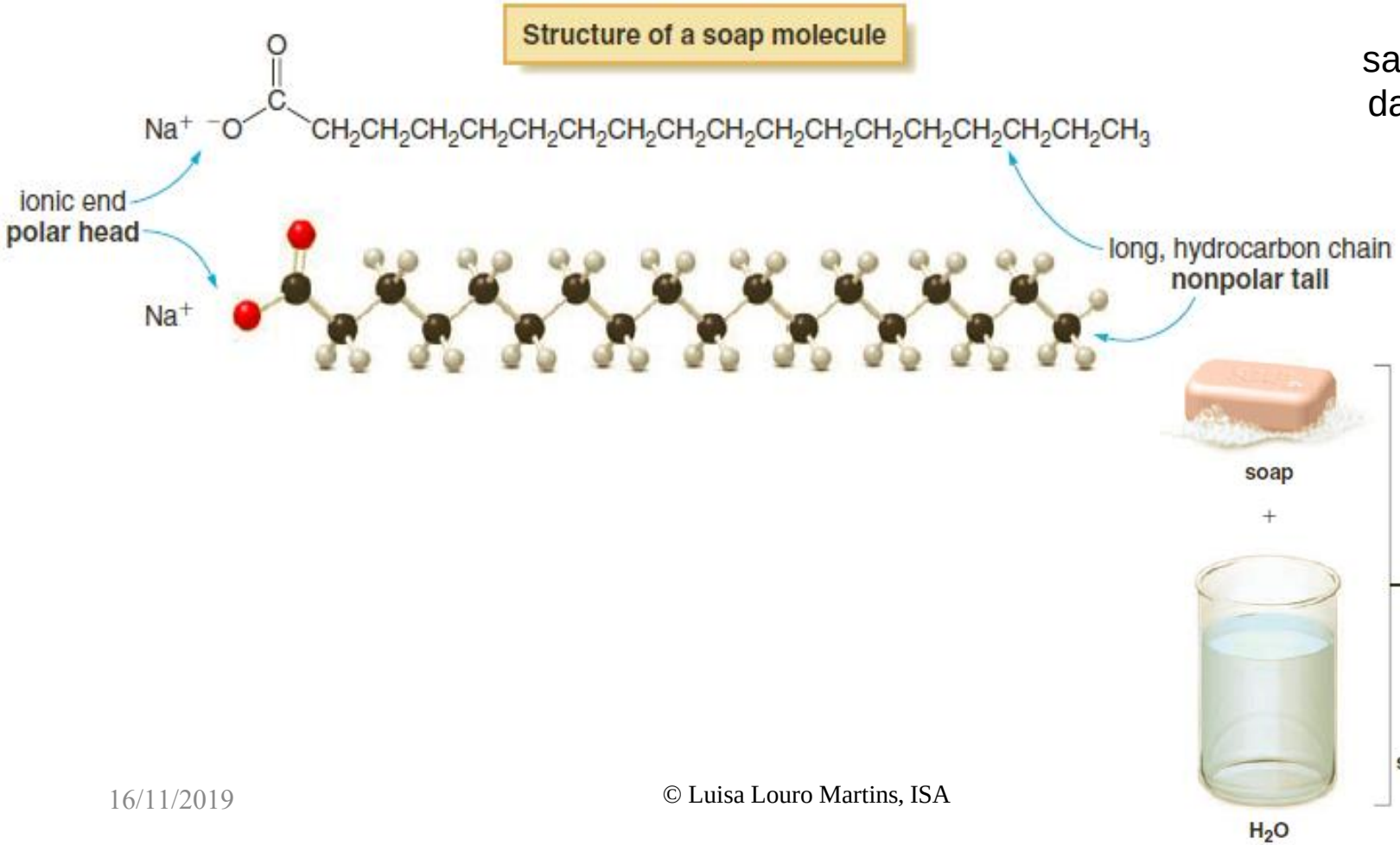
The acid has more than 5 C's, so it is **insoluble** in water.

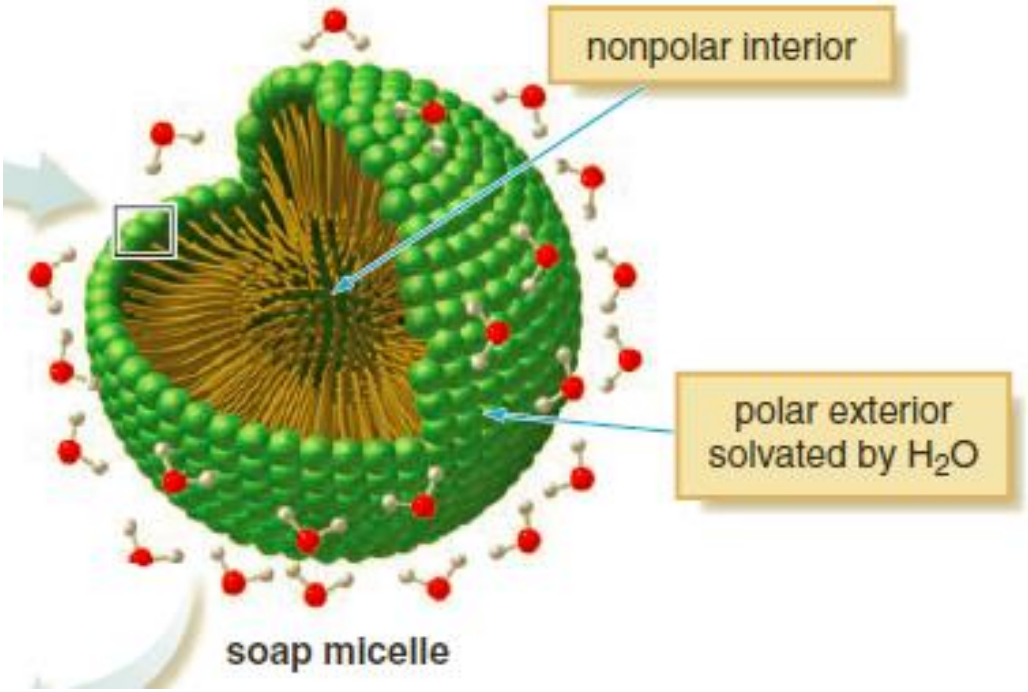
The ionic salt is **soluble** in water.

O caso dos sabões: Sabões são sais solúveis de K, Na, Li, de ácidos gordos (ácidos alifáticos de cadeia longa não ramificada)

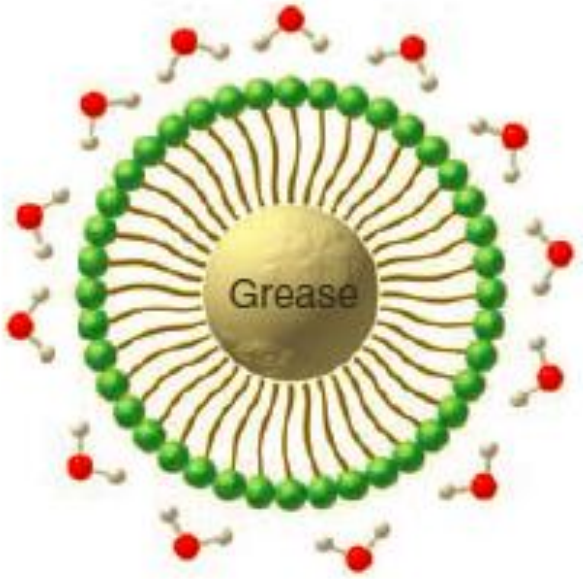
- The ionic end is called the *polar head.*
- The carbon chain of nonpolar C—C and C—H bonds is called the *nonpolar tail.*

São obtidos industrialmente por saponificação das gorduras naturais





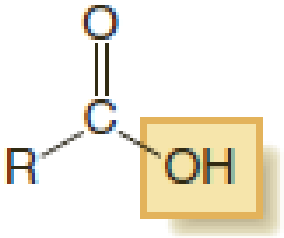
E o caso das águas duras??
Ca^{2+} e Mg^{2+}



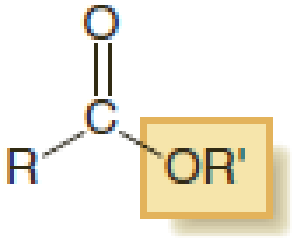
Cross-section of a soap micelle with a grease particle dissolved in the interior

Reações de **substituição** nos ácidos orgânicos:

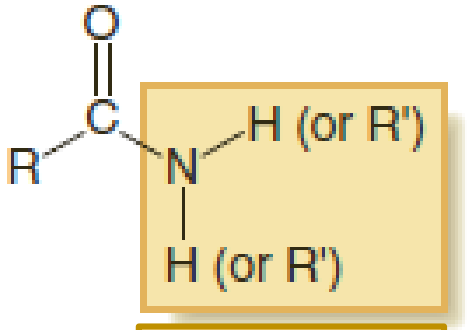
-Formação de ésteres e amidas



ácido carboxilico



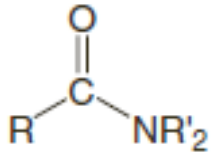
éster



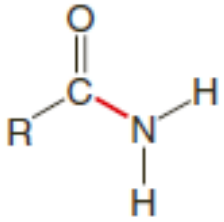
amida

Amidas:

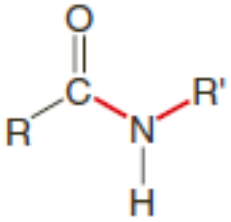
General structure



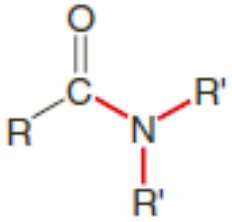
amide
R' = H or alkyl



1° amide
1 C—N bond



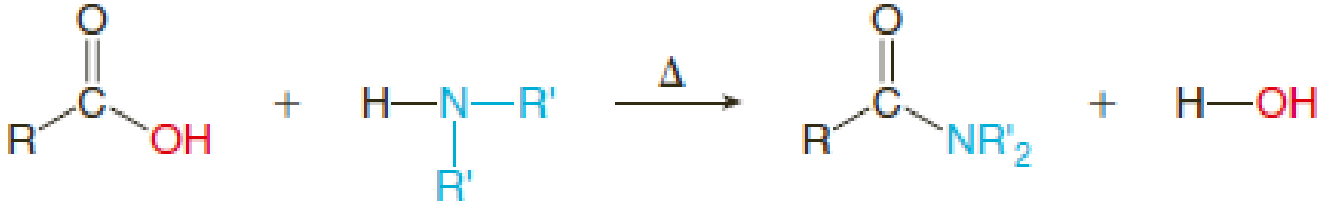
2° amide
2 C—N bonds



3° amide
3 C—N bonds

Formação:

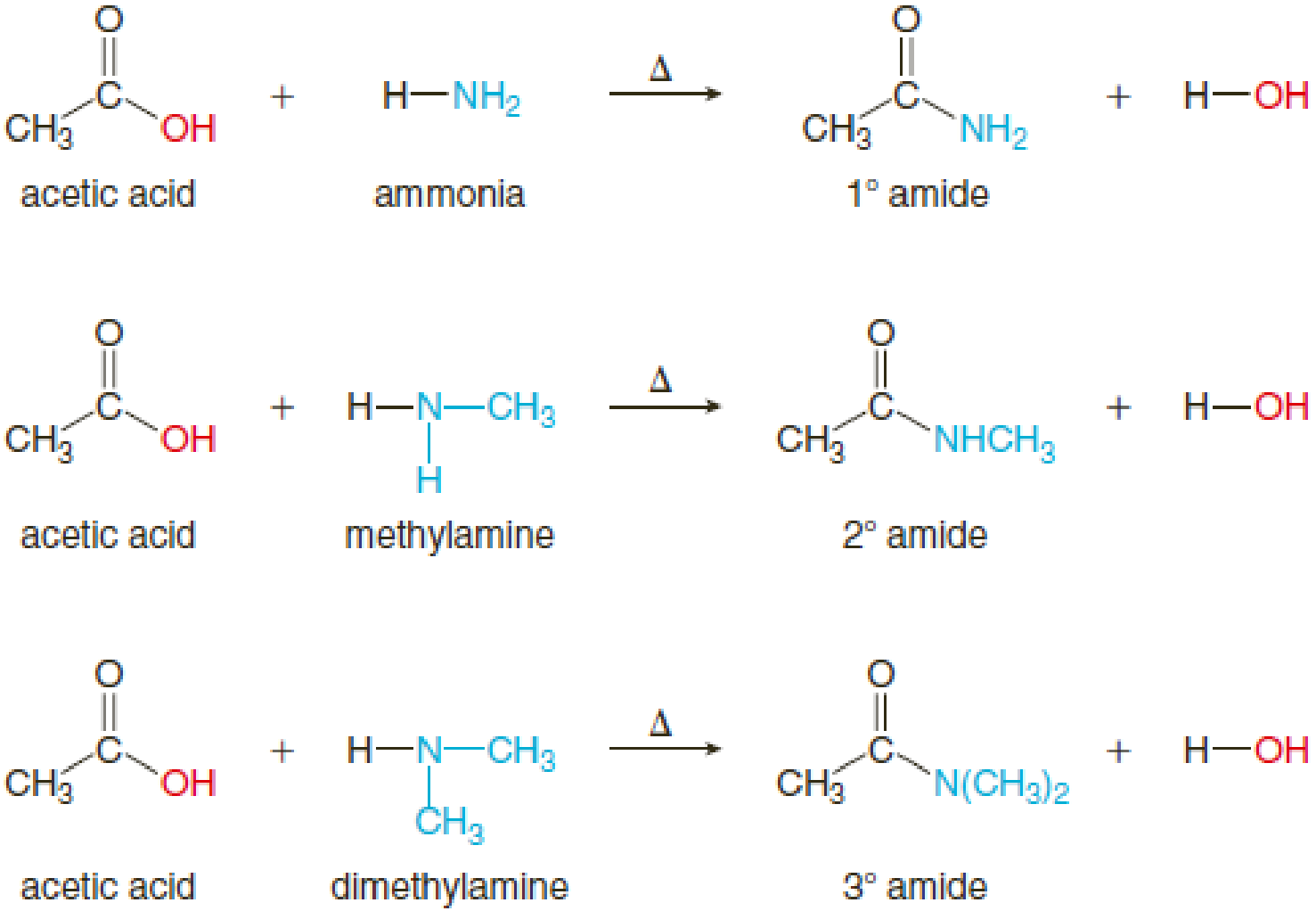
Amide formation



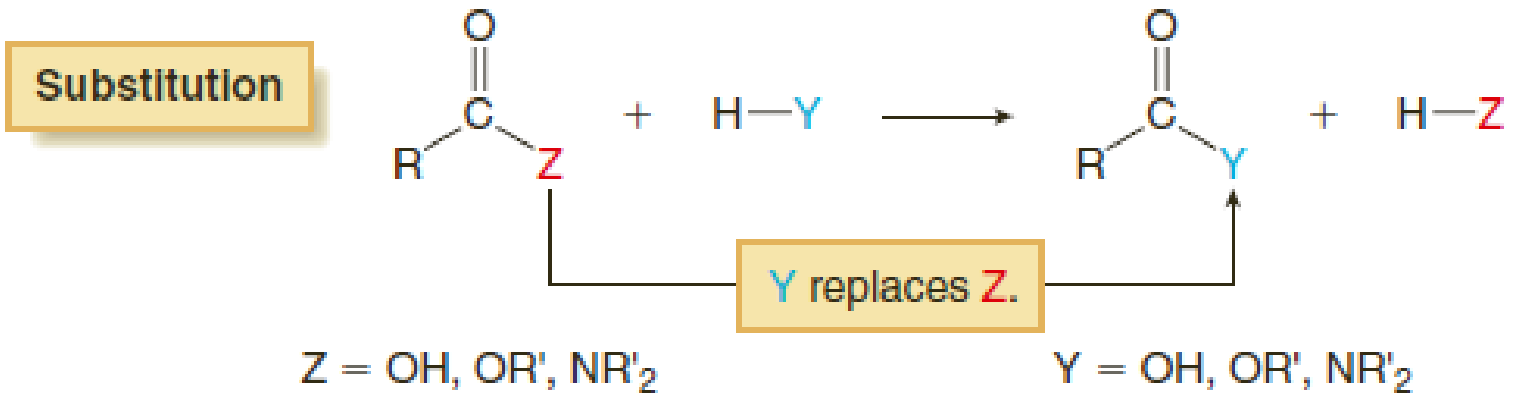
carboxylic acid R' = H or alkyl amide

- Reaction of RCOOH with NH_3 forms a 1° amide ($RCONH_2$). — Amida primária
- Reaction of RCOOH with $R'NH_2$ forms a 2° amide ($RCONHR'$). — Amida secundária
- Reaction of RCOOH with R'_2NH forms a 3° amide ($RCONR'_2$). — Amida terciária

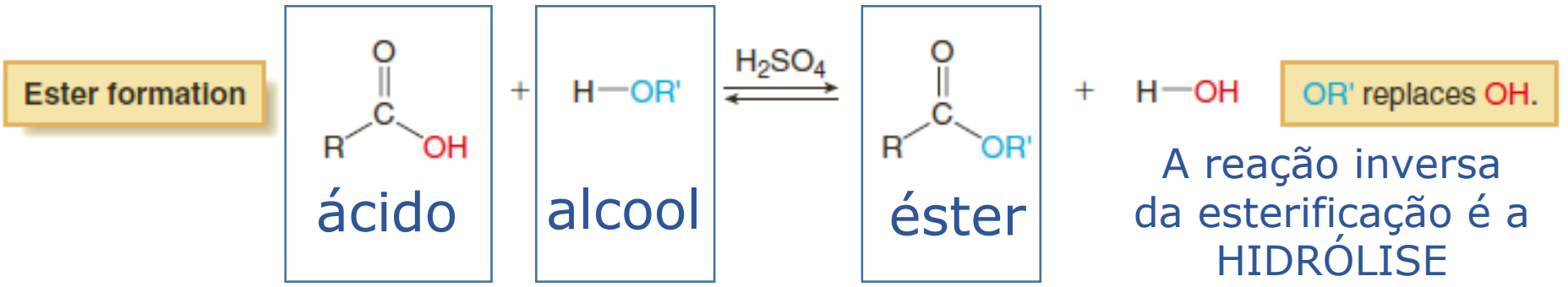
Examples



Reações de substituição nos ácidos orgânicos: **Esterificação:** formação de ésteres

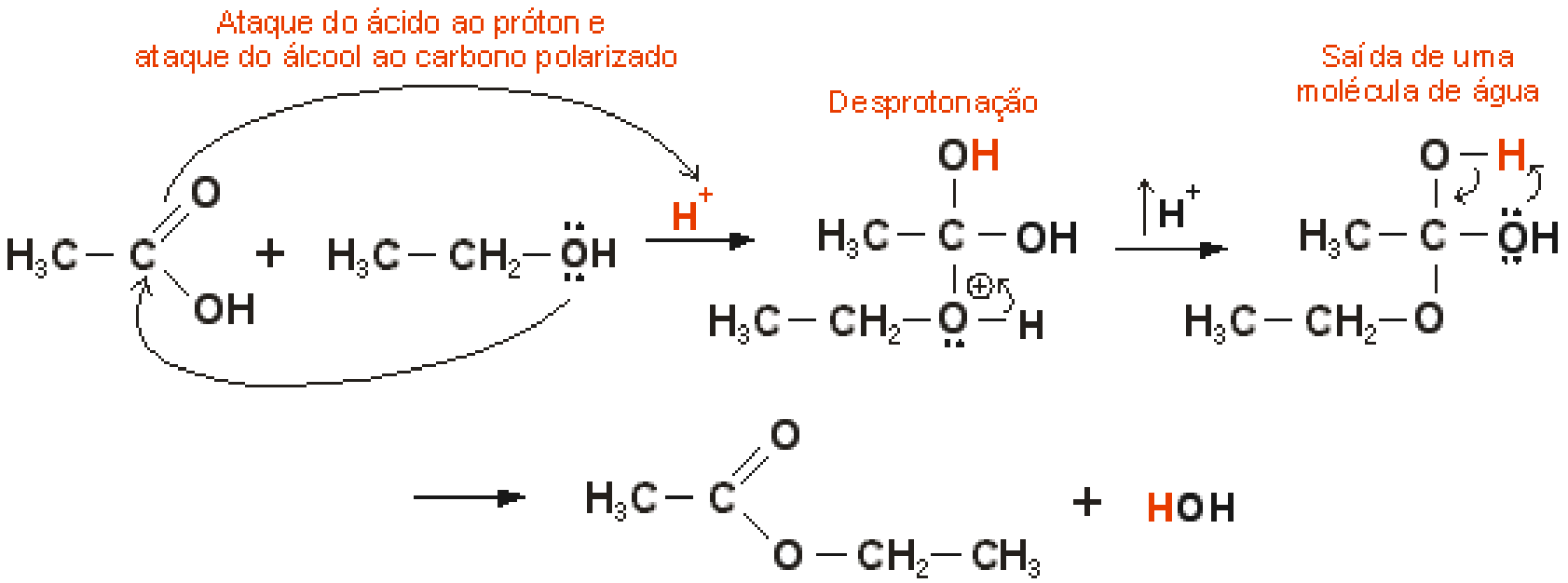


Formação de ésteres: reação de ácidos e álcoois em meio ácido (o equilibrio favorece a formação do éster)



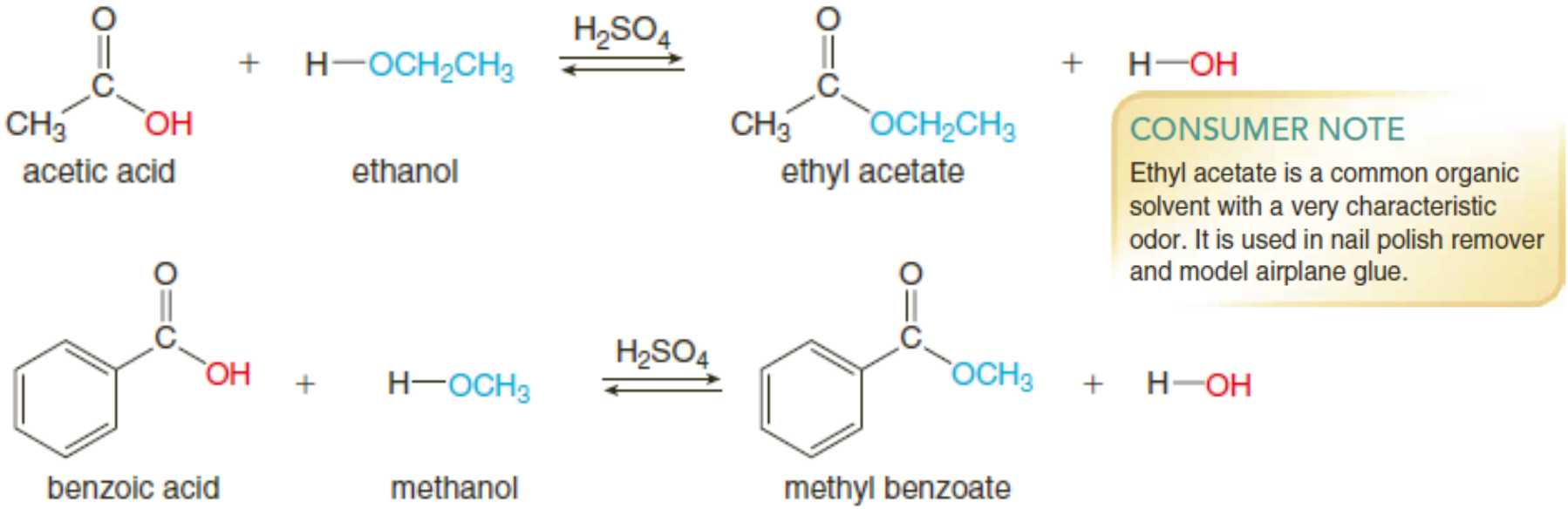
A reação inversa da esterificação é a HIDRÓLISE

Esterificação entre um ácido orgânico e o etanol em meio ácido:



Etanoato de etilo
(éster)

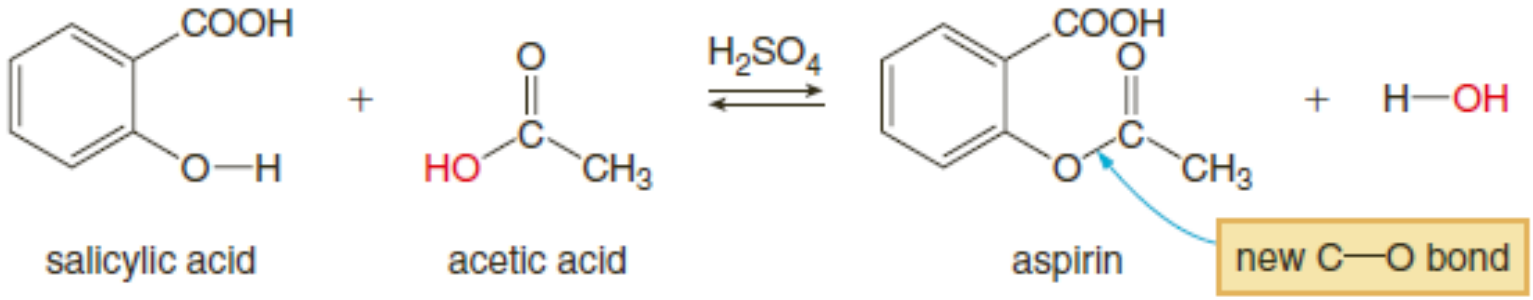
Ex:



CONSUMER NOTE

Ethyl acetate is a common organic solvent with a very characteristic odor. It is used in nail polish remover and model airplane glue.

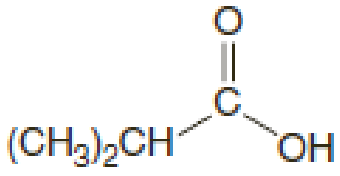
Síntese do ácido acetilsalicílico:



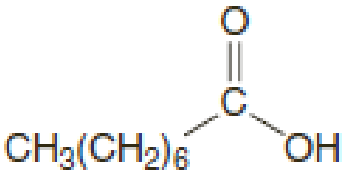
Exercícios:

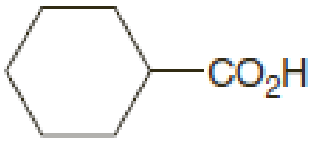
E1.

What ester is formed when each carboxylic acid is treated with ethanol (CH_3CH_2OH) in the presence of H_2SO_4?

a. 

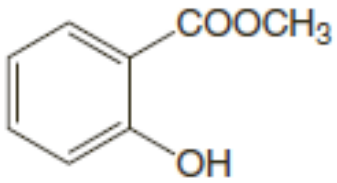
b. HCO_2H

c. 

d. 

E2.

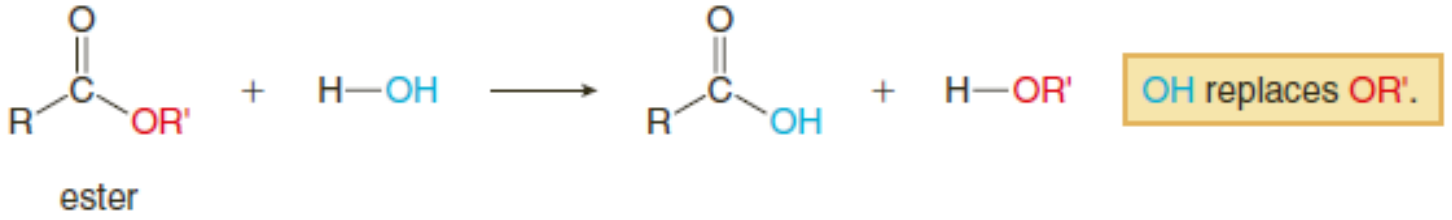
Methyl salicylate is the major component of the oil of wintergreen (Section 17.5). What carboxylic acid and alcohol are needed to synthesize methyl salicylate by Fischer esterification?



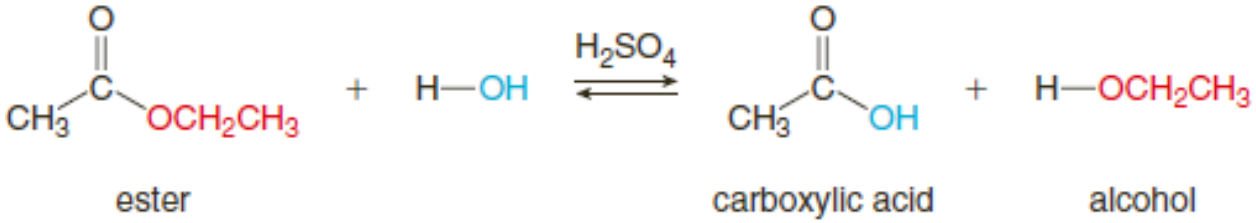
methyl salicylate

Hidrólise dos ésteres:

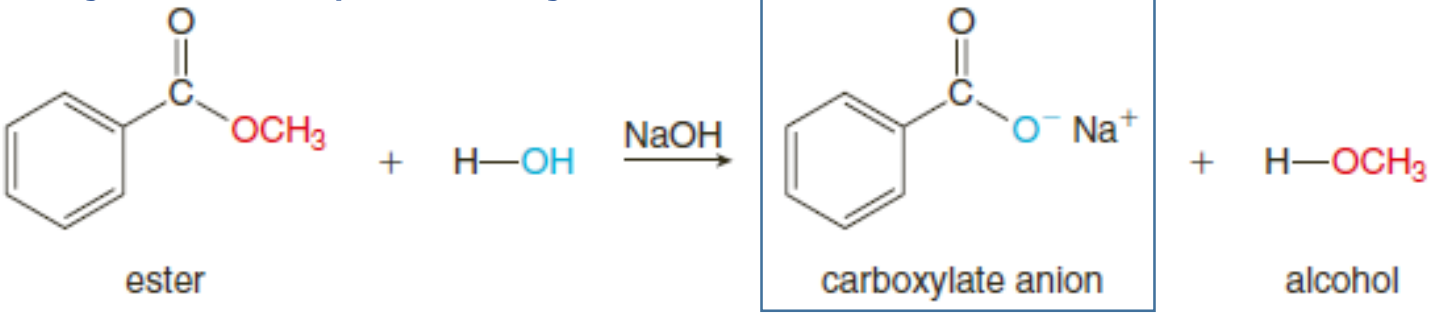
Ester hydrolysis



Hidrólise dos ésteres em meio ácido:
-reação inversa da esterificação



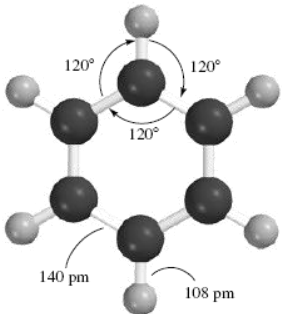
Hidrólise dos ésteres em meio alcalino:
-reação de saponificação



Quando se formam sabões?

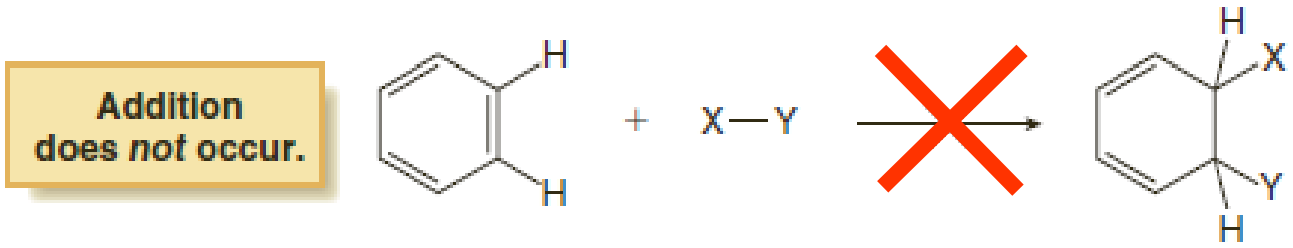
Reatividade dos COMPOSTOS AROMÁTICOS

- São compostos insaturados
  - 6 ligações idênticas
  - 6 e^- π partilhados por 6C
  - anel benzénico muito estável - 36 kcal mol^{-1}



Hibridação sp^2

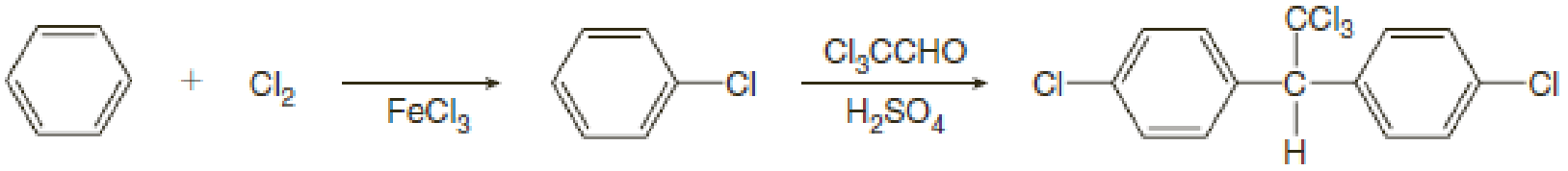
- Ocorrem preferencialmente reações de **substituição**
- Não ocorrem reações de **adição** (como nos alcenos)



The product is *not* aromatic.

A química orgânica no nosso dia-a-dia:

The chlorination of benzene is the first step in the two-step synthesis of the pesticide **DDT** (*d*ichloro*d*iphenyl*t*richloroethane).

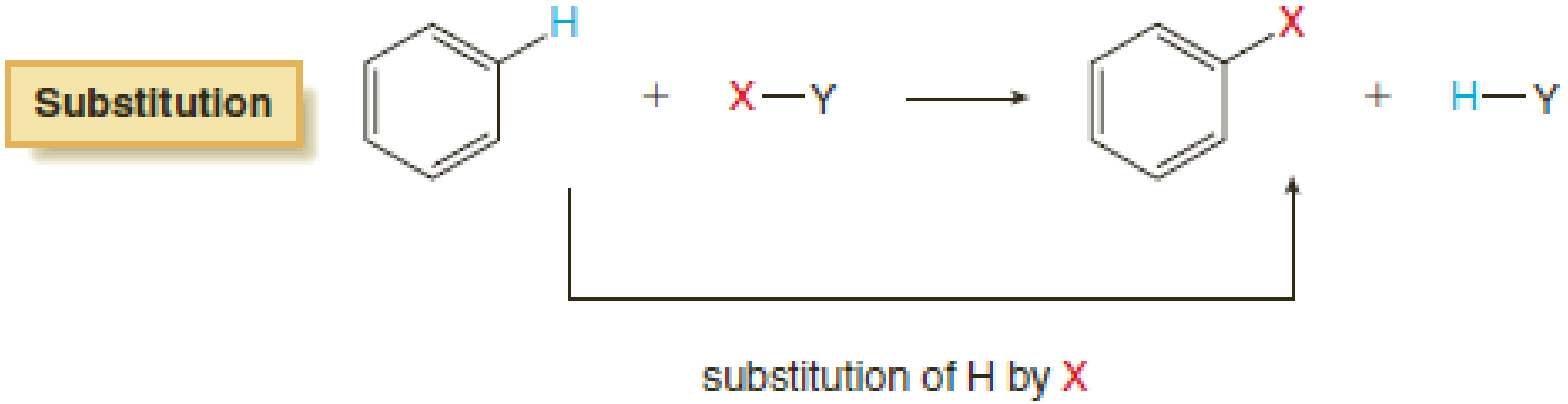


DDT
(nonbiodegradable pesticide)

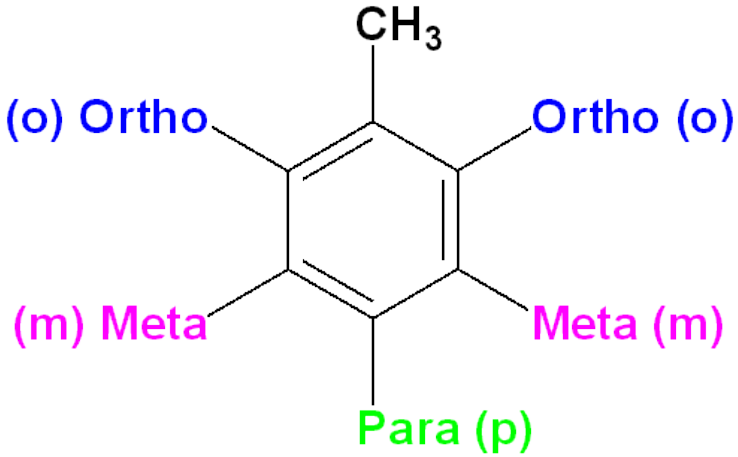
DDT is an organic molecule with valuable short-term effects that has caused long-term problems. DDT kills insects that spread diseases such as malaria and typhus, and in controlling insect populations, DDT has saved millions of lives worldwide. DDT is a weakly polar and very stable organic compound, and so it (and compounds like it) persists in the environment for years. Since DDT is soluble in organic media, it accumulates in the fatty tissues of most animals. Most adults in the U.S. have low concentrations of DDT (or a degradation product of DDT) in them. The long-term effect on humans is not known, but DDT has had a direct harmful effect on the eggshell formation of certain predator birds such as eagles and hawks.

Reatividade dos COMPOSTOS AROMÁTICOS

Reações de **substituição** são as mais frequentes nos compostos aromáticos

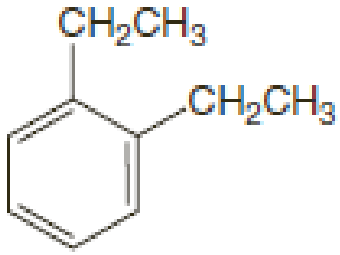
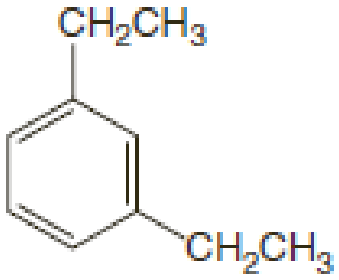
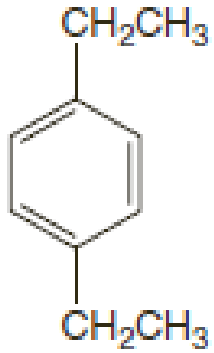


A **substituição** do H no anel aromático por Br, Cl, NO_2 mantém as características aromáticas do composto final



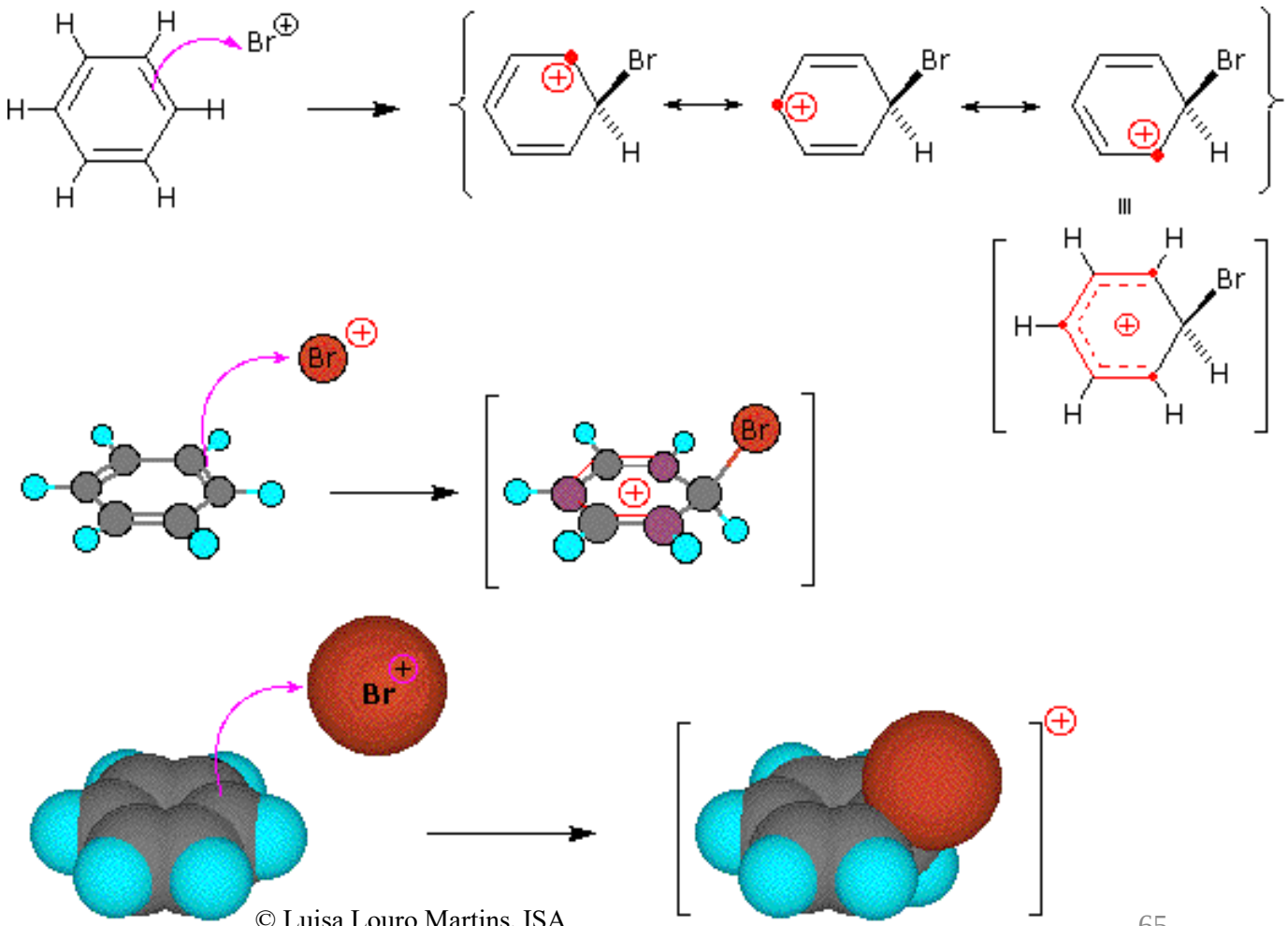
Orientação nas reações de substituição

There are three different ways that two groups can be attached to a benzene ring, so a prefix—**ortho**, **meta**, or **para**—is used to designate the relative position of the two substituents. Ortho, meta, and para are also abbreviated as *o*, *m*, and *p*, respectively.

1,2-Disubstituted benzene **ortho** isomer	**1,3**-Disubstituted benzene **meta** isomer	**1,4**-Disubstituted benzene **para** isomer
		
***ortho*-diethylbenzene** or ***o*-diethylbenzene** or **1,2**-diethylbenzene	***meta*-diethylbenzene** or ***m*-diethylbenzene** or **1,3**-diethylbenzene	***para*-diethylbenzene** or ***p*-diethylbenzene** or **1,4**-diethylbenzene

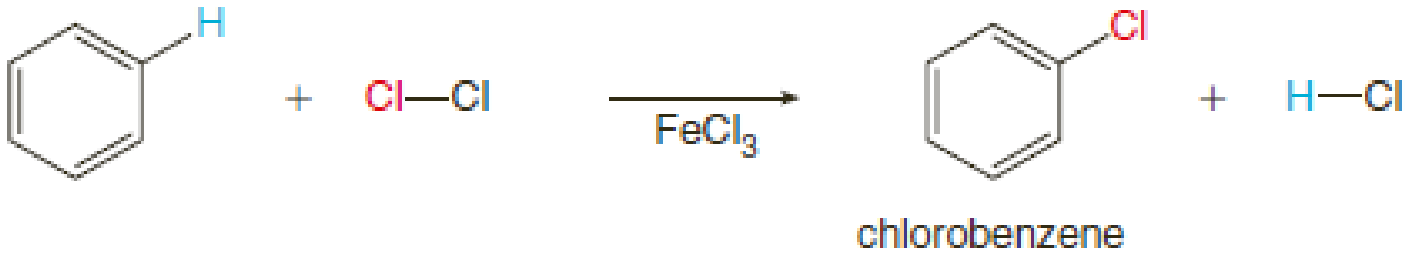
Reatividade dos COMPOSTOS AROMÁTICOS:

A **substituição eletrófila** no anel benzénico ocorre devido a forte densidade eletrónica do anel (ex: halogenação)



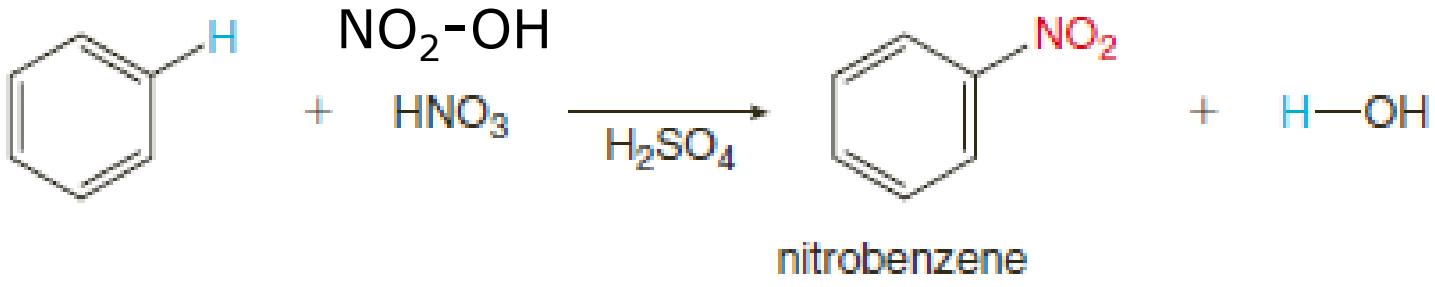
Substituição eletrófila do H pelo Cl no anel benzénico:
O benzeno reage com o Cl_2 na presença de catalisador ($FeCl_3$) e forma o clorobenzeno:

Chlorination

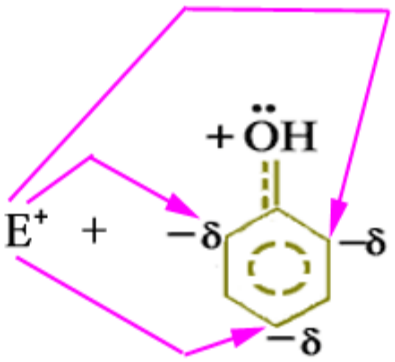


Nitração do anel benzénico:
Substituição eletrófila do H pelo NO_2^+ (O=N=O)

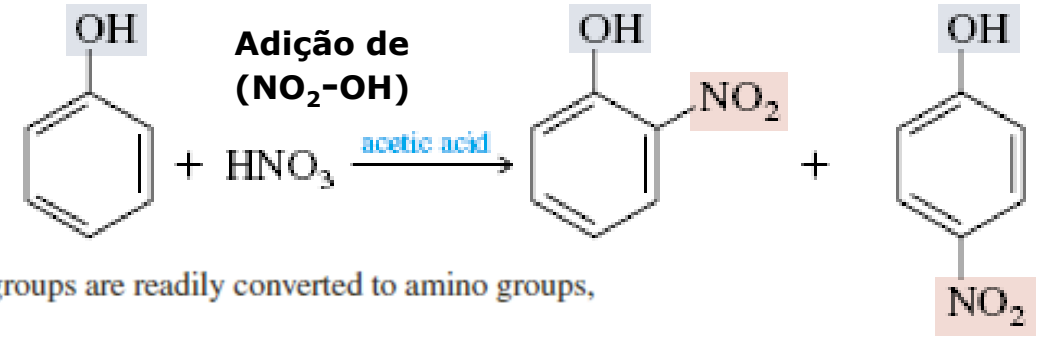
Nitration



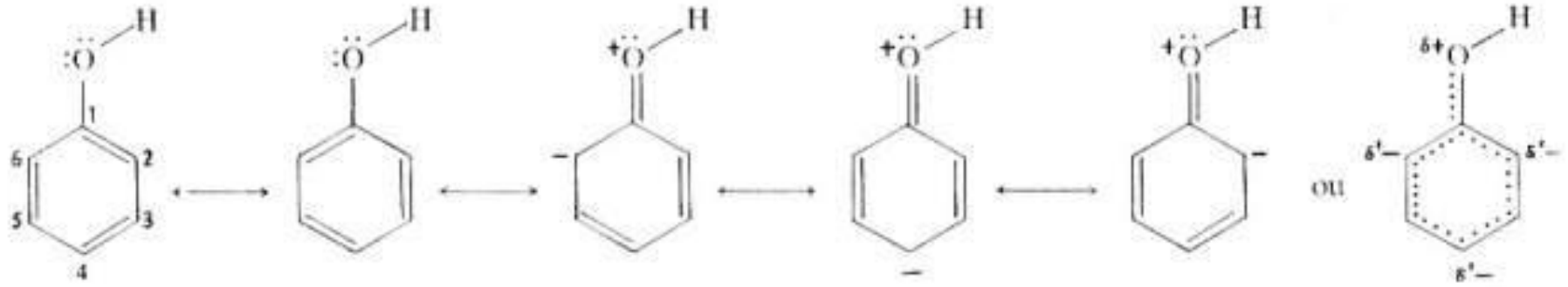
Os grupos substituintes do anel benzénico influenciam a posição dos substituintes:



Na substituição eletrófila o grupo OH é ***orto/para*** orientador pois **acentua** a densidade eletrónica nessas posições (2 e 4), tornando esses carbonos mais reativos



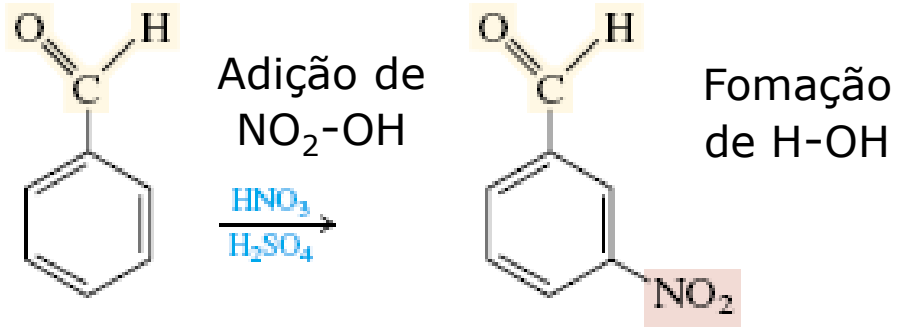
Nitration is a very valuable reaction because nitro groups are readily converted to amino groups, (NH_2) with H_2 and a palladium catalyst.

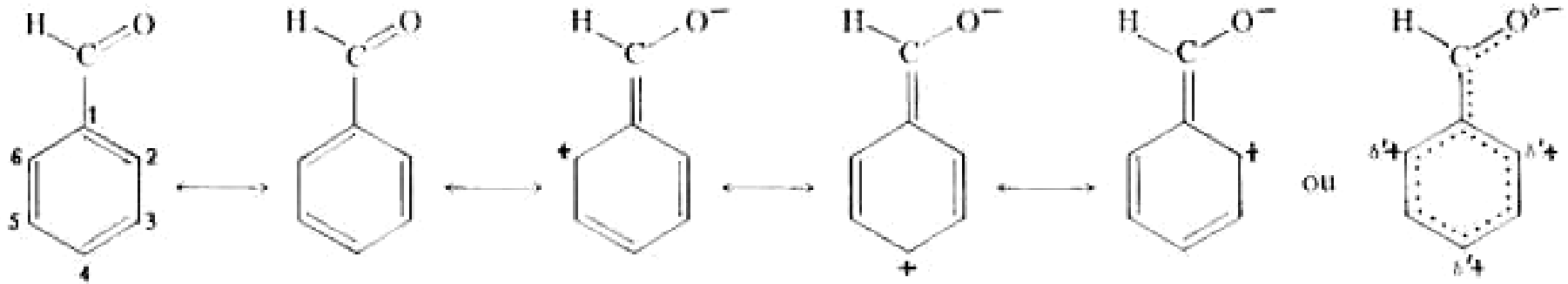


Os grupos substituintes do anel benzénico influenciam a posição dos substituintes:

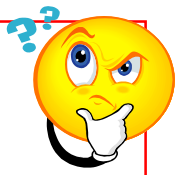
Na substituição eletrófila, o grupo COH é ***meta*** orientador, **cria défice eletrónico** nas posições ***orto*** e ***para*** tornando esses carbonos menos reativos

-é assim que facilita a substituição eletrófila na posição **meta**

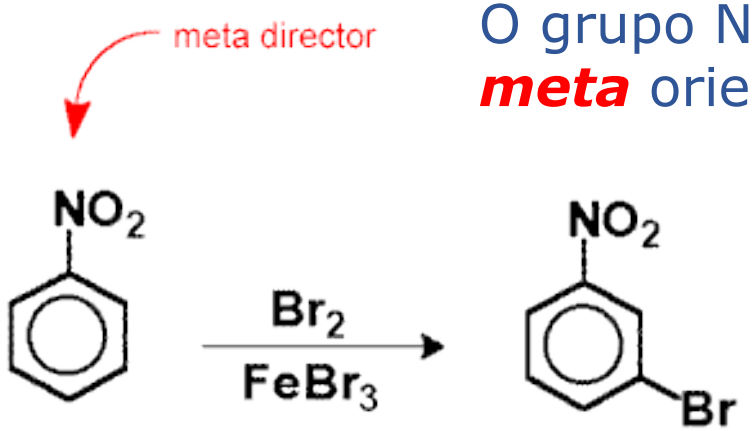


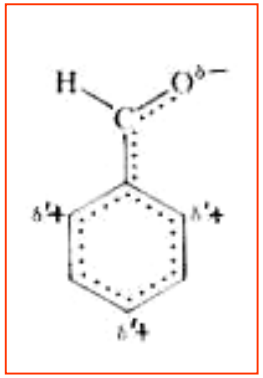


Os grupos substituintes do anel benzénico influenciam a orientação da posição dos substituintes:

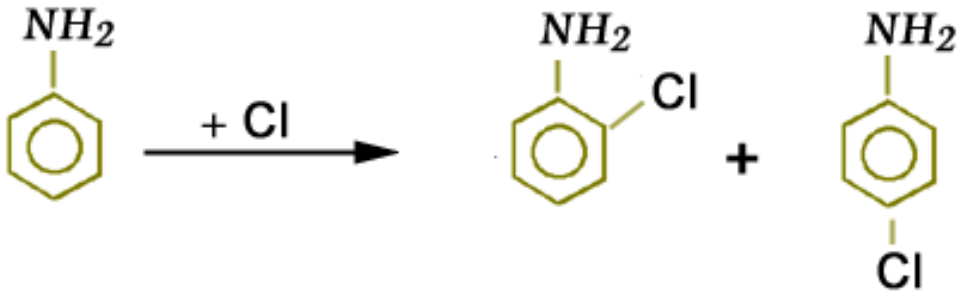


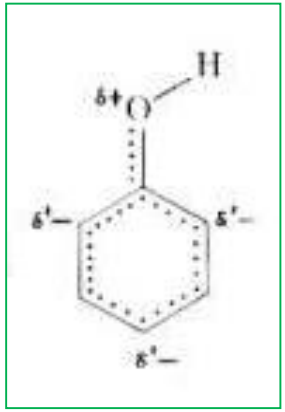
O grupo NO_2 é ***meta*** orientador





O grupo NH_2 é ***orto/para*** orientador

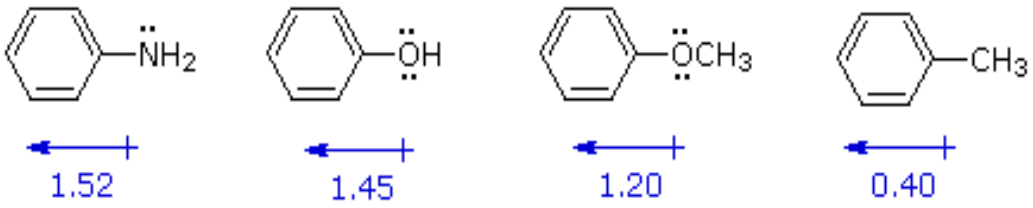




Os grupos substituintes do anel benzénico alteram o momento dipolar e influenciam a reatividade por interação de dois efeitos:
-efeito indutor atrativo (elementos eletronegativos)
-estabilização do anel por ressonância envolvendo os pares de eletrões não emparelhados
-Substituintes favorecem orientação orto e para enquanto outros favorecem a orientação meta

substituintes que ativam o anel benzénico para ataque eletrófílo

Activating Substituents

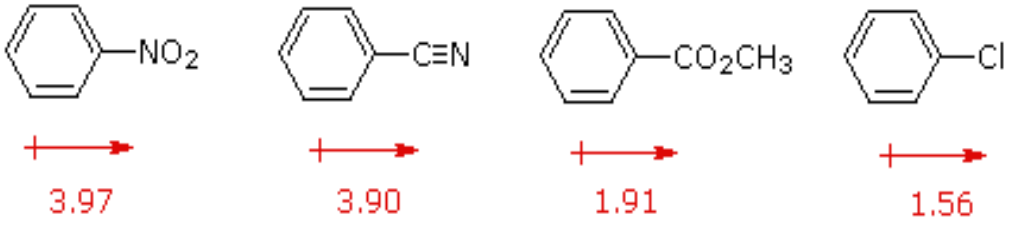


são ***orto*** e ***para*** orientadores

(—OH, —OR, —NH_2, —CH_3, —R, —C_6H_5)

substituintes que tornam o anel benzénico menos suscetível de ataque eletrófílo

Deactivating Substituents



são ***meta*** orientadores

(NO_2, —CH_2Cl, CHO, CO—R, COOH)

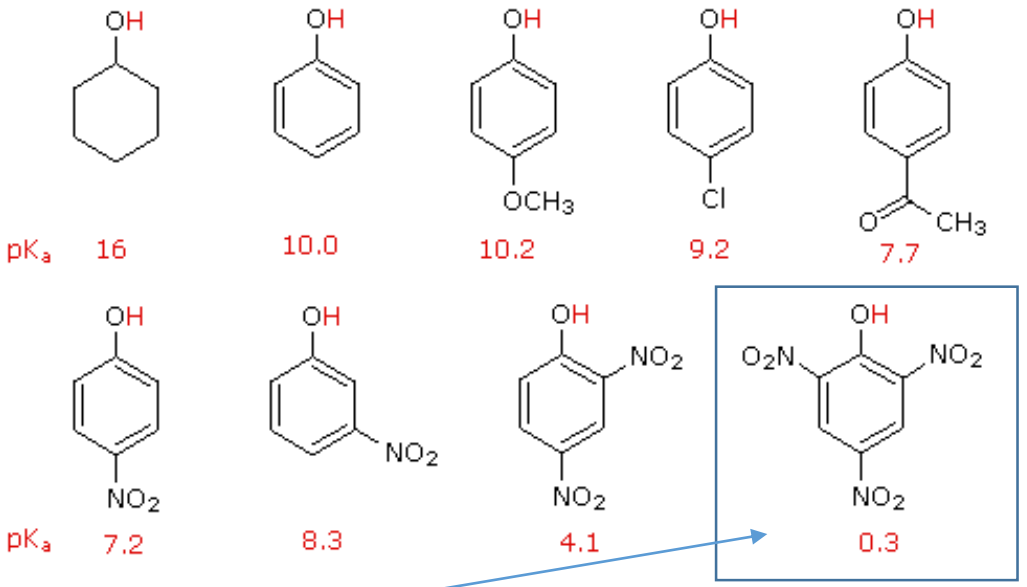
FENÓIS: reatividade

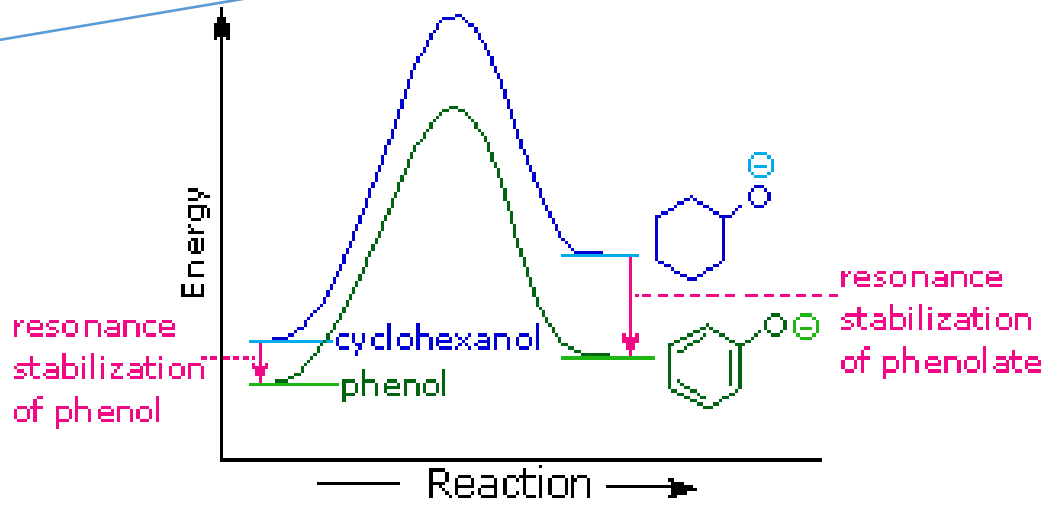
Deslocalização dos eletrões π no **anel benzénico** é responsável pelas reações de substituição

Comportamento de **ácido** devido à polarização da ligação **O—H**

-caráter ácido é favorecido pela orientação ***orto*** e ***para*** em relação ao grupo OH (ex: NO_2)

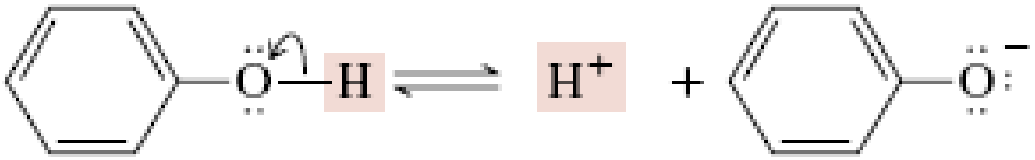
-caráter ácido é favorecido pela estabilização por ressonância do ião fenolato





Os fenóis têm um caráter ácido mais forte que os álcoois (e não formam ésteres por reação com os ácidos):

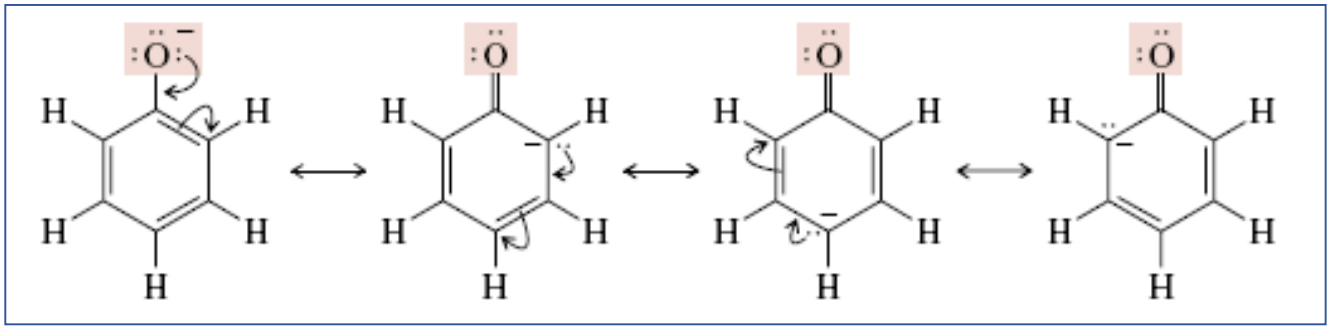
$K_a = 10^{-16}$ ($pK_a = 16$)



$K_a = 10^{-10}$ ($pK_a = 10$)

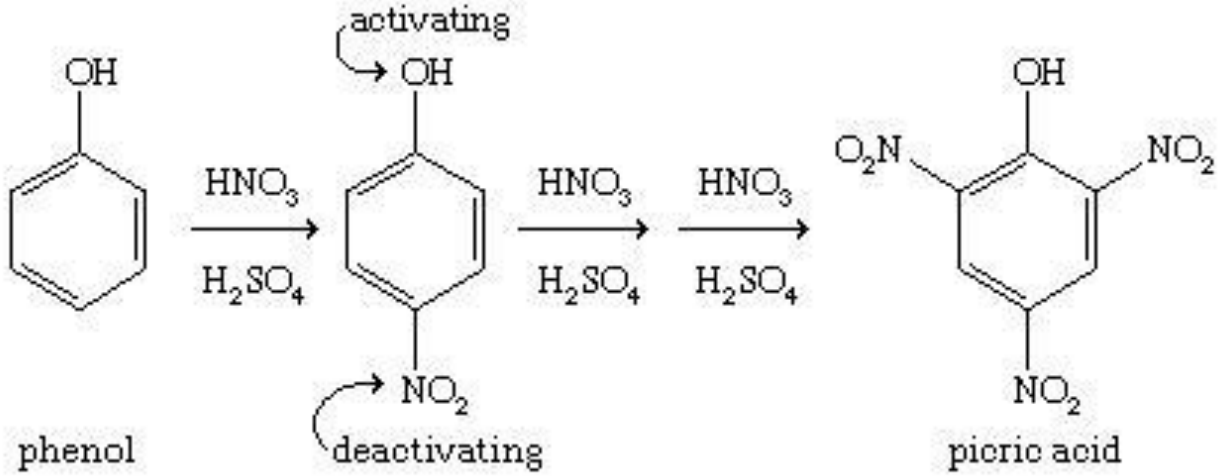
$$K_a = \frac{[ArO^-] \cdot [H^+]}{[ArOH]}$$

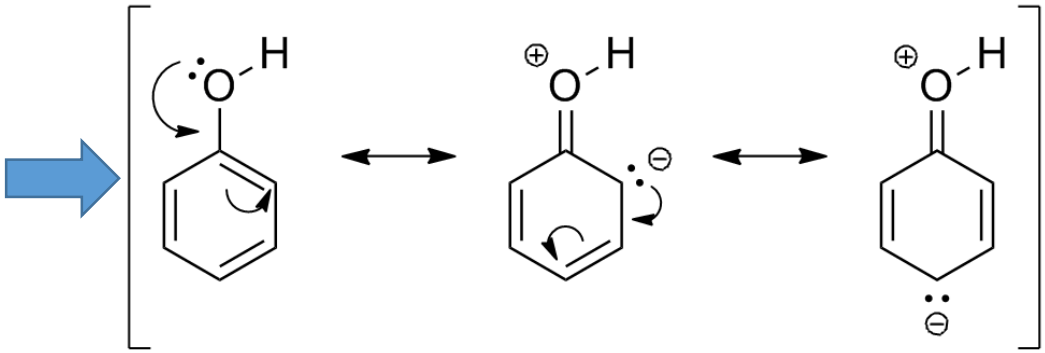
Estabilização do ArO^- por ressonância



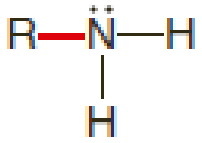
Exercicio E1:

Explique porque se formam os seguintes produtos a partir do fenol:

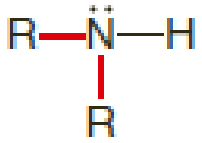




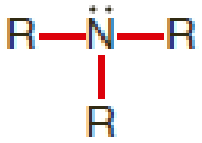
Aminas



Amina primária



Amina secundária

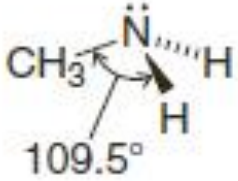


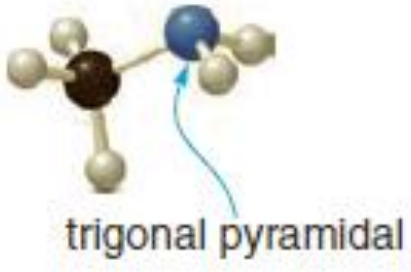
Amina terciária

- A primary (1°) amine has one C—N bond and the general structure RNH_2.
- A secondary (2°) amine has two C—N bonds and the general structure R_2NH.
- A tertiary (3°) amine has three C—N bonds and the general structure R_3N.

Exemplos de aminas:

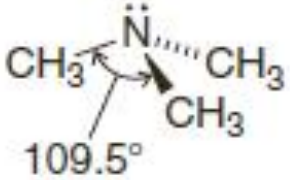
CH_3NH_2
methylamine

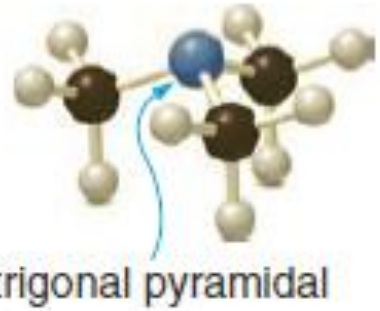




Amina terciária N-substituida

$(CH_3)_3N$
trimethylamine





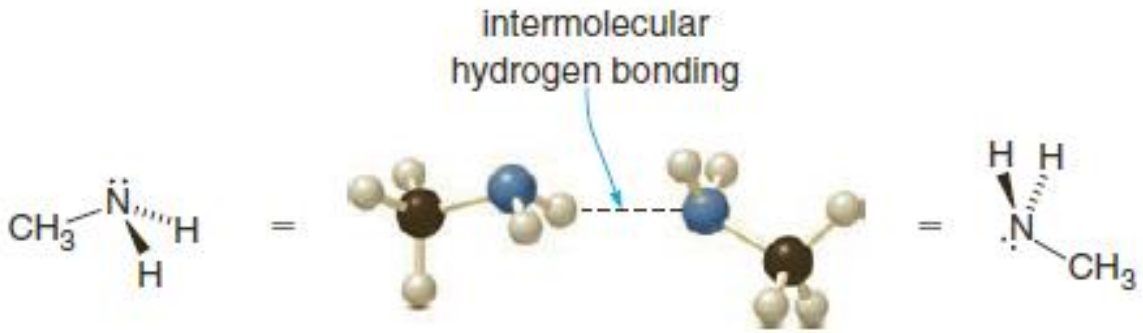
Aminas: propriedades físicas

- In comparing compounds of similar size, 1° and 2° amines have higher boiling points than compounds incapable of hydrogen bonding, but lower boiling points than alcohols that have stronger intermolecular hydrogen bonds.

$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2NH_2$	$CH_3CH_2CH_2CH_2OH$
diethyl ether	1-butanamine	1-butanol
bp = 38 °C	bp = 78 °C	bp = 117 °C

Increasing intermolecular forces
Increasing boiling point

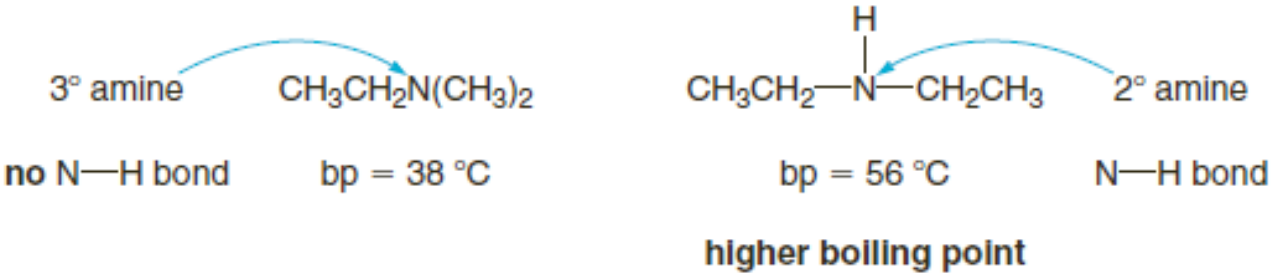
Aminas primárias e secundárias estabelecem pontes de H, embora mais fracas que com o oxigénio



Aminas terciárias dificilmente estabelecem pontes de H pelo que apresentam pontos de ebulição menores que aminas primárias e secundárias

-apenas aminas 3árias com menos que 6 C são solúveis em água

- Tertiary (3°) amines have lower boiling points than 1° and 2° amines of comparable size, because they have no N—H bonds.



Amines are soluble in organic solvents regardless of size. Amines with fewer than six carbons are water soluble since they can hydrogen bond with water. Larger amines are water insoluble since the nonpolar alkyl portion is too large to dissolve in the polar water solvent.

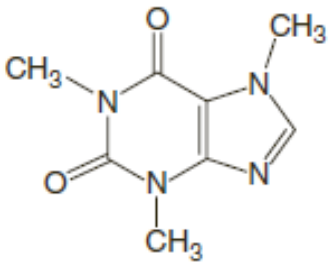
A química orgânica no nosso dia-a-dia:

cafeína e nicotina são alcalóides

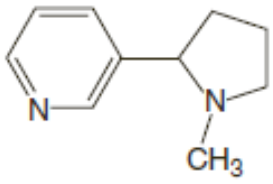
São aminas heterocíclicas de origem vegetal

Caffeine and **nicotine** are widely used stimulants of the central nervous system

caffeine increases glucose production, making an individual feel energetic



caffeine



nicotine

CONSUMER NOTE

Some chocolate bars contain as much caffeine as a 12-oz can of cola.

TABLE 18.1 Average Caffeine Content in Common Foods and Drugs

Product	Serving Size	Caffeine (mg)
Coffee, brewed	8 oz	133
Coffee, instant	16 oz	47
Coffee, decaffeinated	8 oz	5
Tea, brewed	8 oz	53
Coca-Cola Classic	12 oz	35
Diet Coke	12 oz	47

1 oz
28 mL

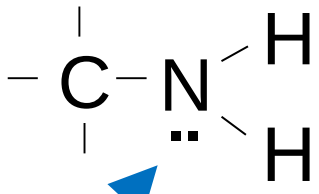
Aminas: reatividade

As aminas são bases (bases fracas)

(aceitadores de protões, dadores de eletrões)

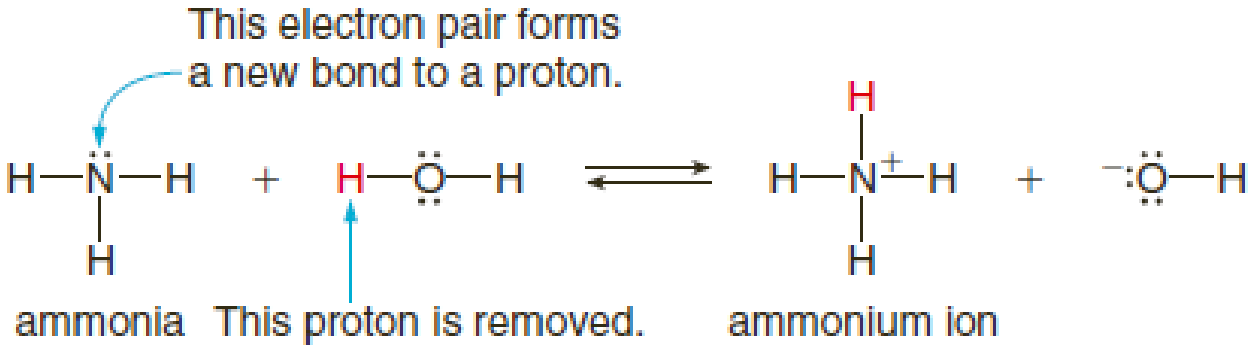
-caráter básico resulta da presença de um dupleto livre no N

Ataque por bases
(caráter ácido)
-pouco acentuado



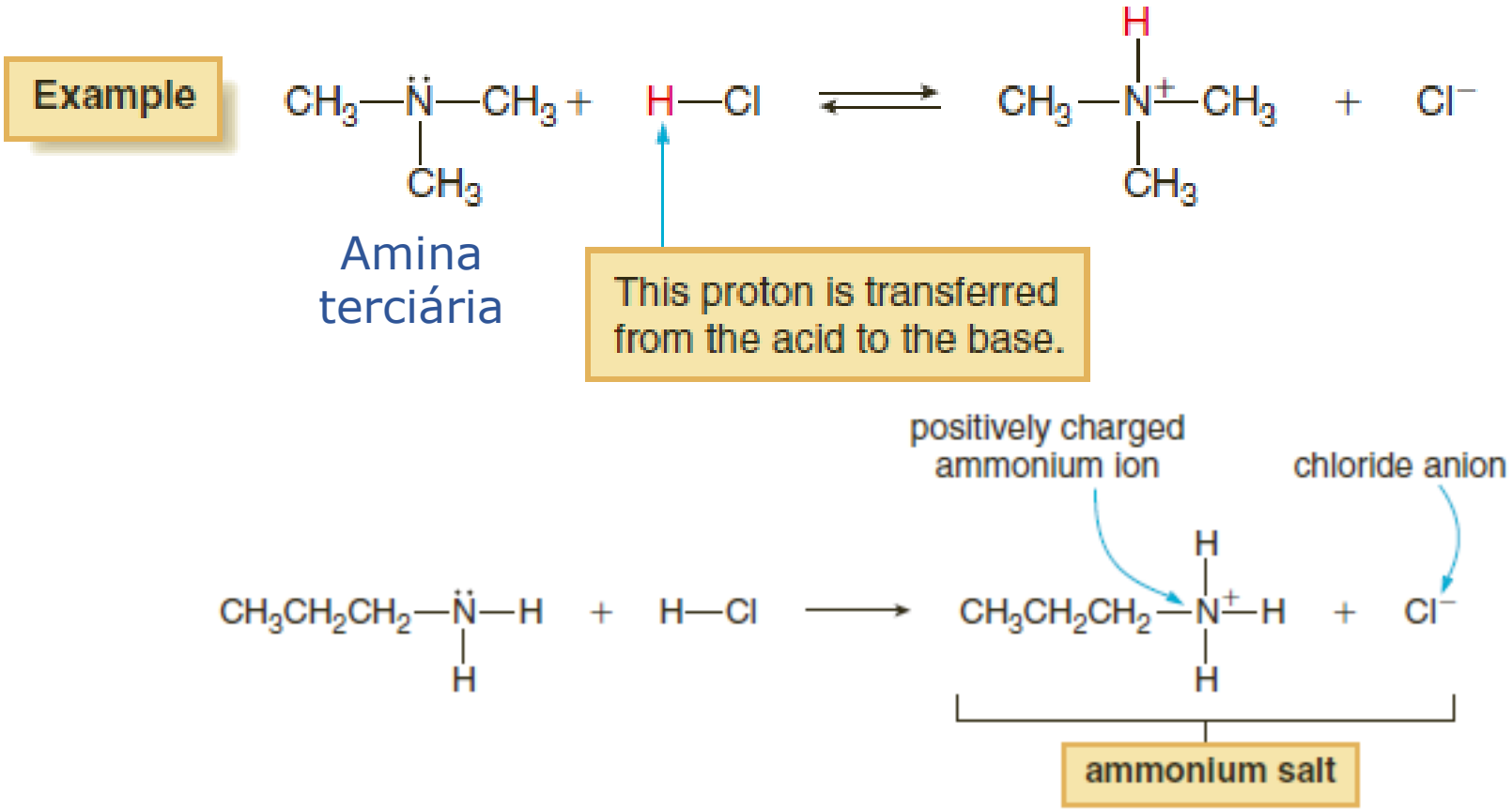
Ataque por ácidos
e eletrófilos
(caráter básico)

General reactions



As aminas reagem com ácidos fortes formando sais solúveis em água:

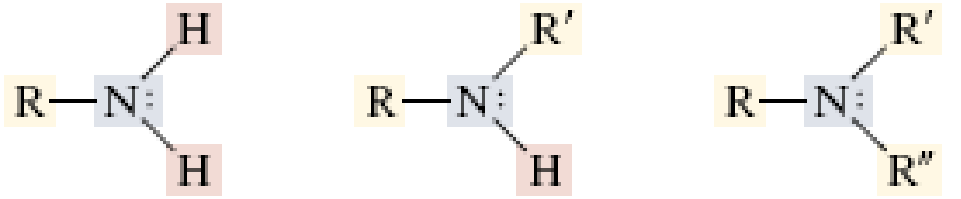
-a reação ocorre por ataque eletrófilo devido à presença de um par de eletrões no N



Influência dos substituintes na reatividade das aminas:

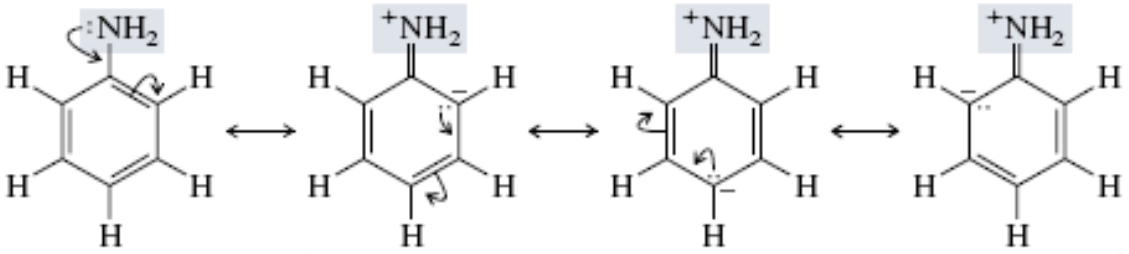
O efeito indutor repulsivo dos radicais alquilo acentua a densidade eletrónica sobre o azoto

Caráter básico aumenta



Reatividade aumenta

As aminas aromáticas são menos reativas (menor caráter básico) pois há menor densidade eletrónica sobre o azoto:



O par de eletrões está menos presente sobre o azoto devido ao **efeito de ressonância**

Apresentam caráter ácido mais acentuado do que as aminas alifáticas