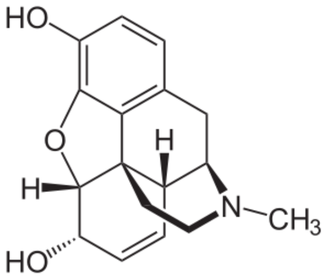
QFL0341 - Estrutura e Propriedades de Compostos Orgânicos - Noturno (2019)

20/agosto/2019

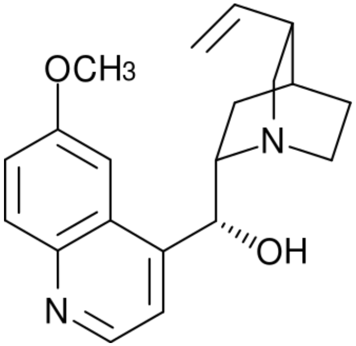
Estruturas, nomenclatura e caracterização de álcoois, cetonas, ácidos carboxílicos.

Compostos nitrogenados.

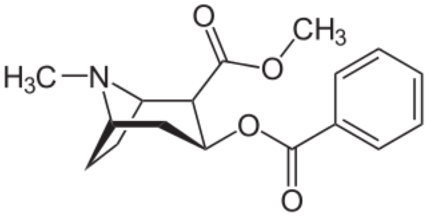
Diversidade de funções orgânicas



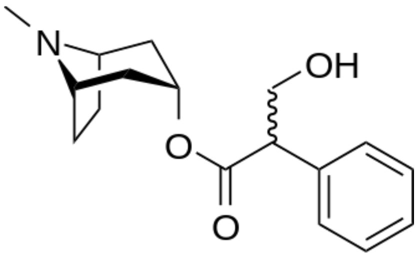
Morfina: Sertürner, 1805



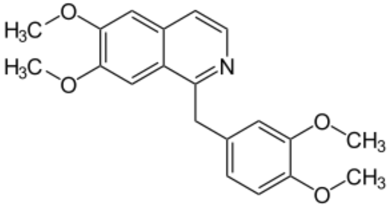
Quinina: Pelletier e Magendie, 1820



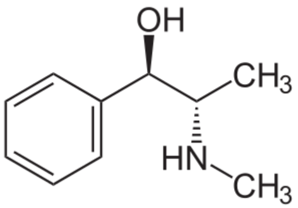
Cocaína: Wöhler, 1859.



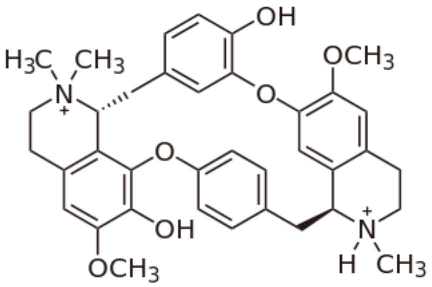
Atropina: Mein, 1831.



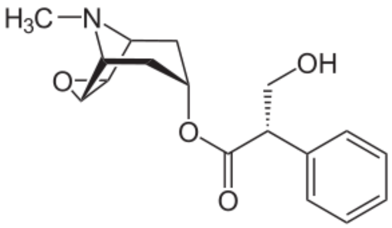
Papaverina: Merck, 1848.



Efedrina: Nagai, 1885.

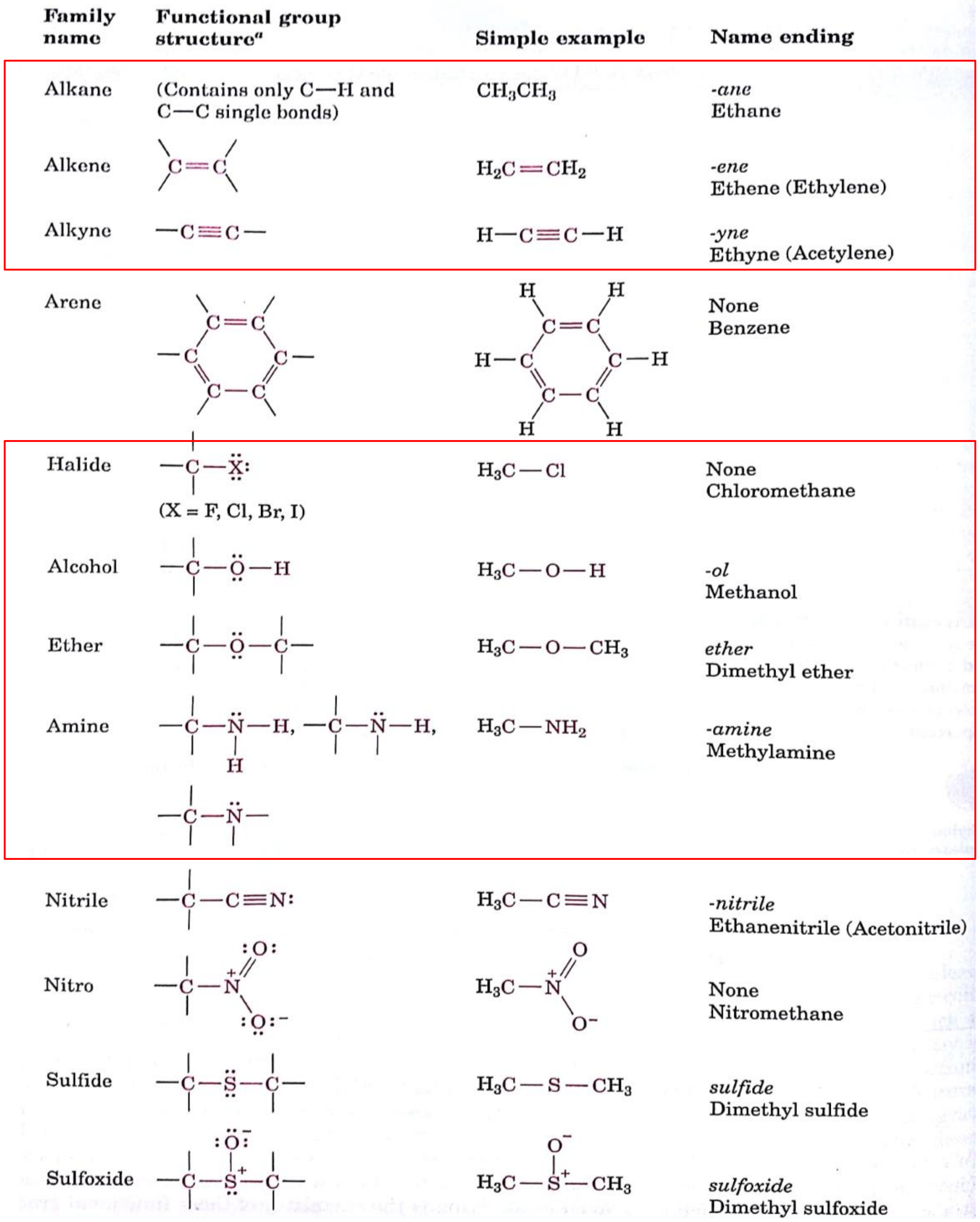


Tubocurarina: Boehm, 1895.



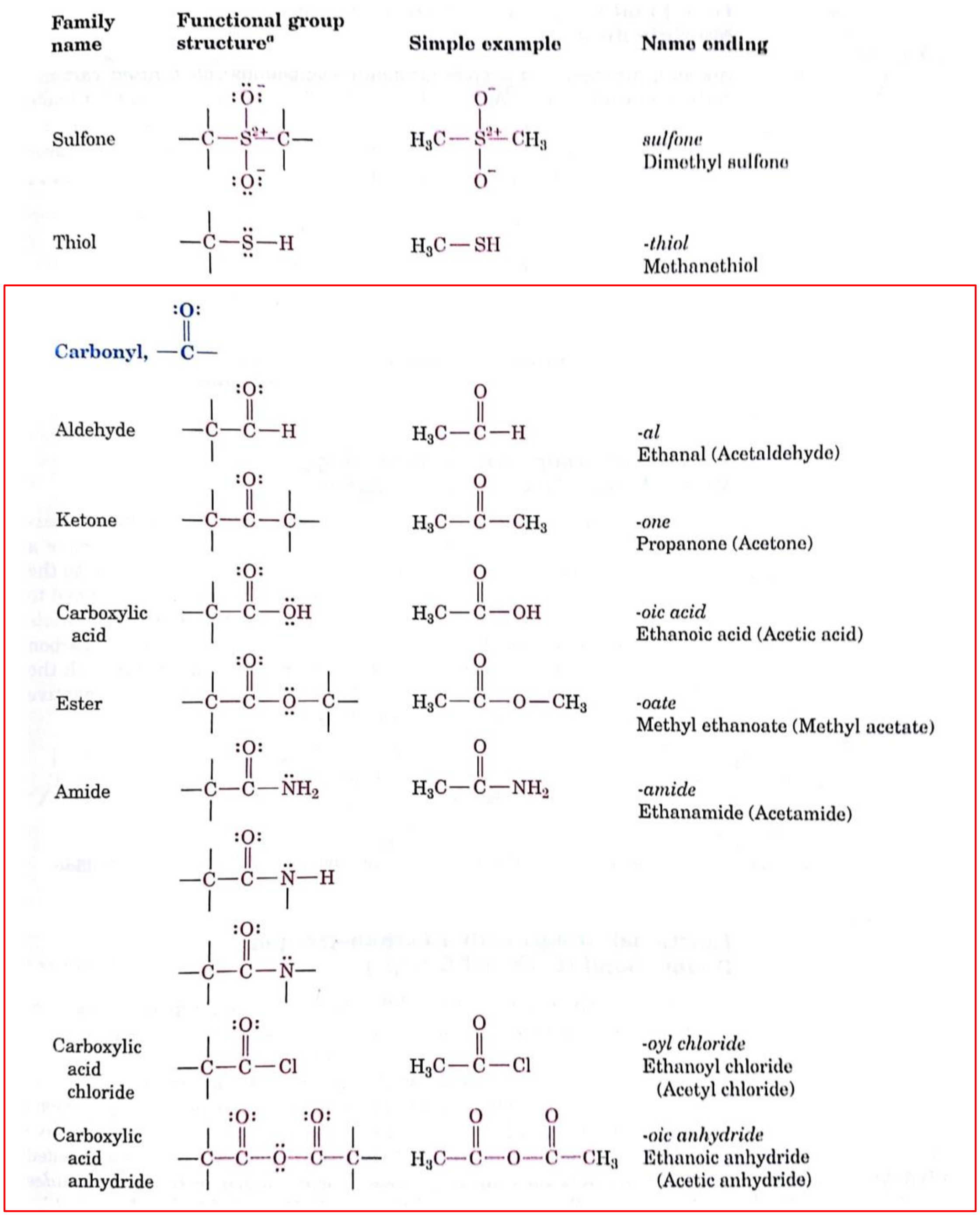
Escopolamina: Landenburg, 1881.

Functional groups



Family name	Functional group structure[a]	Simple example	Name ending
Alkane	(Contains only C—H and C—C single bonds)	CH_3CH_3	*-ane* Ethane
Alkene	$C=C$	$H_2C=CH_2$	*-ene* Ethene (Ethylene)
Alkyne	$-C\equiv C-$	$H-C\equiv C-H$	*-yne* Ethyne (Acetylene)
Arene			None Benzene
Halide	$-C-\ddot{X}:$ (X = F, Cl, Br, I)	H_3C-Cl	None Chloromethane
Alcohol	$-C-\ddot{O}-H$	H_3C-O-H	*-ol* Methanol
Ether	$-C-\ddot{O}-C-$	$H_3C-O-CH_3$	*ether* Dimethyl ether
Amine	$-C-\ddot{N}(H)-H$, $-C-\ddot{N}-H$, $-C-\ddot{N}-$	H_3C-NH_2	*-amine* Methylamine
Nitrile	$-C-C\equiv N:$	$H_3C-C\equiv N$	*-nitrile* Ethanenitrile (Acetonitrile)
Nitro	$-C-\overset{+}{N}(=\ddot{O}:)-\ddot{O}:^-$	$H_3C-\overset{+}{N}(=O)-O^-$	None Nitromethane
Sulfide	$-C-\ddot{S}-C-$	$H_3C-S-CH_3$	*sulfide* Dimethyl sulfide
Sulfoxide	$-C-\overset{+}{S}(\ddot{O}:^-)-C-$	$H_3C-\overset{+}{S}(O^-)-CH_3$	*sulfoxide* Dimethyl sulfoxide

Functional groups



Family name	Functional group structure[a]	Simple example	Name ending
Sulfone	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:\ddot{O}:^-}{\underset{:\ddot{O}:^-}{S^{2+}}}-\overset{\mid}{\underset{\mid}{C}}-$	$H_3C-\overset{O^-}{\underset{O^-}{S^{2+}}}-CH_3$	*sulfone* Dimethyl sulfone
Thiol	$-\overset{\mid}{\underset{\mid}{C}}-\ddot{\underset{..}{S}}-H$	H_3C-SH	*-thiol* Methanethiol
Carbonyl,	$-\overset{:O:}{\overset{\|}{C}}-$		
Aldehyde	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-H$	$H_3C-\overset{O}{\overset{\|}{C}}-H$	*-al* Ethanal (Acetaldehyde)
Ketone	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$	*-one* Propanone (Acetone)
Carboxylic acid	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}H$	$H_3C-\overset{O}{\overset{\|}{C}}-OH$	*-oic acid* Ethanoic acid (Acetic acid)
Ester	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-\overset{\mid}{\underset{\mid}{C}}-$	$H_3C-\overset{O}{\overset{\|}{C}}-O-CH_3$	*-oate* Methyl ethanoate (Methyl acetate)
Amide	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{N}H_2$	$H_3C-\overset{O}{\overset{\|}{C}}-NH_2$	*-amide* Ethanamide (Acetamide)
	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\underset{\mid}{\ddot{N}}-H$		
	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\underset{\mid}{\ddot{N}}-$		
Carboxylic acid chloride	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-Cl$	$H_3C-\overset{O}{\overset{\|}{C}}-Cl$	*-oyl chloride* Ethanoyl chloride (Acetyl chloride)
Carboxylic acid anhydride	$-\overset{\mid}{\underset{\mid}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-\overset{:O:}{\overset{\|}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$	*-oic anhydride* Ethanoic anhydride (Acetic anhydride)

Carbonyl derivatives

Álcoois

(al-kohul, al-kuhul ou al-ghawl, “fino composto utilizado para a maquiagem obtido através da destilação”)

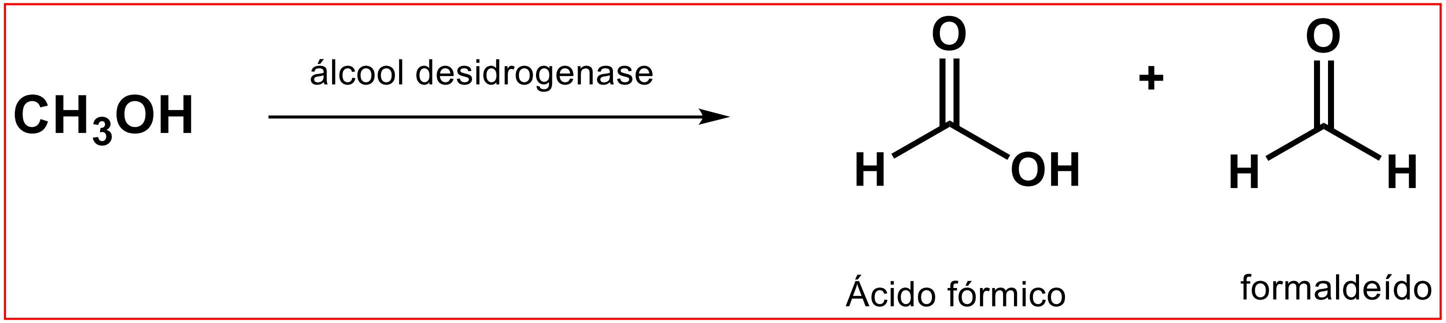
✓ Grupo funcional: Hidroxila (-OH) ligada a um átomo de carbono saturado (com hibridização sp^3).

✓ Um álcool pode ser considerado como tendo propriedades intermediárias entre um alcano e a água:

R-H	**H-OH**	**R-OH**	**R-O-R**
um alcano	**água**	**um álcool**	**um éter**

Metanol (álcool da madeira)

methy: intoxicar (Grego)

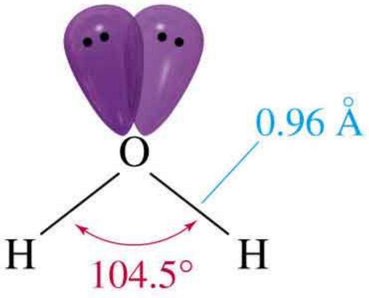


atacam gânglios da retina degenerando o nervo ótico

A ingestão de 10 mL causa cegueira de forma irreversível; 30 mL é fatal.

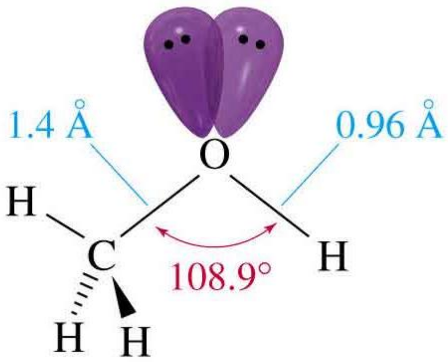
Structure of Alcohols

- Hydroxyl (OH) functional group
- Oxygen is *sp*^{3} hybridized.

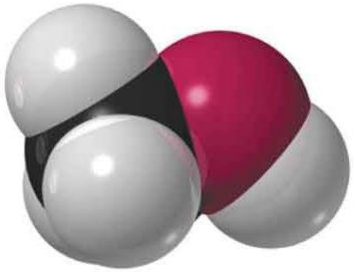


water

water

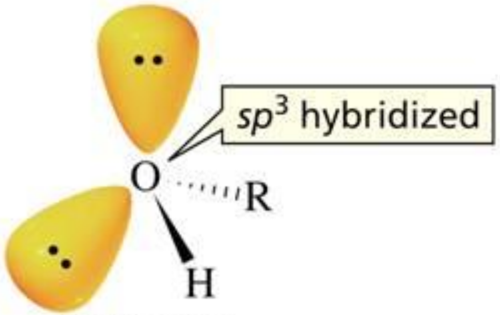


methyl alcohol



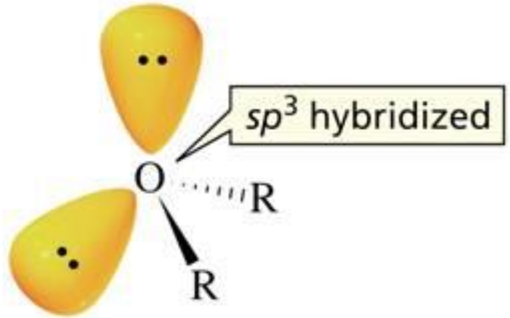
methyl alcohol

Estruturas de Álcool e Éter

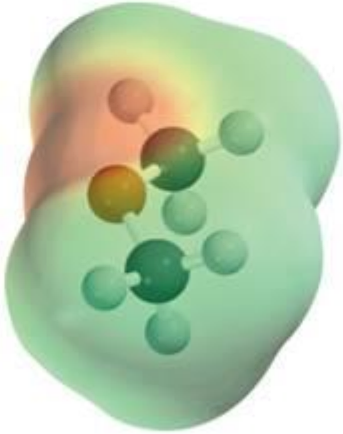


an alcohol

electrostatic potential map for methanol



an ether



electrostatic potential map for dimethyl ether

Oldest known organic synthesis:

“fermentation”

Sugar + yeast → ethyl alcohol + CO_2

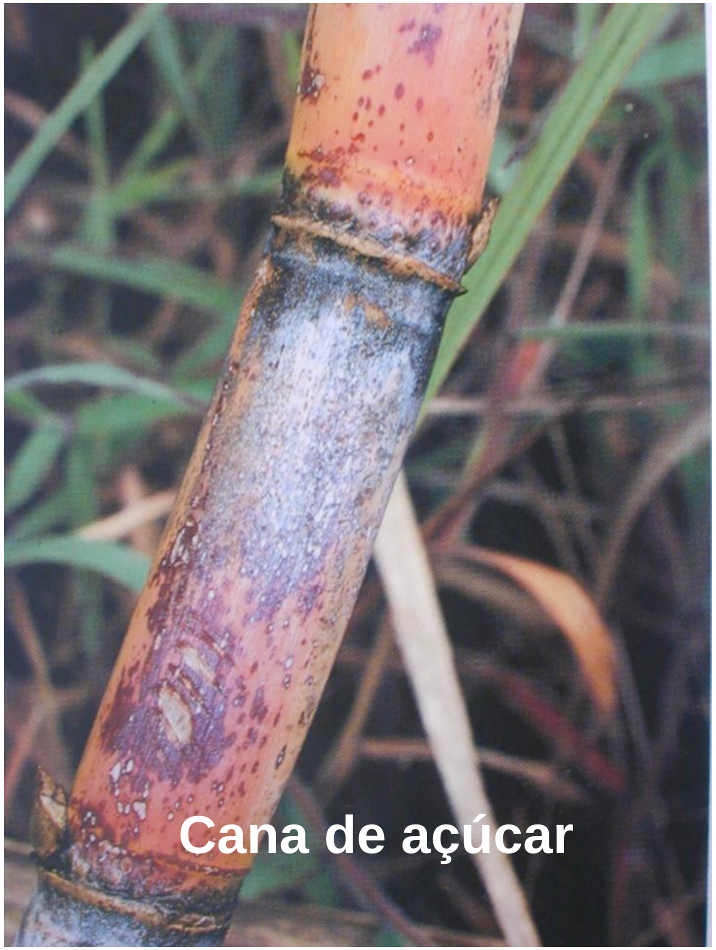
Grape juice => “wine”

Barley => “beer”

Honey => “mead” (tradução: hidromel)

Rice => “sake”

~5-11% ethanol



Cana de açúcar

→ Fermentação da sacarose → etanol

Produção brasileira de álcool combustível:

33,1 bilhões de litros (2016)

https://veja.abril.com.br/economia/brasil-tera-producao-recorde-de-etanol-de-331-bilhoes-de-litros/

Distillation of fermented beverages to produce “distilled spirits” with a greater percentage of ethyl alcohol (bp 78.3 ^{o}C).

Ethyl alcohol forms a binary azeotrope with water:

95% ethanol + 5% water (bp 78.15^{o}C)

Diluted with water => “vodka” 40% ethyl alcohol in water.

“proof”: when aqueous alcohol is placed on a sample of gunpowder and ignited, the gunpowder will burn at a minimum concentration of 50% alcohol. This is called “100-proof”.

Add oil of juniper (Juniperus communis, “zimbro”) => gin

Add peat smoke (“fumaça de turfa”) => scotch

Age in a burned barrel => whiskey

Add peppermint => schnapps

Etc.

Ethyl alcohol is a poison. LD_{50} = ~10g/Kg orally in mice.

Nausea, vomiting, flushing, mental excitement or depression, drowsiness, impaired perception, loss of coordination, stupor, coma, death may occur. (intoxication)

Economist.com SCIENCE & TECHNOLOGY

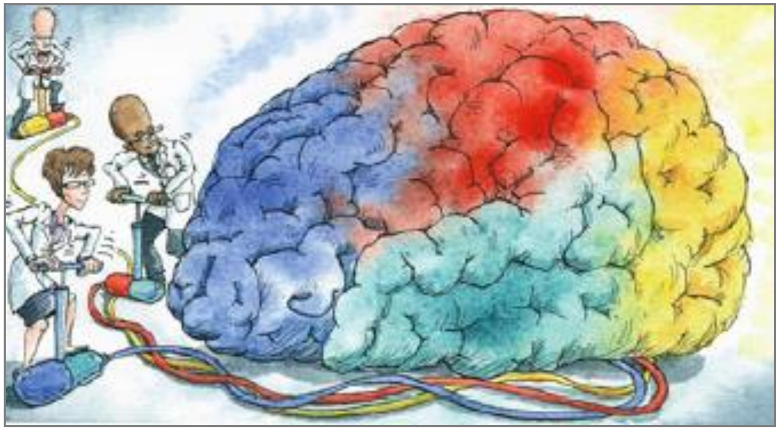
Cognitive enhancement

All on the mind

May 22nd 2008

From The Economist print edition

Stress? memory? cognition?



Propranolol é uma das substâncias proibidas nos Jogos Olímpicos, provavelmente para a sua utilização no controle de tremores. Ela foi tomada por um atirador norte-coreano que ganhou duas medalhas nos Jogos Olímpicos de 2008. Ele foi o primeiro atirador olímpico a ser desclassificado por uso de drogas.

Propranolol: orally administered anti-hypertensive

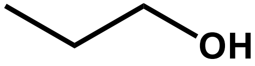
β-Blocker: blocks the action of epinephrine and norepinephrine on both β_1- and β_2-adrenergic receptors

“Basic sciences in the history of cardiovascular pharmacology”

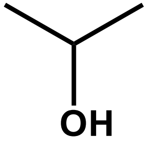
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC325477/

Classificação de álcoois CH_3, 1^o, 2^o, 3^o

álcool primário

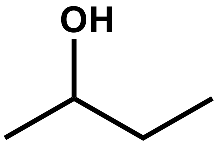


álcool n-propílico
(IUPAC: 1-propanol)

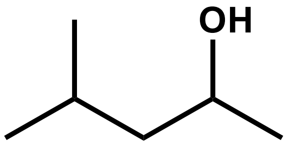


álcool iso-propílico
(2-propanol)

álcool secundário

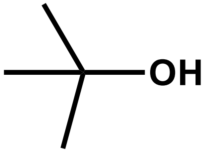


álcool sec-butílico
(2-butanol)



IUPAC: 4-metil-2-pentanol

álcool terciário



álcool t-butílico (t-butanol)
(2-metil-2-propanol)

Nomenclature of alcohols

Common names: “alkyl alcohol”

IUPAC: parent = longest continuous carbon chain containing the –OH group.

alkane drop -*e*, add –*ol*

prefix locant for –OH (lower number for OH)

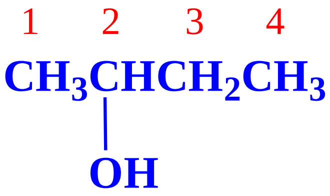
Number and name all substituents

Examples of alcohols and nomenclature (replace “e” by “ol”)

Type	Formula	IUPAC Name	Common name
Monohydric alcohols	CH_3OH	Methanol	Wood alcohol
	C_2H_5OH	Ethanol	Alcohol
	C_3H_7OH	Propan-2-ol	Isopropyl alcohol, Rubbing alcohol
	C_4H_9OH	Butan-1-ol	Butanol, Butyl alcohol
	$C_5H_{11}OH$	Pentan-1-ol	Pentanol, Amyl alcohol
	$C_{16}H_{33}OH$	Hexadecan-1-ol	Cetyl alcohol
Polyhydric alcohols	$C_2H_4(OH)_2$	Ethane-1,2-diol	Ethylene glycol
	$C_3H_6(OH)_2$	Propane-1,2-diol	Propylene glycol
	$C_3H_5(OH)_3$	Propane-1,2,3-triol	Glycerol
	$C_4H_6(OH)_4$	Butane-1,2,3,4-tetraol	Erythritol, Threitol
	$C_5H_7(OH)_5$	Pentane-1,2,3,4,5-pentol	Xylitol
	$C_6H_8(OH)_6$	hexane-1,2,3,4,5,6-hexol	Mannitol, Sorbitol
	$C_7H_9(OH)_7$	Heptane-1,2,3,4,5,6,7-heptol	Volemitol
Unsaturated aliphatic alcohols	C_3H_5OH	Prop-2-ene-1-ol	Allyl alcohol
	$C_{10}H_{17}OH$	3,7-Dimethylocta-2,6-dien-1-ol	Geraniol
	C_3H_3OH	Prop-2-yn-1-ol	Propargyl alcohol
Alicyclic alcohols	$C_6H_6(OH)_6$	Cyclohexane-1,2,3,4,5,6-hexol	Inositol
	$C_{10}H_{19}OH$	5-Methyl-2-(propan-2-yl)cyclohexan-1-ol	Menthol

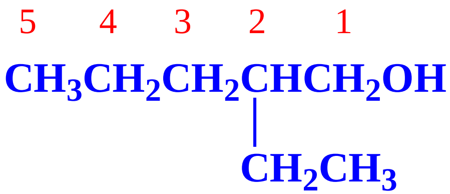
Nomenclatura de álcoois

1. Determine a cadeia principal contendo o grupo functional OH



$CH_3CH(OH)CH_2CH_3$

2-butanol
or
butan-2-ol



$CH_3CH_2CH_2CH(CH_2CH_3)CH_2OH$

2-ethyl-1-pentanol
or
2-ethylpentan-1-ol

3 2 1

$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2OH$

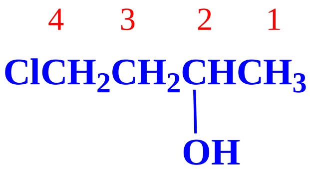
3-butoxy-1-propanol
or
3-butoxypropan-1-ol

2. O sufixo do grupo funcional deve ter o menor número

1 2 3

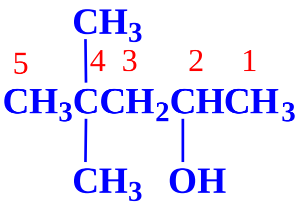
$HOCH_2CH_2CH_2Br$

3-bromo-1-propanol



$ClCH_2CH_2\underset{OH}{CH}CH_3$

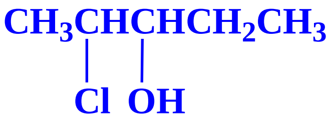
4-chloro-2-butanol



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{OH}{CH}CH_3$

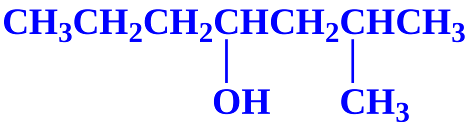
4,4-dimethyl-2-pentanol

3. Se há um sufixo de grupo funcional e um substituinte, o sufixo do grupo funcional recebe o menor número possível



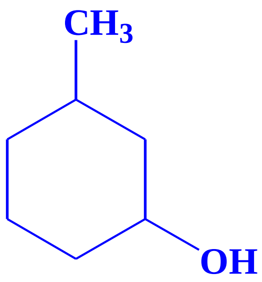
$CH_3\underset{Cl}{CH}\underset{OH}{CH}CH_2CH_3$

2-chloro-3-pentanol
not
4-chloro-3-pentanol



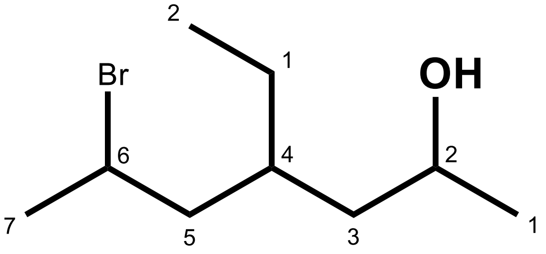
$CH_3CH_2CH_2\underset{OH}{CH}CH_2\underset{CH_3}{CH}CH_3$

2-methyl-4-heptanol
not
6-methyl-4-heptanol

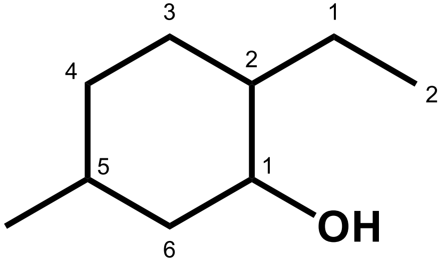


3-methylcyclohexanol
not
5-methylcyclohexanol

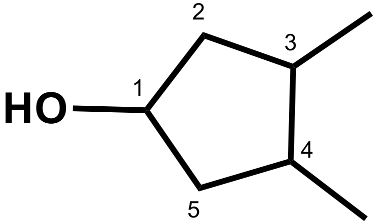
4. Se houver mais que um substituinte, os substituintes são citados em ordem alfabética



6-bromo-4-ethylheptan-2-ol



2-ethyl-5-methylcyclohexan-1-ol



3,4-dimethylcyclopentan-1-ol

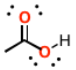
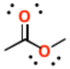
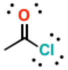
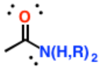
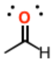
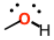
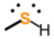
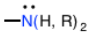
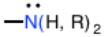
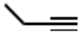
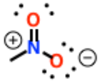
Naming Priority

- Acids
- Esters
- Aldehydes
- Ketones
- Alcohols
- Amines

- Alkenes
- Alkynes
- Alkanes
- Ethers
- Halides
- Nitro compounds

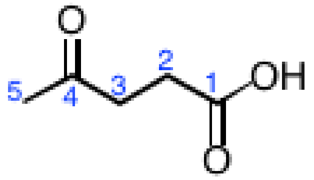
Naming Priority

HIGHEST PRIORITY

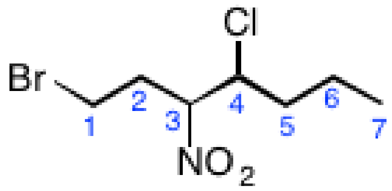
Group	Prefix	Suffix	Example
 **carboxylic acid**	carboxy-	-carboxylic acid -oic acid	ethanoic acid
 **ester**	(R)-oxycarbonyl	-oate	methyl ethanoate
 **acid chloride**	halocarbonyl-	-oyl halide	ethanoyl chloride
 **amide**	carbamoyl-	-carboxamide -amide	ethanamide
$-C\equiv N:$ **nitrile**	cyano-	-nitrile	ethanonitrile
 **aldehyde**	formyl-	-al -carbaldehyde	ethanal
 **ketone**	oxo-	-one	2-propanone
 **alcohol**	hydroxy-	-ol	methanol
 **thiol**	mercapto-	-thiol	methanethiol
 $-\ddot{N}(H, R)_2$ **amine**	amino-	-amine	methylamine
 $-\ddot{N}(H, R)_2$ **amine**	amino-	-amine	methylamine
 **alkene**	alkenyl	-ene	propene
 **alkyne**	alkynyl	-yne	butyne
 **alkane**	alkyl	**-ane**	butane
 **ether**	alkoxy	**-ane**	methoxy methane (or methyl methyl ether)
 **alkyl halide**	halo-	**-ane**	bromomethane
 **nitro**	nitro-	**-ane**	nitromethane

EVERYTHING FROM HERE ON BELOW ENDS IN "–ANE"

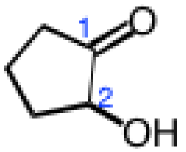
Applying the priorities (suffixes are **highlighted**)



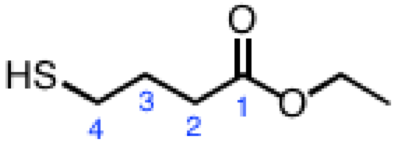
4-oxo-pentan**oic acid**



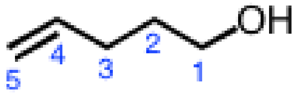
1-bromo-4-chloro-3-nitrohept**ane**



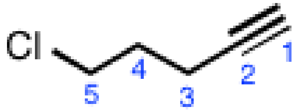
2-hydroxycyclopentan**one**



ethyl 4-mercaptobutan**oate**



4-penten**ol**
(pent-4-en-1-ol)



5-chloropent-1-**yne**

Unsaturated Alcohols

- Hydroxyl group takes precedence. Assign that carbon the lowest number.
- Use alkene or alkyne name.

$$CH_2{=}CHCH_2\overset{\overset{OH}{|}}{C}HCH_3$$

4-penten-2-ol (old)

pent-4-ene-2-ol
(1997 revision of IUPAC rules)

Physical properties of alcohols:

polar + hydrogen bonding

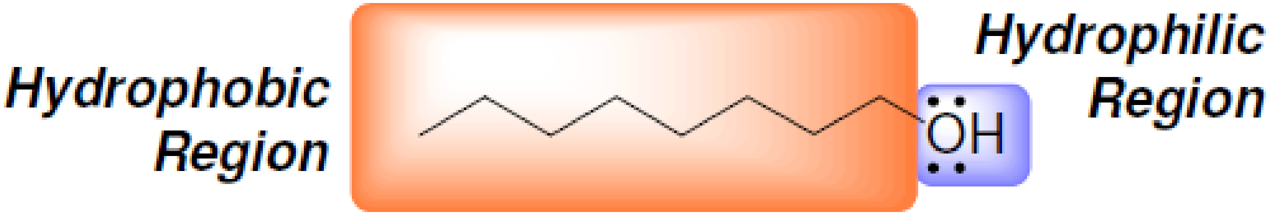
relatively higher mp/bp

water insoluble!

(except for alcohols of three carbons or less)

Physical Properties of Alcohols

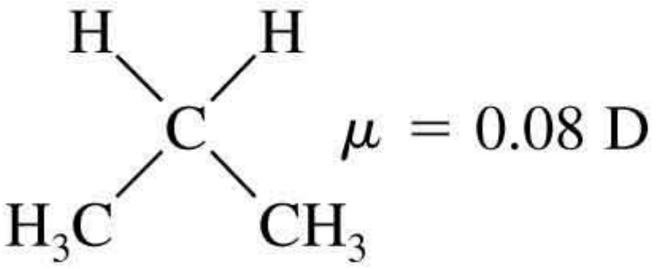
octanol-water partitioning



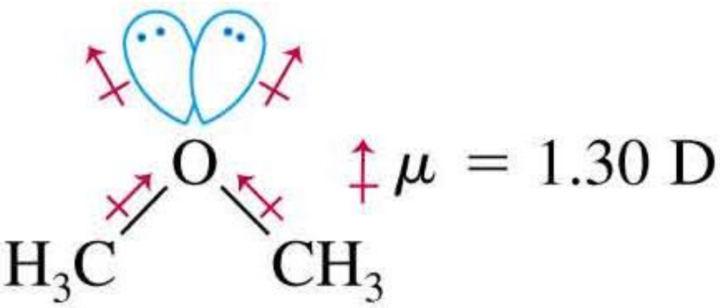
- Molecules with large hydrophobic groups are generally insoluble in water.
- Alcohols with three or less carbons are generally water miscible.
- Alcohols with more than three carbons are not miscible, and their solubility decreases as the size of the hydrophobic group increases.
- *Partition Coefficient*: relative solubility of a compound (ratio) in octanol vs. water (Drug absorbtion & transport)

- **ADME** (Adsorption, distribution, metabolism, excretion)

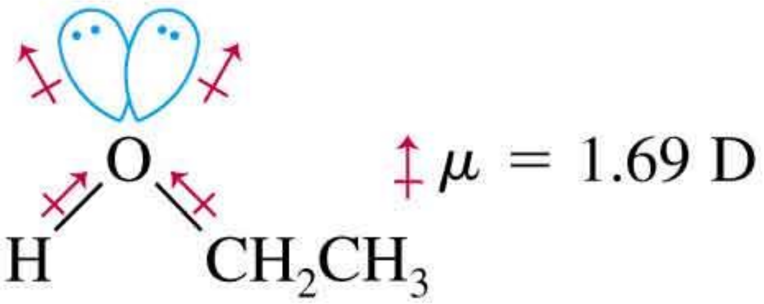
Boiling Points


$\mu = 0.08$ D

propane, MW 44
bp −42°C

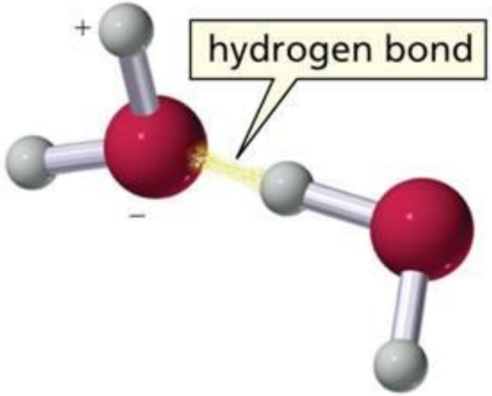

$\mu = 1.30$ D

dimethyl ether, MW 46
bp −25°C

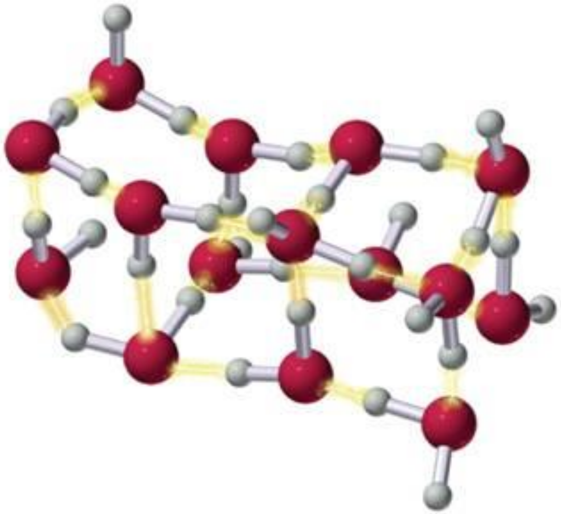

$\mu = 1.69$ D

ethanol, MW 46
bp 78°C

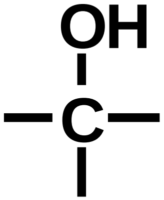
- Uma ligação de hidrogênio é um tipo especial de interação dipolo–dipolo

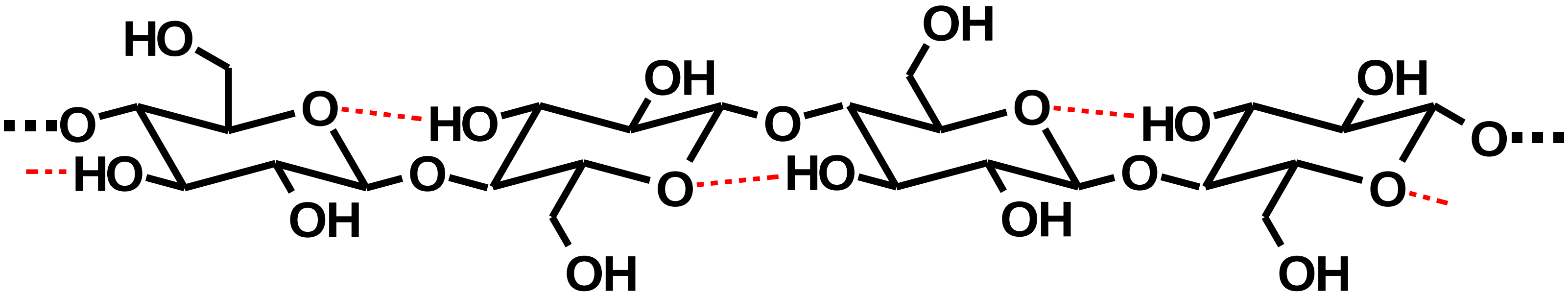


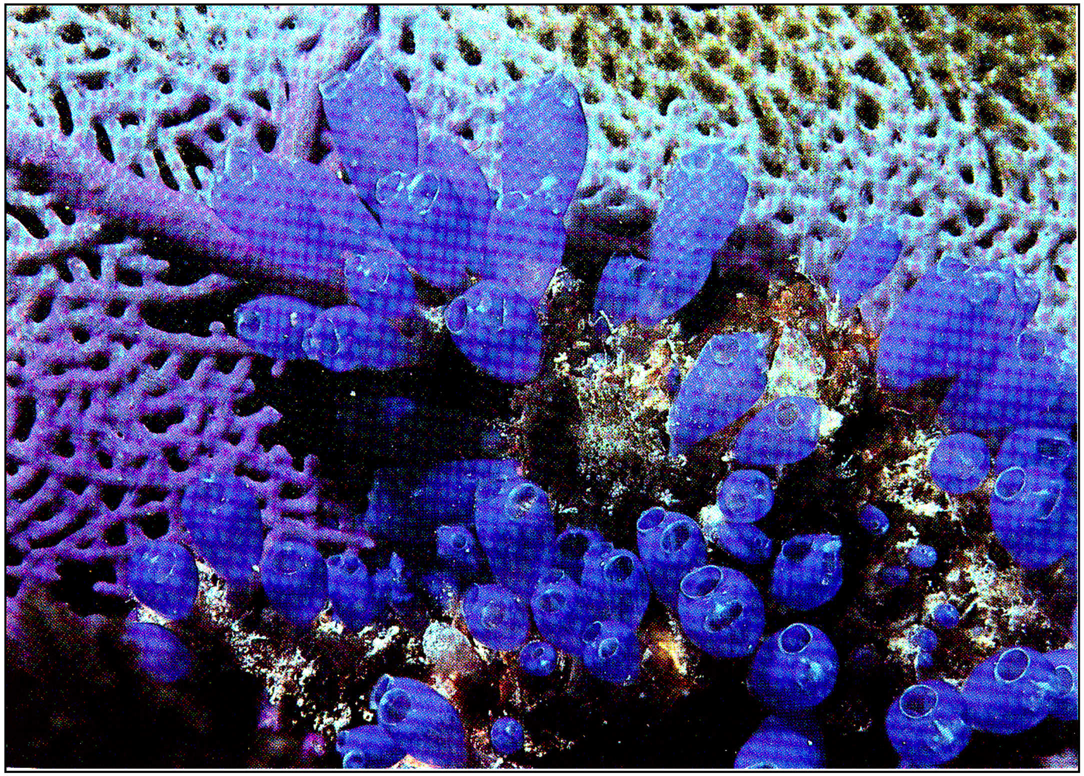
hydrogen bonding in water

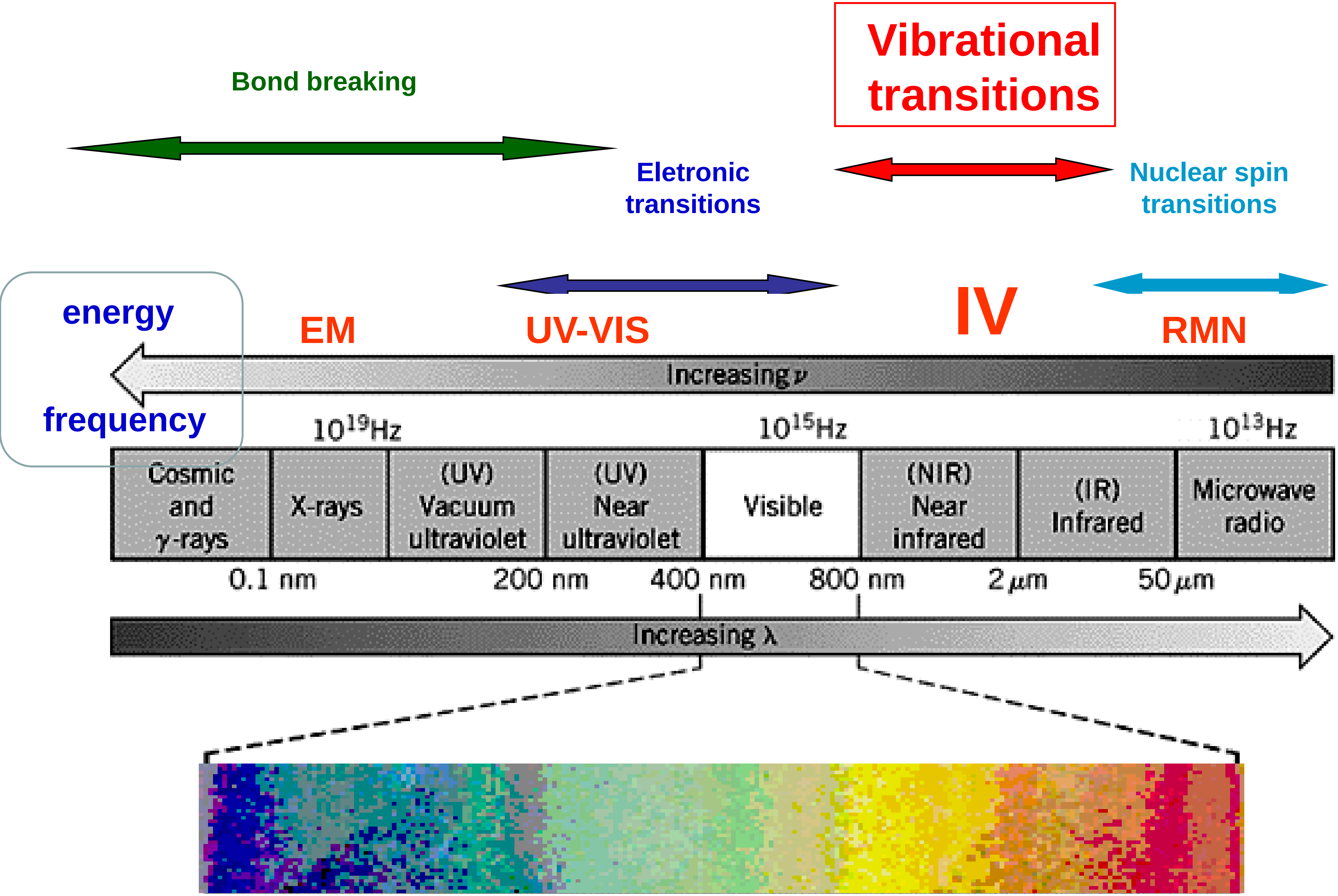


ÁLCOOIS: Polissacarídeos I (Celulose)









Vibrational transitions

Bond breaking

Eletronic transitions

Nuclear spin transitions

energy

frequency

EM

UV-VIS

IV

RMN

Infrared radiation

λ = 2.5 to 17 μm

ν (número de onda) = 4000 to 600 cm^{-1}

These frequencies match the frequencies of covalent bond stretching and bending vibrations.

Infrared spectroscopy can be used to find out about **covalent bonds** in molecules.

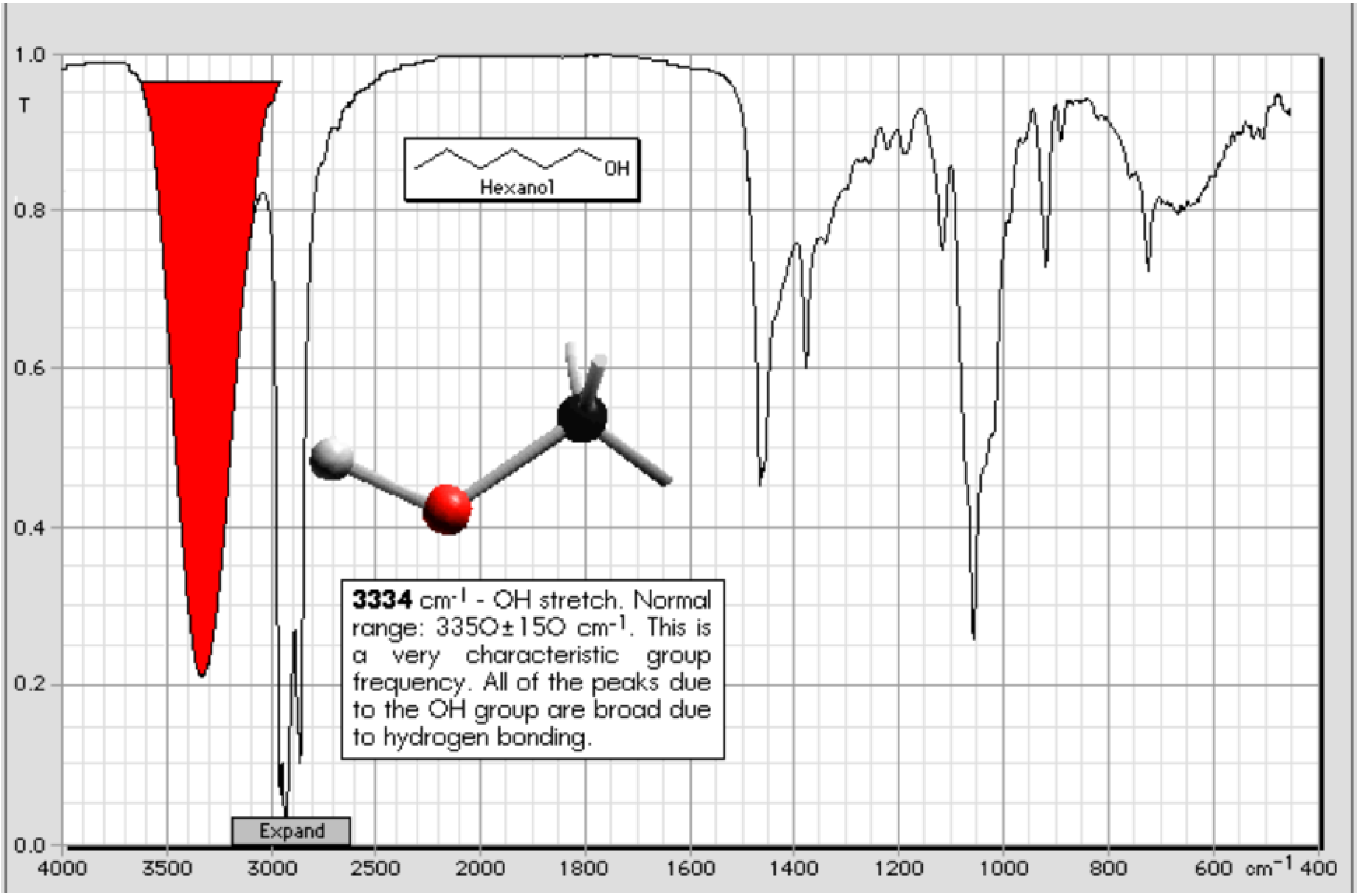
IR is used to tell:

1. what type of bonds are present

2. some structural information

Absorption bands for alcohols (streching of O-H)

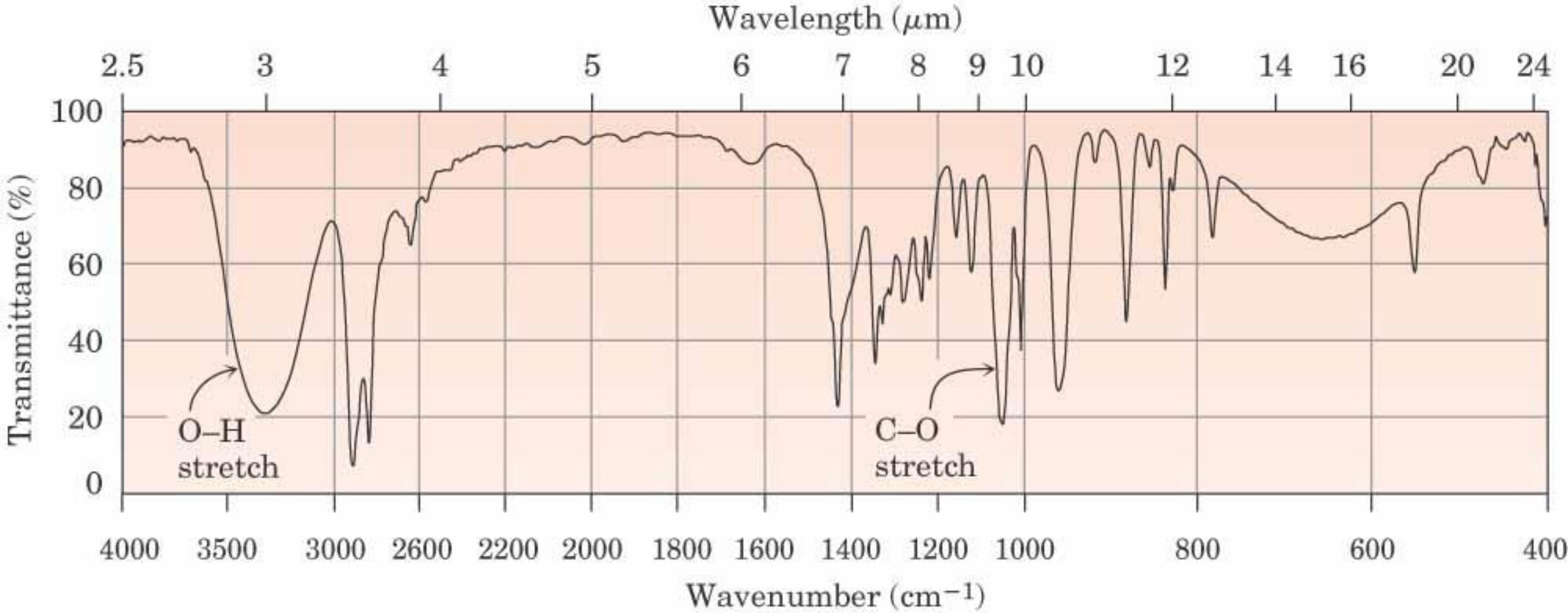
Broadening caused by different extension of hydrogen bonding)



3334 cm^{-1} - OH stretch. Normal range: 3350±150 cm^{-1}. This is a very characteristic group frequency. All of the peaks due to the OH group are broad due to hydrogen bonding.

Espectro no Infravermelho do hexanol

Cyclohexanol

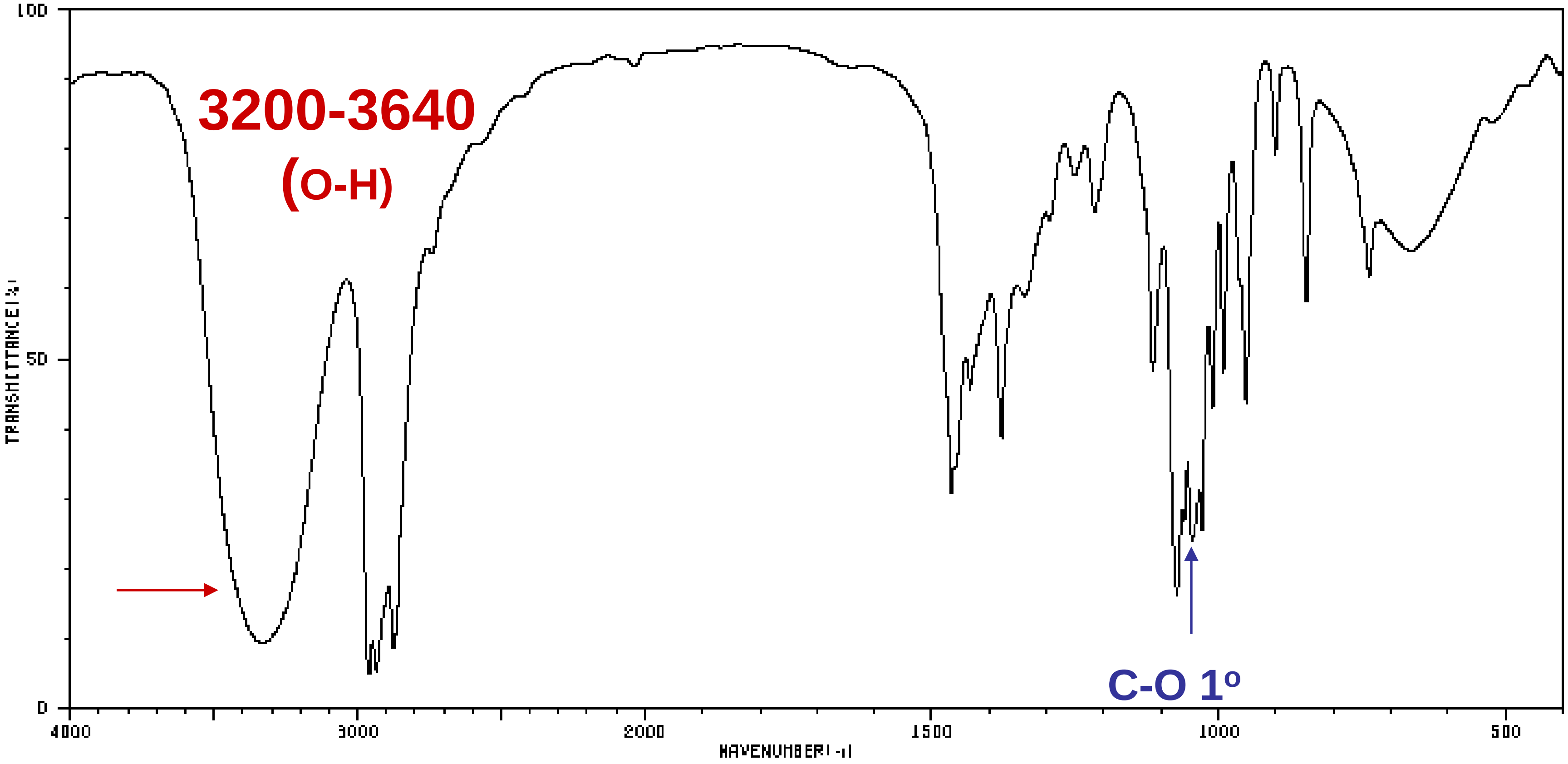


HIT-NO=1418	SCORE= ( )	SDBS-NO=1374	IR-NIDA-05408 : LIQUID FILM

1-BUTANOL

1-butanol

$C_4H_{10}O$



3200-3640

(O-H)

C-O 1º

3333	9	1434	49	1073	16	901	77
3323	9	1379	37	1060	26	847	57
2960	4	1338	57	1047	23	738	58
2934	6	1296	68	1029	24	670	62
2875	8	1252	74	1011	42	665	62
1466	30	1217	68	992	46		
1461	33	1116	46	963	42		

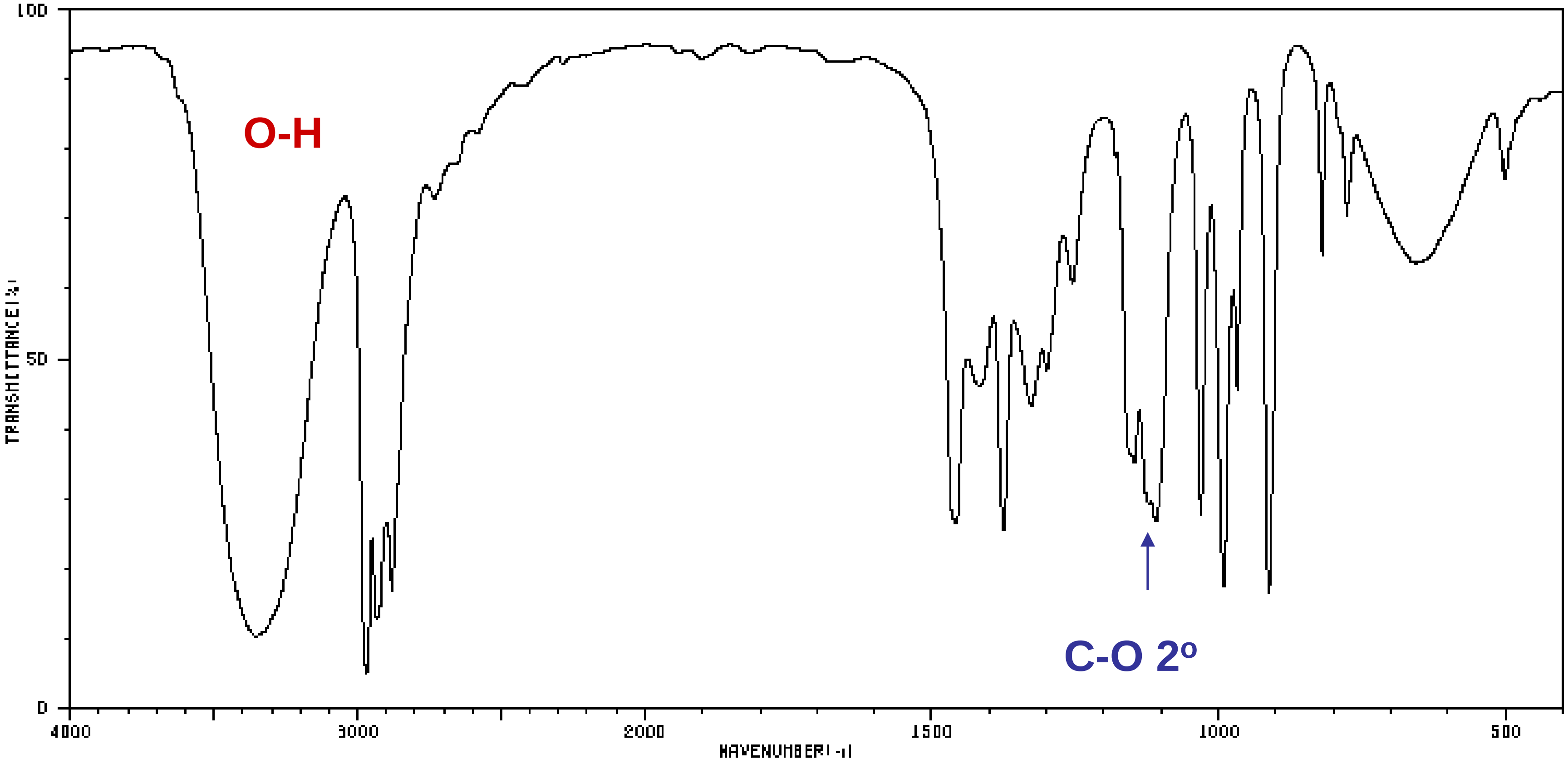
$CH_3CH_2CH_2CH_2$-OH

HIT-NO=1035	SCORE= ( )	SDBS-NO=507	IR-NIDA-04700 : LIQUID FILM

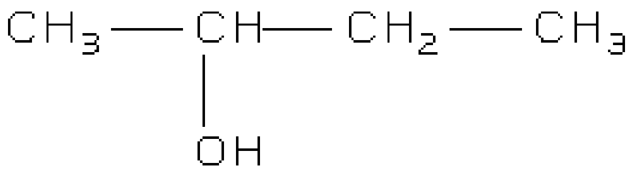
2-BUTANOL

2-butanol

$C_4H_{10}O$



3363	10	1376	24	1110	26	666	60
2968	4	1327	42	1031	26	651	60
2932	12	1300	46	991	16	501	72
2880	16	1266	58	968	43		
2734	70	1154	35	913	15		
1457	25	1148	34	820	82		
1416	44	1122	28	777	68		



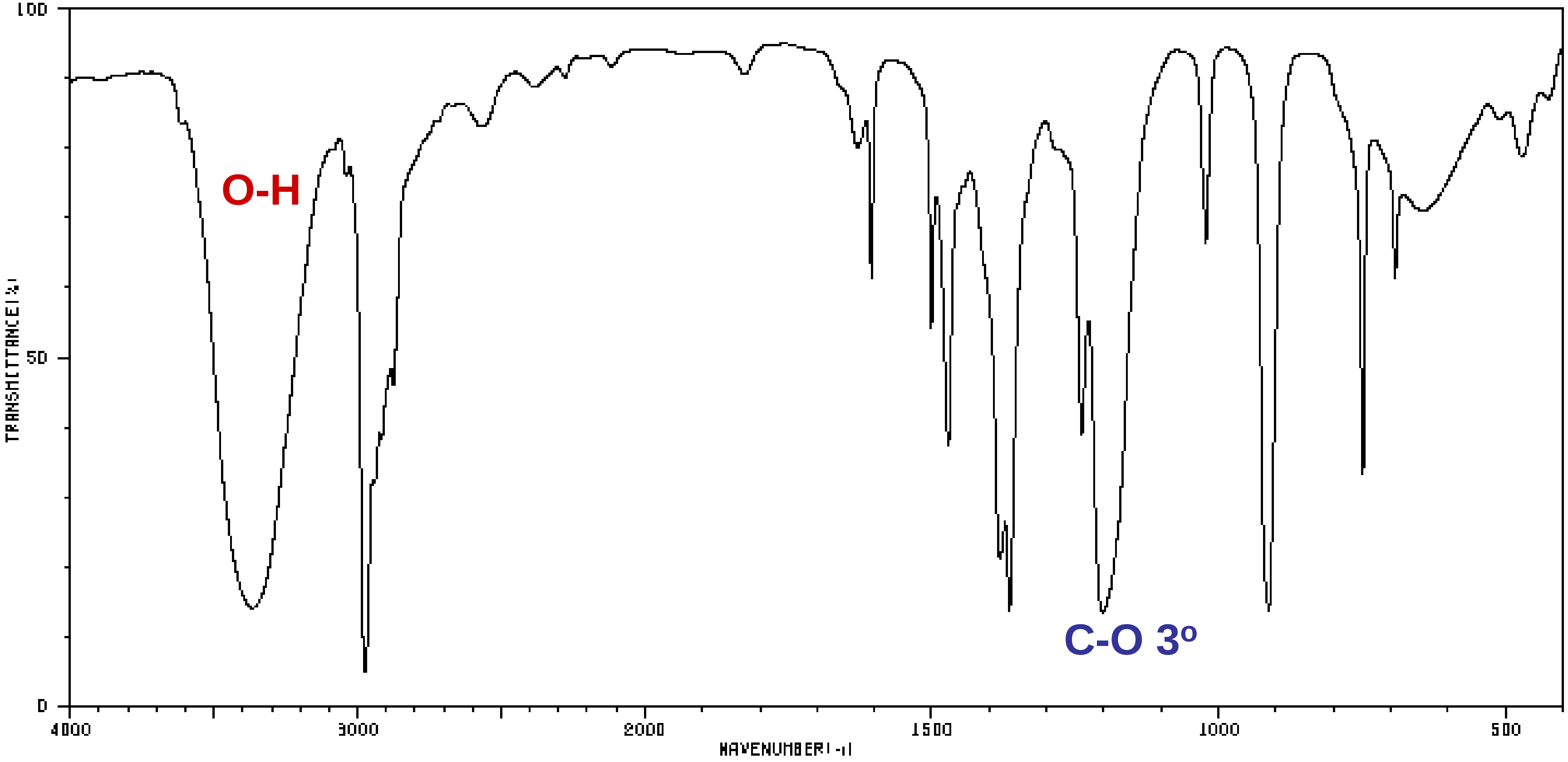
$CH_3—CH(OH)—CH_2—CH_3$

HIT-NO=1034	SCORE= ( )	SDBS-NO=506	IR-NIDA-05409 : LIQUID FILM

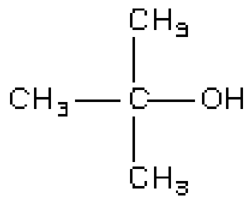
2-METHYL-2-PROPANOL

tert-butyl alcohol

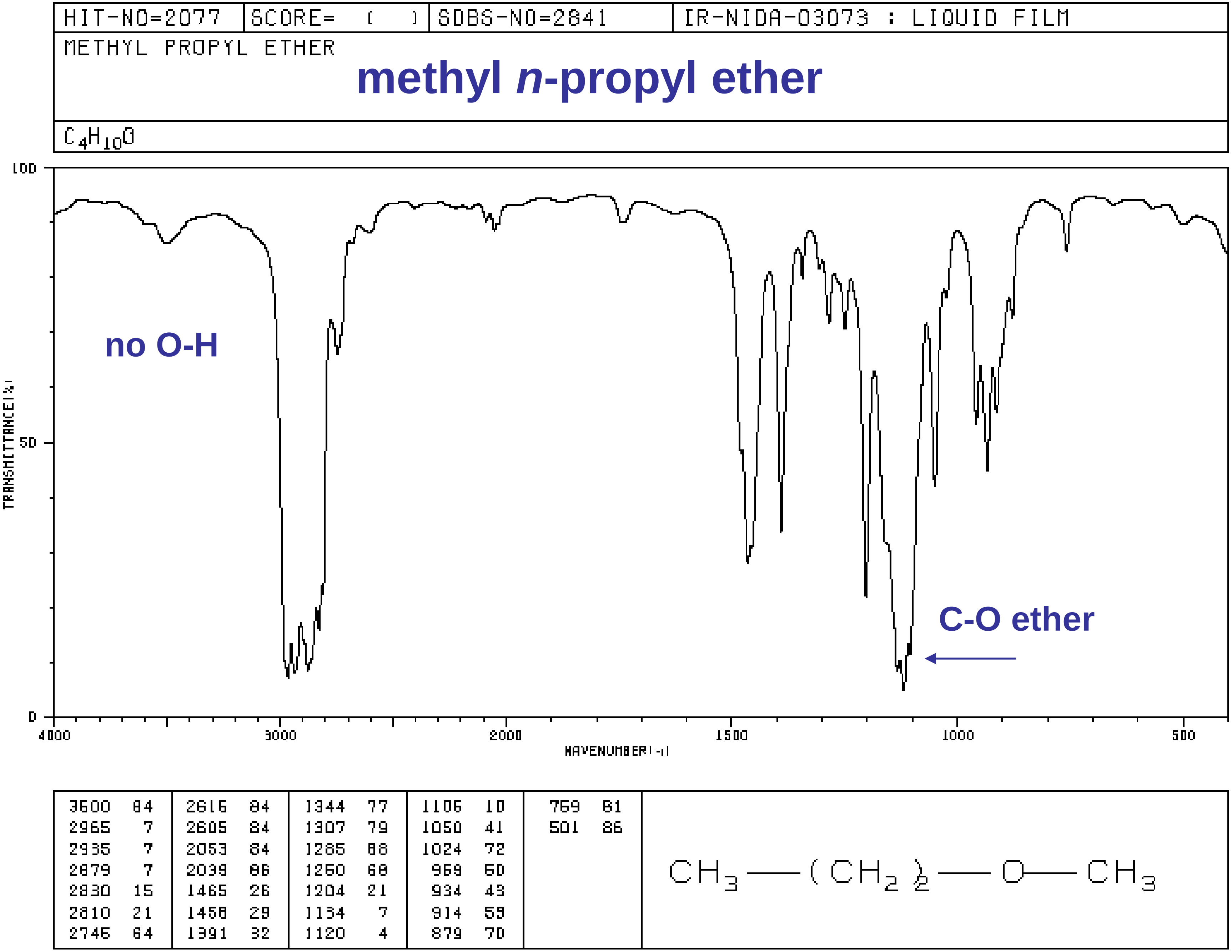
$C_4H_{10}O$



3366	13	1630	77	1202	12	511	81
3038	72	1606	58	1022	64	471	77
2974	4	1501	52	913	13		
2940	31	1471	36	749	32		
2875	44	1381	20	693	58		
2564	79	1365	15	648	68		
2386	86	1239	37	643	68		



methyl *n*-propyl ether



HIT-NO=2077	SCORE= ( )	SDBS-NO=2841	IR-NIDA-03073 : LIQUID FILM

METHYL PROPYL ETHER

$C_4H_{10}O$

no O-H

C-O ether

3600	84	2616	84	1344	77	1106	10	769	81
2965	7	2605	84	1307	79	1050	41	501	86
2935	7	2053	84	1285	88	1024	72		
2879	7	2039	86	1260	68	969	50		
2830	15	1465	26	1204	21	934	43		
2810	21	1458	29	1134	7	914	59		
2746	64	1391	32	1120	4	879	70		

$CH_3-(CH_2)_2-O-CH_3$

Solubility in Water

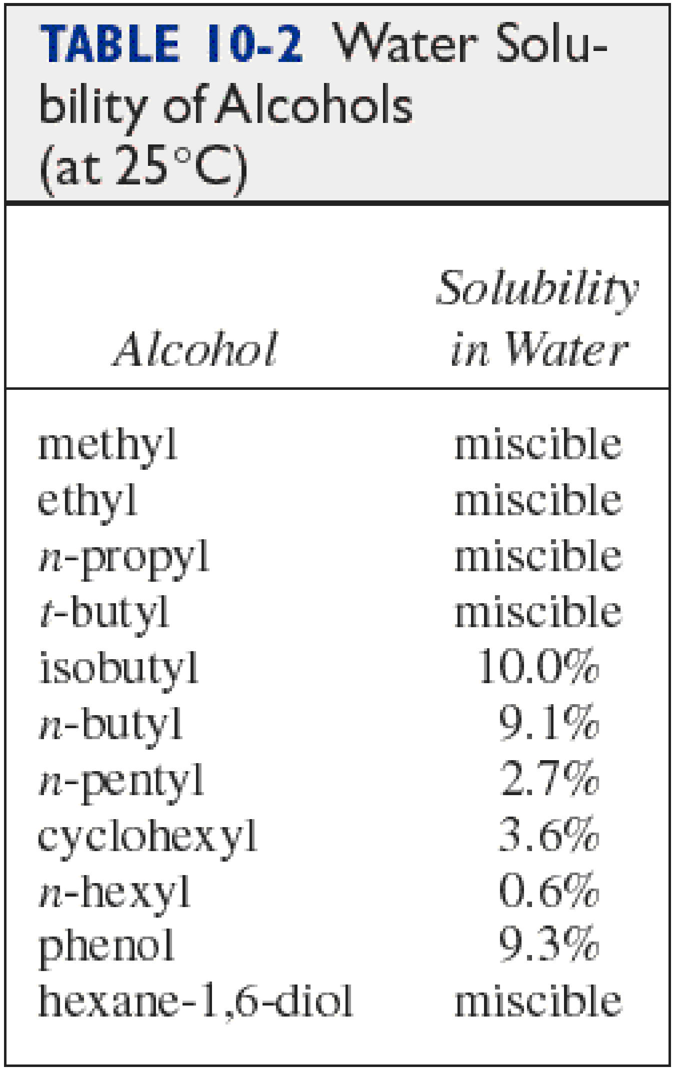
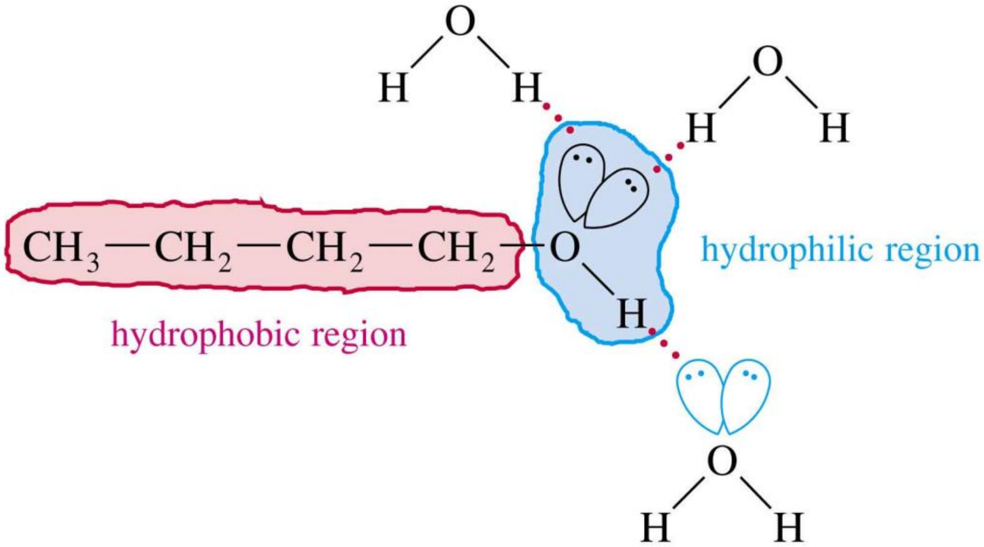


TABLE 10-2 Water Solubility of Alcohols (at 25°C)

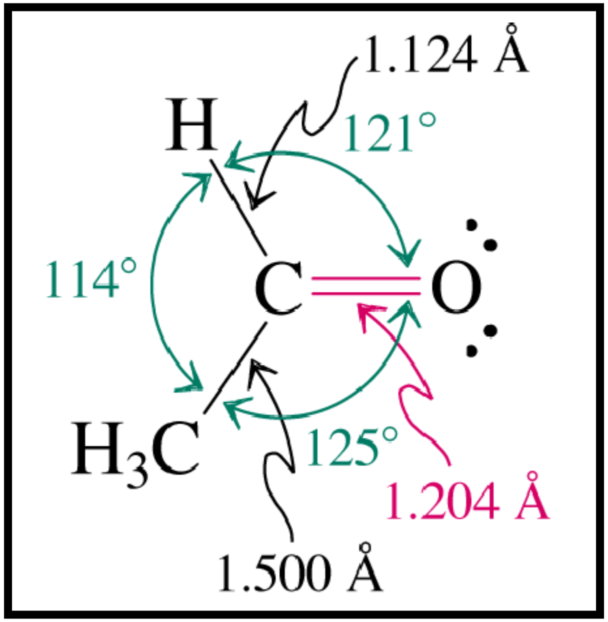
Alcohol	*Solubility in Water*
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible

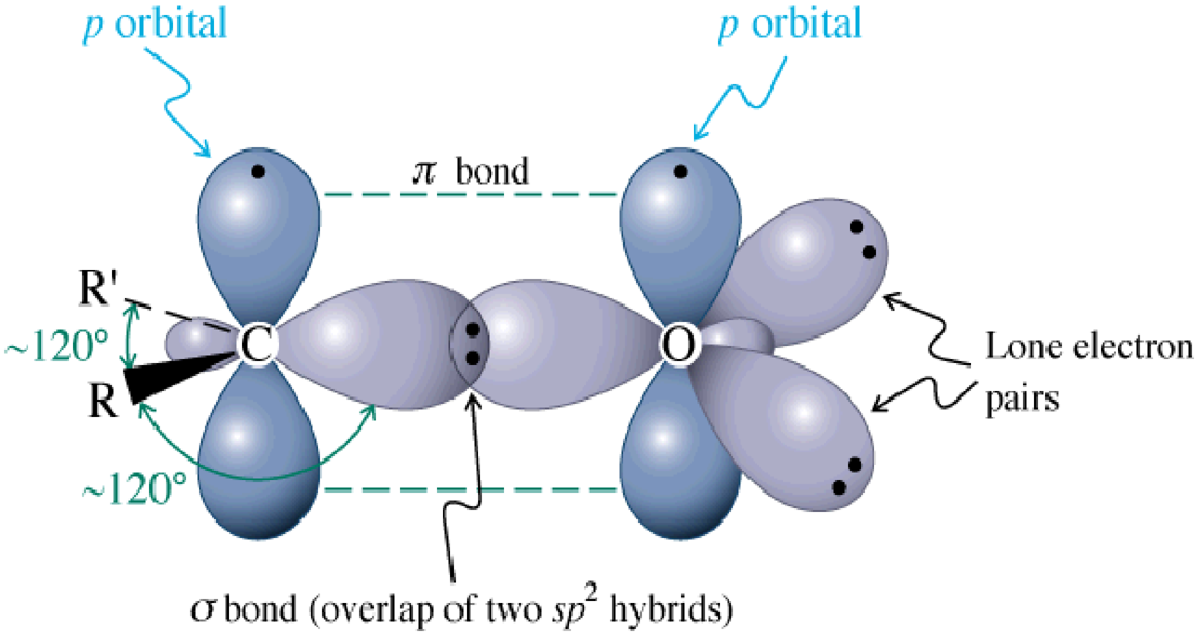


Solubility decreases as the size of the alkyl group increases.

Aldeídos e Cetonas

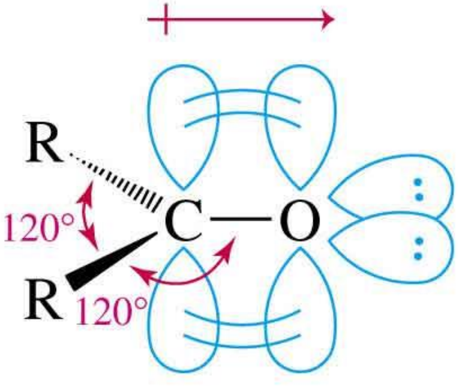
- ✓ Grupo funcional em aldeídos e cetonas é trigonal planar. Ângulos de ligação são aproximadamente 120º.
- ✓ Hibridização do C e do O é sp^2.





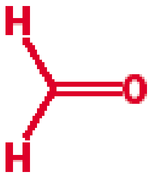
Carbonyl Structure

- Carbon is *sp*^{2} hybridized.
- C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.

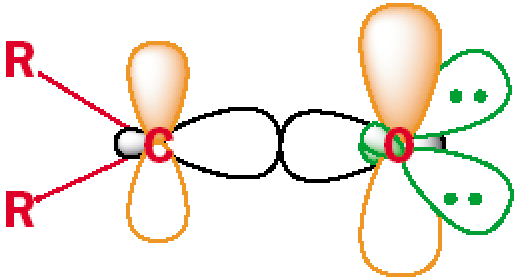


	length	*energy*
ketone C═O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C═C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

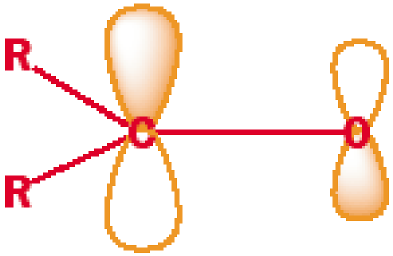
A Ligação π C=O



formaldehyde
(methanal, CH_2O)

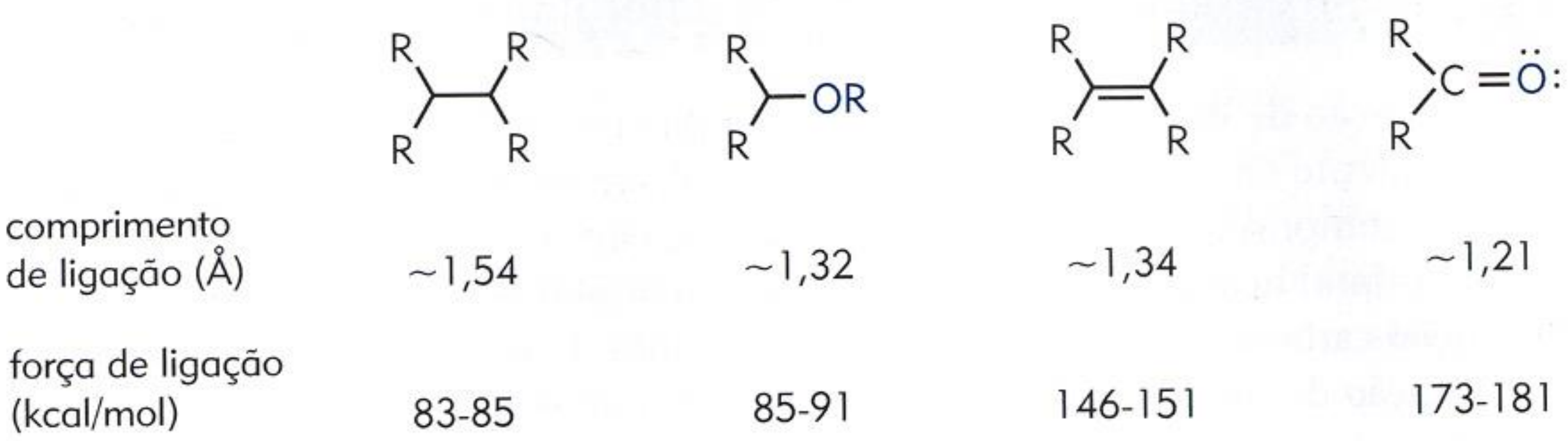


complete diagram of filled orbitals of C=O bond



empty, antibonding π* orbital

Como podem ser explicadas as diferenças nos comprimentos de ligação e de energia de ligação mostradas abaixo?



comprimento de ligação (Å)	~1,54	~1,32	~1,34	~1,21
força de ligação (kcal/mol)	83-85	85-91	146-151	173-181

Um alto valor de energia de ligação não implica necessariamente em baixa reatividade. Compostos carbonílicos são reativos frente a nucleófilos.

Carbonyl Compounds

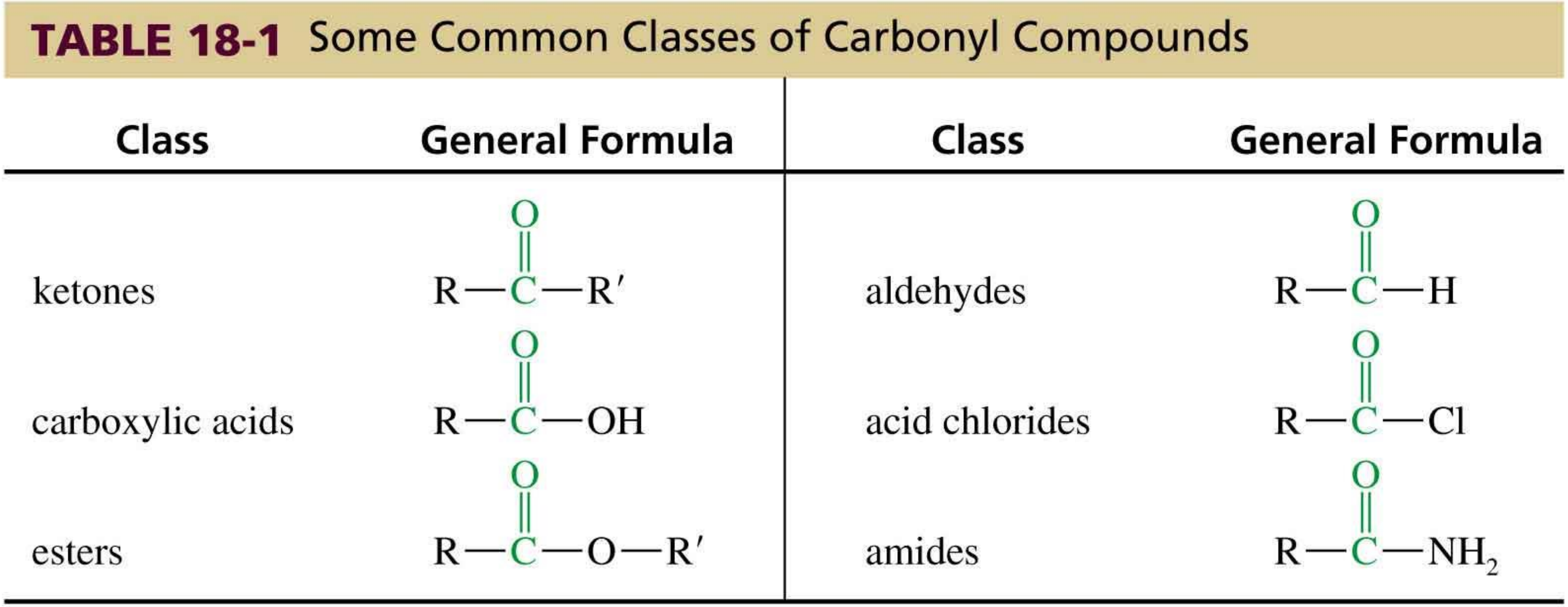
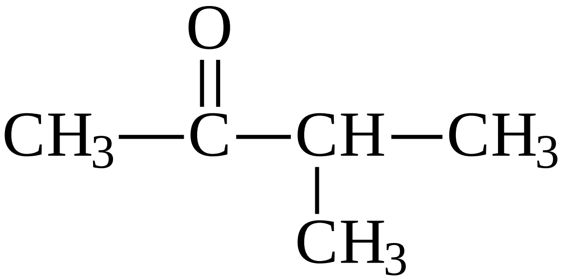


TABLE 18-1 Some Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones	$R-\overset{O}{\overset{\|}{C}}-R'$	aldehydes	$R-\overset{O}{\overset{\|}{C}}-H$
carboxylic acids	$R-\overset{O}{\overset{\|}{C}}-OH$	acid chlorides	$R-\overset{O}{\overset{\|}{C}}-Cl$
esters	$R-\overset{O}{\overset{\|}{C}}-O-R'$	amides	$R-\overset{O}{\overset{\|}{C}}-NH_2$

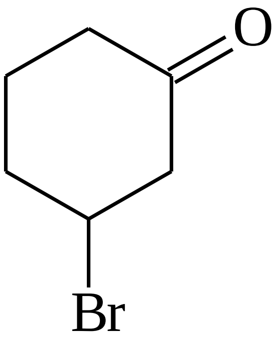
IUPAC Names for Ketones

- Replace -*e* with -*one*. Indicate the position of the carbonyl with a number.
- Number the chain so that carbonyl carbon has the lowest number.
- For cyclic ketones the carbonyl carbon is assigned the number 1.



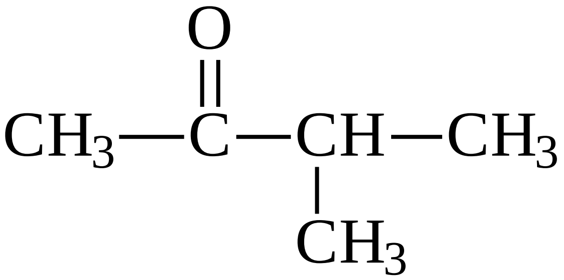
$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

3-methyl-2-butanone



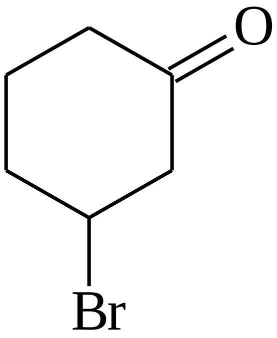
3-bromocyclohexanone

Examples

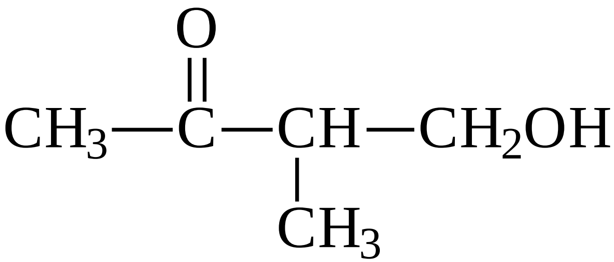


$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$

3-methyl-2-butanone



3-bromocyclohexanone

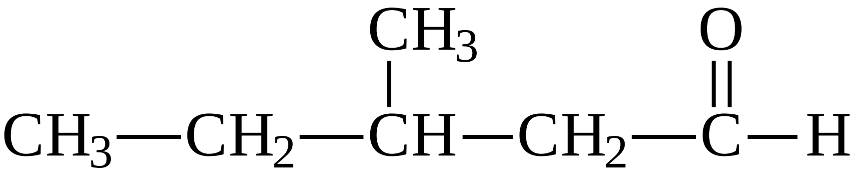


$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2OH}$$

4-hydroxy-3-methyl-2-butanone

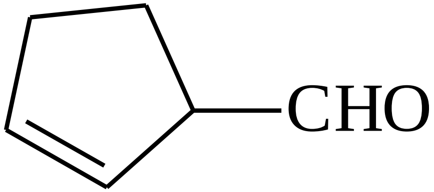
Naming Aldehydes

- IUPAC: Replace -*e* with -*al*.
- The aldehyde carbon is number 1.
- If -CHO is attached to a ring, use the suffix -*carbaldehyde*.



$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H$$

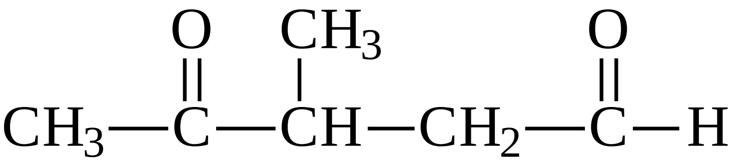
3-methylpentanal



2-cyclopentenecarbaldehyde

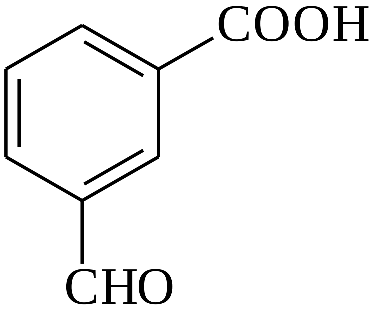
Name as Substituent

- On a molecule with a higher priority functional group, C=O is *oxo*- and -CHO is *formyl.*
- Aldehyde priority is higher than ketone.



$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$

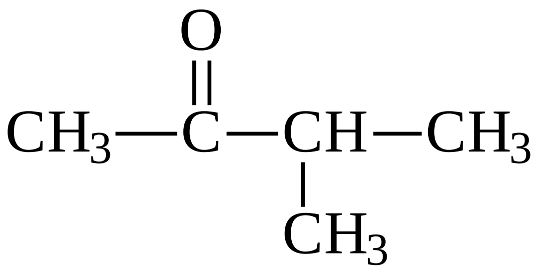
3-methyl-4-oxopentanal



3-formylbenzoic acid

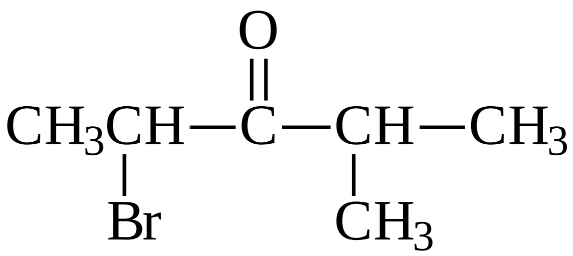
Common Names for Ketones

- Named as alkyl attachments to -C=O.
- Use Greek letters instead of numbers.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

methyl isopropyl ketone



$$CH_3\underset{\underset{\displaystyle Br}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

α–bromoethyl isopropyl ketone

Aldehyde Common Names

- Use the common name of the acid.
- Drop -*ic acid* and add -*aldehyde*.

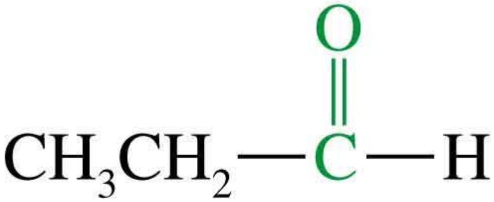
  - 1 C: formic acid, formaldehyde
  - 2 C's: acetic acid, acetaldehyde
  - 3 C's: propionic acid, propionaldehyde
  - 4 C's: butyric acid, butyraldehyde.

Boiling Points of carbonyl compounds

- Higher boiling point than comparable alkane or ether.
- Lower boiling point than comparable alcohol.

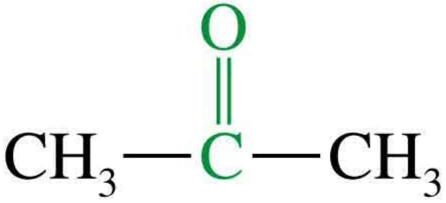
$CH_3CH_2CH_2CH_3$
butane
bp 0°C

$CH_3{-}O{-}CH_2CH_3$
methoxyethane
bp 8°C



$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$

propanal
bp 49°C



$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$

acetone
bp 56°C

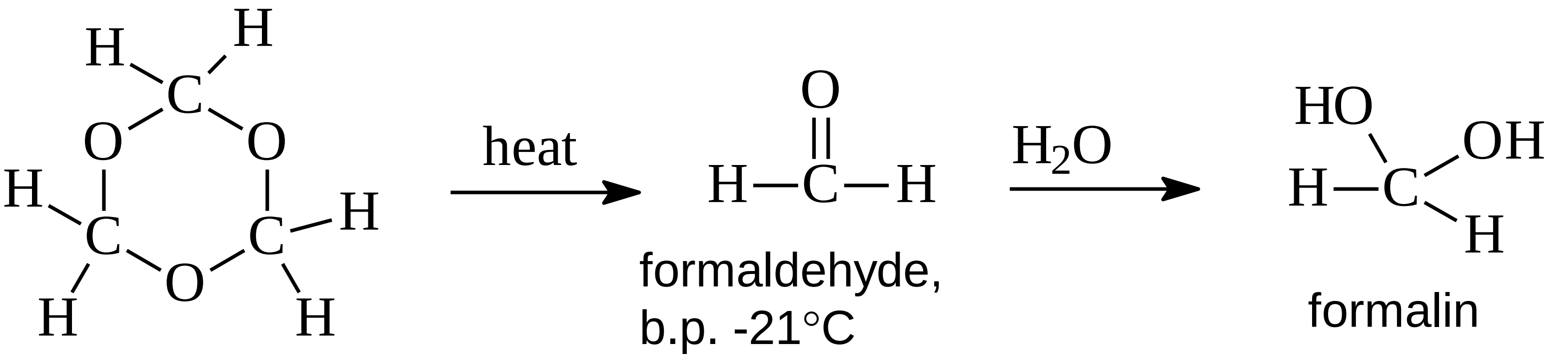
$CH_3CH_2CH_2{-}OH$
1-propanol
bp 97°C

Solubility of carbonyl compounds

- Good solvent for alcohols.
- Lone pair of electrons on oxygen of carbonyl can accept a hydrogen bond from O-H or N-H.
- Acetone and acetaldehyde are miscible in water.

Formaldehyde

- Gas at room temperature.
- Formalin is a 40% aqueous solution.



formaldehyde, b.p. -21°C

formalin

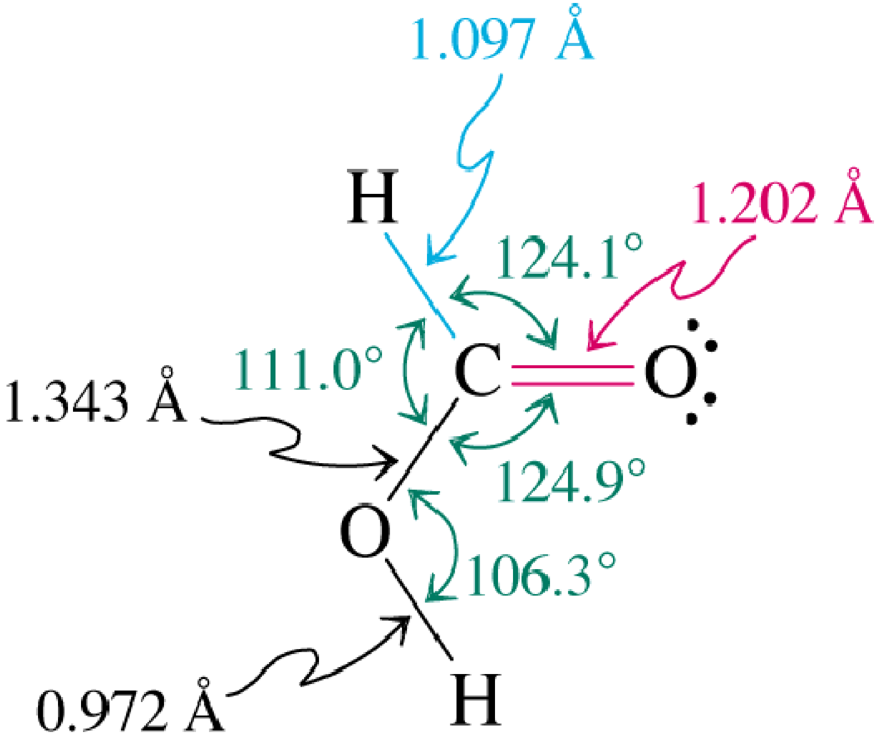
trioxane, m.p. 62°C

Ácidos Carboxílicos

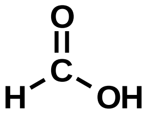
Ácido fórmico:

i) planar;

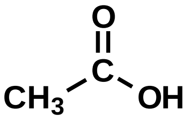
ii) carbono carbonílico é trigonal planar.



Exemplos de ácidos carboxílicos simples e a origem de seus nomes



ácido fórmico
(Latin: *formica* = formiga)



ácido acético
(*acetum* = vinagre)

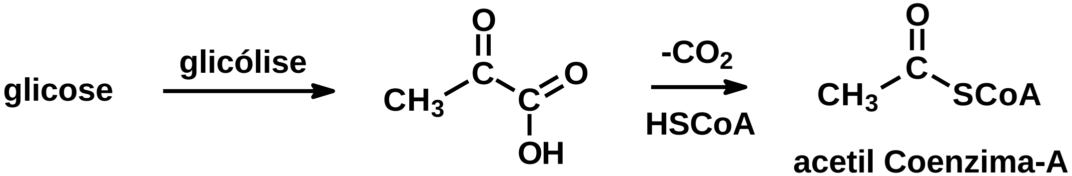
$CH_3CH_2CH_2CO_2H$

ácido propiônico
(*pro*= o primeiro;
pion= gordura)

$CH_3CH_2CH_2CH_2CO_2H$

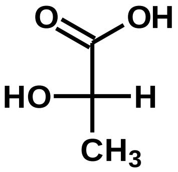
ácido butírico
(*butirum*=manteiga)

Derivados de ácidos carboxílicos naturais biologicamente importantes

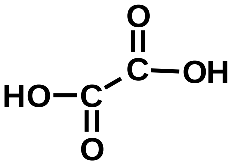


ácido pirúvico

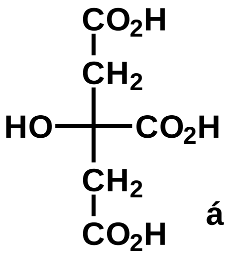
acetil Coenzima-A
(um tioéster)



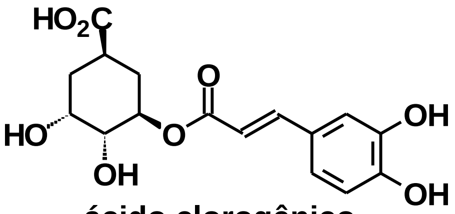
ácido (*S*)-(+)-lático



ácido oxálico



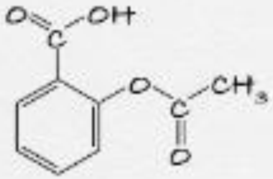
ácido cítrico



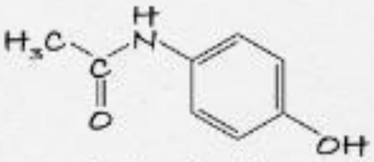
ácido clorogênico
(maçã)

Some significant examples

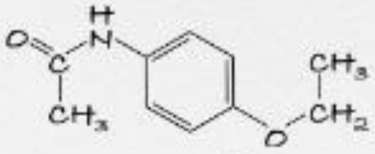
Analgesics - pain killers
Antipyetics - fever reducers



Acetylsalicylc acid
(Aspirin)



Acetaminophen
(Tylenol)

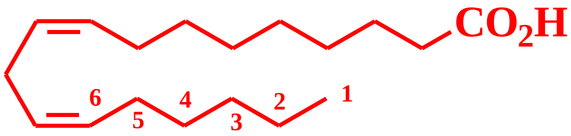


Phenacetin
(APC tablets)

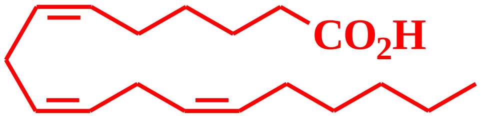
Formula	**Common Name**	**Source**	**IUPAC Name**	**Melting Point**	**Boiling Point**
HCO_2H	formic acid	ants (L. formica)	methanoic acid	8.4 ºC	101 ºC
CH_3CO_2H	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 ºC	118 ºC
$CH_3CH_2CO_2H$	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 ºC	141 ºC
$CH_3(CH_2)_2CO_2H$	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 ºC	164 ºC
$CH_3(CH_2)_3CO_2H$	valeric acid	valerian root	pentanoic acid	-34.5 ºC	186 ºC
$CH_3(CH_2)_4CO_2H$	caproic acid	goats (L. caper)	hexanoic acid	-4.0 ºC	205 ºC
$CH_3(CH_2)_5CO_2H$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 ºC	223 ºC
$CH_3(CH_2)_6CO_2H$	caprylic acid	goats (L. caper)	octanoic acid	16.3 ºC	239 ºC
$CH_3(CH_2)_7CO_2H$	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 ºC	253 ºC
$CH_3(CH_2)_8CO_2H$	capric acid	goats (L. caper)	decanoic acid	31.0 ºC	219 ºC

Ácidos graxos da série n-6

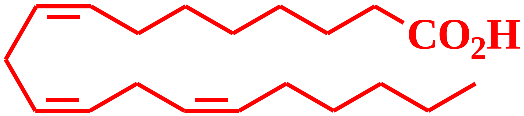
(gordura animal, óleos do girassol,
soja, açafrão e algodão)



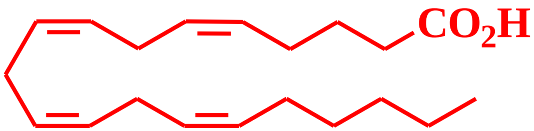
Ácido linolêico 18:2



Ácido γ-linolênico 18:3



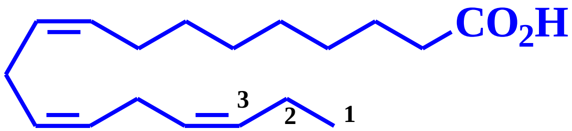
Ácido dihomo-γ-linolênico 20:3



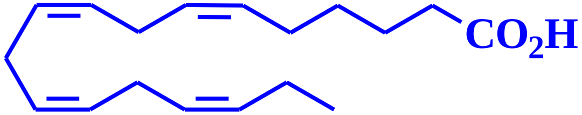
Ácido araquidônico 20:4

Ácidos graxos da série n-3

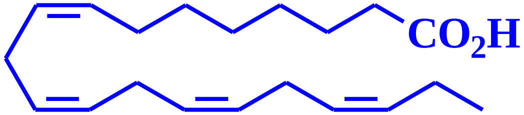
(folhas verdes, óleos de peixes,
óleos de soja e linhaça)



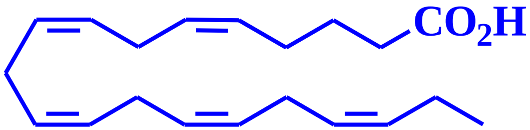
Ácido α-linolênico 18:3



Ácido octadecatetraenóico 18:4



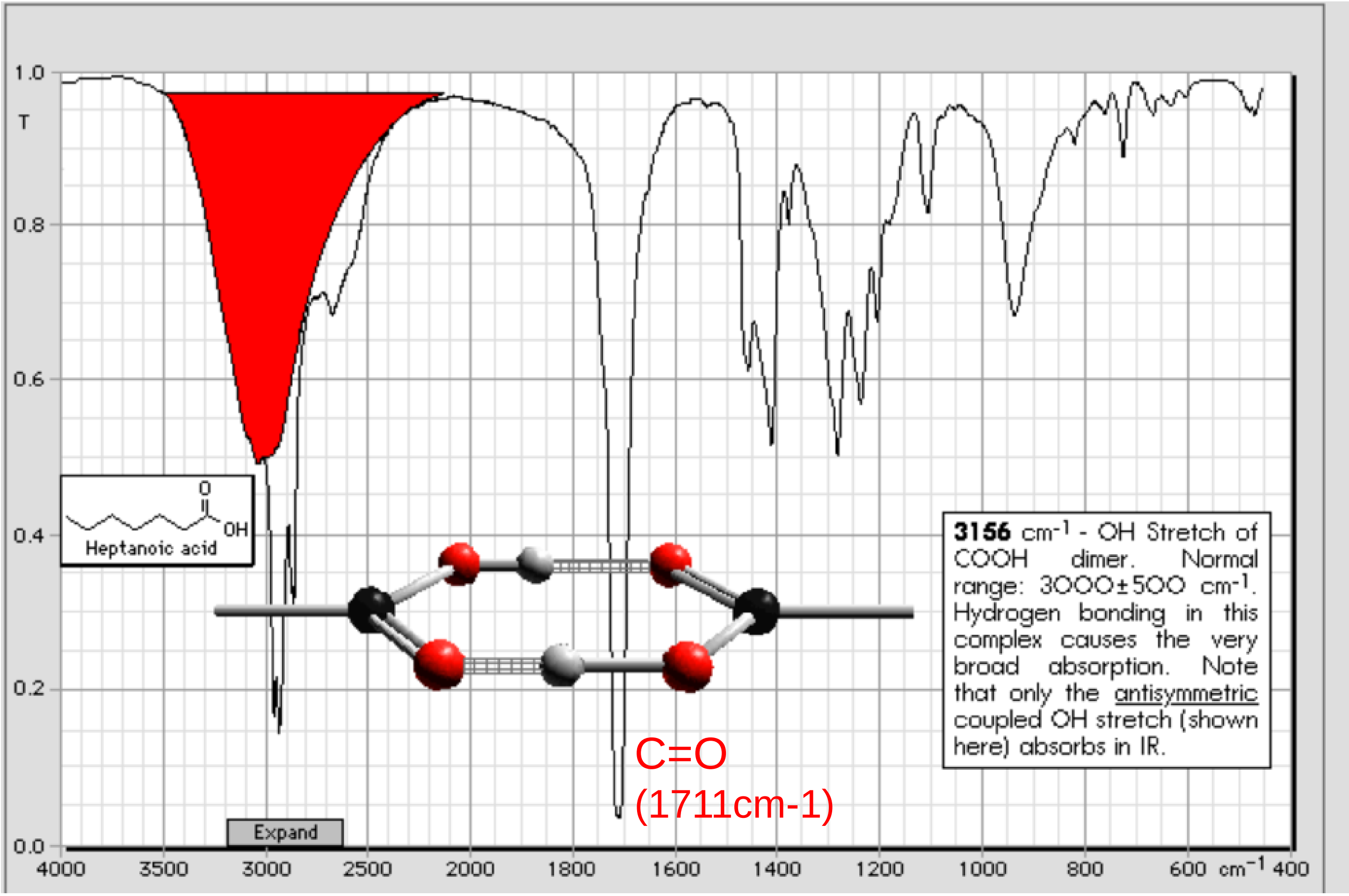
Ácido eicosa-8,11,14,17-tetraenóico 20:4



Ácido eicosapentaenóico (EPA) 20:5

Absorption bands for carboxylic acids (streching of O-H)

The broadening of bands in carboxylic acids are very effective



3156 cm^{-1} - OH Stretch of COOH dimer. Normal range: 3000±500 cm^{-1}. Hydrogen bonding in this complex causes the very broad absorption. Note that only the antisymmetric coupled OH stretch (shown here) absorbs in IR.

C=O
(1711cm-1)

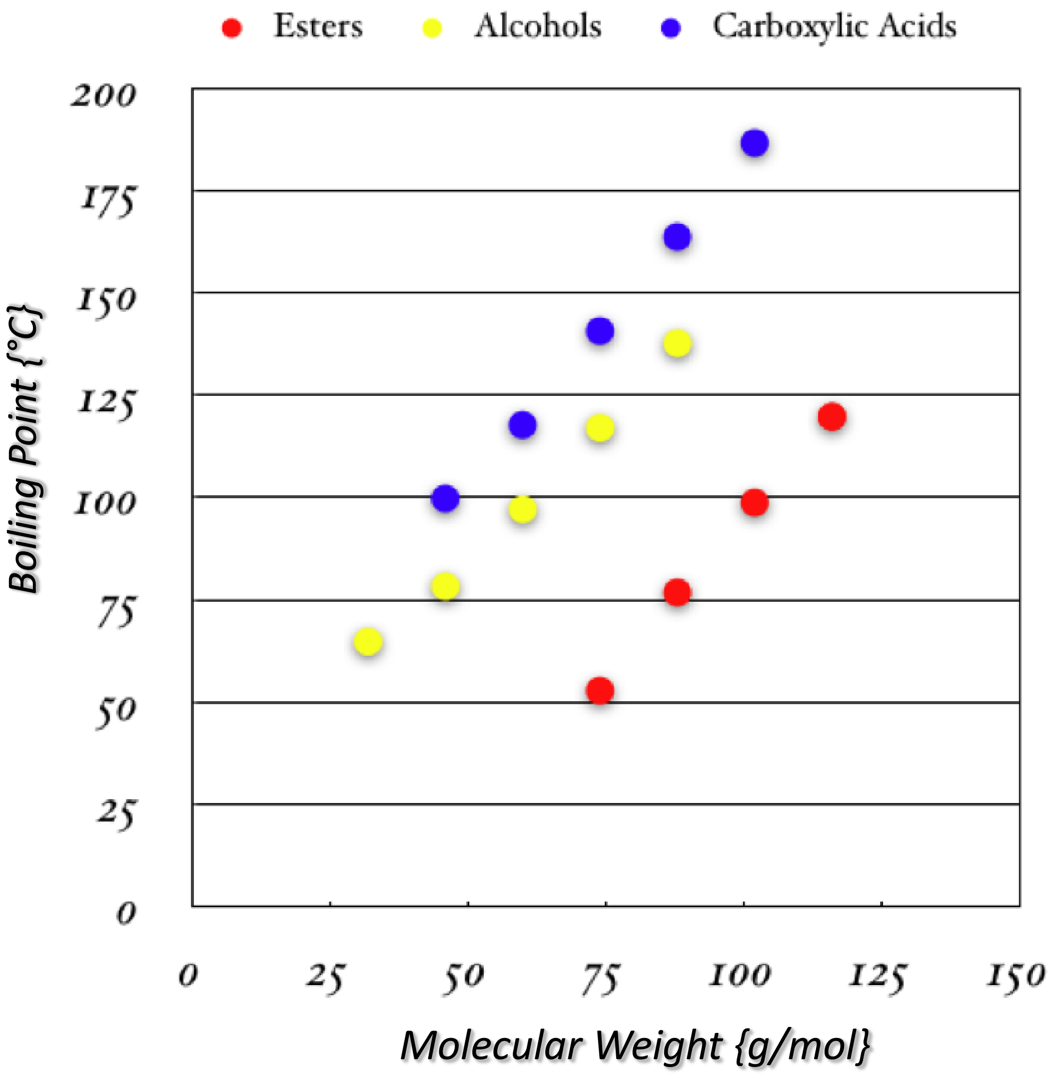
Espectro no Infravermelho do ácido heptanoico

Physical Properties of Some Organic Compounds

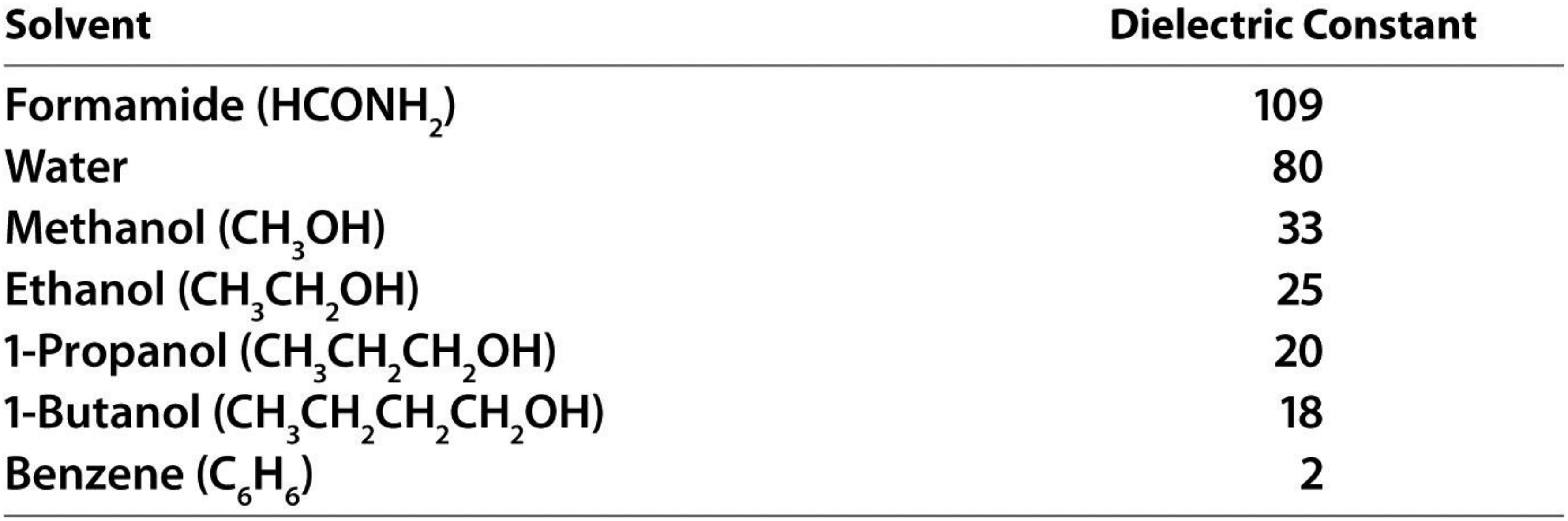
Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
$CH_3(CH_2)_2CO_2H$	butanoic acid	88	164 °C	very soluble
$CH_3(CH_2)_4OH$	1-pentanol	88	138 °C	slightly soluble
$CH_3(CH_2)_3CHO$	pentanal	86	103 °C	slightly soluble
$CH_3CO_2C_2H_5$	ethyl ethanoate	88	77 °C	moderately soluble
$CH_3CH_2CO_2CH_3$	methyl propanoate	88	80 °C	slightly soluble
$CH_3(CH_2)_2CONH_2$	butanamide	87	216 °C	soluble
$CH_3CON(CH_3)_2$	N,N-dimethylethanamide	87	165 °C	very soluble
$CH_3(CH_2)_4NH_2$	1-aminobutane	87	103 °C	very soluble
$CH_3(CH_2)_3CN$	pentanenitrile	83	140 °C	slightly soluble
$CH_3(CH_2)_4CH_3$	hexane	86	69 °C	insoluble

Alcohols, Carboxylic Acids & Esters

- The boiling points for members of all three families increases with molecular weight (London dispersion interactions).
- Alcohols and carboxylic acids have a higher boiling point than esters (why?)
- The carboxylic acids have a slightly higher boiling point than alcohols (they can form two hydrogen bonds with a neighboring molecule).



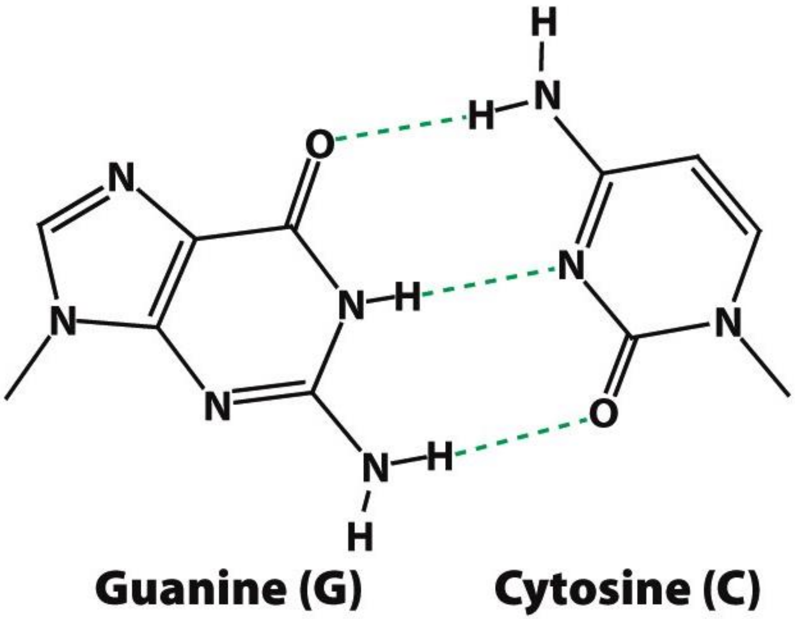
Dielectric Solvent Constants[1]

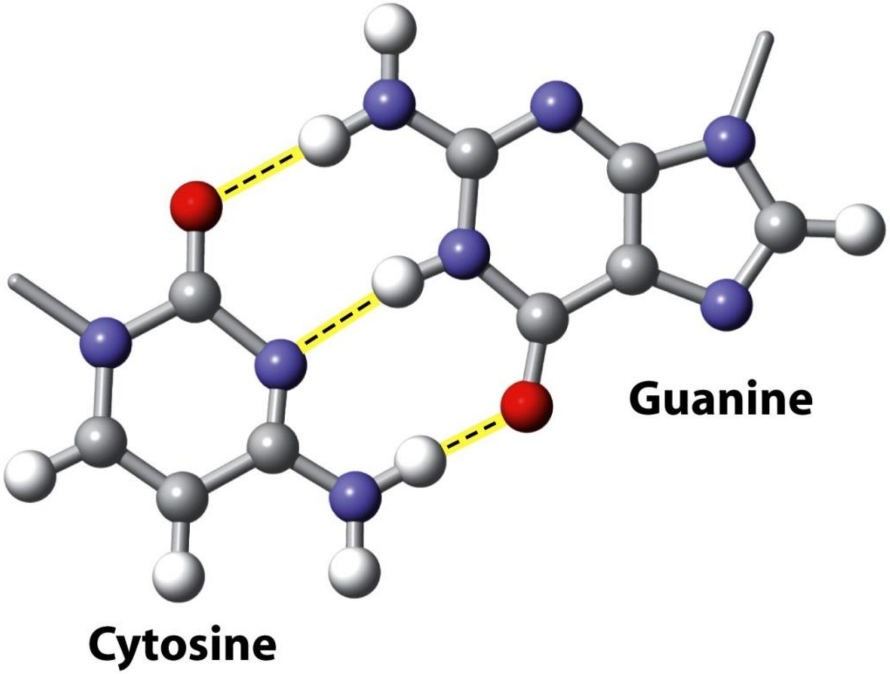


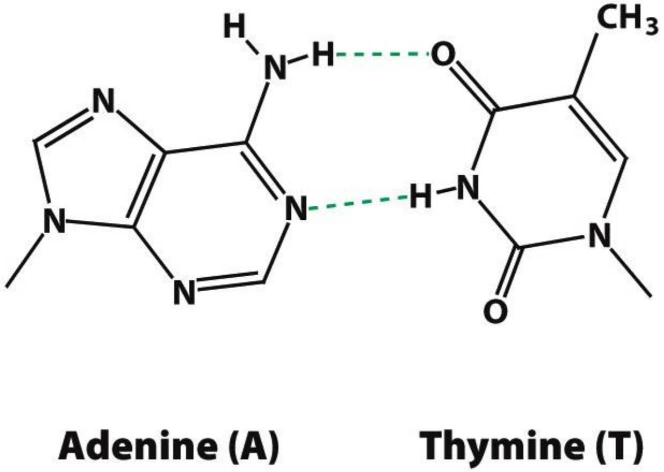
Solvent	Dielectric Constant
Formamide ($HCONH_2$)	109
Water	80
Methanol (CH_3OH)	33
Ethanol (CH_3CH_2OH)	25
1-Propanol ($CH_3CH_2CH_2OH$)	20
1-Butanol ($CH_3CH_2CH_2CH_2OH$)	18
Benzene (C_6H_6)	2

[1] Dielectric solvent constant is a measure of the ability of a solvent to diminish electrostatic attraction between dissolved ions

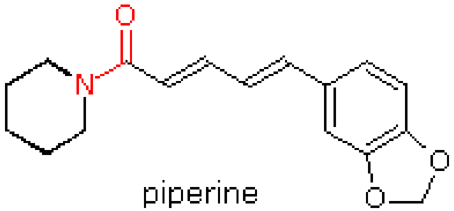
DNA Base Pair Hydrogen Bonding



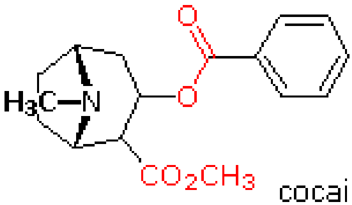




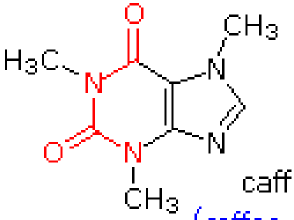
Exemplos de derivados de ácidos carboxílicos naturais (quais são as funções?)



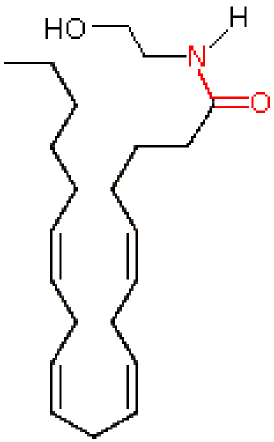
piperine
(from black pepper)



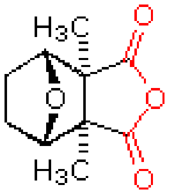
cocaine
(the coca bush)



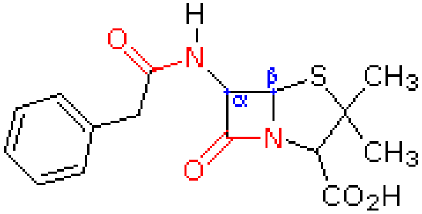
caffeine
(coffee and tea)



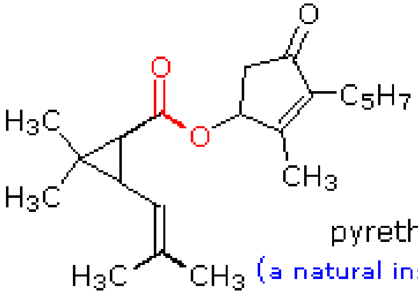
anandamide
(from chocolate)



cantharidin
(blister beetle)

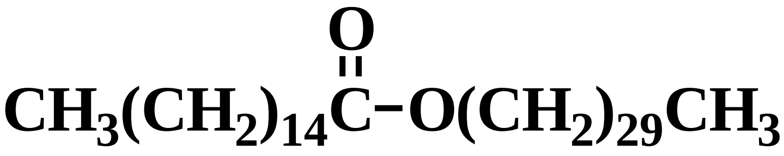


penicillin G
(an antibiotic)



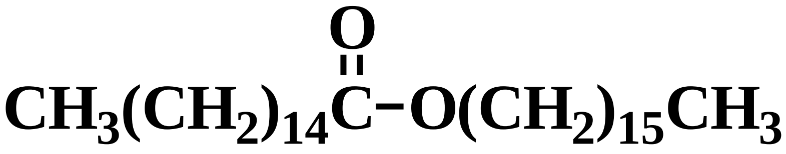
pyrethrin
(a natural insecticide)

Ceras: ésteres de ácidos e álcoois graxos



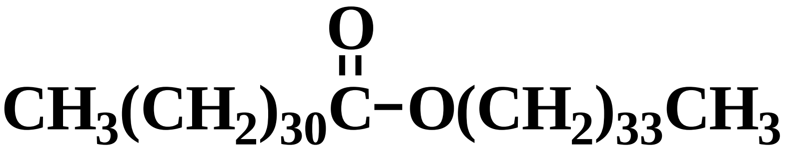
$$CH_3(CH_2)_{14}\overset{\overset{O}{\|}}{C}-O(CH_2)_{29}CH_3$$

éster de cera de abelhas



$$CH_3(CH_2)_{14}\overset{\overset{O}{\|}}{C}-O(CH_2)_{15}CH_3$$

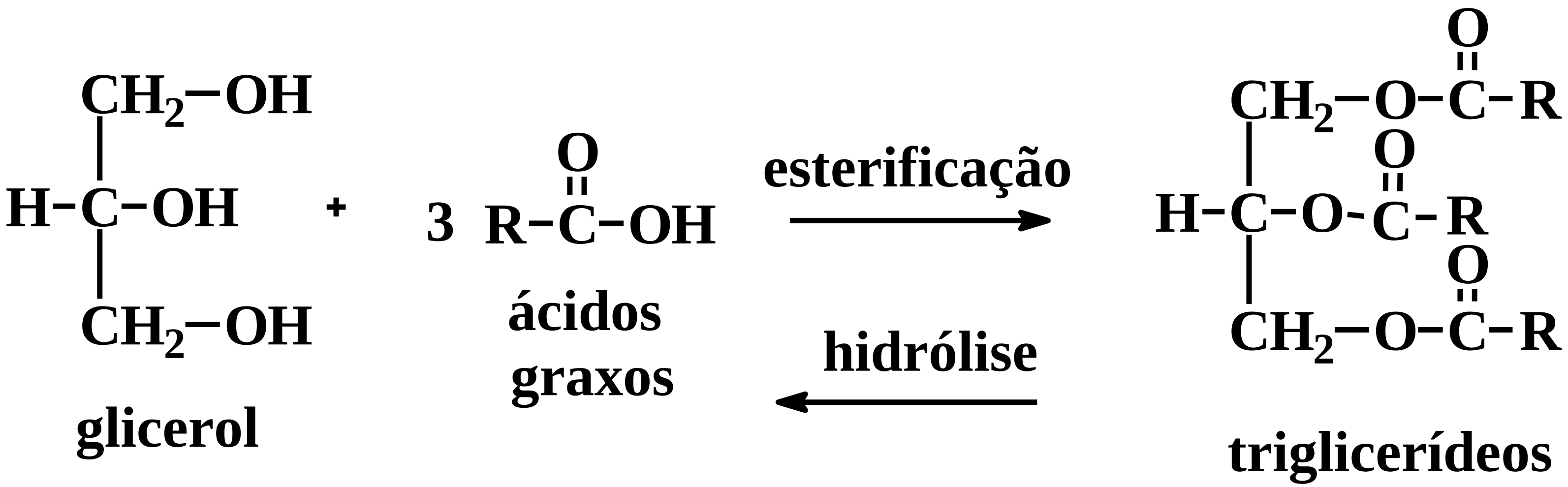
principal constituínte do esperma de baleias



$$CH_3(CH_2)_{30}\overset{\overset{O}{\|}}{C}-O(CH_2)_{33}CH_3$$

principal constituínte da cera de carnaúba

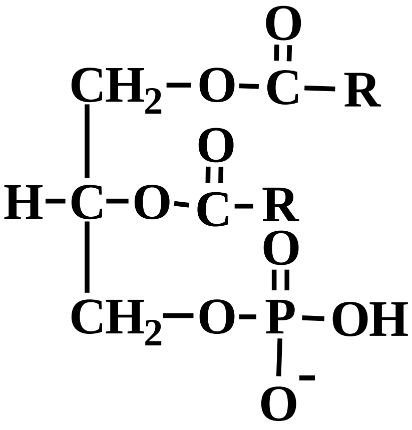
Triglicerídeos: fornecem mais energia do que carboidratos por serem menos oxidados. Ao contrário do glicogênio, sendo menos polares, não se ligam a moléculas de água.



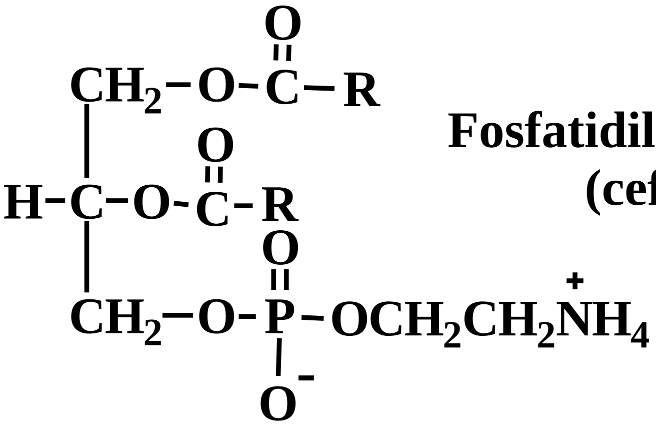
O estoque energético de humanos, baseado em gorduras (21% para homens e 25% para mulheres), fornece necessidades para 2-3 meses.

O estoque de carboidratos (glicogênio) é consumido em menos de um dia.

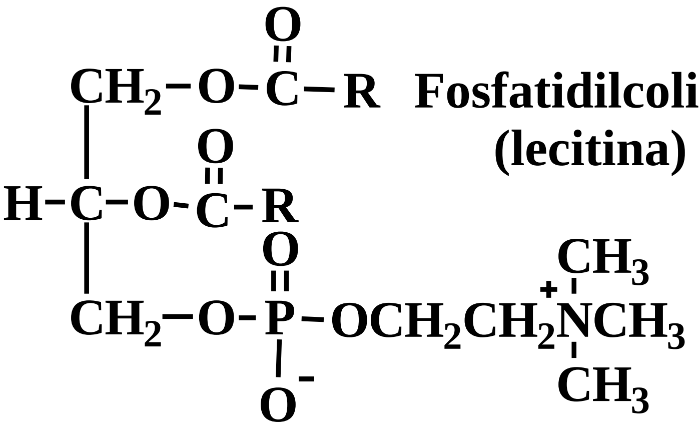
Fosfolipídeos (principais componentes de membranas)



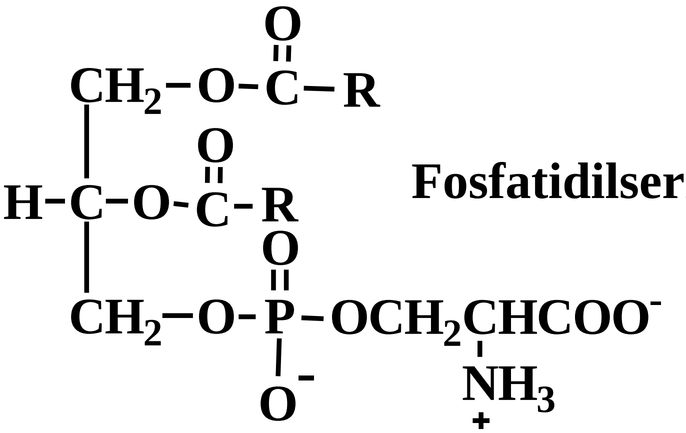
Ácido fosfatídico



Fosfatidiletanolamina
(cefalina)



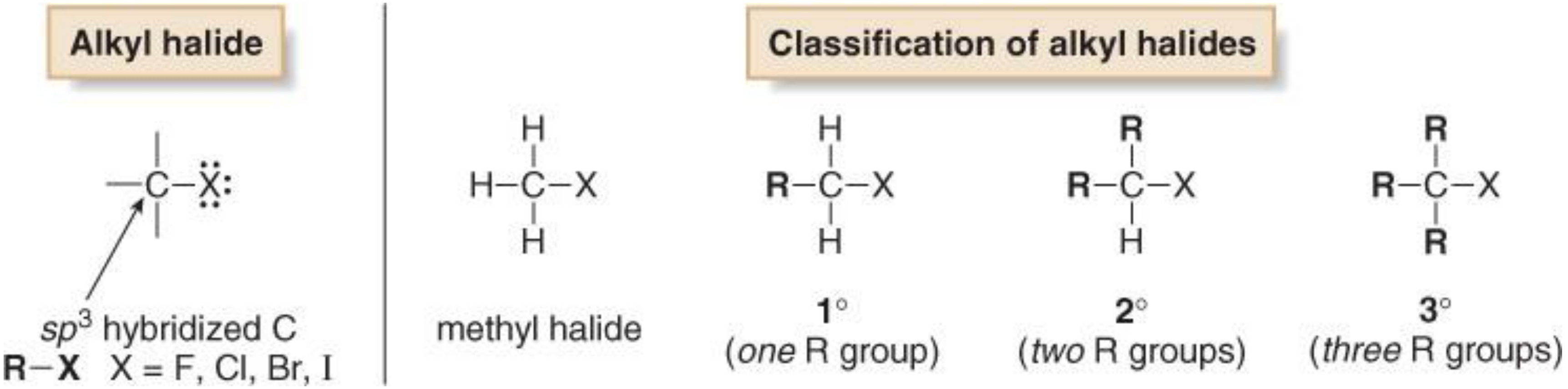
Fosfatidilcolina
(lecitina)



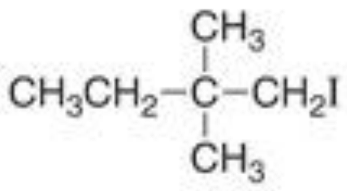
Fosfatidilserina

Alkyl Halides

- Alkyl halides are organic molecules containing a halogen atom bonded to an sp^3 hybridized carbon atom.
- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom in halides is often denoted by the symbol “X”.

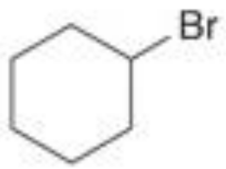


Examples of 1°, 2°, and 3° alkyl halides

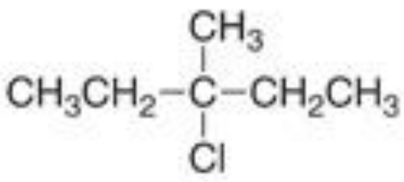


$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2I$$

1° iodide



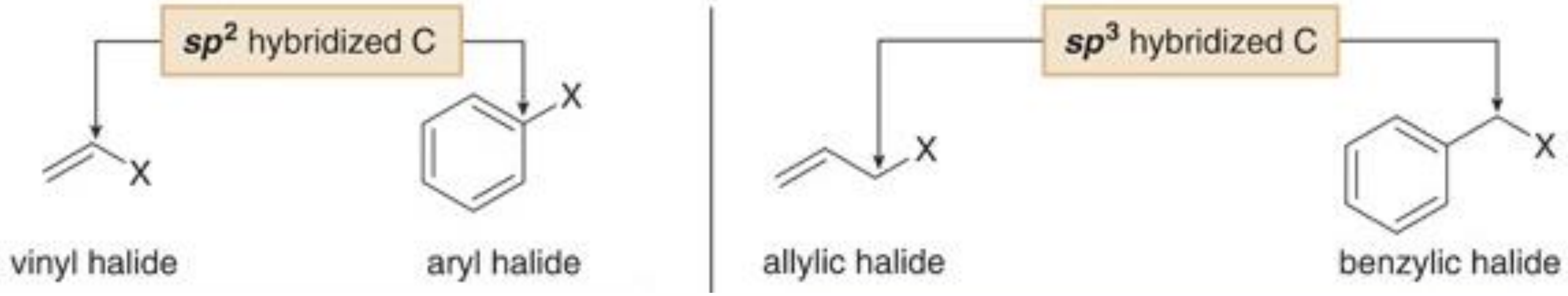
2° bromide



$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$$

3° chloride

Four types of organic halides (RX) having X near a π bond



vinyl halide

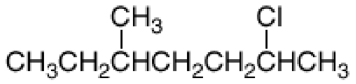
aryl halide

allylic halide

benzylic halide

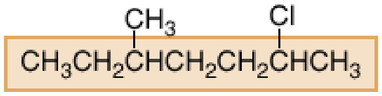
Nomenclatura de haletos de alquila

Example Give the IUPAC name of the following alkyl halide:



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3$

Step [1] Find the parent carbon chain containing the halogen.



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3$

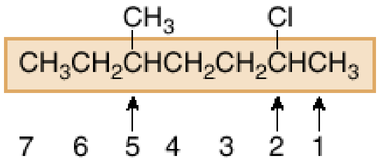
- Name the parent chain as an ***alkane,*** with the halogen as a substituent bonded to the longest chain.

7 C's in the longest chain

7 C's - - - → **heptane**

Step [2] Apply all other rules of nomenclature.

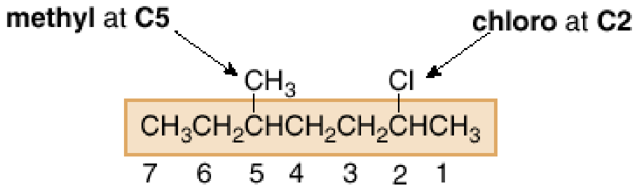
a. **Number** the chain.



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3$

- Begin at the end nearest the first substituent, either alkyl or halogen.

b. **Name** and **number** the substituents.



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3$

methyl at **C5**

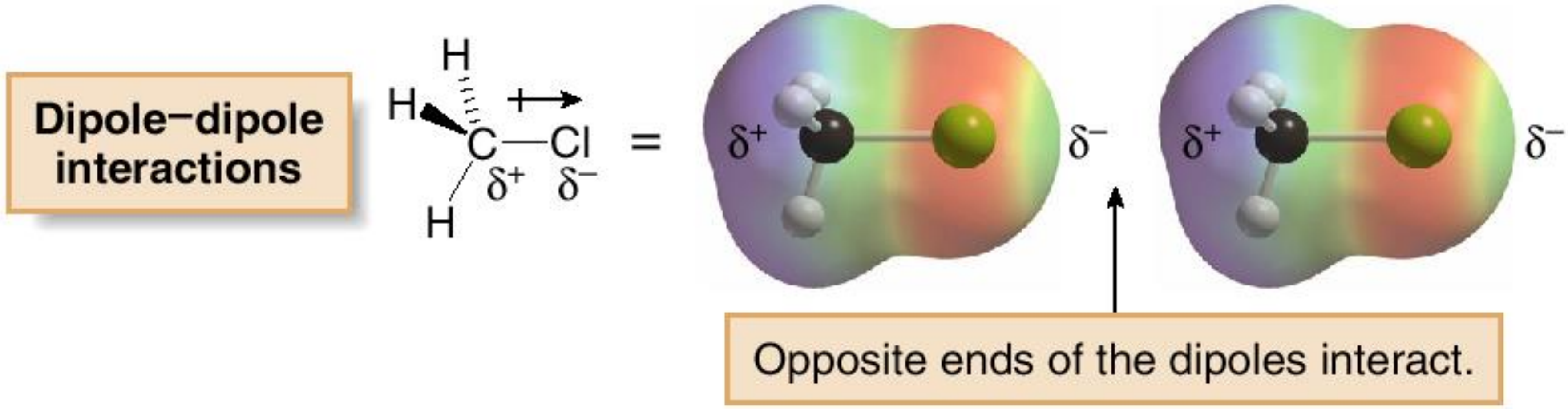
chloro at **C2**

c. **Alphabetize: c** for **c**hloro, then **m** for **m**ethyl.

ANSWER: 2-chloro-5-methylheptane

Physical Properties

- Alkyl halides are weak polar molecules.
- They exhibit dipole-dipole interactions because of their polar C—X bond, but because the rest of the molecule contains only C—C and C—H bonds, they are incapable of intermolecular hydrogen bonding.



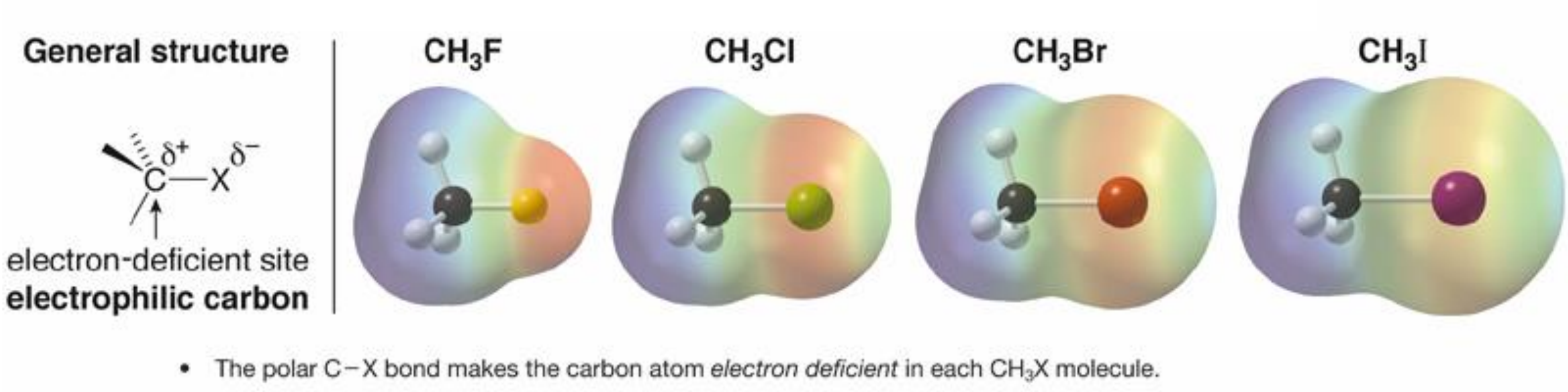
Dipole–dipole interactions

Opposite ends of the dipoles interact.

The Polar Carbon-Halogen Bond

- The electronegative halogen atom in alkyl halides creates a polar C—X bond, making the carbon atom electron deficient.

Electrostatic potential maps of four halomethanes (CH_3X)



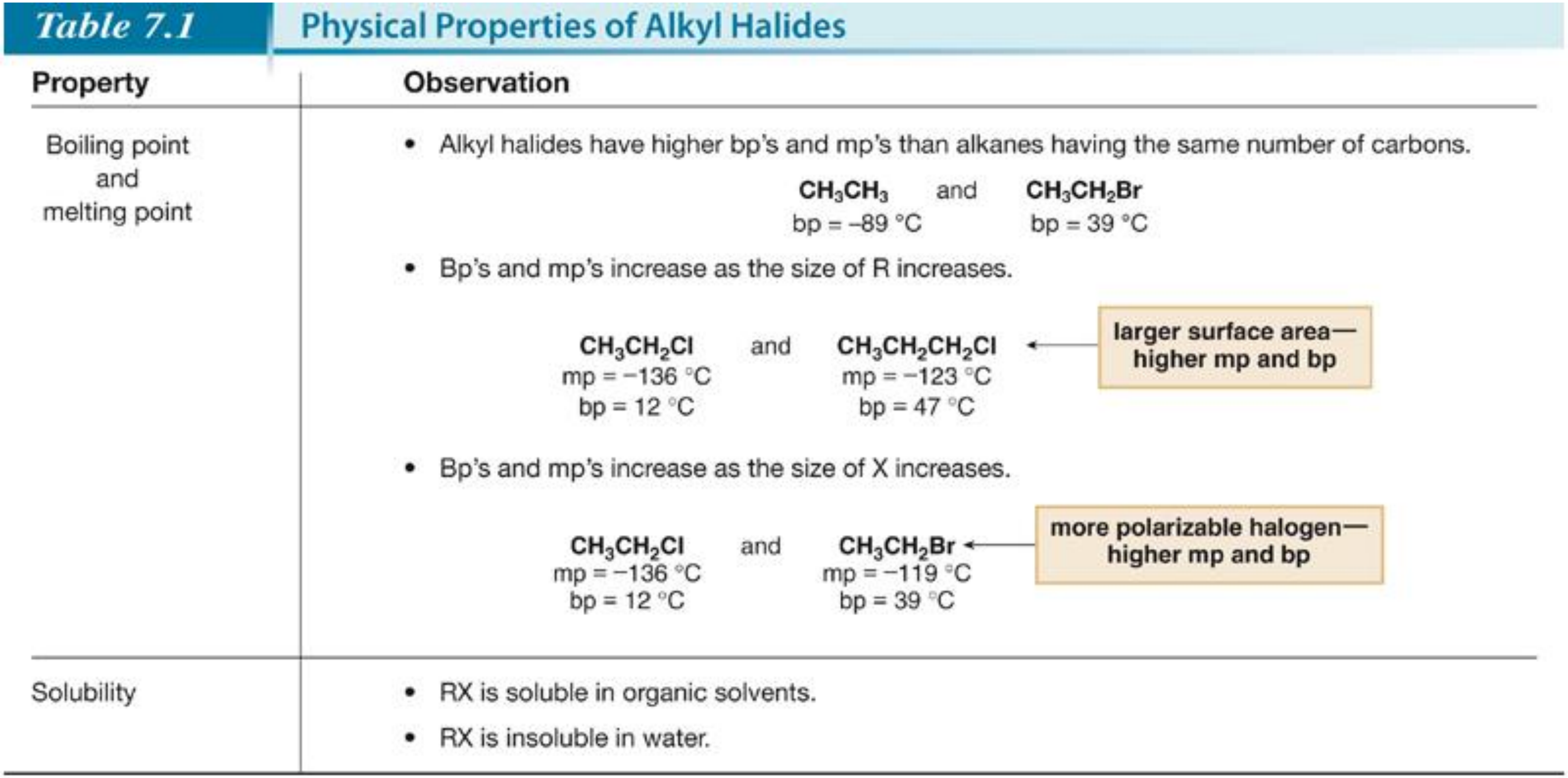


Table 7.1 Physical Properties of Alkyl Halides

Property	Observation
Boiling point and melting point	• Alkyl halides have higher bp's and mp's than alkanes having the same number of carbons. CH_3CH_3 bp = −89 °C and CH_3CH_2Br bp = 39 °C • Bp's and mp's increase as the size of R increases. CH_3CH_2Cl mp = −136 °C, bp = 12 °C and $CH_3CH_2CH_2Cl$ mp = −123 °C, bp = 47 °C ← **larger surface area— higher mp and bp** • Bp's and mp's increase as the size of X increases. CH_3CH_2Cl mp = −136 °C, bp = 12 °C and CH_3CH_2Br mp = −119 °C, bp = 39 °C ← **more polarizable halogen— higher mp and bp**
Solubility	• RX is soluble in organic solvents. • RX is insoluble in water.

Nomenclatura de Éteres

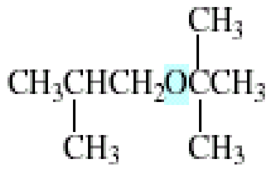
$CH_3OCH_2CH_3$

éter etilmetílico

$CH_3CH_2OCH_2CH_3$

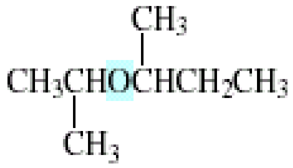
éter dietílico

muitas vezes chamado éter etílico



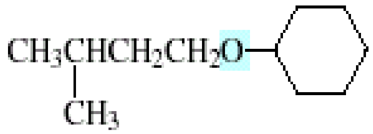
$CH_3CHCH_2OC(CH_3)_2CH_3$ with CH_3 on CH

éter *terc*-butilisobutílico



$CH_3CH(CH_3)OCH(CH_3)CH_2CH_3$

éter *sec*-butilisopropílico



éter ciclo-hexilisopentílico

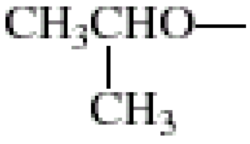
Como substituintes:

$CH_3O—$

metoxi

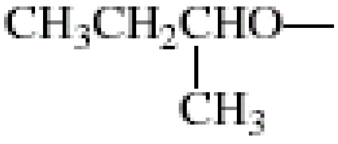
$CH_3CH_2O—$

etoxi



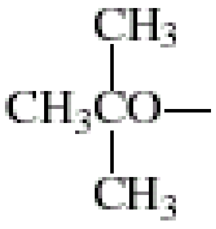
$CH_3CH(CH_3)O—$

isopropoxi



$CH_3CH_2CH(CH_3)O—$

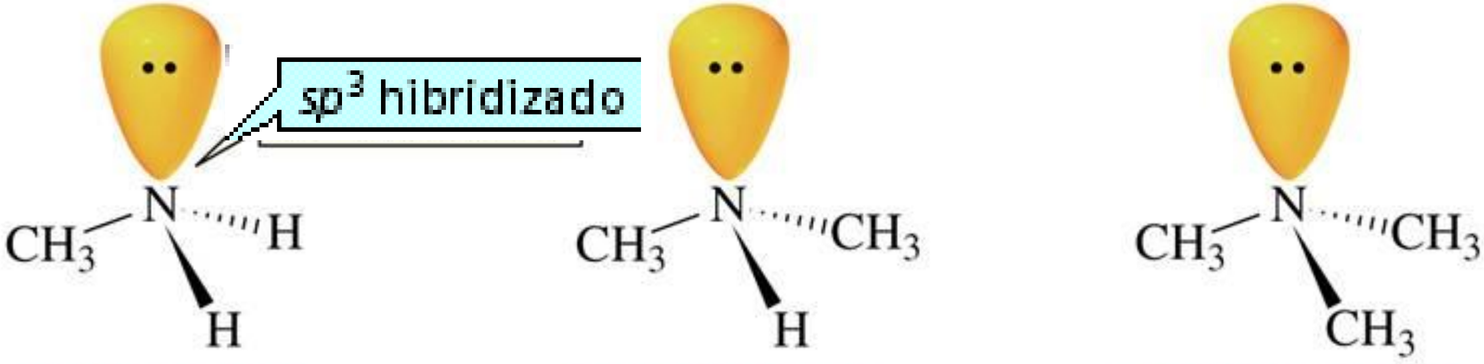
***sec*-butoxi**



$CH_3C(CH_3)_2O—$

***terc*-butoxi**

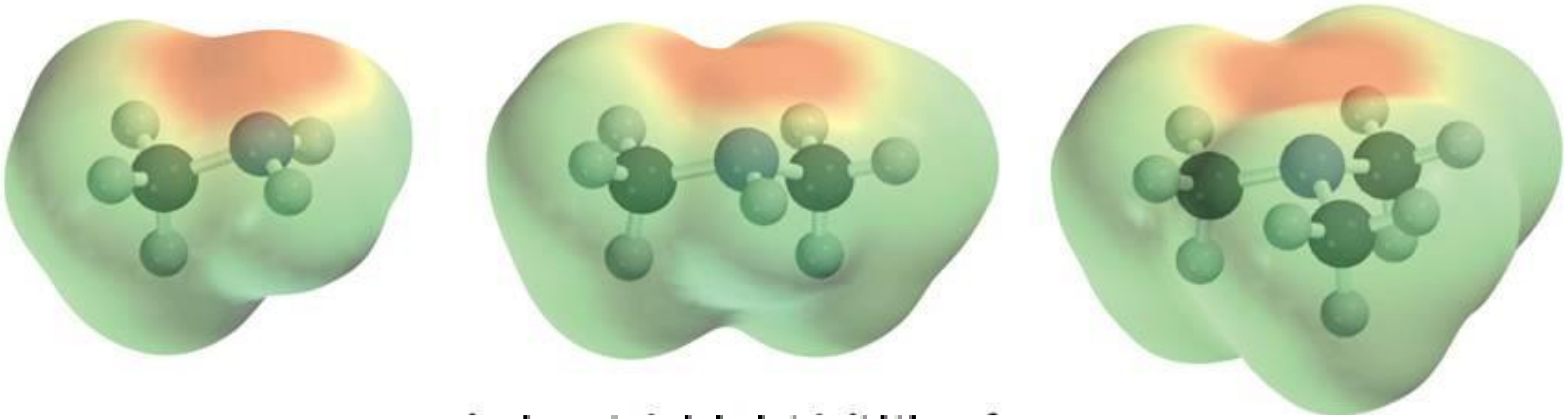
Estruturas de Aminas



metilamina
amina primária

dimetilamina
amina secundária

trimetilamina
amina terciária



mapas de potencial eletrostático para

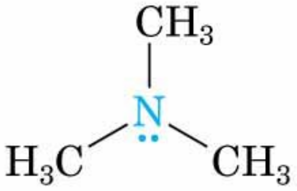
metilamina

dimetilamina

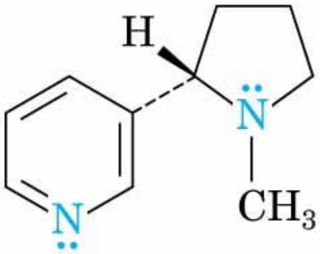
trimetilamina

Amines – Organic Nitrogen Compounds

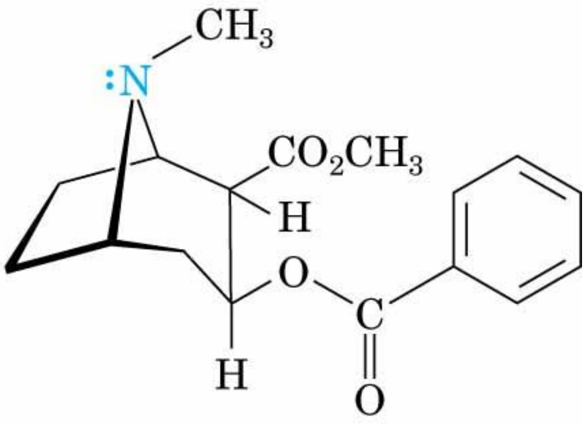
- Organic derivatives of ammonia, NH_3,
- Nitrogen atom with a lone pair of electrons, making amines both basic and nucleophilic
- Occur in plants and animals



Trimethylamine



Nicotine

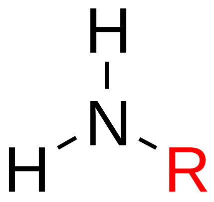


Cocaine

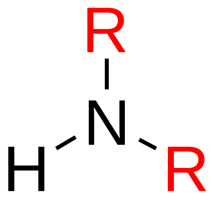
alcaloides!!!

Naming Amines

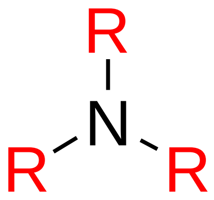
- Alkyl-substituted (alkylamines) or aryl-substituted (arylamines)
- Classified:
  - 1° (RNH_2) primary amine
  - 2° (R_2NH) secondary amine
  - Tertiary amine 3° (R_3N)



Primary



Secondary

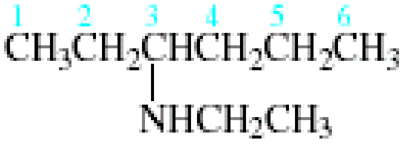


Tertiary

Nomenclatura de Aminas

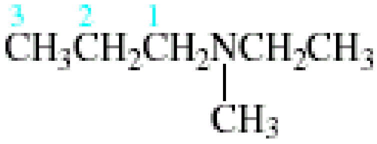
$CH_3CH_2CH_2CH_2NH_2$

1-butanamina
ou butan-1-amina



$CH_3CH_2CH(NHCH_2CH_3)CH_2CH_2CH_3$

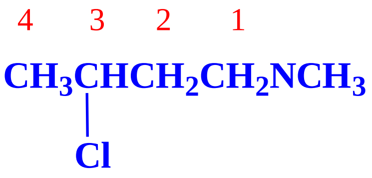
N-etil-3-hexanamina
ou *N*-etil-hexan-3-amina



$CH_3CH_2CH_2N(CH_3)CH_2CH_3$

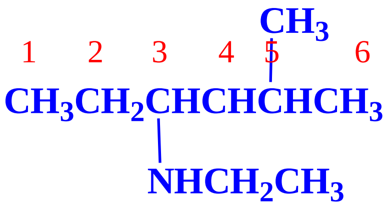
N-etil-*N*-metil-1-propanamina
ou *N*-etil-*N*-metil-propano-1-amina

- Os substituintes são listados em ordem alfabética e depois um número ou um “*N*” é designado para cada um



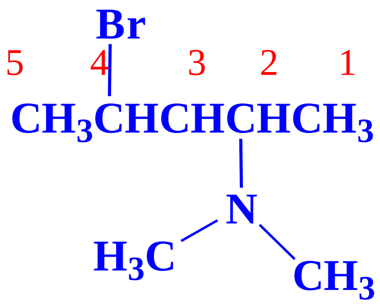
$CH_3CH(Cl)CH_2CH_2NHCH_3$

3-cloro-*N*-metil-1-butanamina



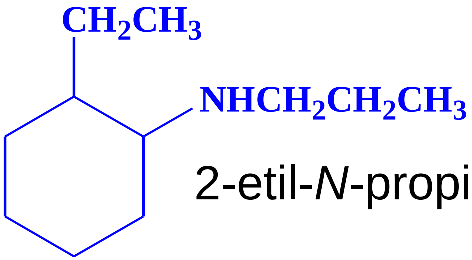
$CH_3CH_2CH(NHCH_2CH_3)CH(CH_3)CH_3$

N-etil-5-metil-3-hexanamina



$CH_3CH(Br)CH_2CH(N(CH_3)_2)CH_3$

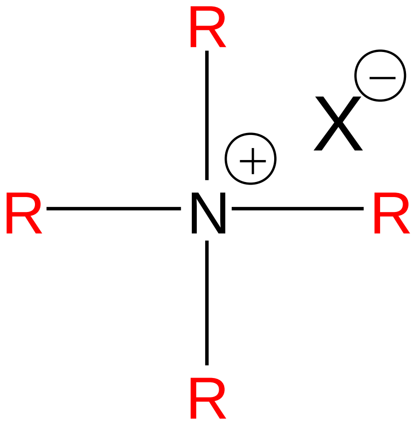
4-bromo-*N*,*N*-dimetil-2-pentanamina



2-etil-*N*-propilcicloexanamina

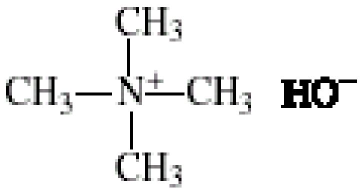
Quaternary Ammonium Ions

- A nitrogen atom with four attached groups is positively charged
- Compounds are quaternary ammonium salts



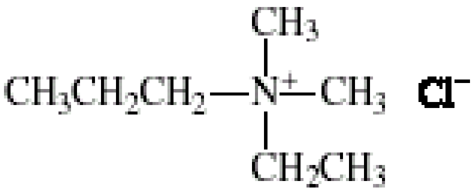
Quaternary ammonium salts are used as disinfectants, surfactants, fabric softeners, and as antistatic agents (e.g. in shampoos).
In liquid fabric softeners, the chloride salts are often used.
In dryer anticling strips, the sulfate salts are often used.
Spermicidal jellies also contain quaternary ammonium salts.

Nomenclatura de Sais de Amônio Quaternário



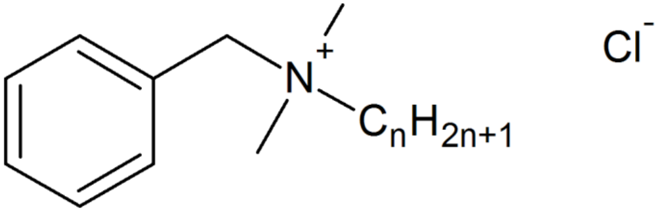
$$CH_3-\overset{CH_3}{\underset{CH_3}{N^{+}}}-CH_3 \quad HO^{-}$$

Hidróxido de tetrametilamônio



$$CH_3CH_2CH_2-\overset{CH_3}{\underset{CH_2CH_3}{N^{+}}}-CH_3 \quad Cl^{-}$$

Cloreto de etil-dimetil-propilamônio



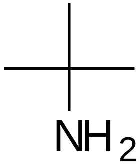
n = 8, 10, 12, 14, 16, 18

Exemplos:

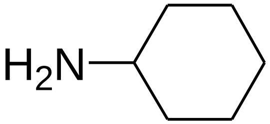
1.**Cloreto de Benzalcônio** *(cloreto de alquilbenzil-dimetilamônio 50% SOLN. AQU);*
Sinônimo*: BENZALKONIUM CHLORIDE; QUARTERNARY AMMONIUM COMPOUND);*
Nome comercial*: ZEPHIRAN*
2.Cloreto de Cetilpiridínio (CEEPRYN; CEPACOL)
3.Cloreto de Benzetônio (CLORETO DE FEMEROL)
4.Cloreto de Metilbenzetônio (DIAPARENE)
5.Brometo de Domifen (BROMETO DE BRADOSOL)

IUPAC Names – Simple Amines

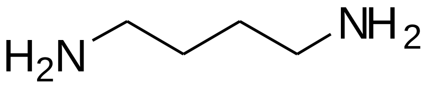
- For simple amines, the suffix -*amine* is added to the name of the alkyl substituent



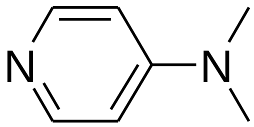
tert-butylamine



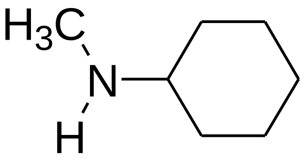
cyclohexanamine



1,4-butandiamine



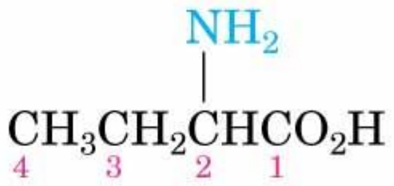
N,N-Dimethyl-4-aminopyridine



N-Methyl-Cyclohexanamine

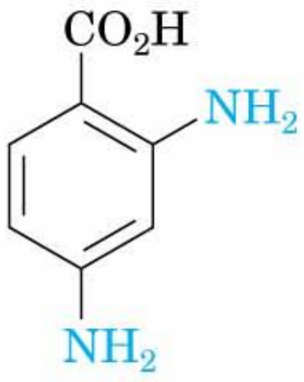
IUPAC Names – Amines With More Than One Functional Group

- Consider the —NH_2 as an *amino* substituent on the parent molecule

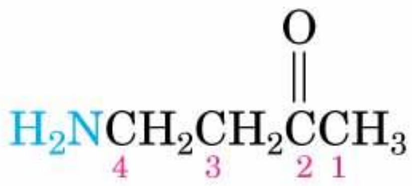


$$\mathrm{CH_3CH_2\overset{\overset{NH_2}{|}}{C}HCO_2H}$$

2-Aminobutanoic acid



2,4-Diaminobenzoic acid

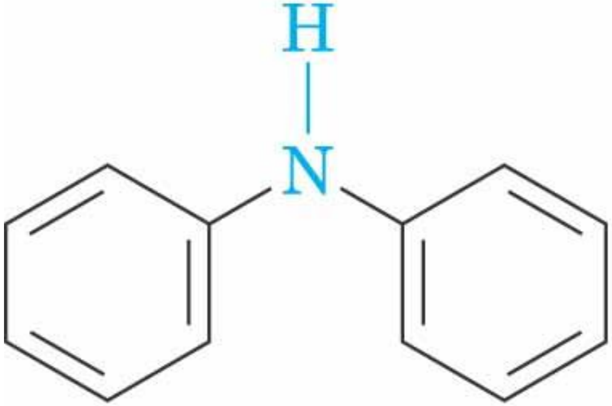


$$\mathrm{H_2NCH_2CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

4-Amino-2-butanone

IUPAC Names – Multiple Alkyl Groups

- Symmetrical secondary and tertiary amines are named by adding the prefix *di*- or *tri*- to the alkyl group



Diphenylamine

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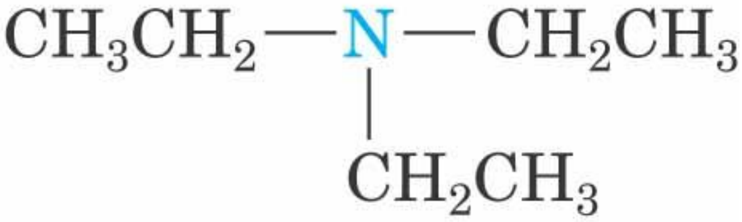
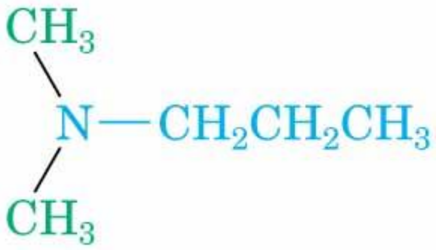


$$CH_3CH_2—N(CH_2CH_3)—CH_2CH_3$$

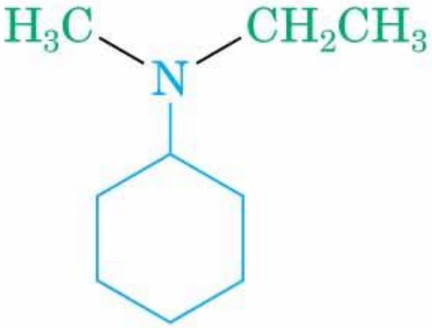
Triethylamine

IUPAC Names – Multiple, Different Alkyl Groups

- Named as *N*-substituted primary amines
- Largest alkyl group is the parent name, and other alkyl groups are considered *N*-substituents



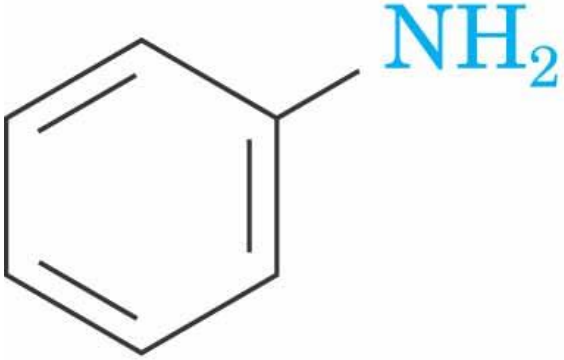
***N*,*N*-Dimethylpropylamine**
(propylamine is the parent name; the two methyl groups are substituents on nitrogen)



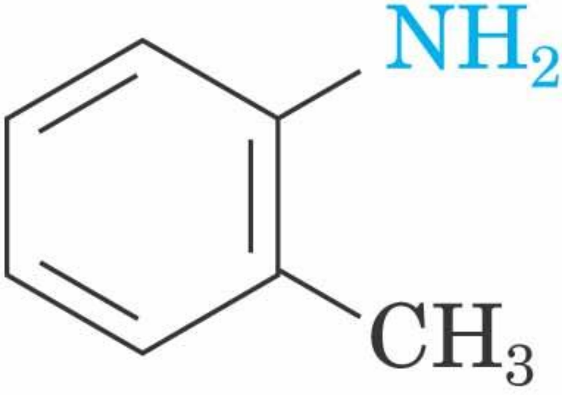
***N*-Ethyl-*N*-methylcyclohexylamine**
(cyclohexylamine is the parent name; methyl and ethyl are *N*-substituents)

Common Names

- Alkylamines do not have common names unless they are biological molecules
- Simple arylamines have common names



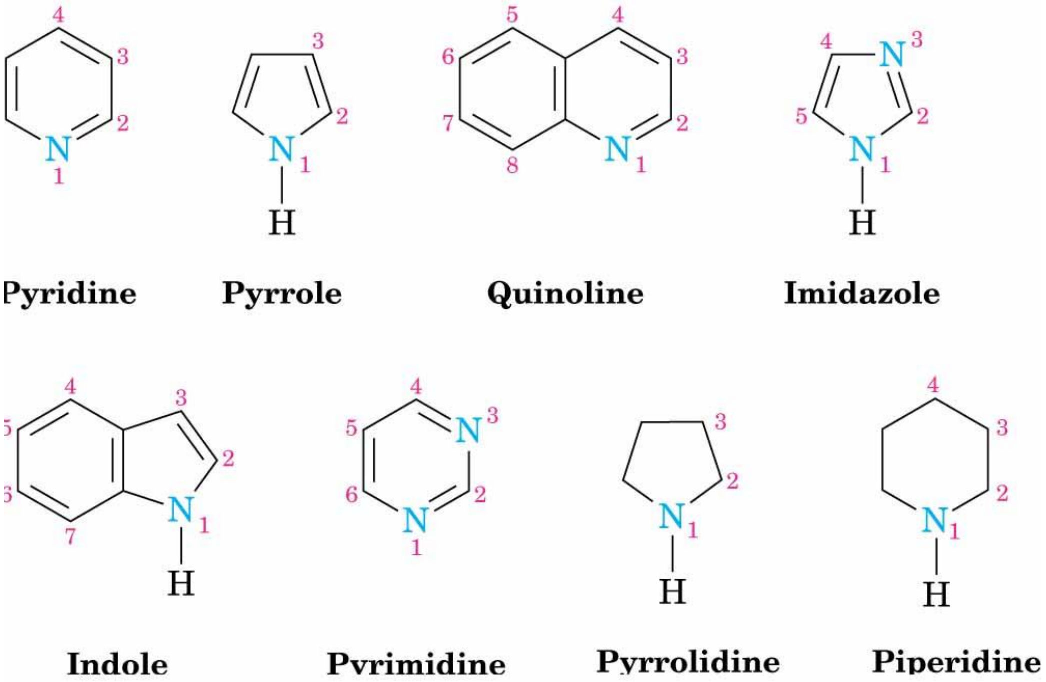
Aniline



***o*-Toluidine**

Heterocyclic Amines

- If the nitrogen atom occurs as part of a ring, the compound is designated as being heterocyclic
- Each ring system has its own parent name



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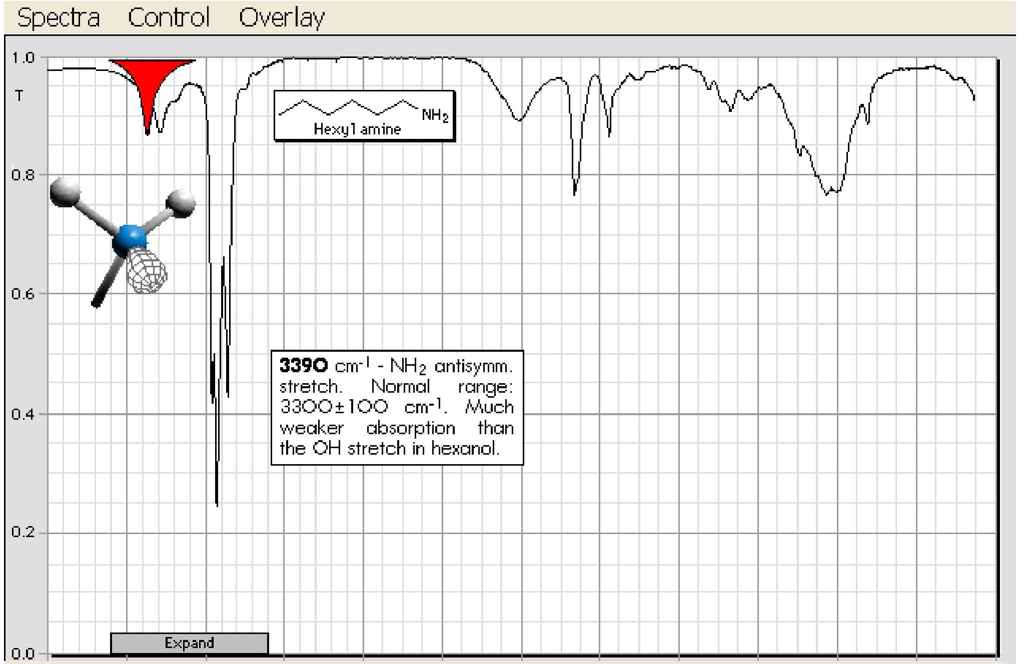
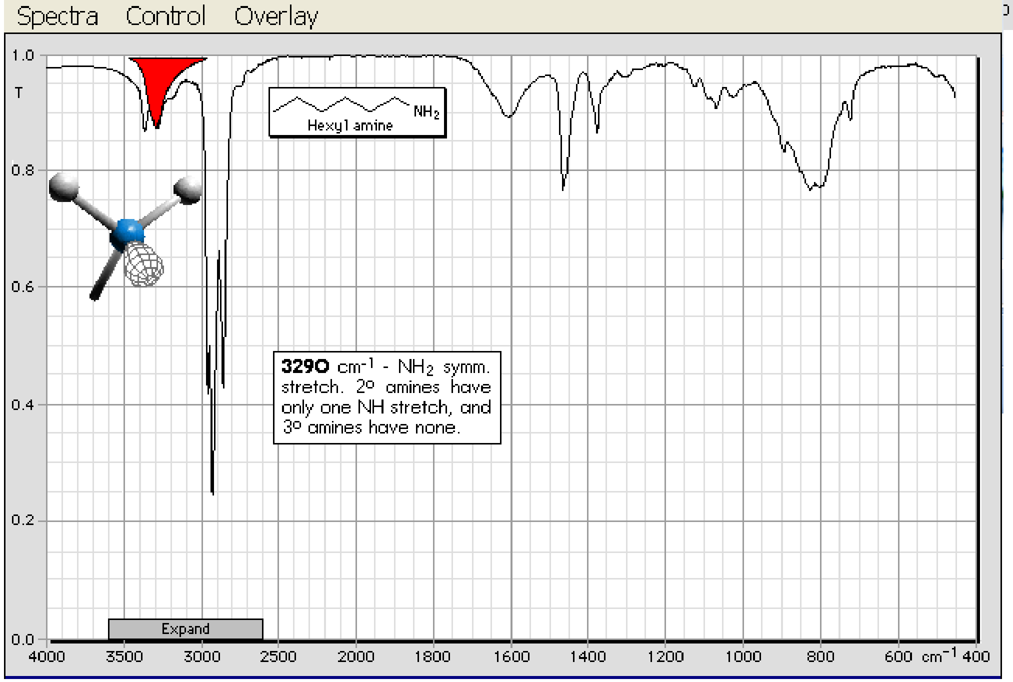
Espectros no Infravermelho de aminas

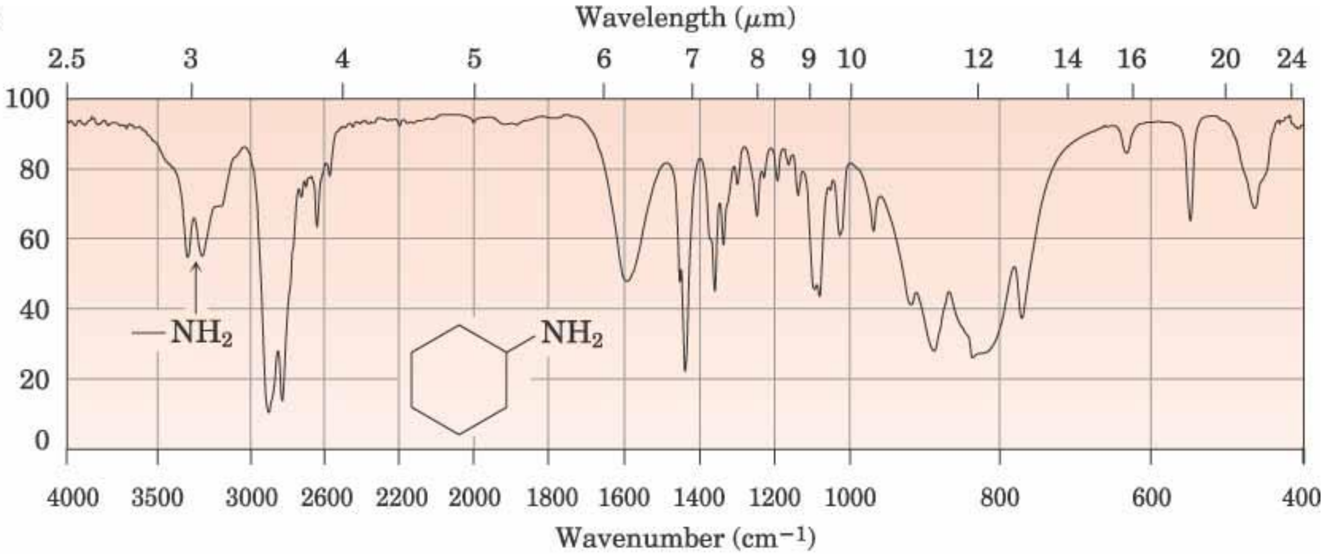


3390 cm^{-1} - NH_2 antisymm. stretch. Normal range: 3300±100 cm^{-1}. Much weaker absorption than the OH stretch in hexanol.

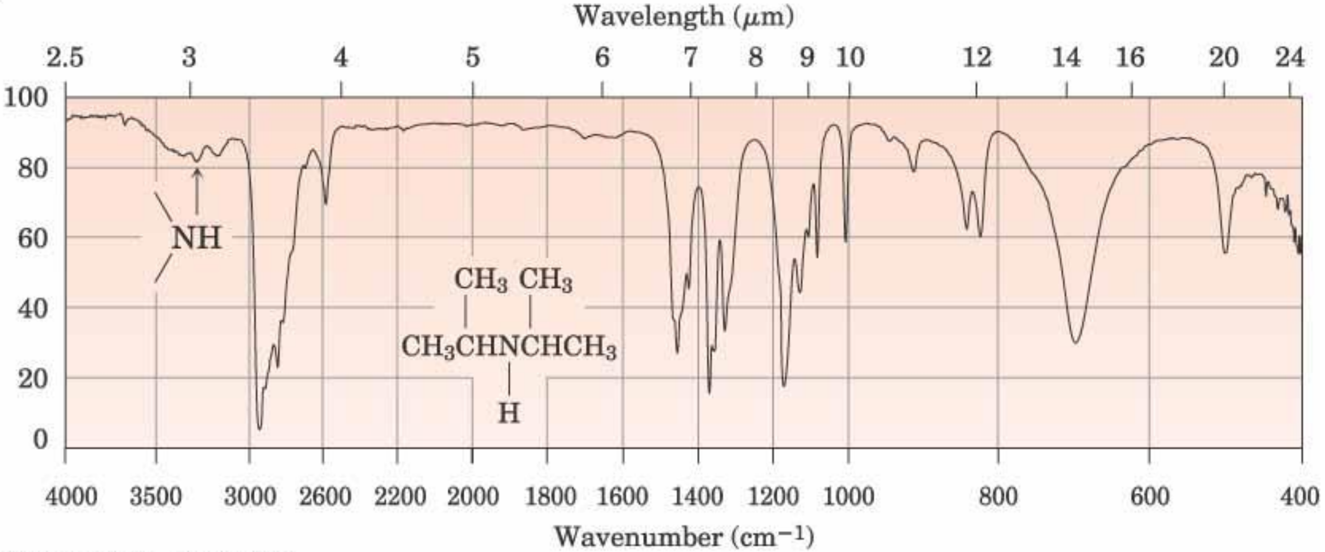


3290 cm^{-1} - NH_2 symm. stretch. 2º amines have only one NH stretch, and 3º amines have none.

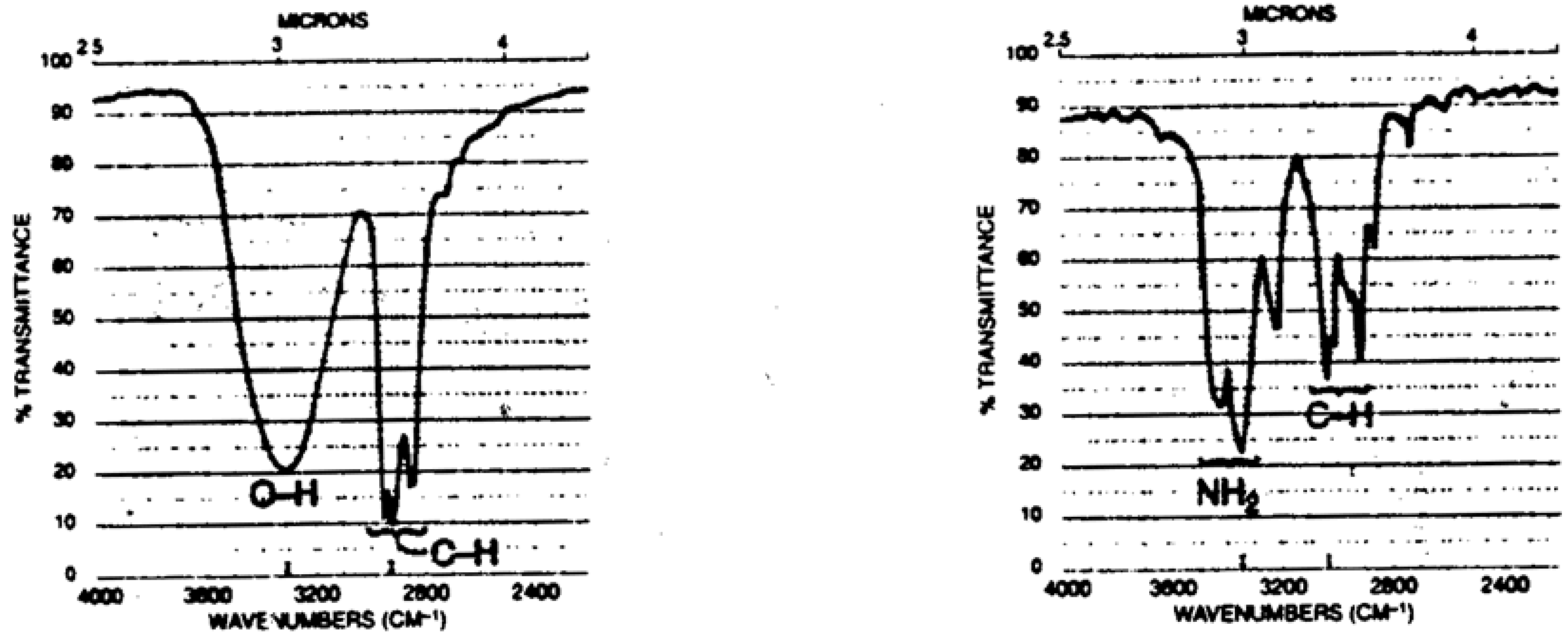
(a)


Wavelength (μm)
2.5
3
4
5
6
7
8
9
10
12
14
16
20
24
Transmittance (%)
100
80
60
40
20
0
—NH₂
NH₂
4000
3500
3000
2600
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm⁻¹)

(b)


Wavelength (μm)
2.5
3
4
5
6
7
8
9
10
12
14
16
20
24
Transmittance (%)
100
80
60
40
20
0
NH
CH₃ CH₃
CH₃CHNCHCH₃
H
4000
3500
3000
2600
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm⁻¹)

Band Shape: OH vs NH2 vs CH

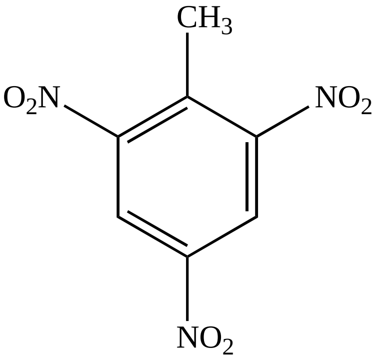


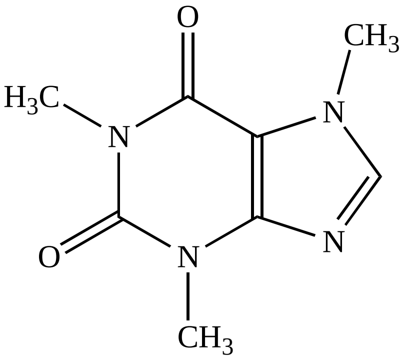
▶ **FIGURE 2.6** A comparison of the shapes of the absorption bands for the O—H and N—H groups.

Characterization of amines by mass spectrometry - How Many Nitrogen Atoms?

Consider these molecules:

NH_3 H_2NNH_2





Formula:	NH_3	N_2H_4	$C_7H_5N_3O_6$	$C_8H_{10}N_4O_2$
m/z (M):	17	32	227	194

Conclusion

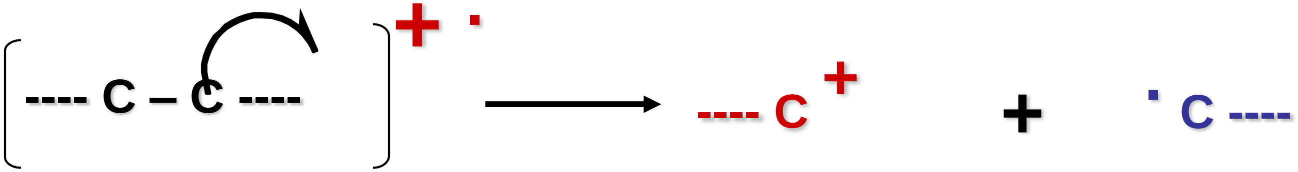
- When m/z (M) = even, number of N in formula is even
- When m/z (M) = odd, number of N in formula is odd

} **The Nitrogen Rule**

Fragmentation process

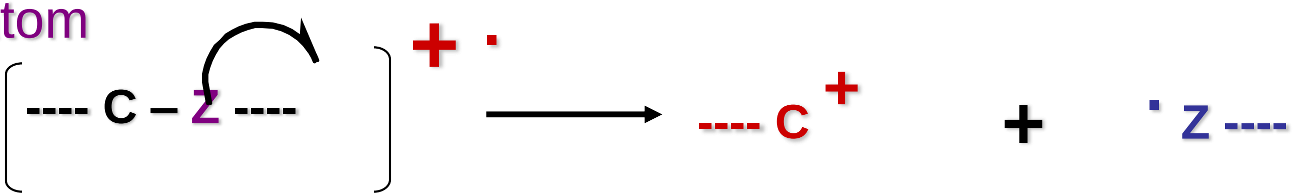
There are 3 type of fragmentations:

1) Cleavage of σ bond



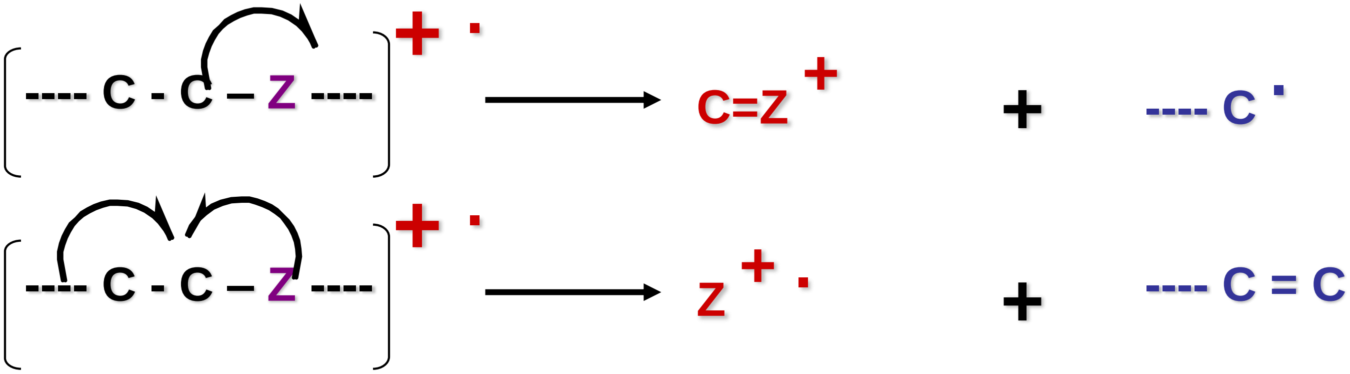
$$[\text{---- C} - \text{C ----}]^{+\cdot} \longrightarrow \text{---- C}^{+} + {}^{\cdot}\text{C ----}$$

At heteroatom



$$[\text{---- C} - \text{Z ----}]^{+\cdot} \longrightarrow \text{---- C}^{+} + {}^{\cdot}\text{Z ----}$$

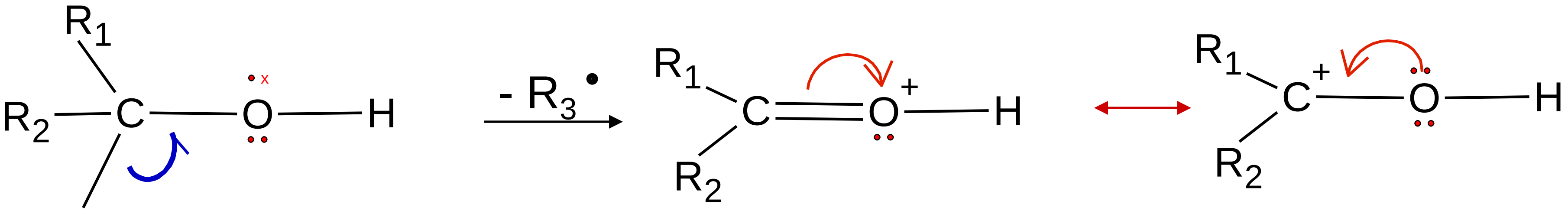
α to heteroatom



$$[\text{---- C - C} - \text{Z ----}]^{+\cdot} \longrightarrow \text{C=Z}^{+} + \text{---- C}^{\cdot}$$

$$[\text{---- C - C} - \text{Z ----}]^{+\cdot} \longrightarrow \text{Z}^{+\cdot} + \text{---- C = C}$$

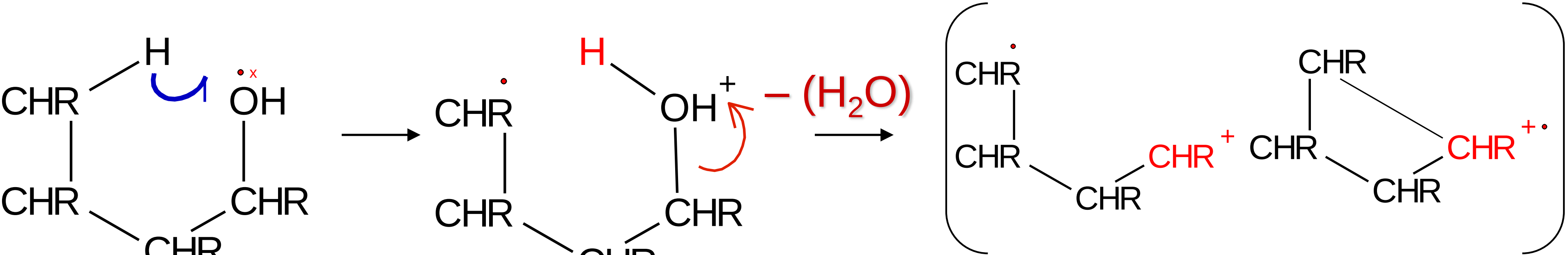
Hydroxy compounds



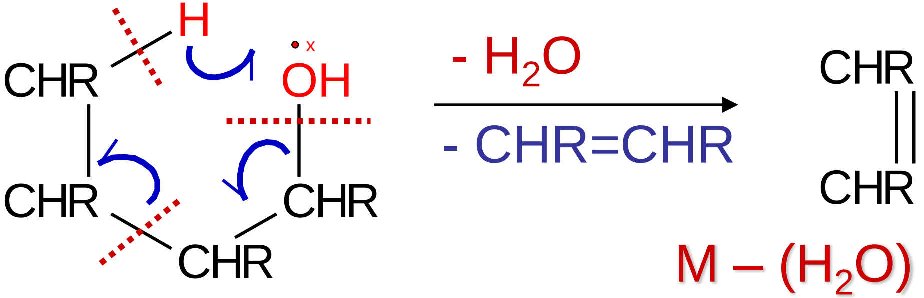
If R_1=H m/z 45, 59, 73 …

Loss of largest group

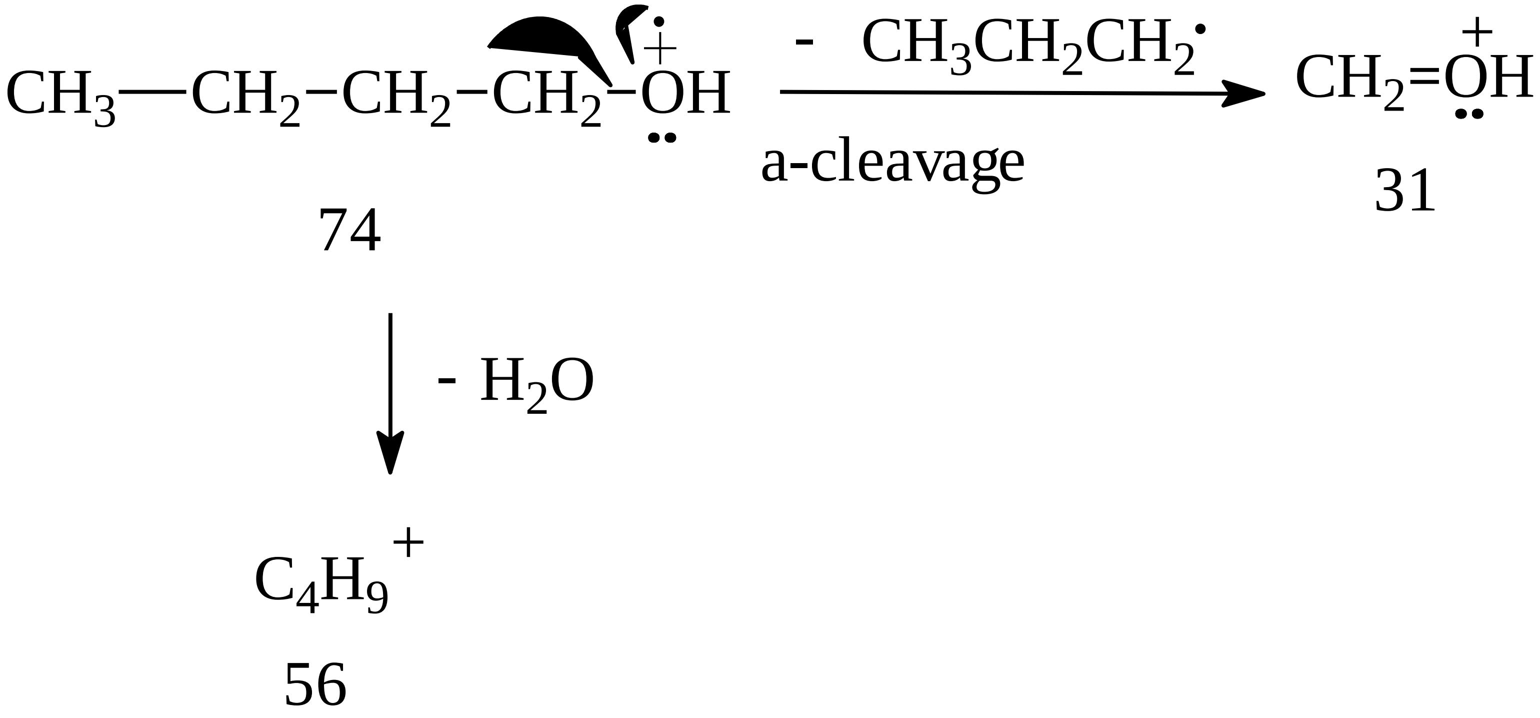
If R_1=alkyl m/z 59, 73, 87 …

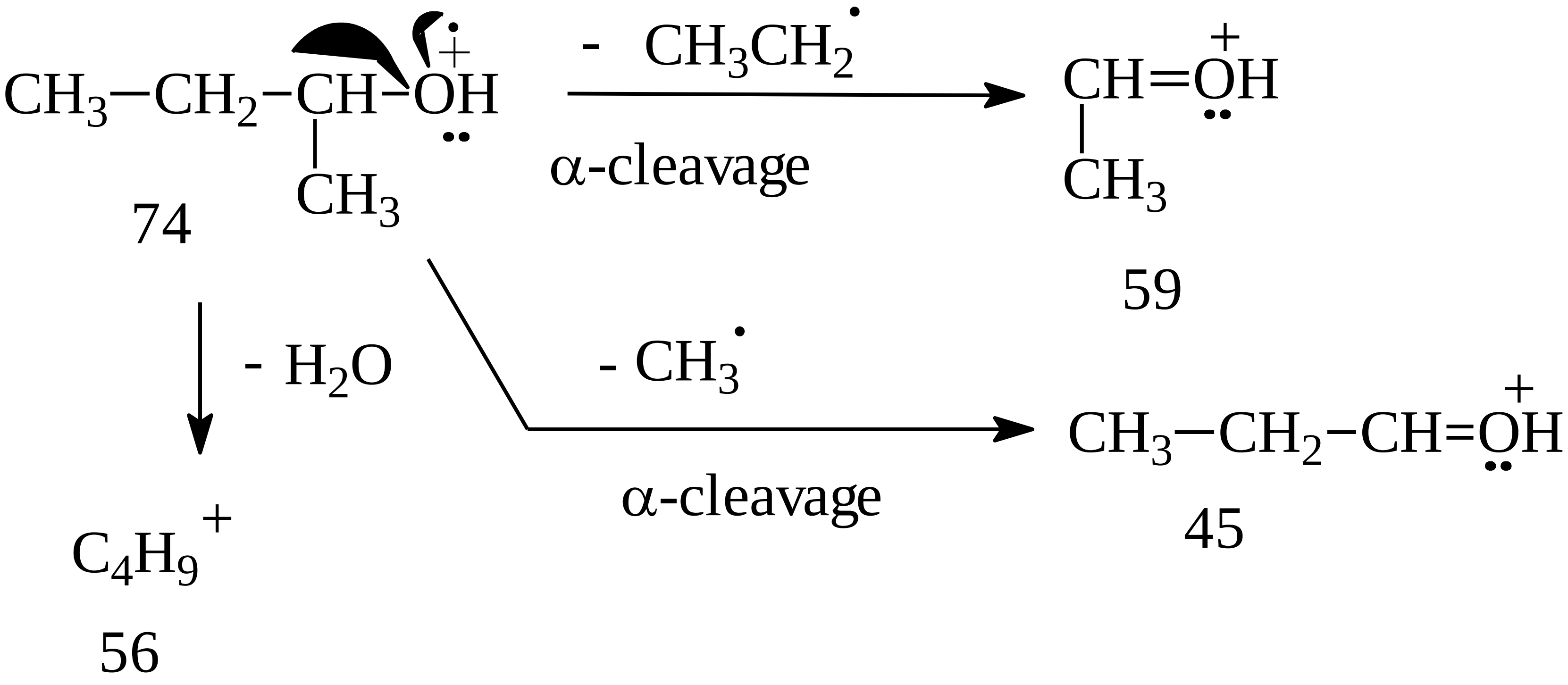


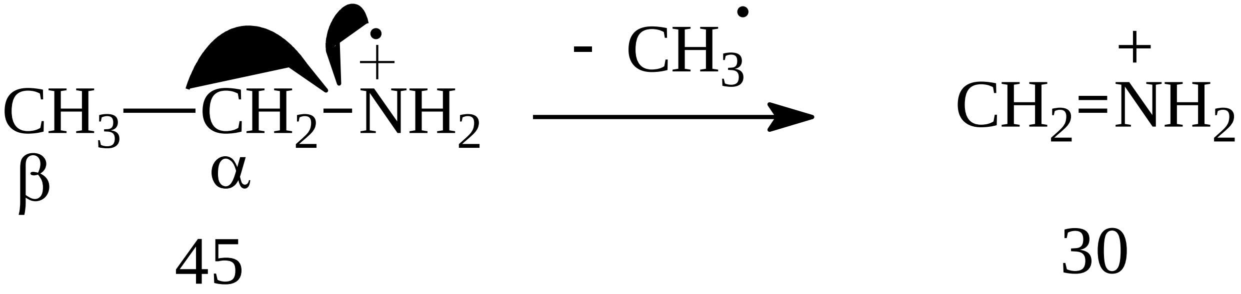
M – (H_2O)



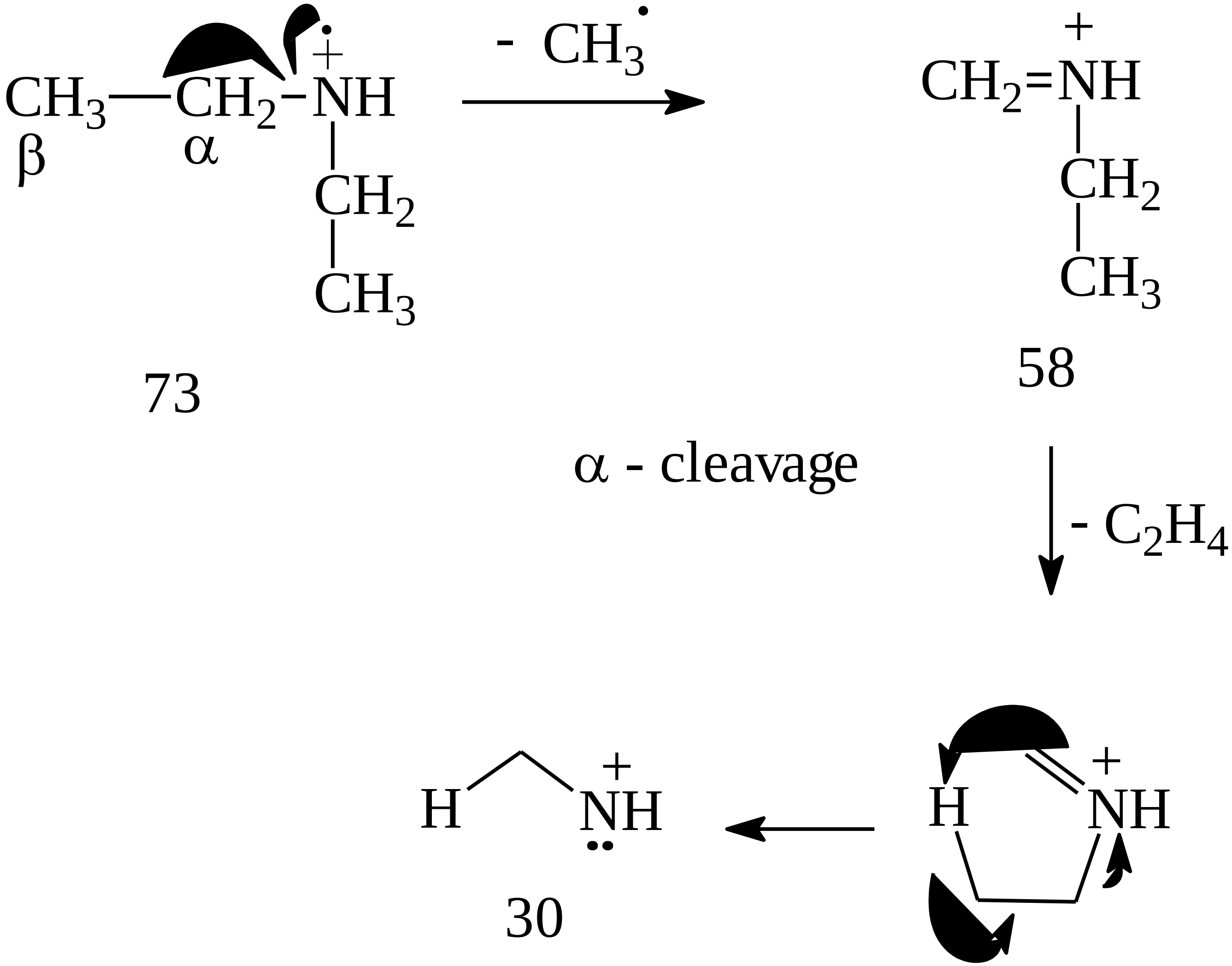
M – (H_2O) – (C1=C2) Alkene


CH3—CH2–CH2–CH2–OH
74
- CH3CH2CH2·
a-cleavage
CH2=OH
31
- H2O
C4H9+
56


CH3–CH2–CH–OH+
CH3
74
- CH3CH2•
α-cleavage
CH=OH+
CH3
59
- H2O
C4H9+
56
- CH3•
α-cleavage
CH3–CH2–CH=OH+
45



α - cleavage



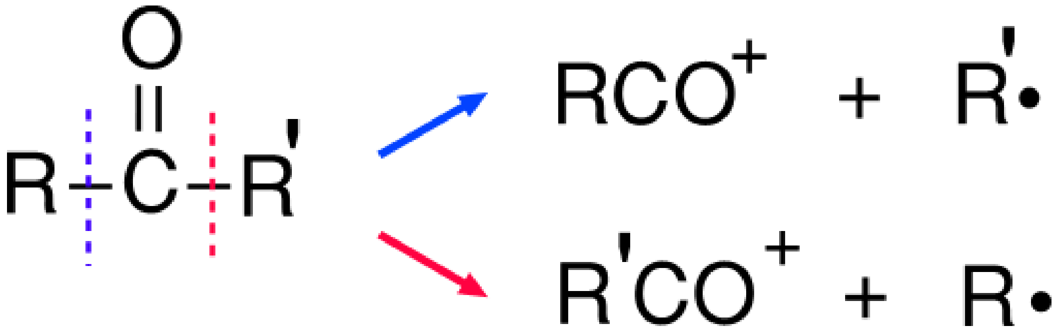
CH3 CH2 NH
β
α
CH2
CH3
73
- CH3
CH2=NH
CH2
CH3
58
α - cleavage
- C2H4
H NH
H NH
30

FRAGMENTATION PATTERNS

ALDEHYDES AND KETONES

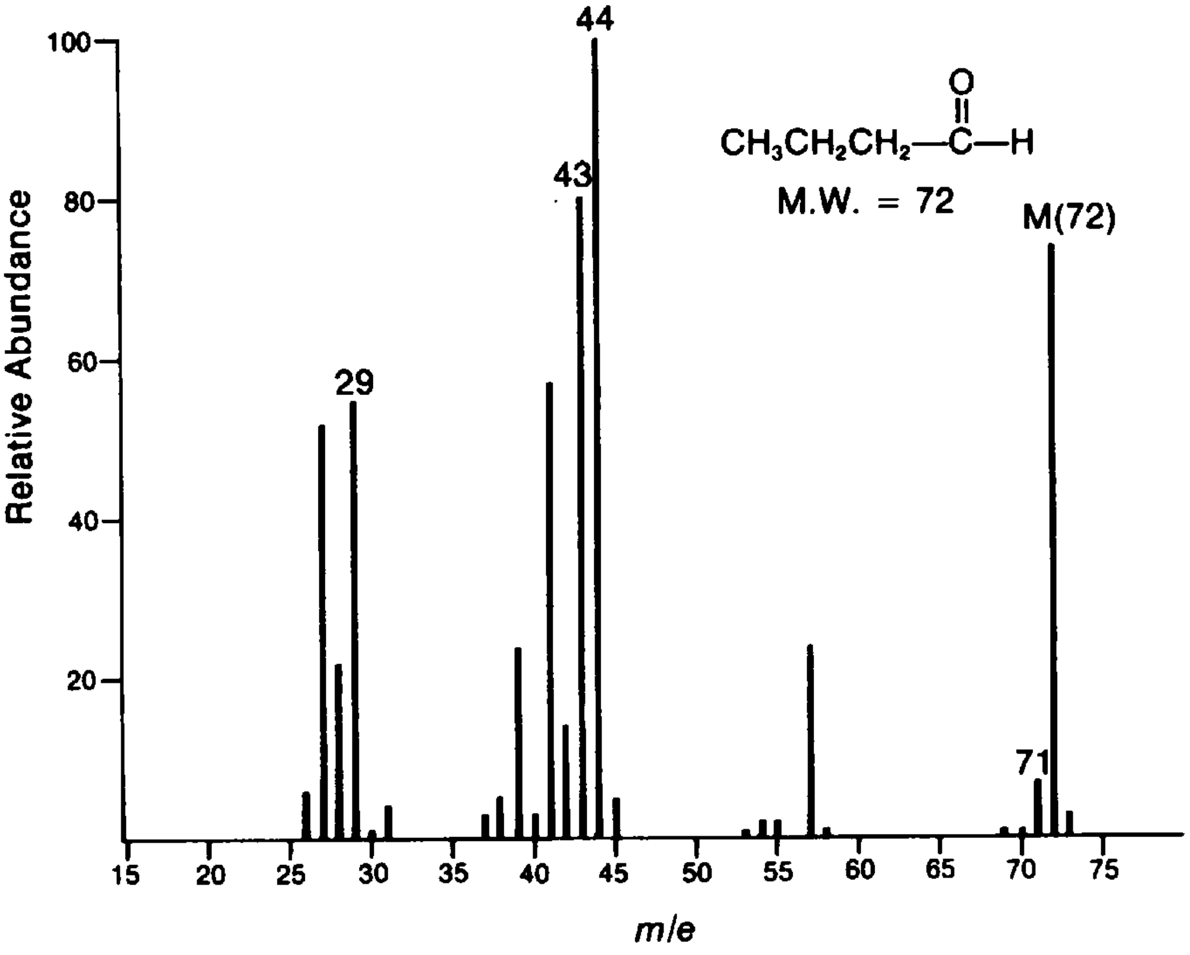
Cleavage of bonds next to the carbonyl group (C=O) is a characteristic fragmentation of aldehydes and ketones. A common fragment is carbon monoxide (CO) but as it is a molecule and thus uncharged it will not produce a peak of its own. However, it will produce an m/z drop of 28 somewhere in the spectrum.

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group

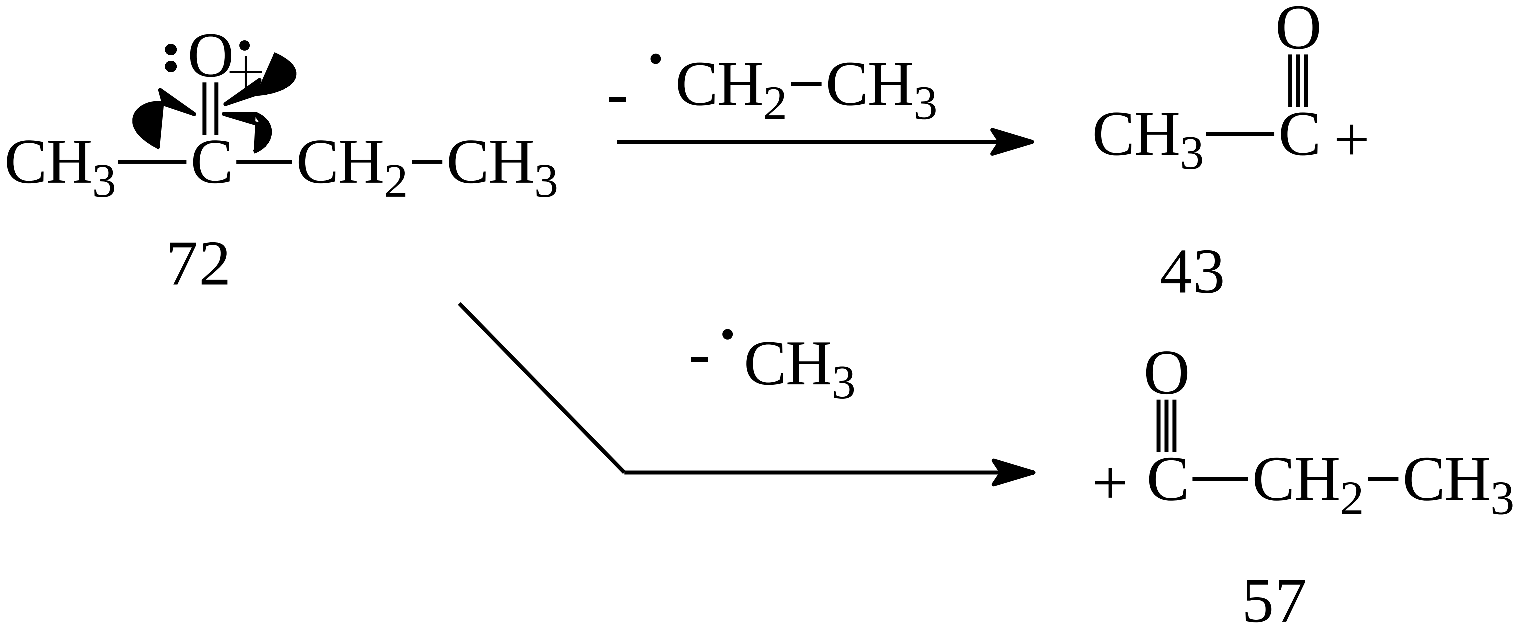


the more stable the acylium ion RCO^+, the more abundant it will be and the more abundant the species the taller its peak in the mass spectrum

butyraldehyde



α-cleavage



favor loss of larger radical