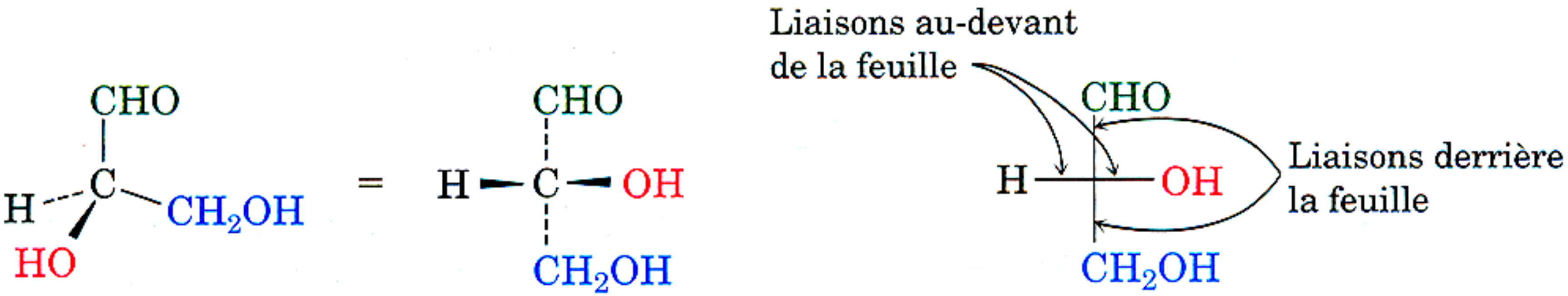
186, 472

(187, 444)

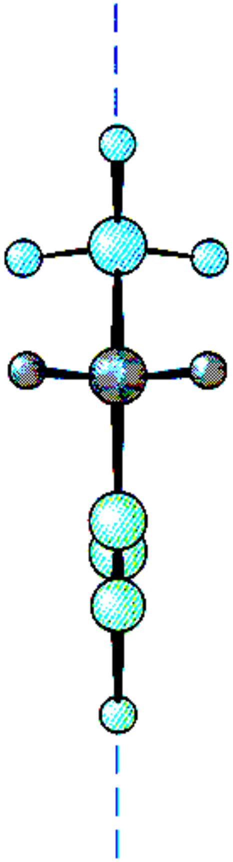
Projection de Fischer - chiralité



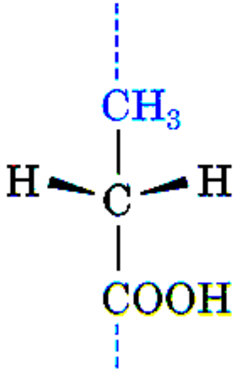
Liaisons au-devant de la feuille

Liaisons derrière la feuille

= Chiralité



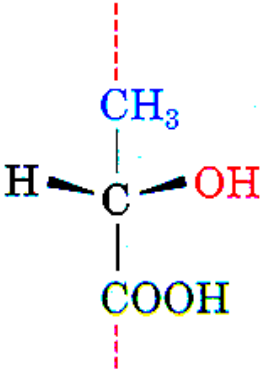
Plan de symétrie

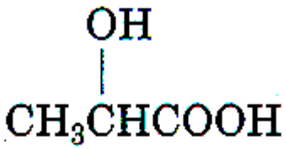


CH_3CH_2COOH

Acide propanoïque (achiral)

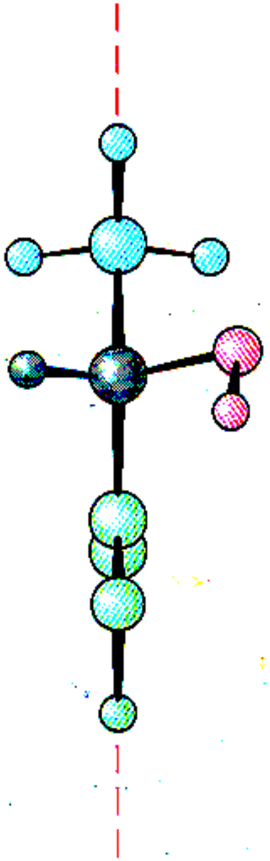
Absence de plan de symétrie





$$CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCOOH$$

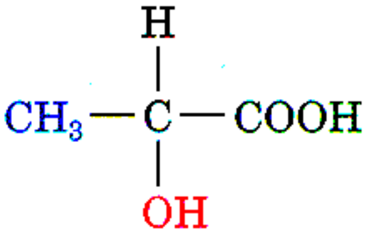
Acide lactique (chiral)



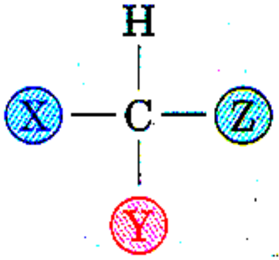
184, 189

(185, 192)

Activité optique



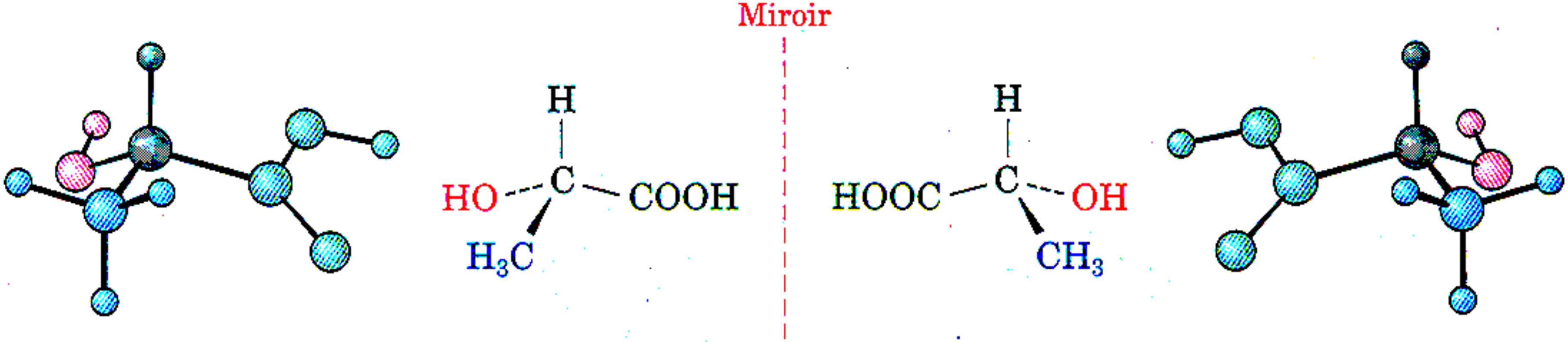
$$CH_3\text{—}\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}\text{—}COOH$$



centre stéréogénique

centre asymétrique

L'acide lactique : une molécule de formule générale CHXYZ



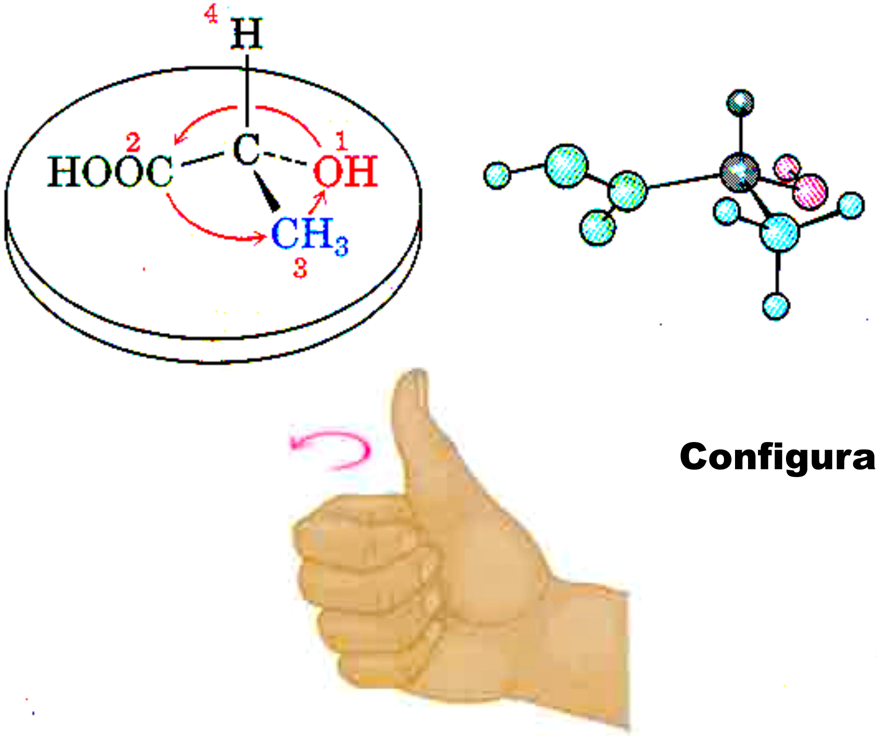
Acide-(+)-lactique
$[\alpha]_D = +3{,}82$

Acide-(−)-lactique
$[\alpha]_D = -3{,}82$

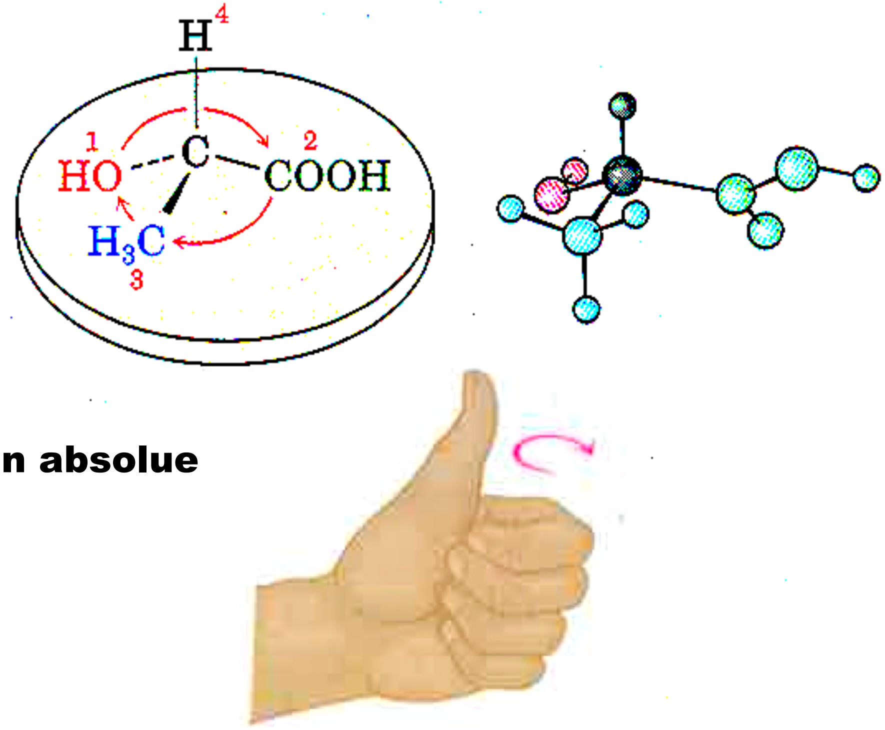
pouvoir rotatoire spécifique

Capacité d'une molécule chirale en solution de faire tourner le plan de la lumière polarisée

Nomenclature



Configuration absolue



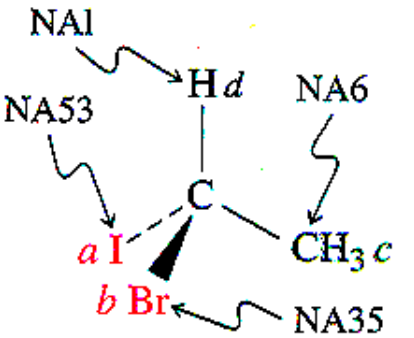
Acide (*R*)-(−)-lactique
(main droite)

Acide (*S*)-(+)-lactique
(main gauche)

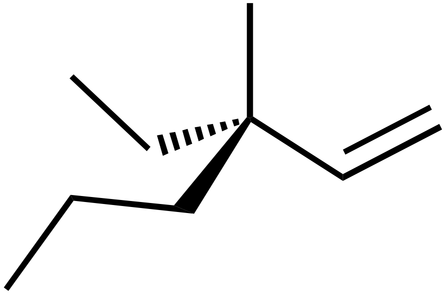
Règles séquencielles

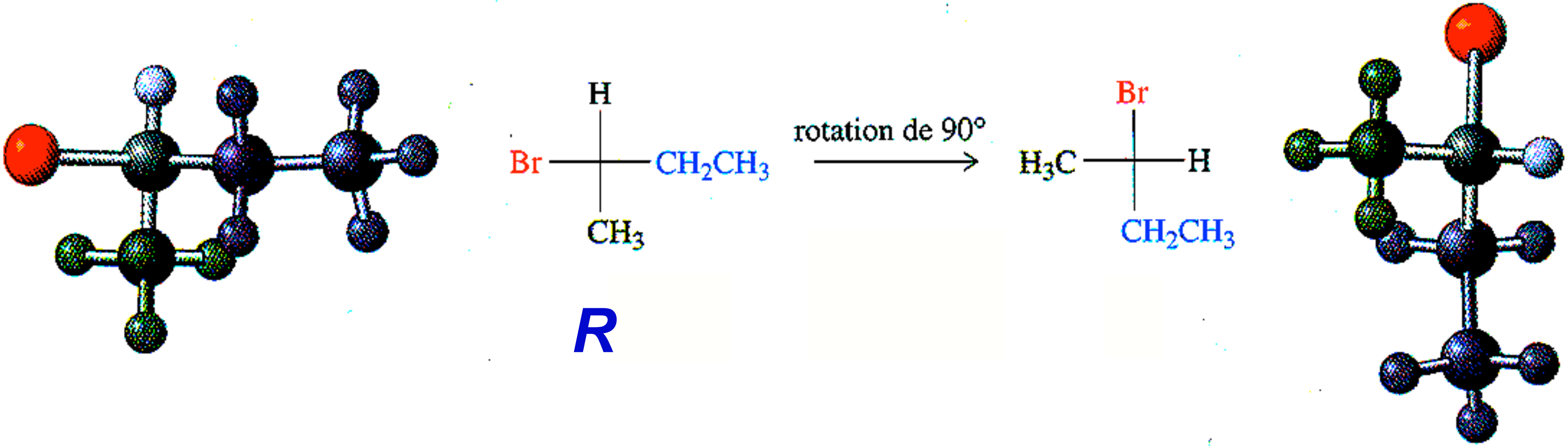
Br > Cl > O > N > C > H

35 17 8 7 6 1

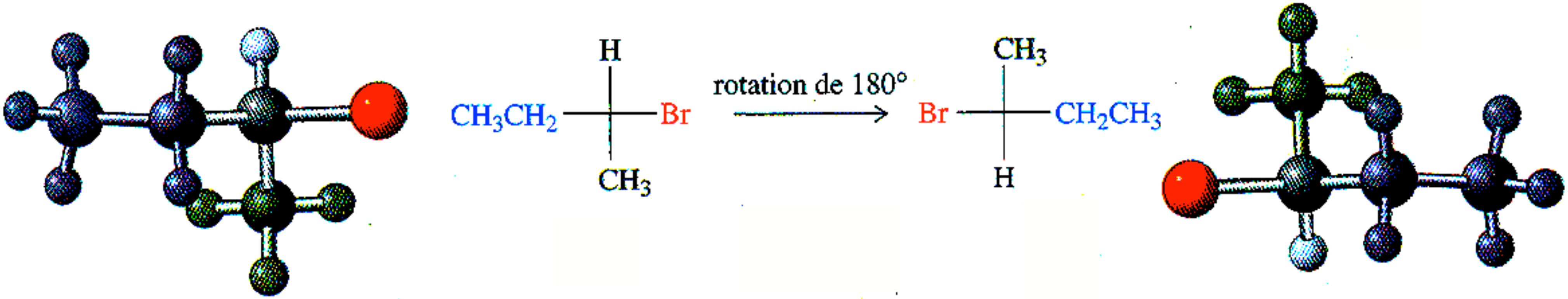


NA = numéro atomique

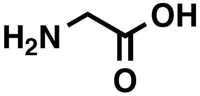



H
Br
CH₂CH₃
CH₃
rotation de 90°
Br
H₃C
H
CH₂CH₃

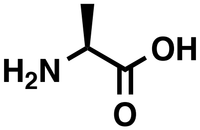
R


H
CH₃CH₂
Br
CH₃
rotation de 180°
CH₃
Br
CH₂CH₃
H

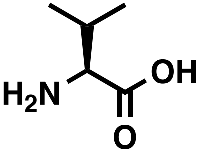
Les acides aminés



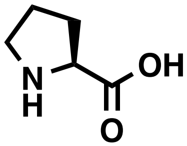
Glycine
(Gly, G)



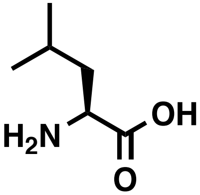
Alanine
(Ala, A)



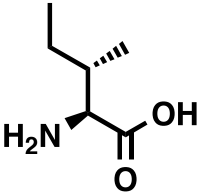
Valine
(Val, V)



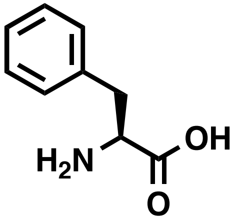
Proline
(Pro, P)



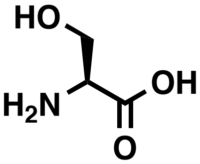
Leucine
(Leu, L)



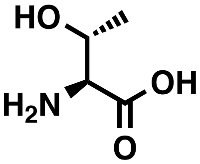
Isoleucine
(Ile, I)



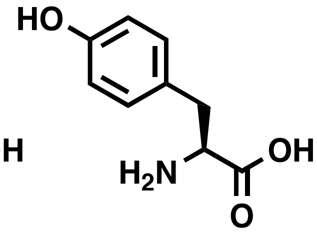
Phénylalanine
(Phe, F)



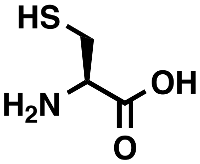
Sérine
(Ser, S)



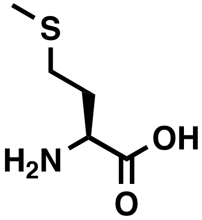
Thréonine
(Thr, T)



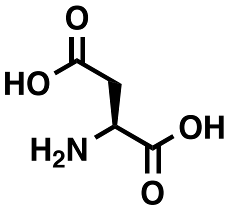
Tyrosine
(Tyr, Y)



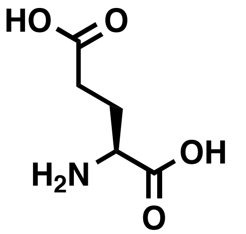
Cystéine
(Cys, C)



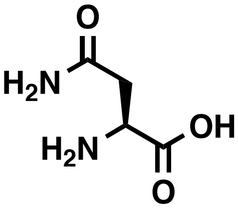
Méthionine
(Met, M)



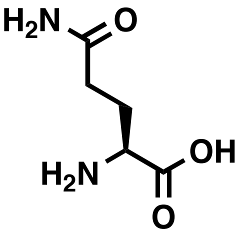
Acide aspartique
(Asp, D)



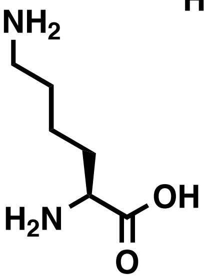
Acide glutamique
(Glu, E)



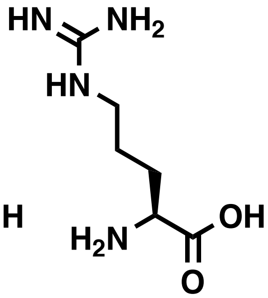
Asparagine
(Asn, N)



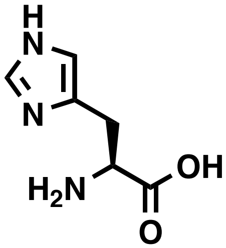
Glutamine
(Gln, Q)



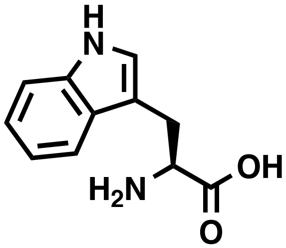
Lysine
(Lys, K)



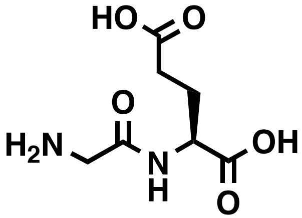
Arginine
(Arg, R)



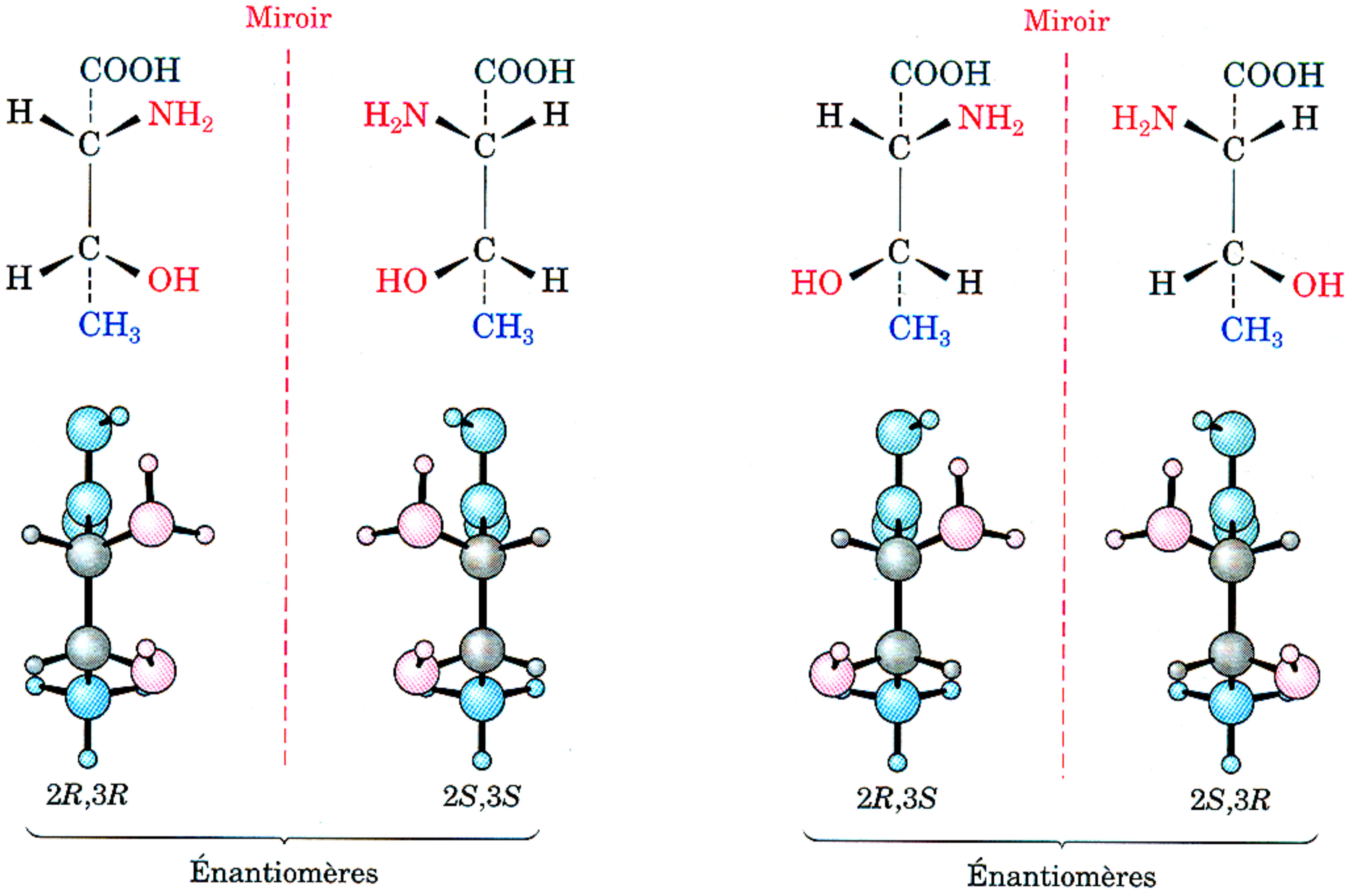
Histidine
(His, H)



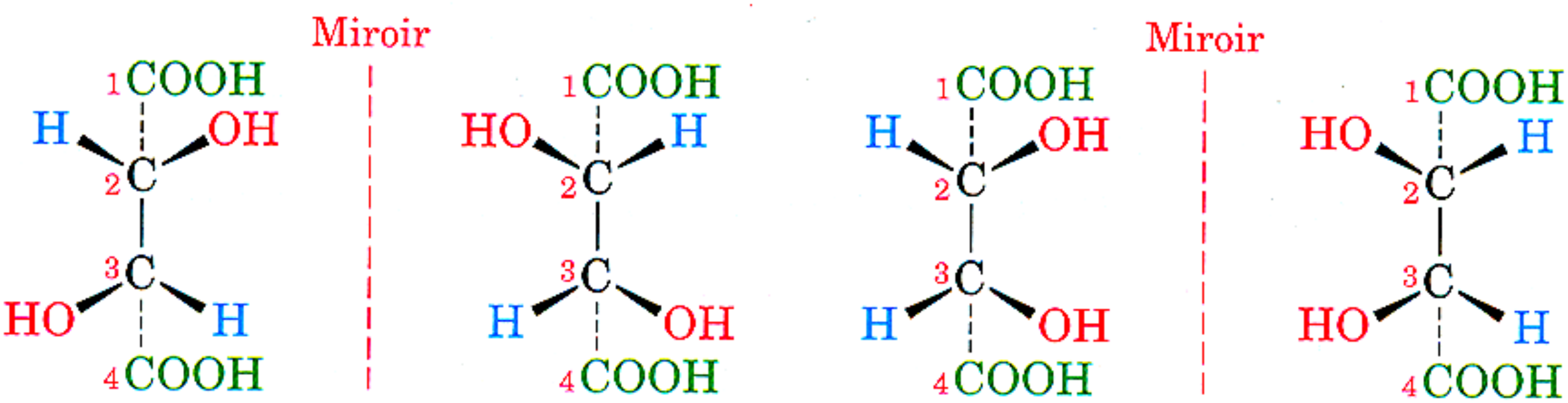
Tryptophane
(Trp, W)



Diastéréoisomères - la thréonine



Composés méso - l'acide tartrique



2*R*,3*R* **2*S*,3*S*** **2*R*,3*S*** **2*S*,3*R***

Stéréoisomère	*Point de fusion (°C)*	*$[\alpha]_D$*	*Densité*	*Solubilité à 20 °C (g / 100 mL d'eau)*
(+)	168-170	+ 12	1,759 8	139,0
(–)	168-170	– 12	1,759 8	139,0
Méso	146-148	0	1,666 0	125,0
(±)	206	0	1,788 0	120,6

Mélange racémique, racémate (201)

Les glucides (carbohydrates, sucres)

$C_n(H_2O)_n$

(449)

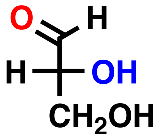
Aldoses (Cétoses)

Aldotriose

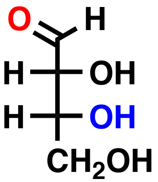
-tetroses

-pentoses

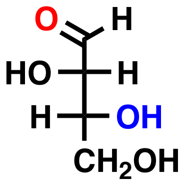
-hexoses



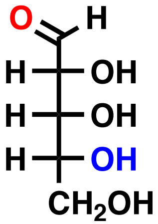
D-Glycéraldéhyde



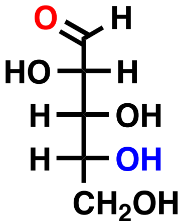
D-Érythrose



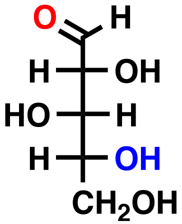
D-Thréose



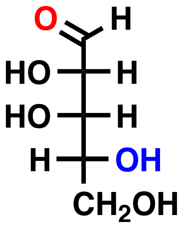
D-Ribose



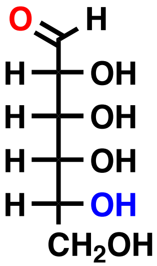
D-Arabinose



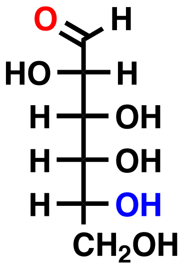
D-Xylose



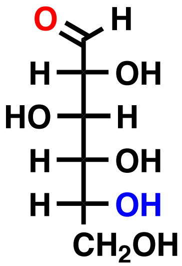
D-Lyxose



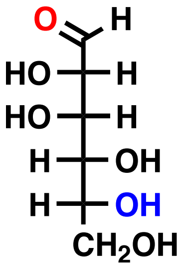
D-Allose



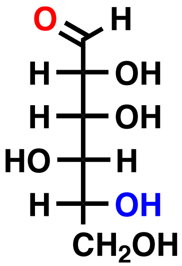
D-Altrose



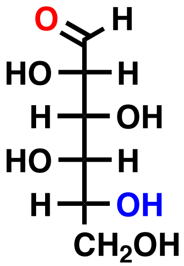
D-Glucose



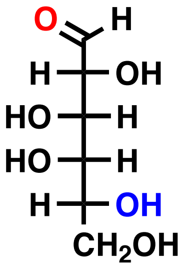
D-Mannose



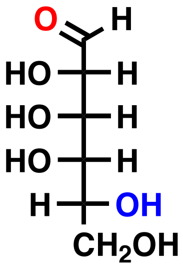
D-Gulose



D-Idose



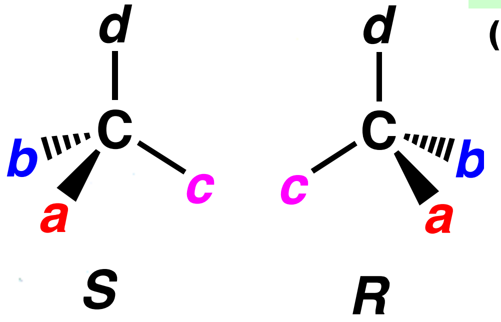
D-Galactose



D-Talose

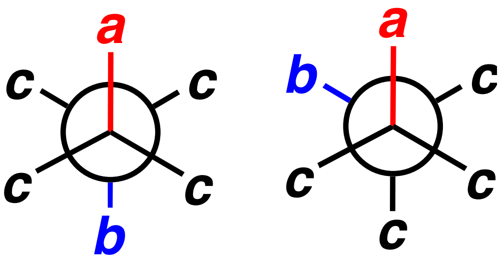
(205-6)

Configuration



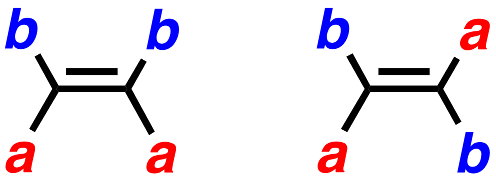
- Isomères
  - Isomères de constitution
  - Stéréoisomères
    - Énantiomères (image dans un miroir)
    - Diastéréoisomères
      - Diastéréoisomères configurationels
      - Diastéréoisomères *cis-trans*

Conformation



anti *gauche*

(décalées)



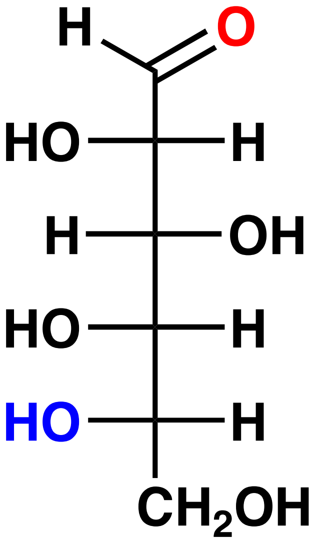
Z (cis) ***E (trans)***

199, 474-6

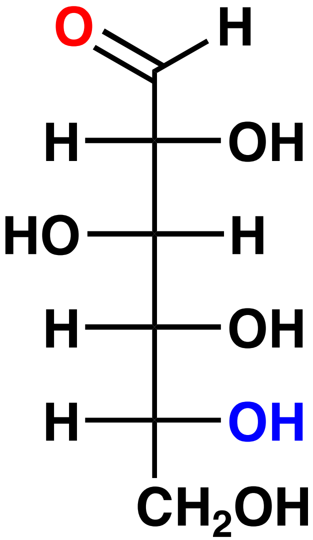
(201, 445-8)

Plus de deux centres stéréogéniques

Miroir



L-Glucose
(composé non naturel)



D-Glucose

n centres

≤ 2^n stéréoisomères

≤ 2^{n-1} couples d'énantiomères

Les glucides (carbohydrates, sucres)

$C_n(H_2O)_n$

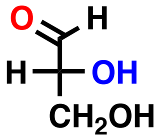
Aldoses (Cétoses)

Aldotriose

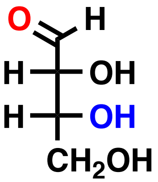
-tetroses

-pentoses

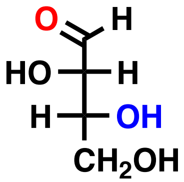
-hexoses



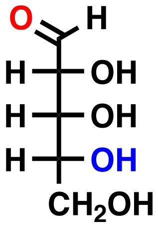
D-Glycéraldéhyde



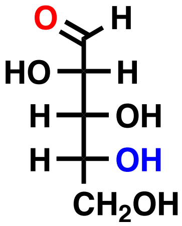
D-Érythrose



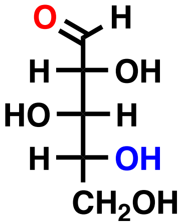
D-Thréose



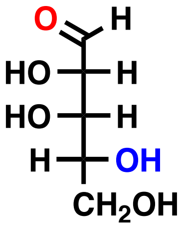
D-Ribose



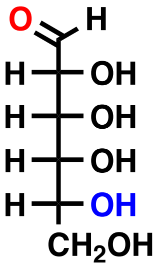
D-Arabinose



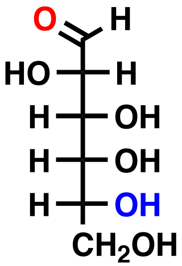
D-Xylose



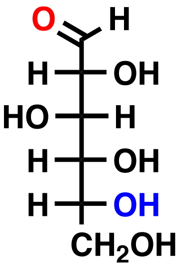
D-Lyxose



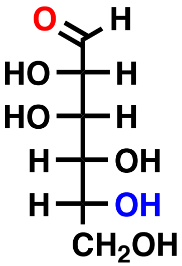
D-Allose



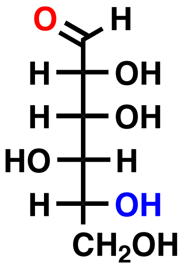
D-Altrose



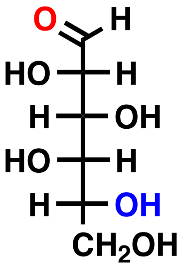
D-Glucose



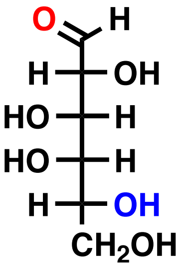
D-Mannose



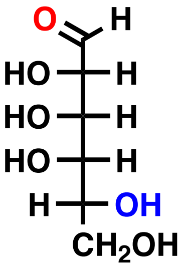
D-Gulose



D-Idose



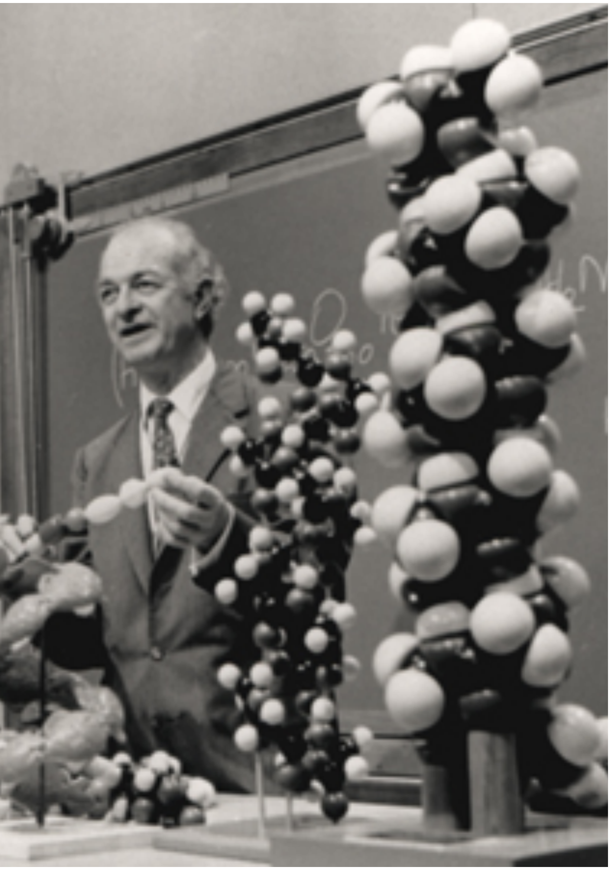
D-Galactose



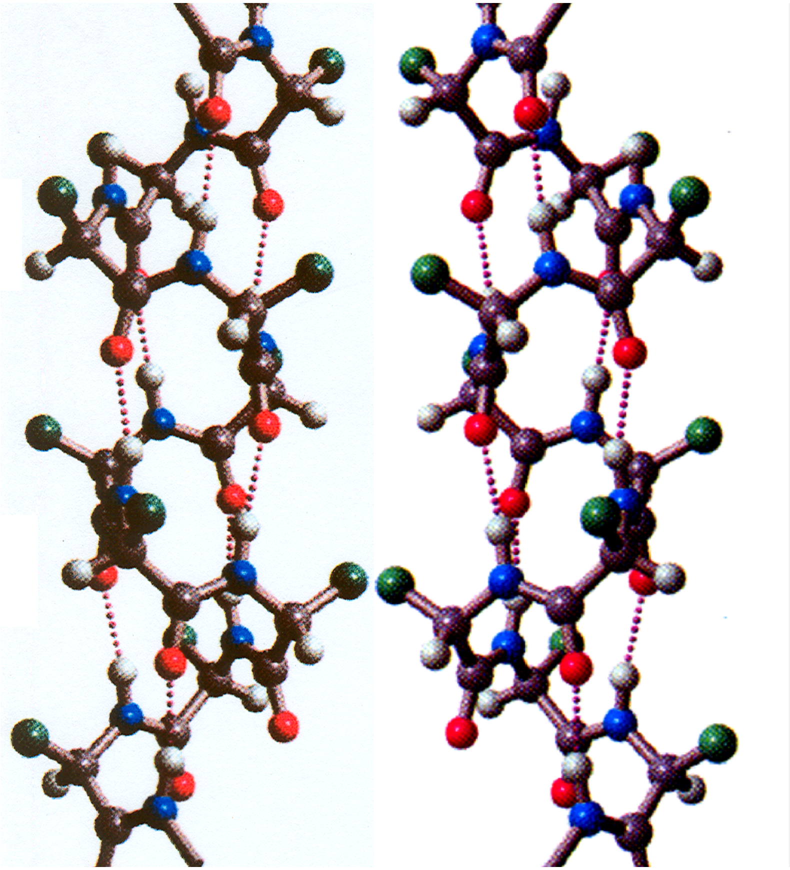
D-Talose

3. Stéréochimie - 4. Alcools - 5. Aldéhydes/cétones

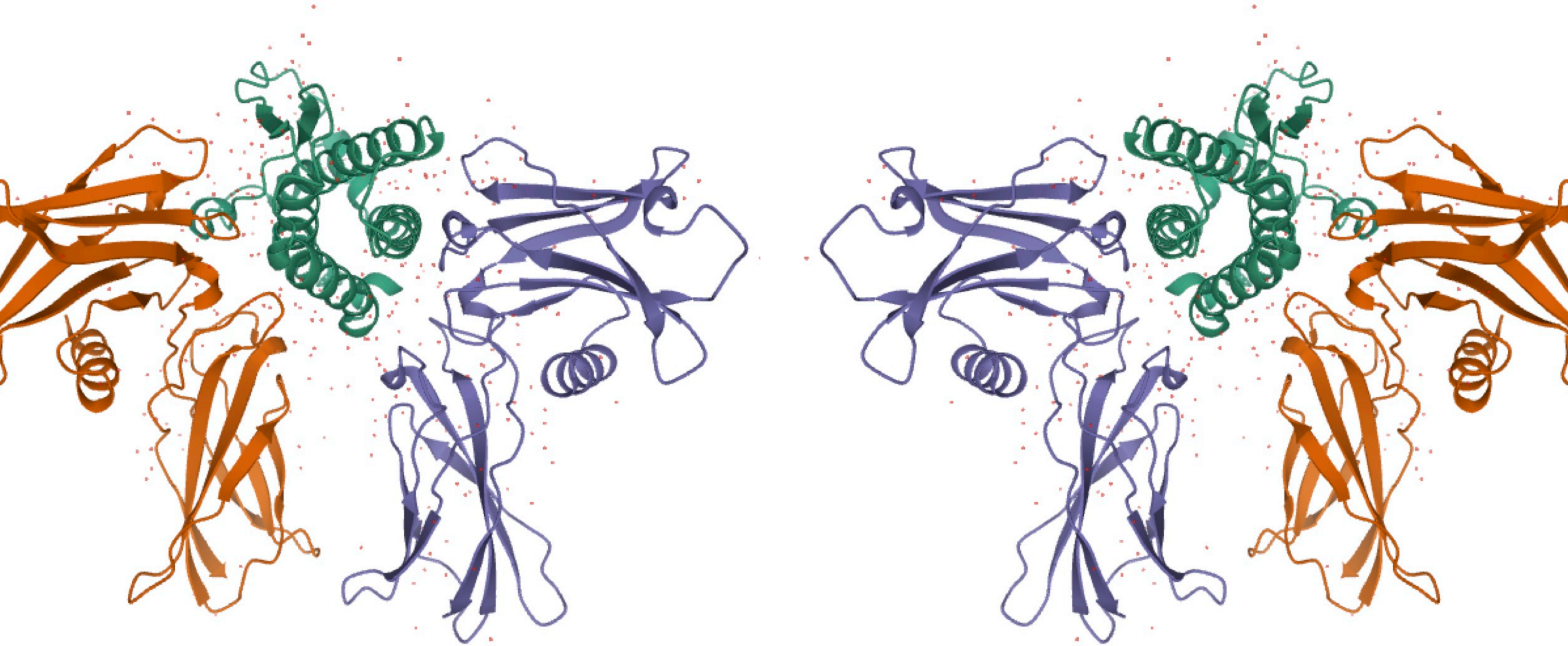
L'hélice α

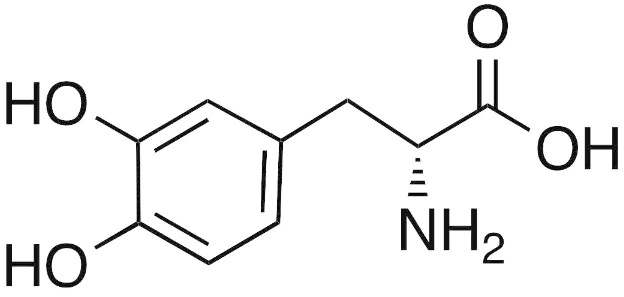


Linus Pauling
Prix Nobel, Chimie, 1954



McMurry

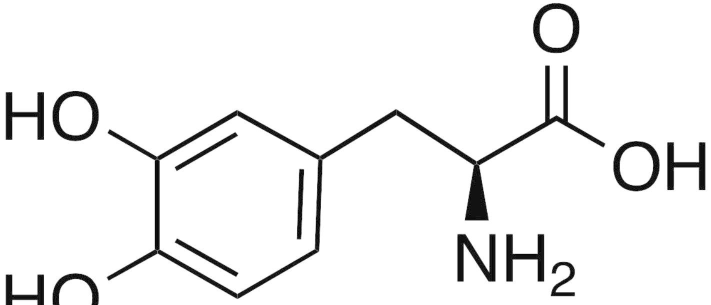




D-Dopa
pas d'effet biologique (208)

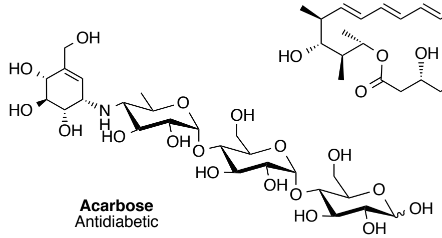
1967
Hoffman-La Roche
Synthesis: William
Knowles, Monsanto,
prix Nobel 2001

N THE BEGINNING L-Dopa was first isolated rom *Vicia faba* seedlings. The aromatic amino acid is ommonly found in plants and animals.

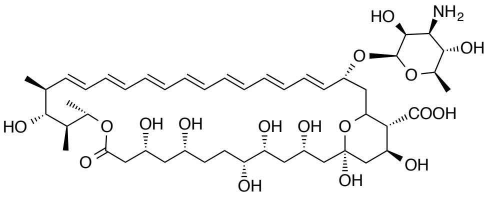


L-Dopa
(Levodopa)
Antiparkinson

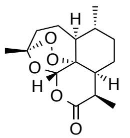
Molécules qui ont changé notre monde...



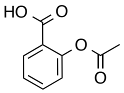
Acarbose
Antidiabetic



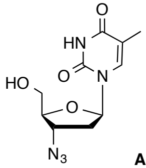
Amphotericin B
Antifungal



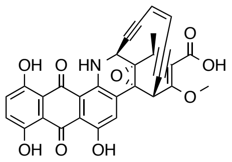
Artemisinin
Antimalarial



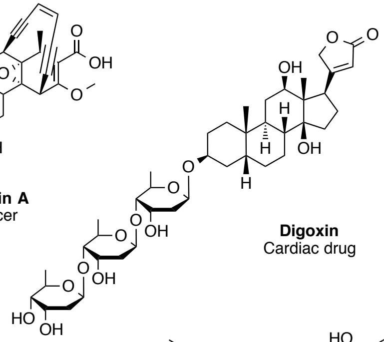
Aspirin
Analgesic



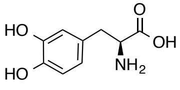
AZT
Antiviral (AIDS)



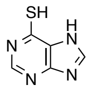
Dynemicin A
Anticancer



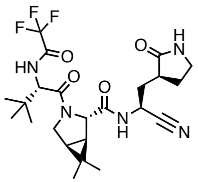
Digoxin
Cardiac drug



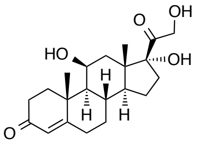
L-Dopa
Antiparkinson



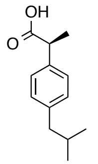
6-Mercaptopurine
Anticancer



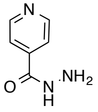
Paxlovid
Antiviral
(SARS-CoV-2)



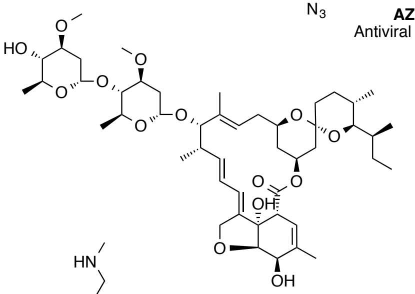
Hydrocortisone
Hormone



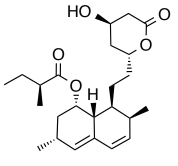
Ibuprofen
Analgesic



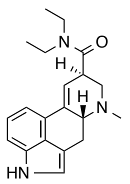
Isoniacid
Antibacterial
(Tuberculosis)



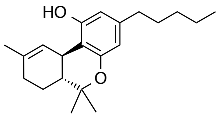
Ivermectin
Antiparasitic
(Onchocerciasis)



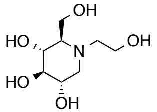
Lovastatin
Anti-cholesterol



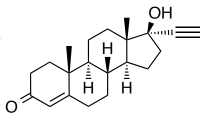
LSD
Psychedelic



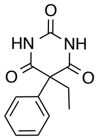
Marijuana
Antiemetic



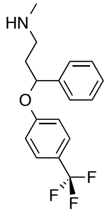
Miglitol
Antidiabetic



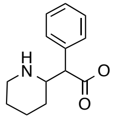
Norethindrone
Hormone
(oral contraceptive)



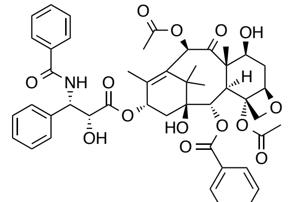
Phenobarbital
Anticonvulsant



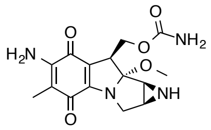
Prozac
Antidepressant



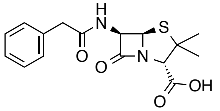
Ritalin
Stimulant



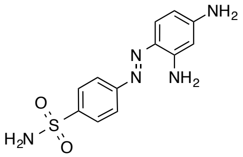
Taxol
Anticancer



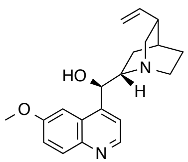
Mitomycin C
Anticancer



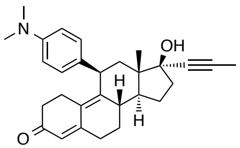
Penicillin
Antibacterial



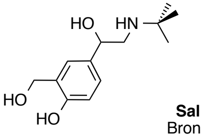
Prontosil
Antibacterial



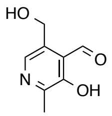
Quinine
Antimalarial



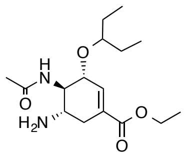
RU-486
Hormone
("abortion pill")



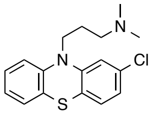
Salbutamol
Bronchodilator
(Asthma)



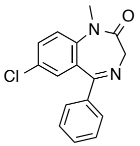
Vitamin B_6
Nutrient



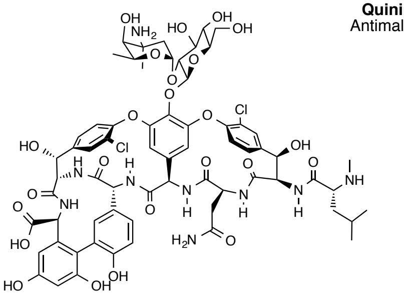
Tamiflu
Antiviral



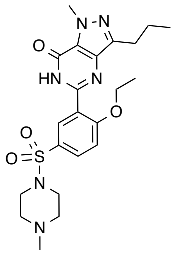
Thorazine
Antipsychotic
(Schizophrenia)



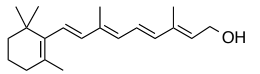
Valium
Tranquilizer



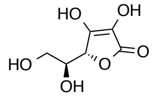
Vancomycin
Antibacterial



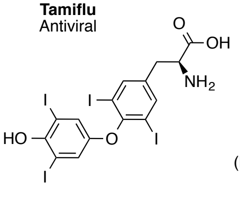
Viagra
Vasodilator



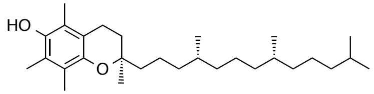
Vitamin A
Nutrient



Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)



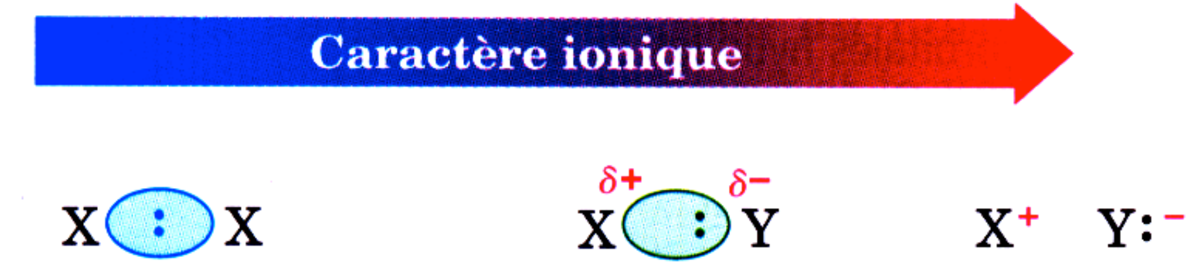
Vitamin E
Nutrient

Résumé 3 (Stéréochimie - carbohydrates -)

- **molécules (a)chirales**
- **centre asymétrique (stéréogénique)**
- **projection de Fischer,** D / L
- **configuration absolue,** *R* / *S* **(***P* / *M***)**
- **activité optique, +** / **-**
- **stéréoisomères (acides aminés, glucides)**
    - **diastéréoisomère**
    - **énantiomère**
    - **composé méso**
    - **mélange racémique**

CONTENU

McMurry

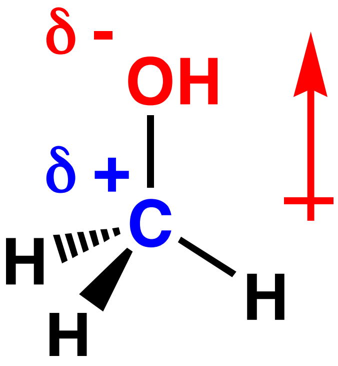


Liaison covalente symétrique

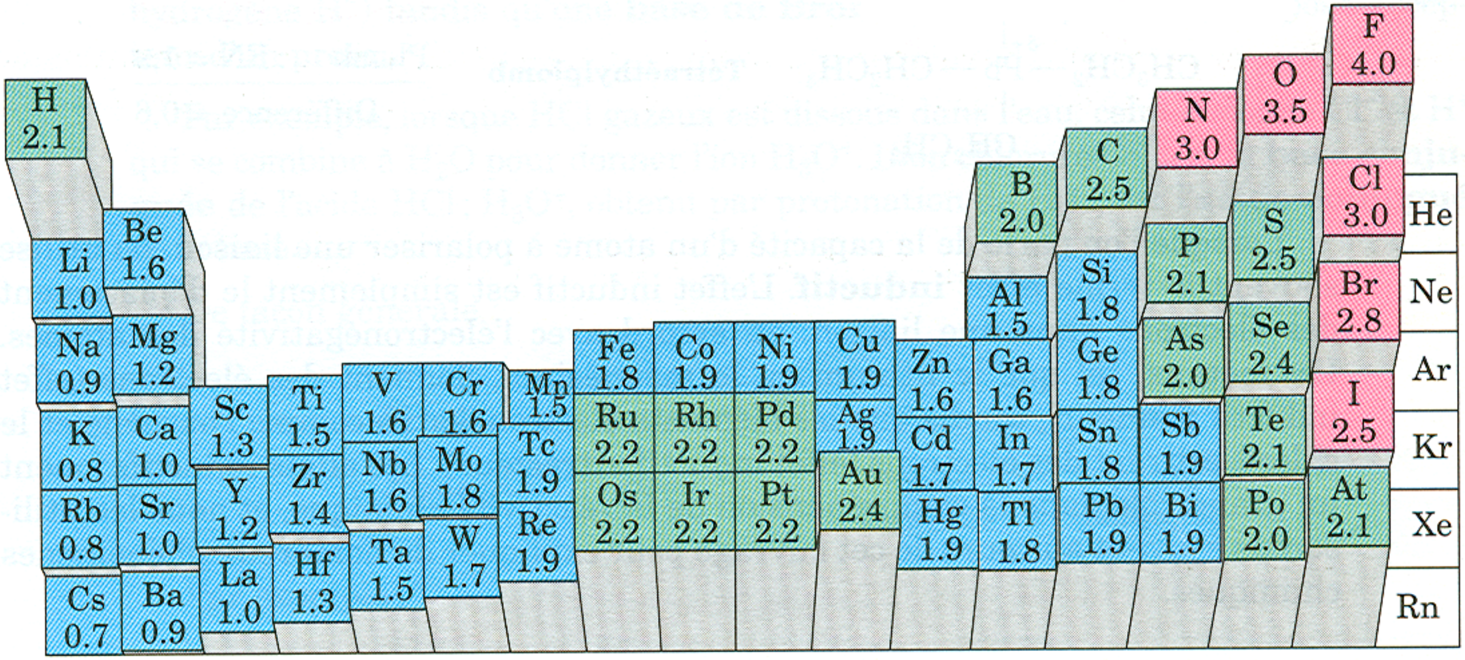
Liaison covalente polaire

Liaison ionique

Electronégativité



dipôle électrique

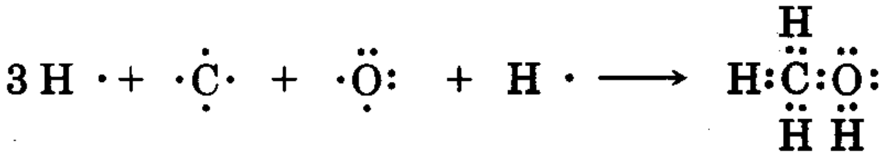


H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

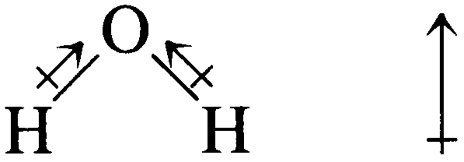
« L’oxygène *sp*³ »

7, 250-1

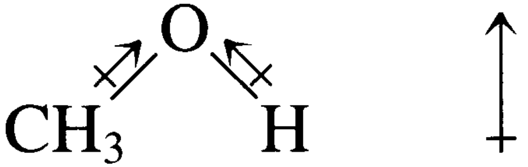
(8, 254-8)



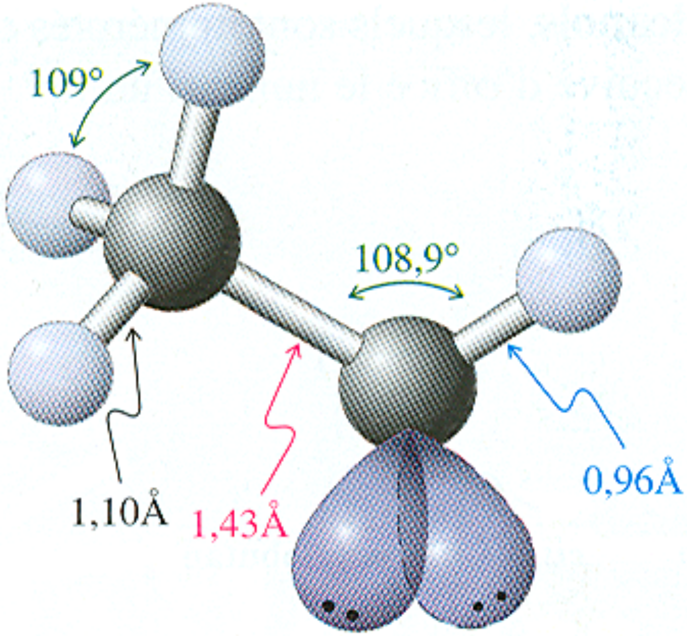
$$3\,\mathrm{H}\cdot + \cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot + \cdot\underset{\cdot}{\ddot{\mathrm{O}}}: + \mathrm{H}\cdot \longrightarrow \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}:\underset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{O}}}}:$$



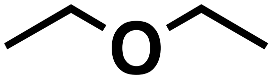
Moment dipolaire résultant



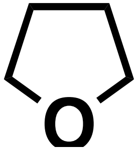
Moment dipolaire résultant



Méthanol

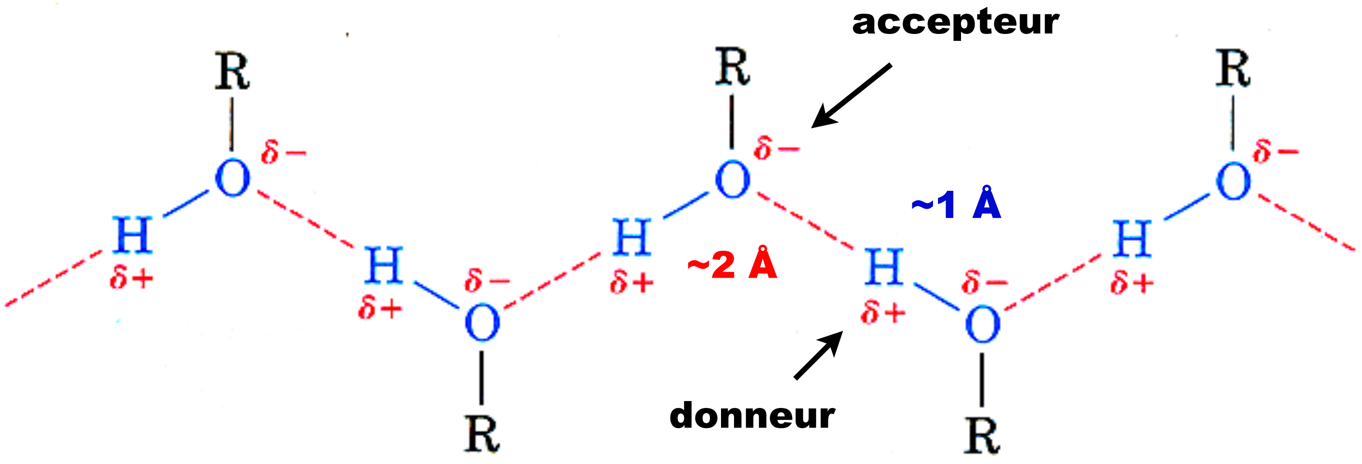


éther (linéaire)



(cyclique)

La liaison hydrogène

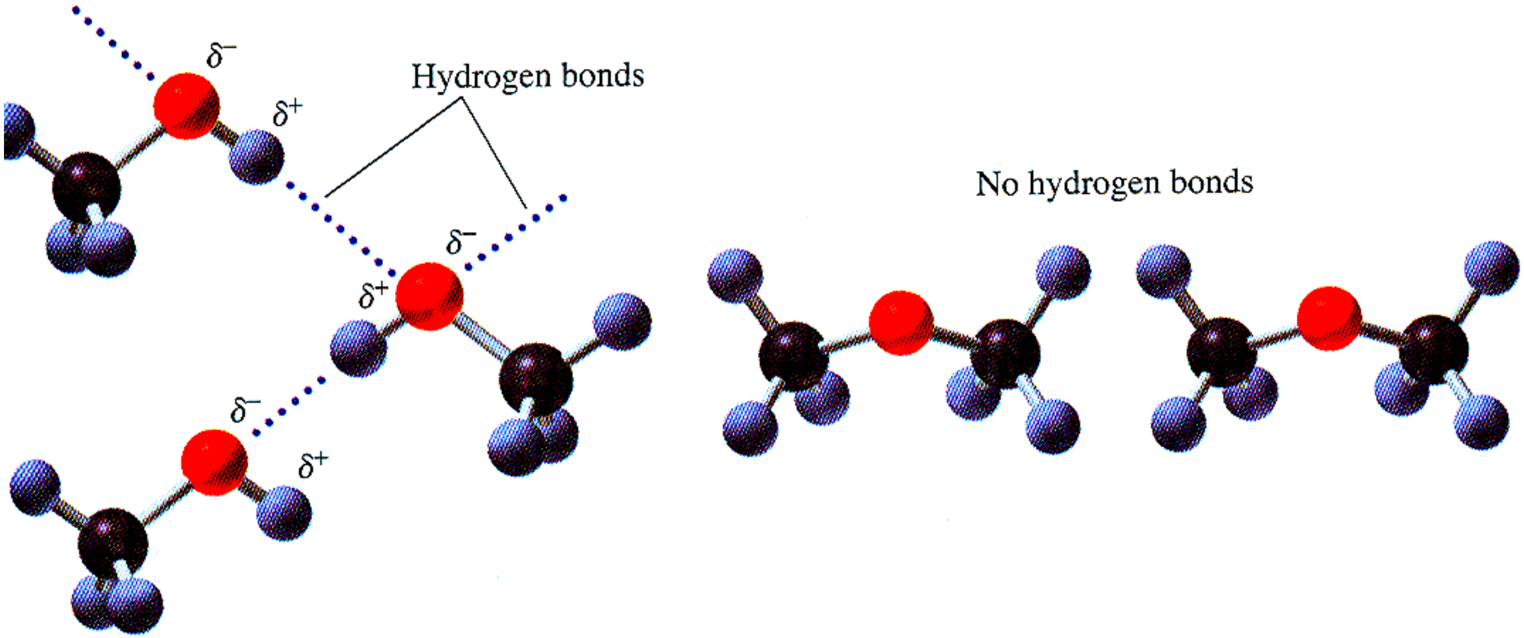


accepteur

~1 Å

~2 Å

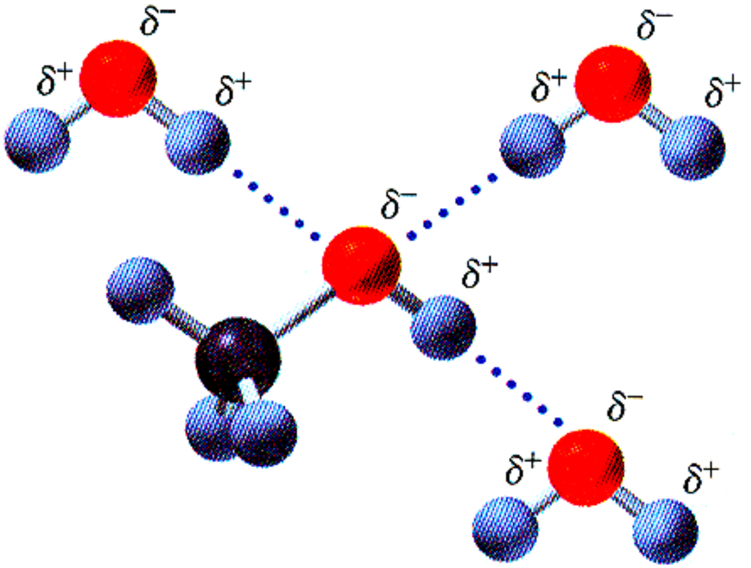
donneur

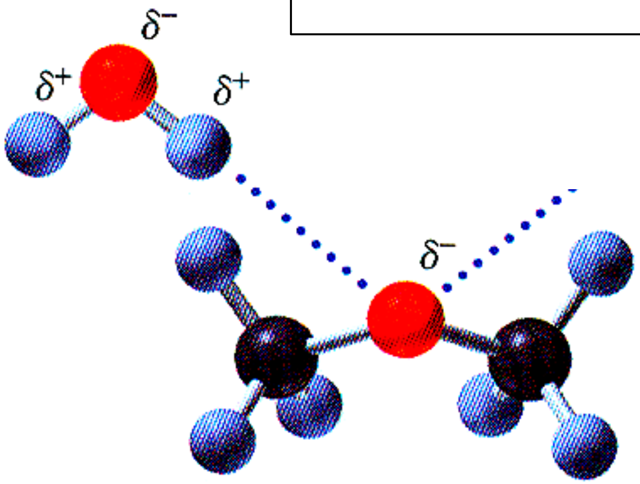


La liaison hydrogène

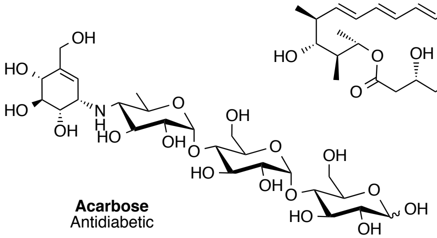
	Solubilité dans H_2O
CH_3CH_2OH	infinie (hydrophile)
CH_3CH_3	5 ml/100 ml (hydrophobe)
	

Point d'ébullition	
CH_3CH_2OH	79 °C
$CH_3CH_2CH_3$	-42 °C
$CH_3(CH_2)_3OH$	117 °C
$CH_3(CH_2)_3CH_3$	36 °C
	34 °C

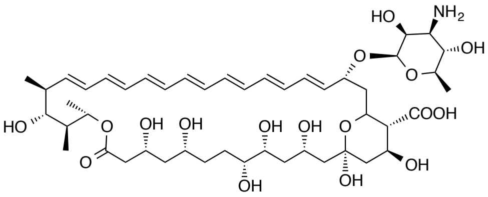




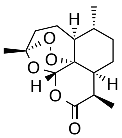
Molécules qui ont changé notre monde...



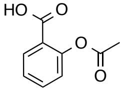
Acarbose
Antidiabetic



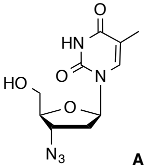
Amphotericin B
Antifungal



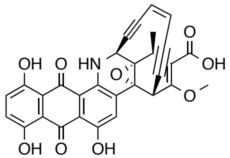
Artemisinin
Antimalarial



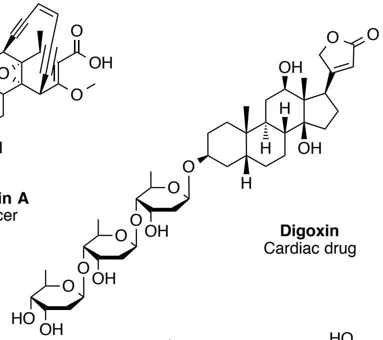
Aspirin
Analgesic



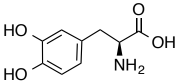
AZT
Antiviral (AIDS)



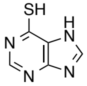
Dynemicin A
Anticancer



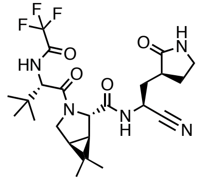
Digoxin
Cardiac drug



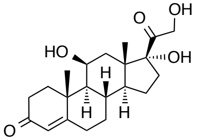
L-Dopa
Antiparkinson



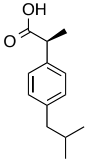
6-Mercaptopurine
Anticancer



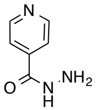
Paxlovid
Antiviral
(SARS-CoV-2)



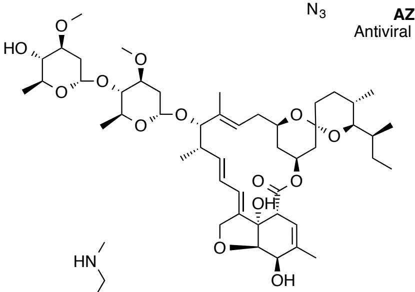
Hydrocortisone
Hormone



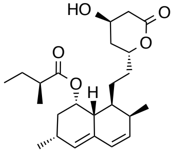
Ibuprofen
Analgesic



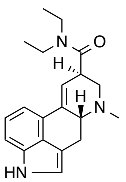
Isoniacid
Antibacterial
(Tuberculosis)



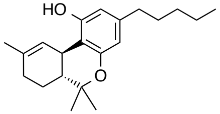
Ivermectin
Antiparasitic
(Onchocerciasis)



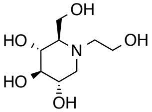
Lovastatin
Anti-cholesterol



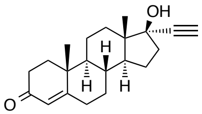
LSD
Psychedelic



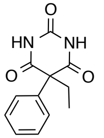
Marijuana
Antiemetic



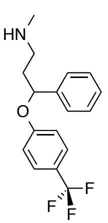
Miglitol
Antidiabetic



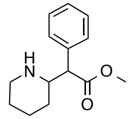
Norethindrone
Hormone
(oral contraceptive)



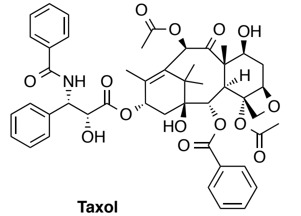
Phenobarbital
Anticonvulsant



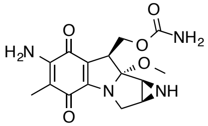
Prozac
Antidepressant



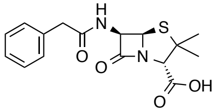
Ritalin
Stimulant



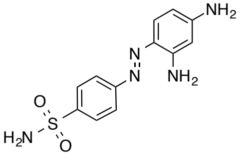
Taxol
Anticancer



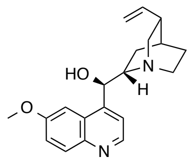
Mitomycin C
Anticancer



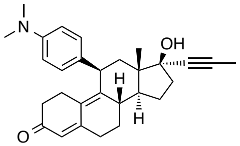
Penicillin
Antibacterial



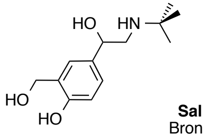
Prontosil
Antibacterial



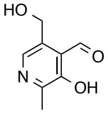
Quinine
Antimalarial



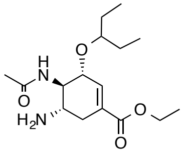
RU-486
Hormone
("abortion pill")



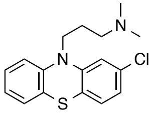
Salbutamol
Bronchodilator
(Asthma)



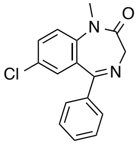
Vitamin B_6
Nutrient



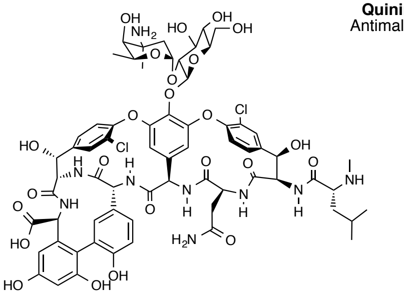
Tamiflu
Antiviral



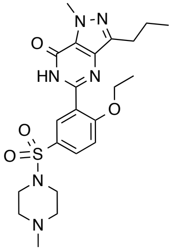
Thorazine
Antipsychotic
(Schizophrenia)



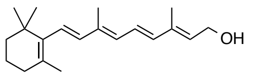
Valium
Tranquilizer



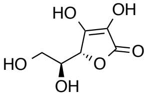
Vancomycin
Antibacterial



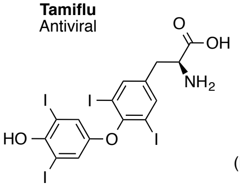
Viagra
Vasodilator



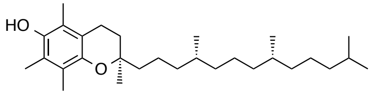
Vitamin A
Nutrient



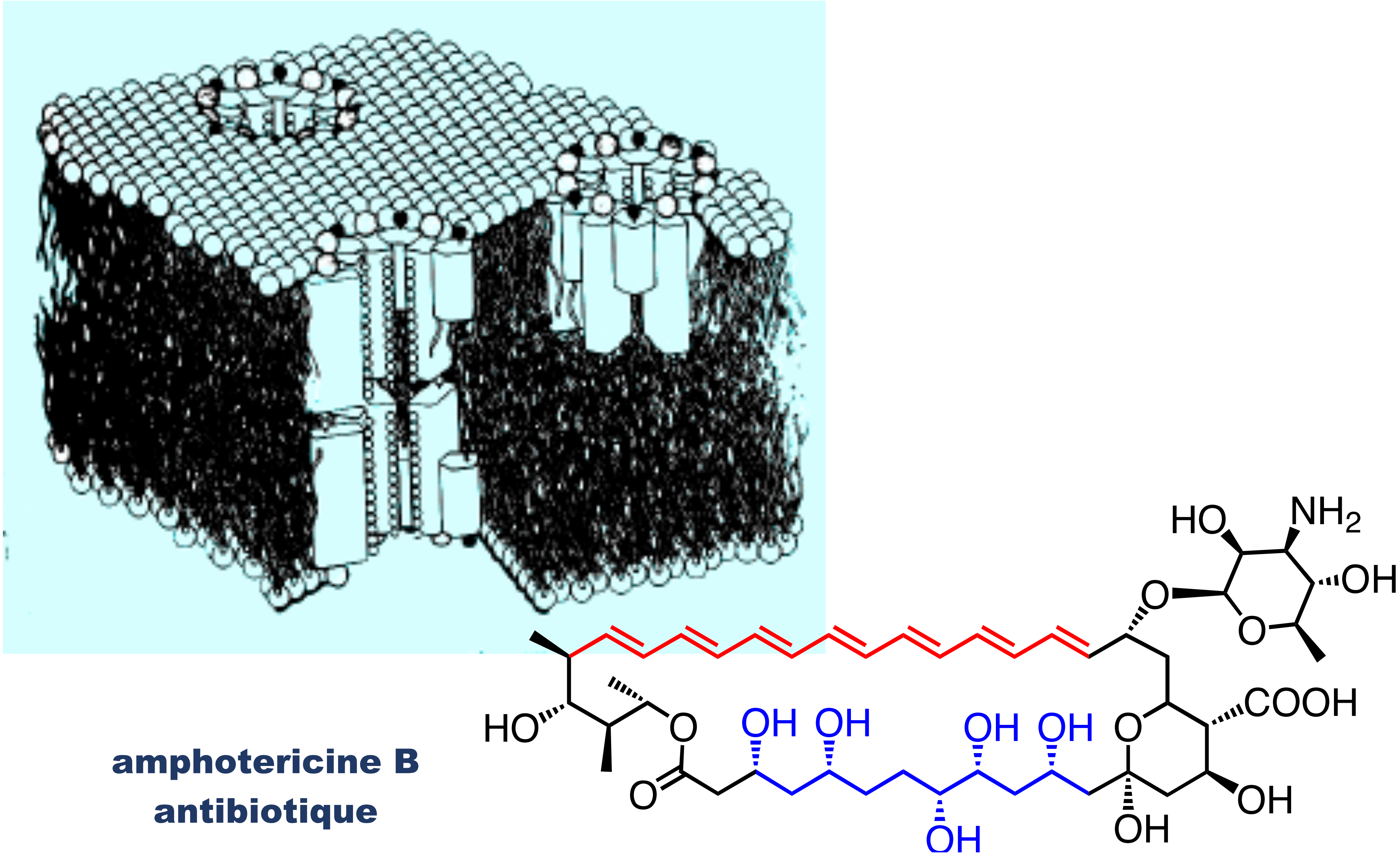
Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)



Vitamin E
Nutrient



amphotericine B
antibiotique

19-22, 252

(22-5, 256)

Acides et bases (Brønsted)

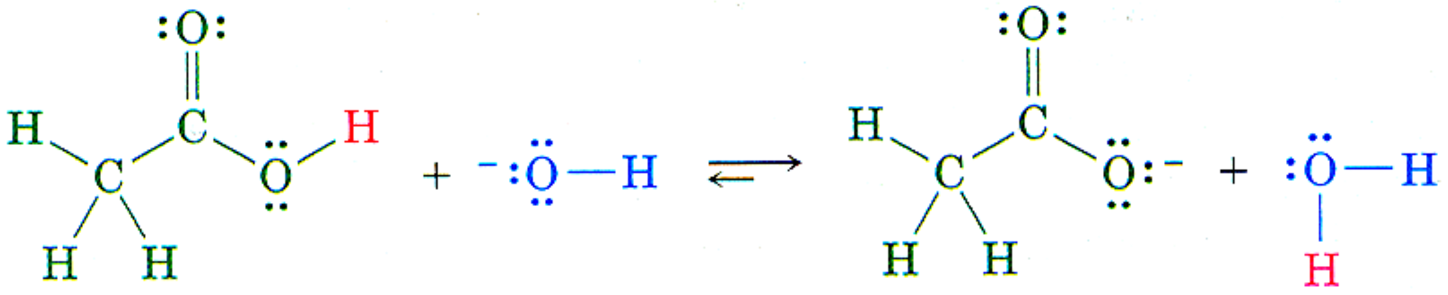
$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$H{-}A + :B \rightleftharpoons A:^- + H{-}B^+$$

Acide — Base — Base conjuguée — Acide conjugué

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$



Acide acétique **(pK_a = 4,76)**

Ion hydroxyde

Ion acétate

Eau **(pK_a = 15,74)**

$$pK_a = pH + \log [HA] / [A^-]$$

19-22, 252

(22-5, 256)

Acides et bases

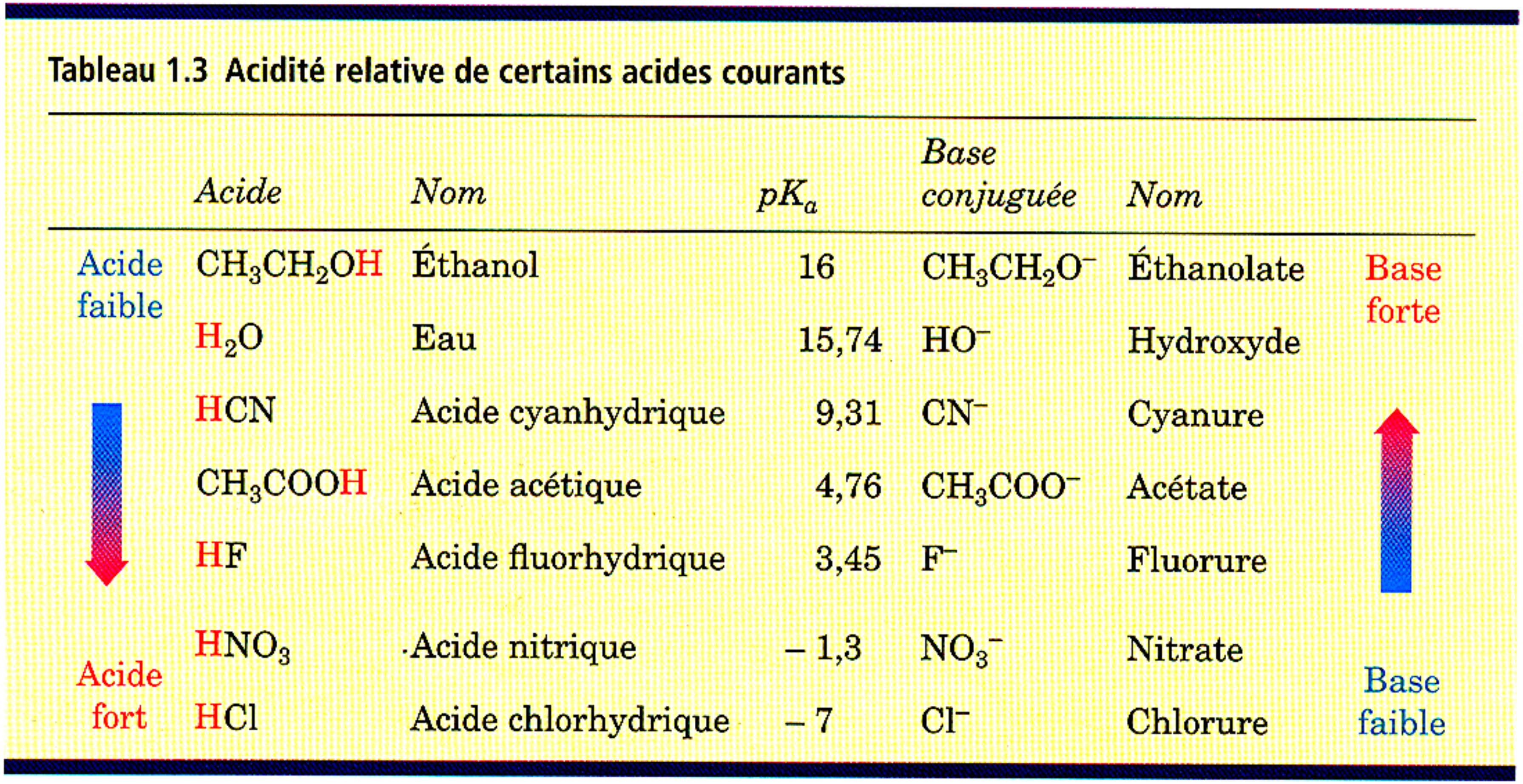
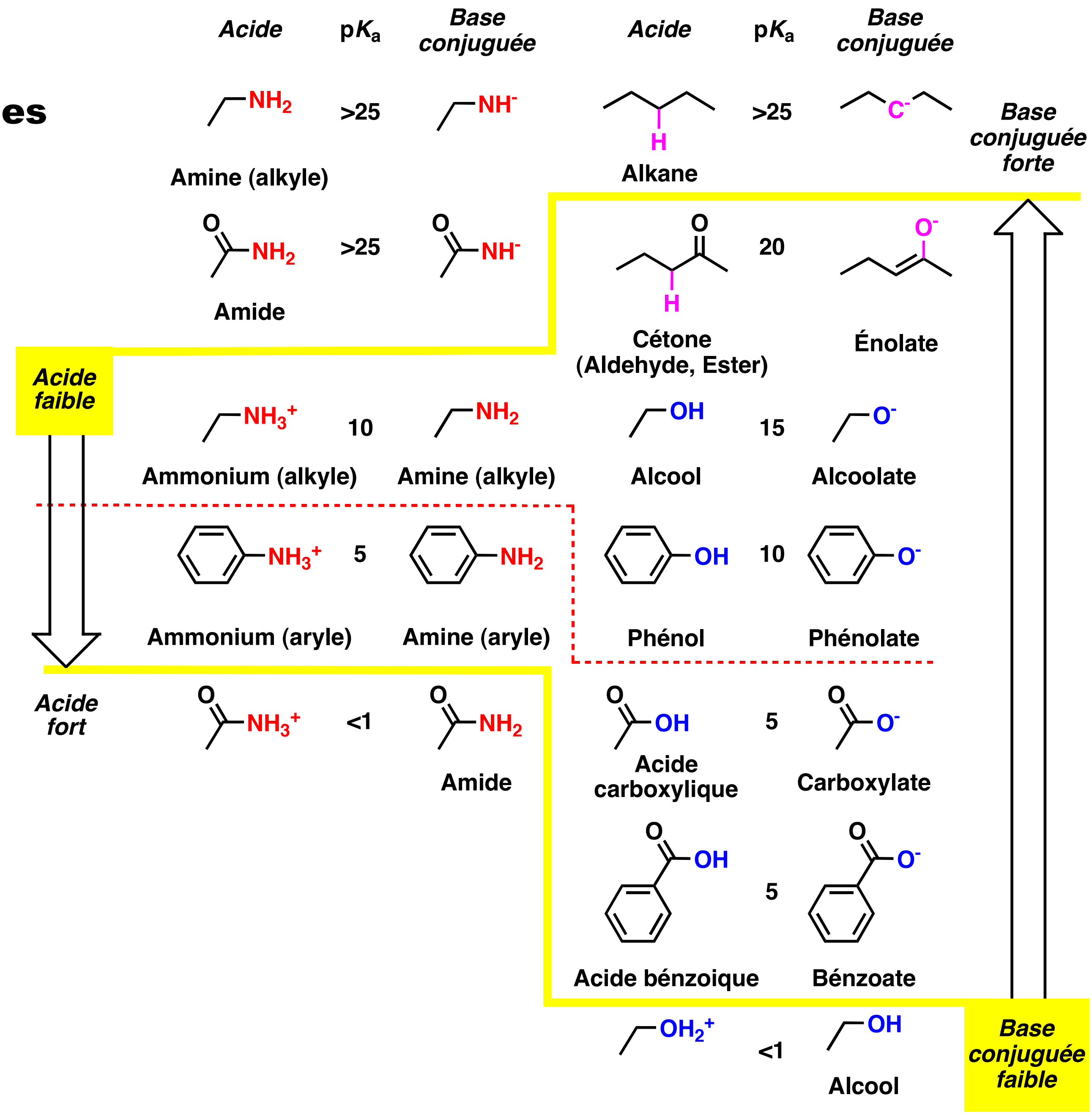


Tableau 1.3 Acidité relative de certains acides courants

	Acide	*Nom*	*pK_a*	*Base conjuguée*	*Nom*	
Acide faible	CH_3CH_2OH	Éthanol	16	$CH_3CH_2O^-$	Éthanolate	Base forte
	H_2O	Eau	15,74	HO^-	Hydroxyde	
	HCN	Acide cyanhydrique	9,31	CN^-	Cyanure	
↓	CH_3COOH	Acide acétique	4,76	CH_3COO^-	Acétate	↑
	HF	Acide fluorhydrique	3,45	F^-	Fluorure	
	HNO_3	Acide nitrique	– 1,3	NO_3^-	Nitrate	
Acide fort	HCl	Acide chlorhydrique	– 7	Cl^-	Chlorure	Base faible

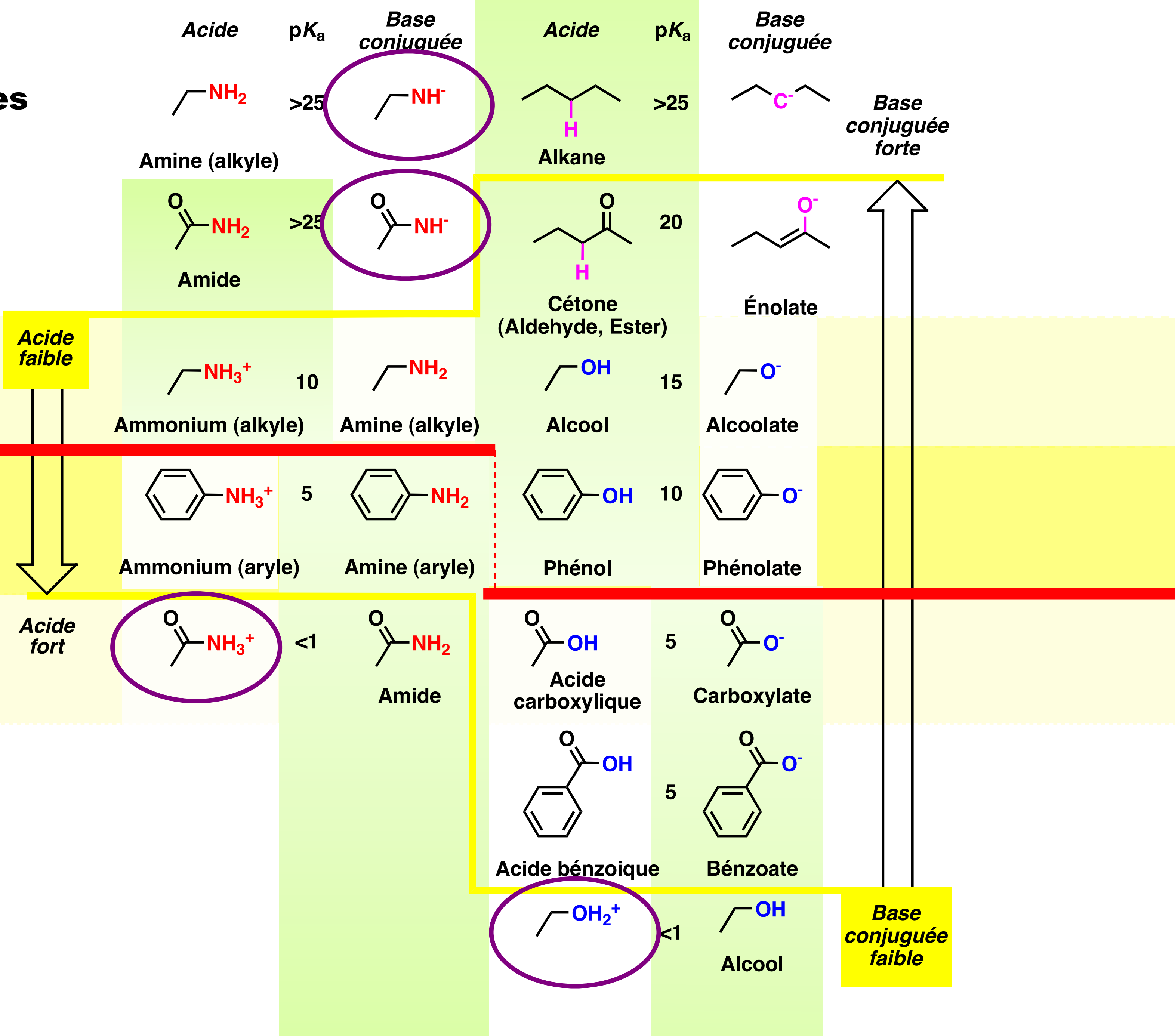
$$pK_a = pH + \log [HA] / [A^-]$$

Résumé
acides et bases



Acide	pK_a	Base conjuguée	Acide	pK_a	Base conjuguée
Amine (alkyle)	>25		Alkane	>25	
Amide	>25		Cétone (Aldehyde, Ester)	20	Énolate
Ammonium (alkyle)	10	Amine (alkyle)	Alcool	15	Alcoolate
Ammonium (aryle)	5	Amine (aryle)	Phénol	10	Phénolate
	<1	Amide	Acide carboxylique	5	Carboxylate
			Acide bénzoique	5	Bénzoate
				<1	Alcool

Résumé
acides et bases



Acide	pK_a	Base conjuguée
Amine (alkyle)	>25	
Amide	>25	
Ammonium (alkyle)	10	Amine (alkyle)
Ammonium (aryle)	5	Amine (aryle)
	<1	Amide

Acide	pK_a	Base conjuguée
Alkane	>25	
Cétone (Aldehyde, Ester)	20	Énolate
Alcool	15	Alcoolate
Phénol	10	Phénolate
Acide carboxylique	5	Carboxylate
Acide bénzoique	5	Bénzoate
	<1	Alcool

Acide faible

Acide fort

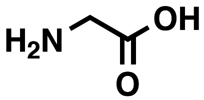
Base conjuguée forte

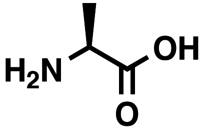
Base conjuguée faible

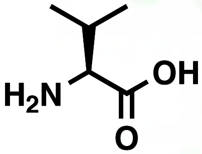
506-9, 513

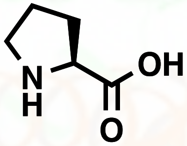
(475-7, 482-3)

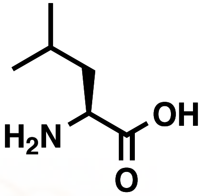
Les acides aminés

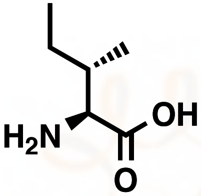

Glycine
(Gly, G)

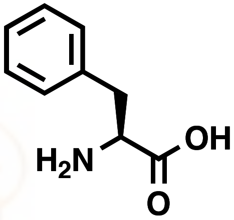

Alanine
(Ala, A)

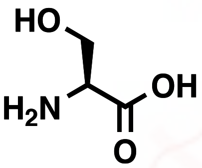

Valine
(Val, V)

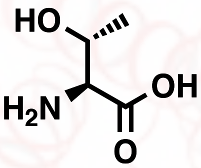

Proline
(Pro, P)

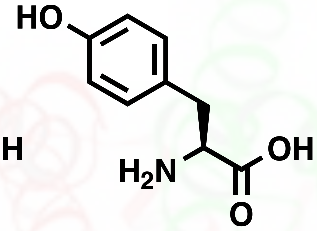

Leucine
(Leu, L)

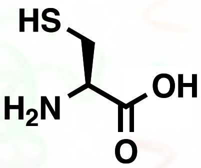

Isoleucine
(Ile, I)

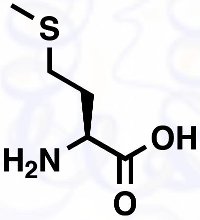

Phénylalanine
(Phe, F)

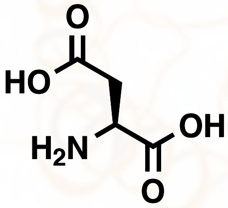

Sérine
(Ser, S)

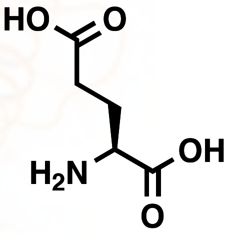

Thréonine
(Thr, T)

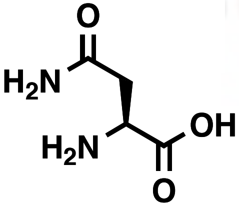

Tyrosine
(Tyr, Y)

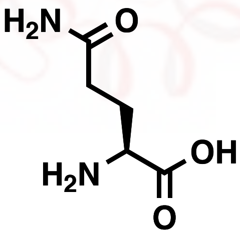

Cystéine
(Cys, C)

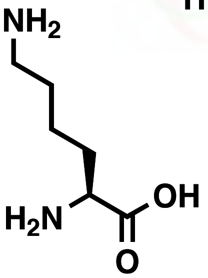

Méthionine
(Met, M)

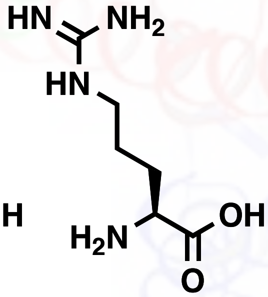

Acide aspartique
(Asp, D)

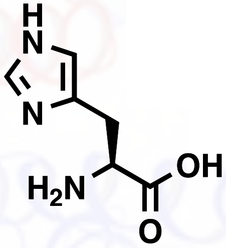

Acide glutamique
(Glu, E)

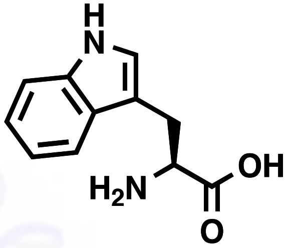

Asparagine
(Asn, N)

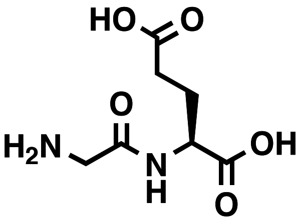

Glutamine
(Gln, Q)


Lysine
(Lys, K)


Arginine
(Arg, R)


Histidine
(His, H)

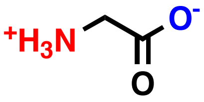

Tryptophane
(Trp, W)



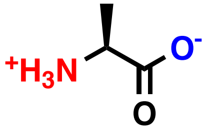
506-13

(476-81)

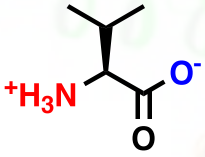
Les acides aminés (pH = 7)



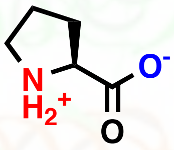
Glycine
(Gly, G)



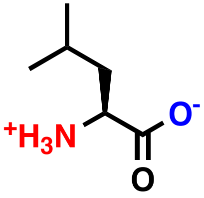
Alanine
(Ala, A)



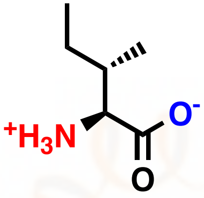
Valine
(Val, V)



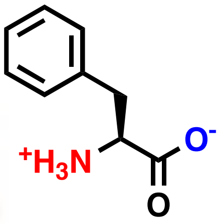
Proline
(Pro, P)



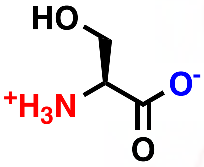
Leucine
(Leu, L)



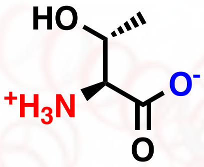
Isoleucine
(Ile, I)



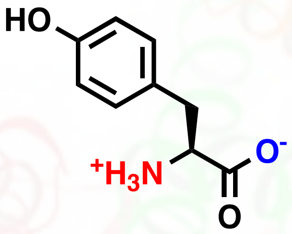
Phénylalanine
(Phe, F)



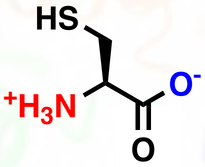
Sérine
(Ser, S)



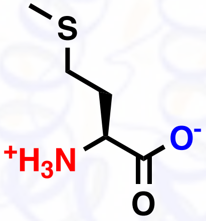
Thréonine
(Thr, T)



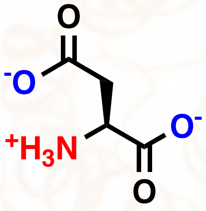
Tyrosine
(Tyr, Y)



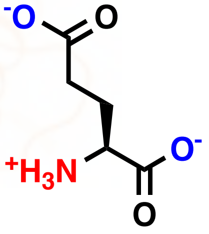
Cystéine
(Cys, C)



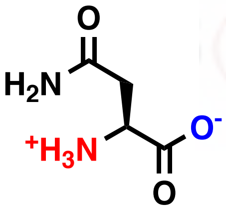
Méthionine
(Met, M)



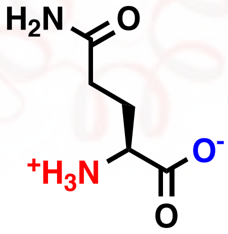
Acide aspartique
(Asp, D)



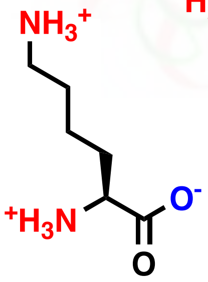
Acide glutamique
(Glu, E)



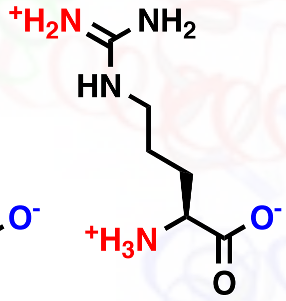
Asparagine
(Asn, N)



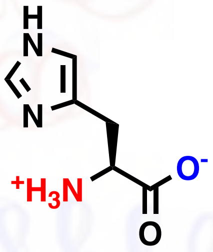
Glutamine
(Gln, Q)



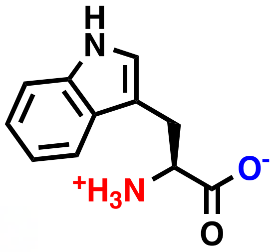
Lysine
(Lys, K)



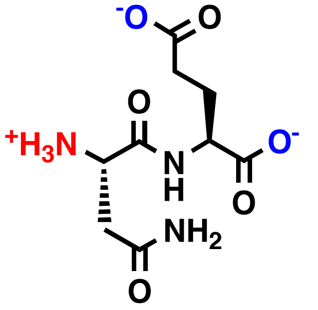
Arginine
(Arg, R)



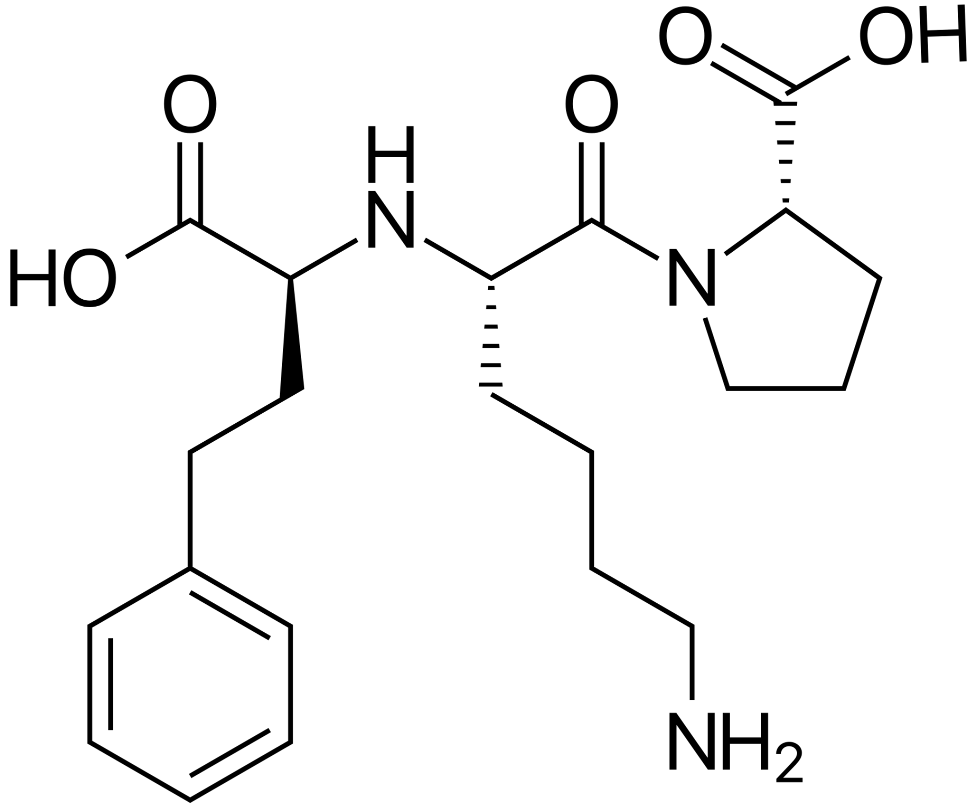
Histidine
(His, H)



Tryptophane
(Trp, W)



Lisitril (Lisinopril)



A	**-2**
B	**-1**
C	**0**
D	**+1**
E	**+2**

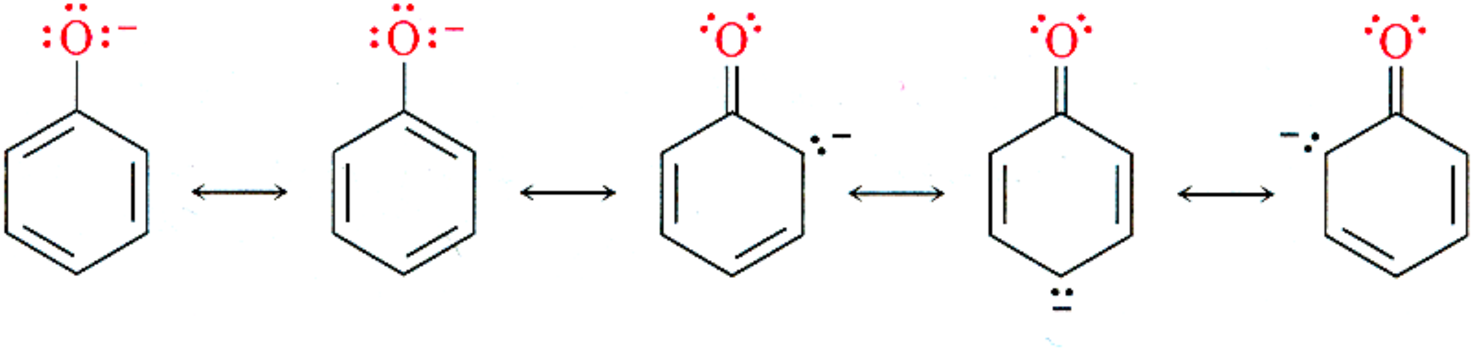
(hypertension, crises cardiaques)

Acidité et résonance

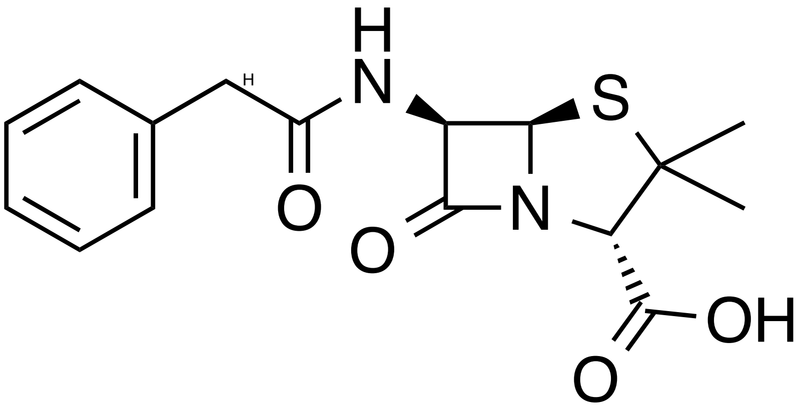
Phénol

Phénolate de sodium

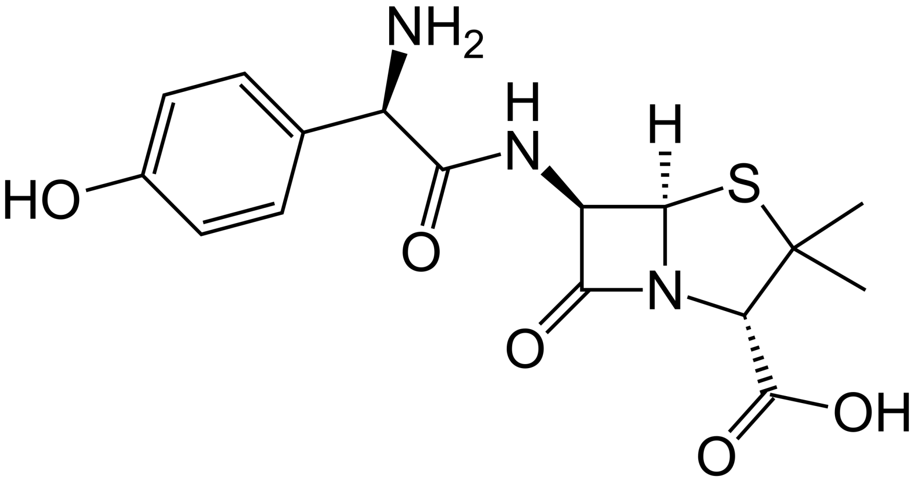
$pK_a \sim 10$



Amoxicilline

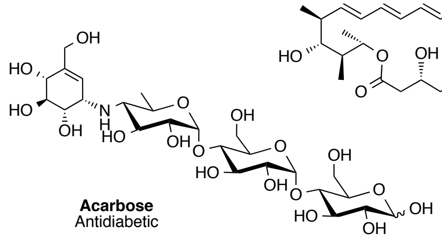


Penicillin
Antibacterial

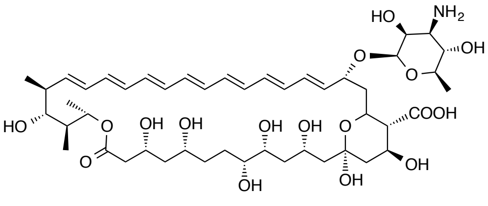


Amoxicillin

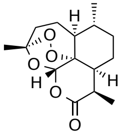
Molécules qui ont changé notre monde...



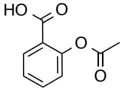
Acarbose
Antidiabetic



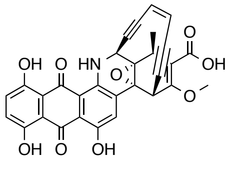
Amphotericin B
Antifungal



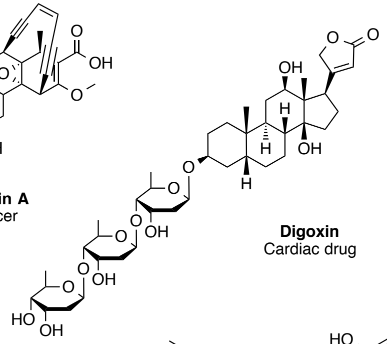
Artemisinin
Antimalarial



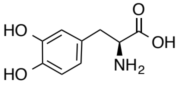
Aspirin
Analgesic



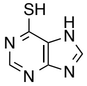
Dynemicin A
Anticancer



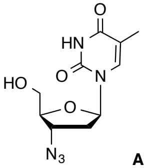
Digoxin
Cardiac drug



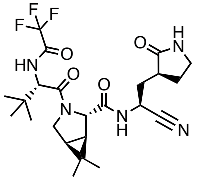
L-Dopa
Antiparkinson



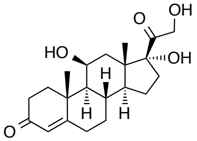
6-Mercaptopurine
Anticancer



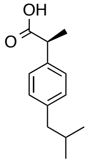
AZT
Antiviral (AIDS)



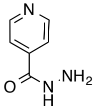
Paxlovid
Antiviral
(SARS-CoV-2)



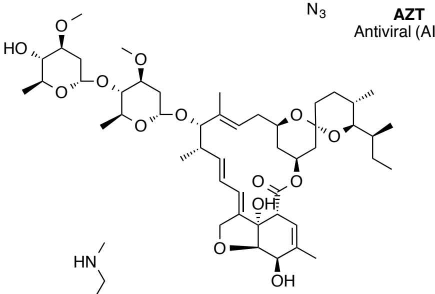
Hydrocortisone
Hormone



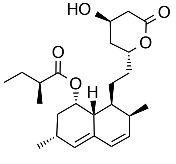
Ibuprofen
Analgesic



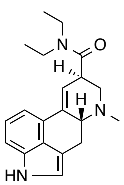
Isoniacid
Antibacterial
(Tuberculosis)



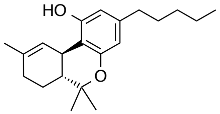
Ivermectin
Antiparasitic
(Onchocerciasis)



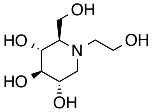
Lovastatin
Anti-cholesterol



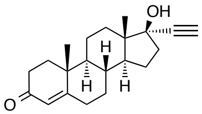
LSD
Psychedelic



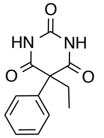
Marijuana
Antiemetic



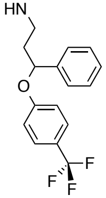
Miglitol
Antidiabetic



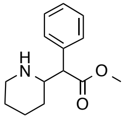
Norethindrone
Hormone
(oral contraceptive)



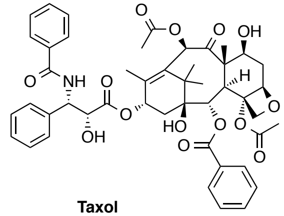
Phenobarbital
Anticonvulsant



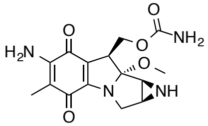
Prozac
Antidepressant



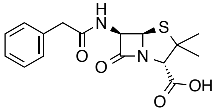
Ritalin
Stimulant



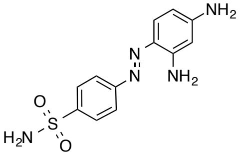
Taxol
Anticancer



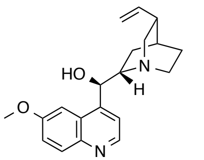
Mitomycin C
Anticancer



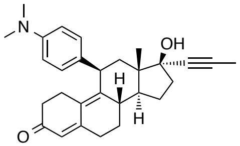
Penicillin
Antibacterial



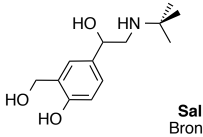
Prontosil
Antibacterial



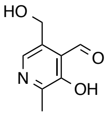
Quinine
Antimalarial



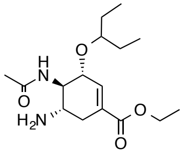
RU-486
Hormone
("abortion pill")



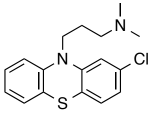
Salbutamol
Bronchodilator
(Asthma)



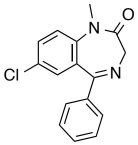
Vitamin B$_6$
Nutrient



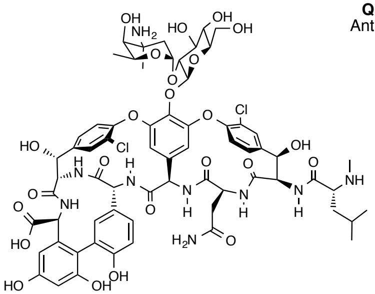
Tamiflu
Antiviral



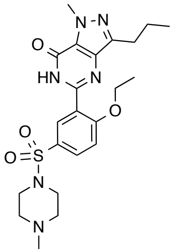
Thorazine
Antipsychotic
(Schizophrenia)



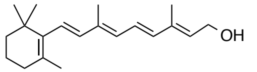
Valium
Tranquilizer



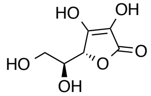
Vancomycin
Antibacterial



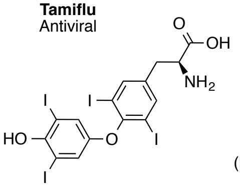
Viagra
Vasodilator



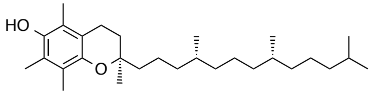
Vitamin A
Nutrient



Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)

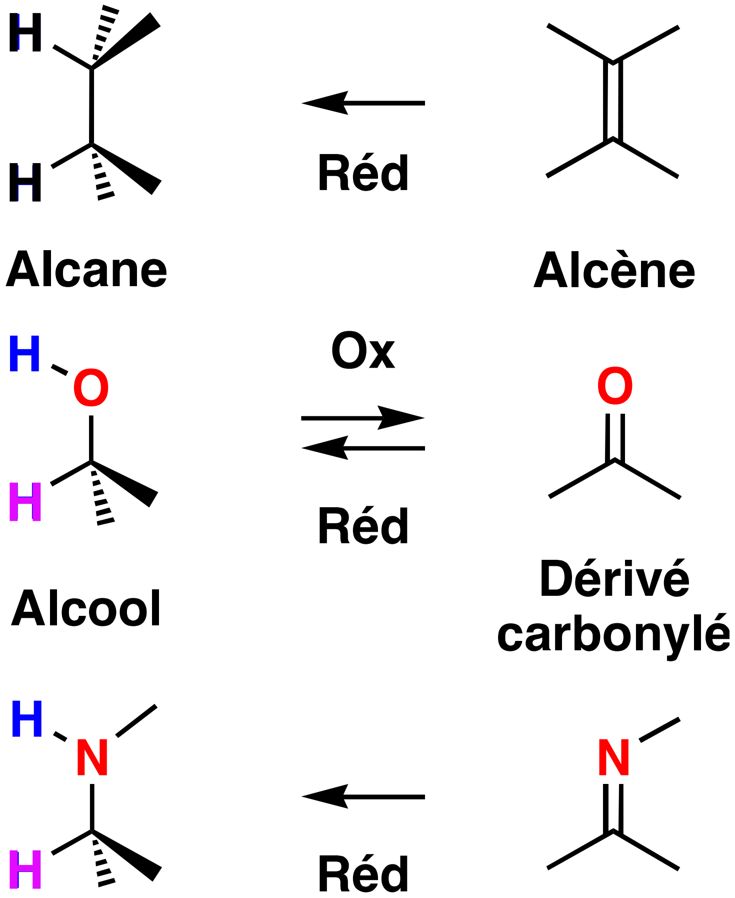


Vitamin E
Nutrient

254-5, 259-60, 484-5

(259-61, 264-5, 458)

Oxydation - réduction



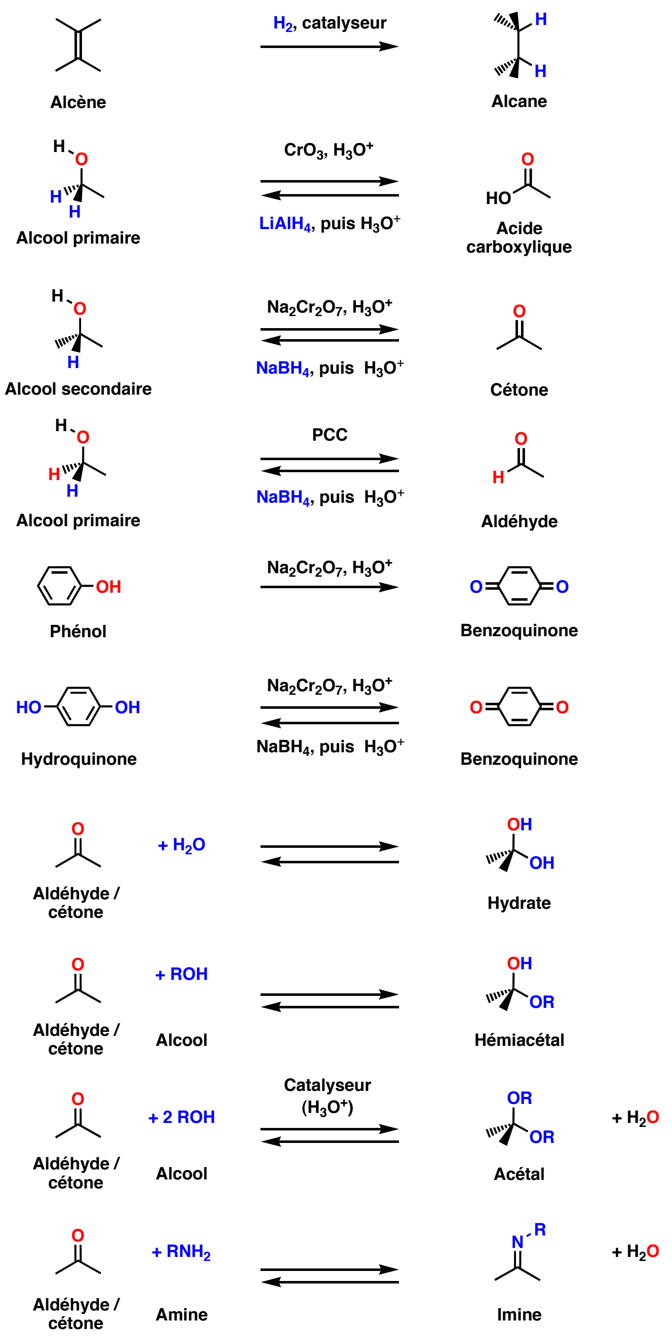
Alcane ← Réd — Alcène

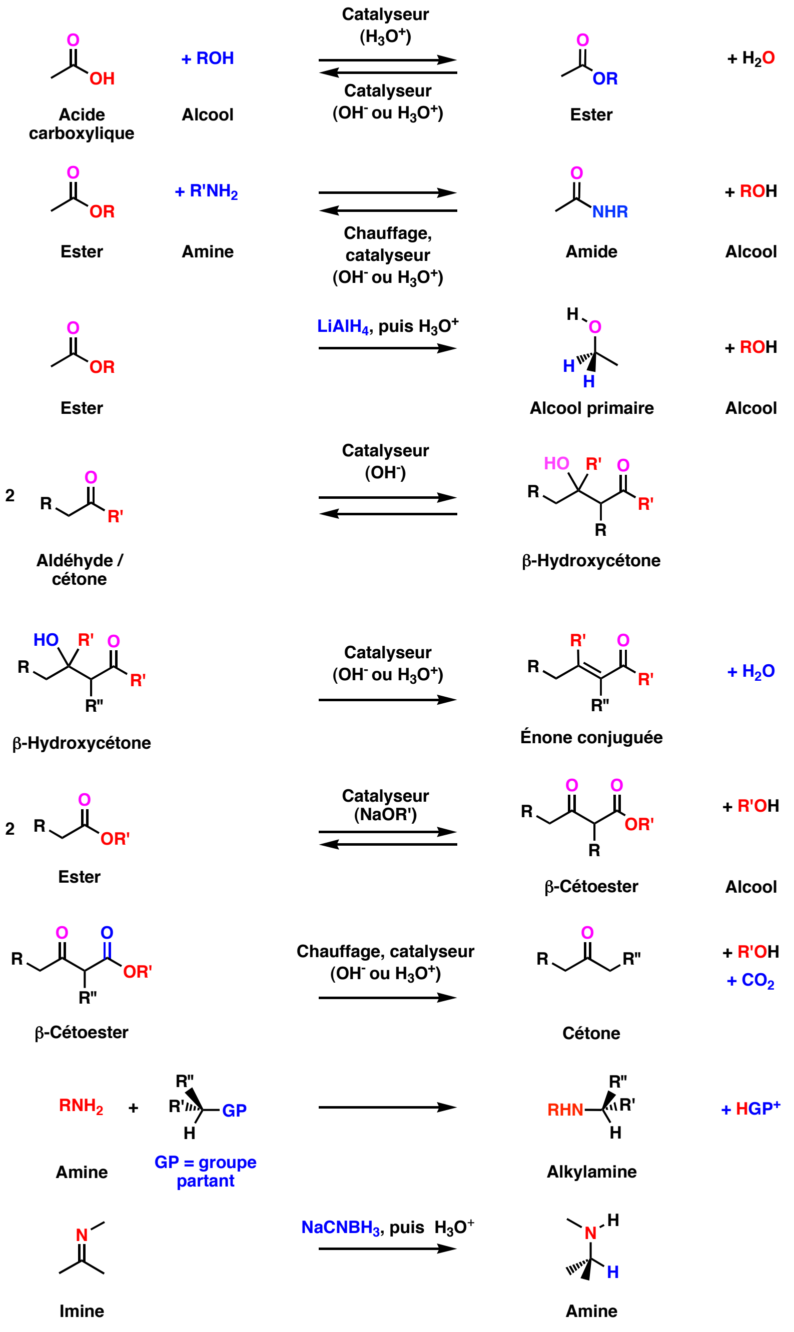
Alcool ⇄ Ox / Réd — Dérivé carbonylé

Amine ← Réd — Imine

Oxydation : Addition d'oxygène à une molécule ou retrait d'hydrogène (583)

Résumé des réactions





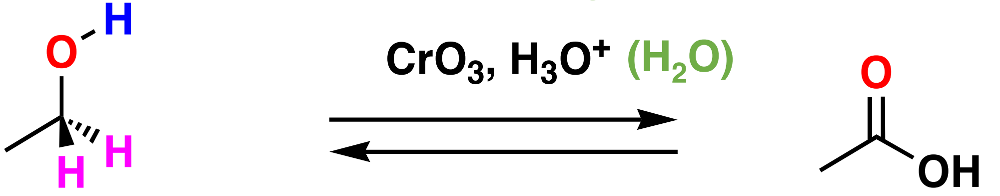
Réactif(s)	Conditions	Produit(s)	2007	2003
Alcène	H_2, catalyseur (→)	Alcane	4.6	4.6
Alcool primaire	CrO_3, H_3O^+ (→)	Acide carboxylique	8.5	8.7
	$LiAlH_4$, puis H_3O^+ (←)		8.4	8.5
Alcool secondaire	$Na_2Cr_2O_7$, H_3O^+ (→)	Cétone	8.5	8.7
	$NaBH_4$, puis H_3O^+ (←)		8.4	8.5
Alcool primaire	PCC (→)	Aldéhyde	8.5	8.7
	$NaBH_4$, puis H_3O^+ (←)		8.4	8.5
Phénol	$Na_2Cr_2O_7$, H_3O^+ (→)	Benzoquinone	8.6	8.8
Hydroquinone	$Na_2Cr_2O_7$, H_3O^+ (→) $NaBH_4$, puis H_3O^+ (←)	Benzoquinone	8.6	8.8
Aldéhyde / cétone + H_2O	⇌	Hydrate	9.7	9.7
Aldéhyde / cétone + ROH (Alcool)	⇌	Hémiacétal	9.8 9.9 14.5 14.6	9.8 14.5 14.6
Aldéhyde / cétone + 2 ROH (Alcool)	Catalyseur (H_3O^+) ⇌	Acétal + H_2O	9.8 9.9 14.7	9.8 14.8
Aldéhyde / cétone + RNH_2 (Amine)	⇌	Imine + H_2O	9.10	9.9
Acide carboxylique + ROH (Alcool)	Catalyseur (H_3O^+) (→)	Ester + H_2O	10.8	10.6
	Catalyseur (OH^- ou H_3O^+) (←)		10.11	10.9
Ester + $R'NH_2$ (Amine)	⇌ Chauffage, catalyseur (OH^- ou H_3O^+)	Amide + ROH (Alcool)	16.13 10.10	10.9 10.10
Ester	$LiAlH_4$, puis H_3O^+ (→)	Alcool primaire + ROH (Alcool)	10.11 8.4	10.9 8.5
2 Aldéhyde / cétone	Catalyseur (OH^-) ⇌	β-Hydroxycétone	11.9	11.8
β-Hydroxycétone	Catalyseur (OH^- ou H_3O^+) (→)	Énone conjuguée + H_2O	11.10	11.9
2 Ester	Catalyseur (NaOR') ⇌	β-Cétoester + R'OH (Alcool)	11.11	11.10
β-Cétoester	Chauffage, catalyseur (OH^- ou H_3O^+) (→)	Cétone + R'OH + CO_2	17.4	17.4
RNH_2 (Amine) + R''R'CH–GP (GP = groupe partant)	→	Alkylamine + HGP^+	12.4 7.5	12.4 7.7 8.11
Imine	$NaCNBH_3$, puis H_3O^+ (→)	Amine	9.10	9.11

254-5, 259-60, 484-5

(259-61, 264-5, 458)

Oxydation - réduction

Réactif Catalyseur (Solvant)



CrO_3, H_3O^+ (H_2O)

$LiAlH_4$, puis H_3O^+

éther Solvant

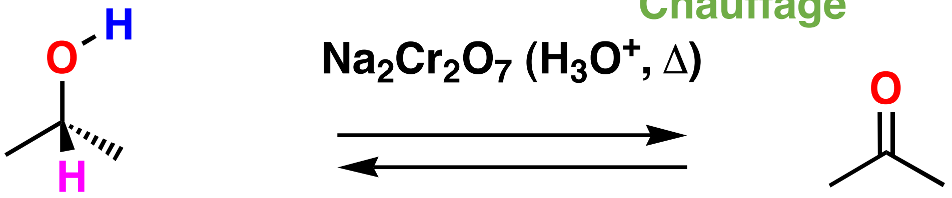
Alcool primaire

Acide carboxylique

Substrat
(Réactant principale)

Produit

Chauffage

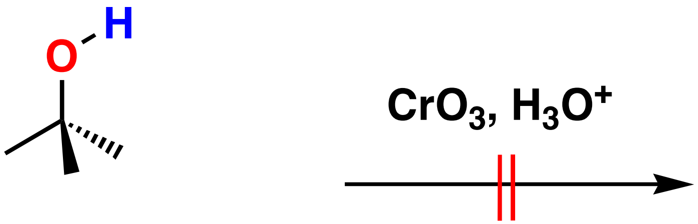


$Na_2Cr_2O_7$ (H_3O^+, Δ)

$NaBH_4$, puis H_3O^+

Alcool secondaire

Cétone



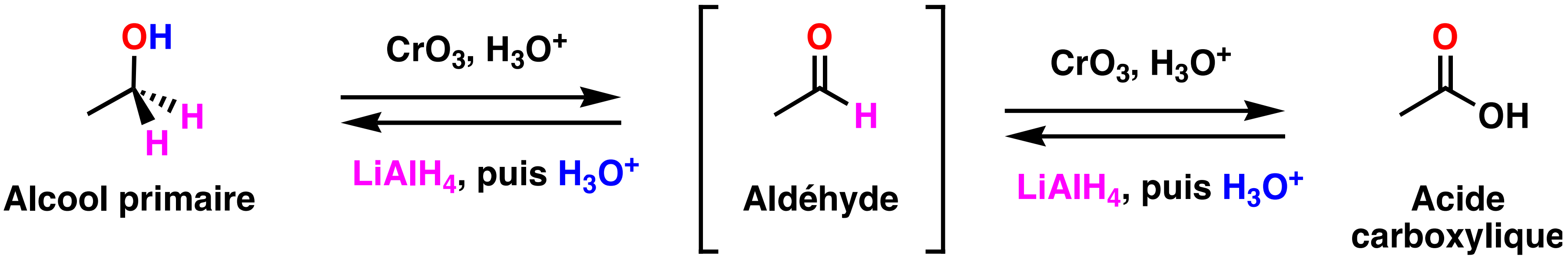
CrO_3, H_3O^+

Alcool tertiaire

259, 285

(264, 286)

Oxydation des alcools - aldéhydes



Alcool primaire

CrO_3, H_3O^+

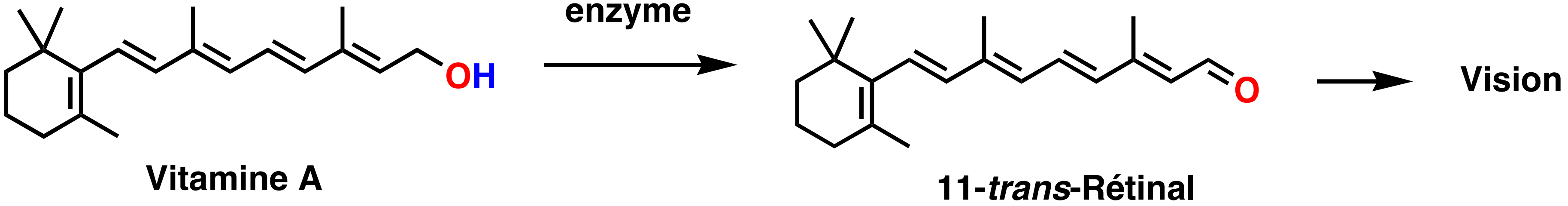
$LiAlH_4$, puis H_3O^+

Aldéhyde

CrO_3, H_3O^+

$LiAlH_4$, puis H_3O^+

Acide carboxylique

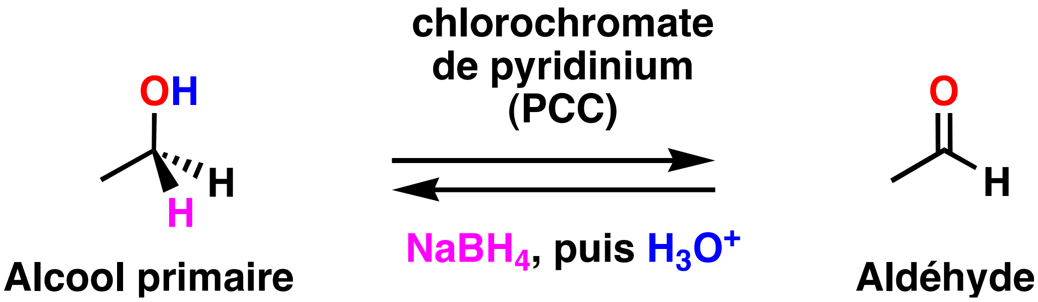


Vitamine A

enzyme

11-*trans*-Rétinal

Vision



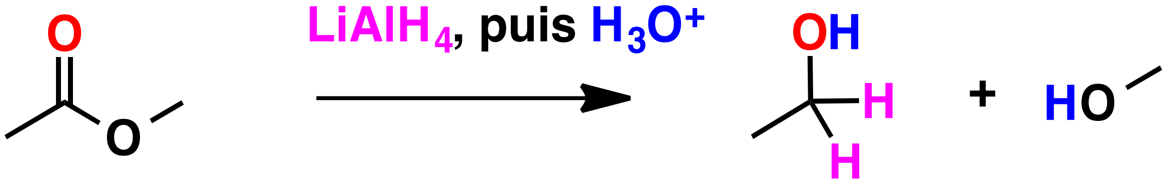
Alcool primaire

chlorochromate de pyridinium (PCC)

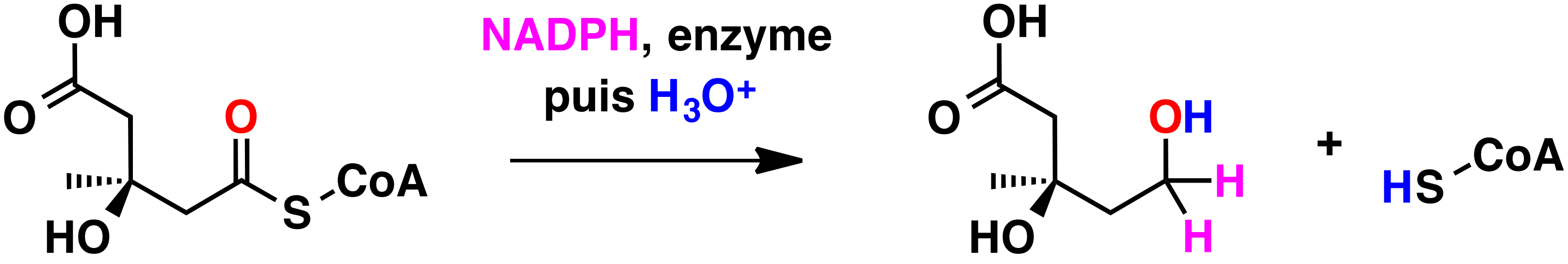
$NaBH_4$, puis H_3O^+

Aldéhyde

Réduction des esters



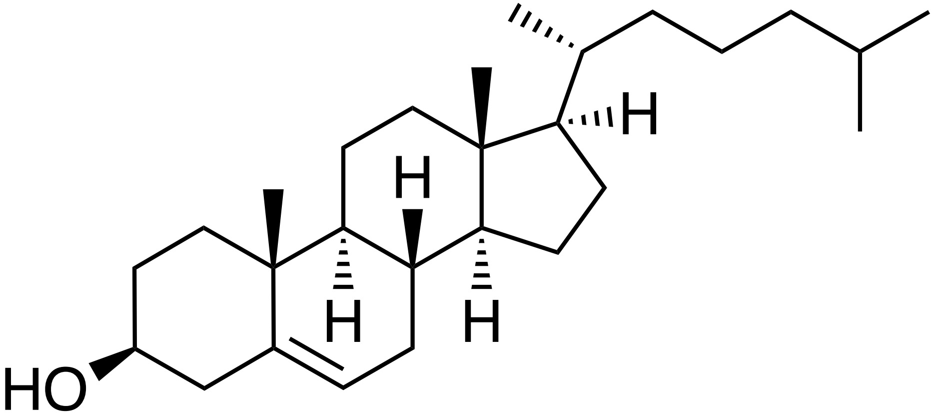
Thioesters, sélectivité



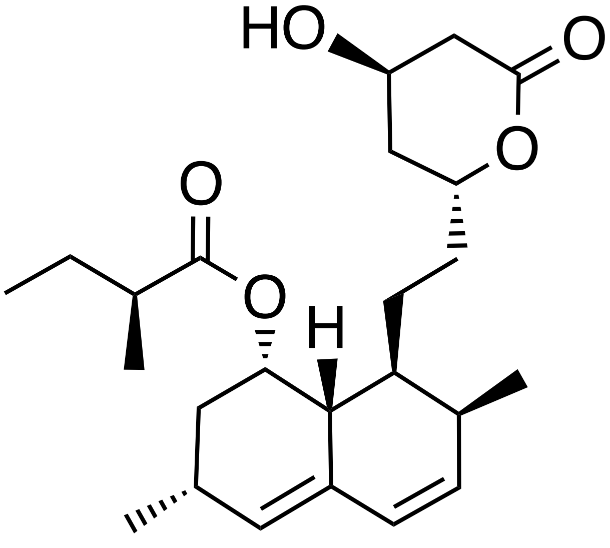
HMG-CoA

Mévalonate

La biosynthèse des stéroïdes
Médicaments anti-cholestérol

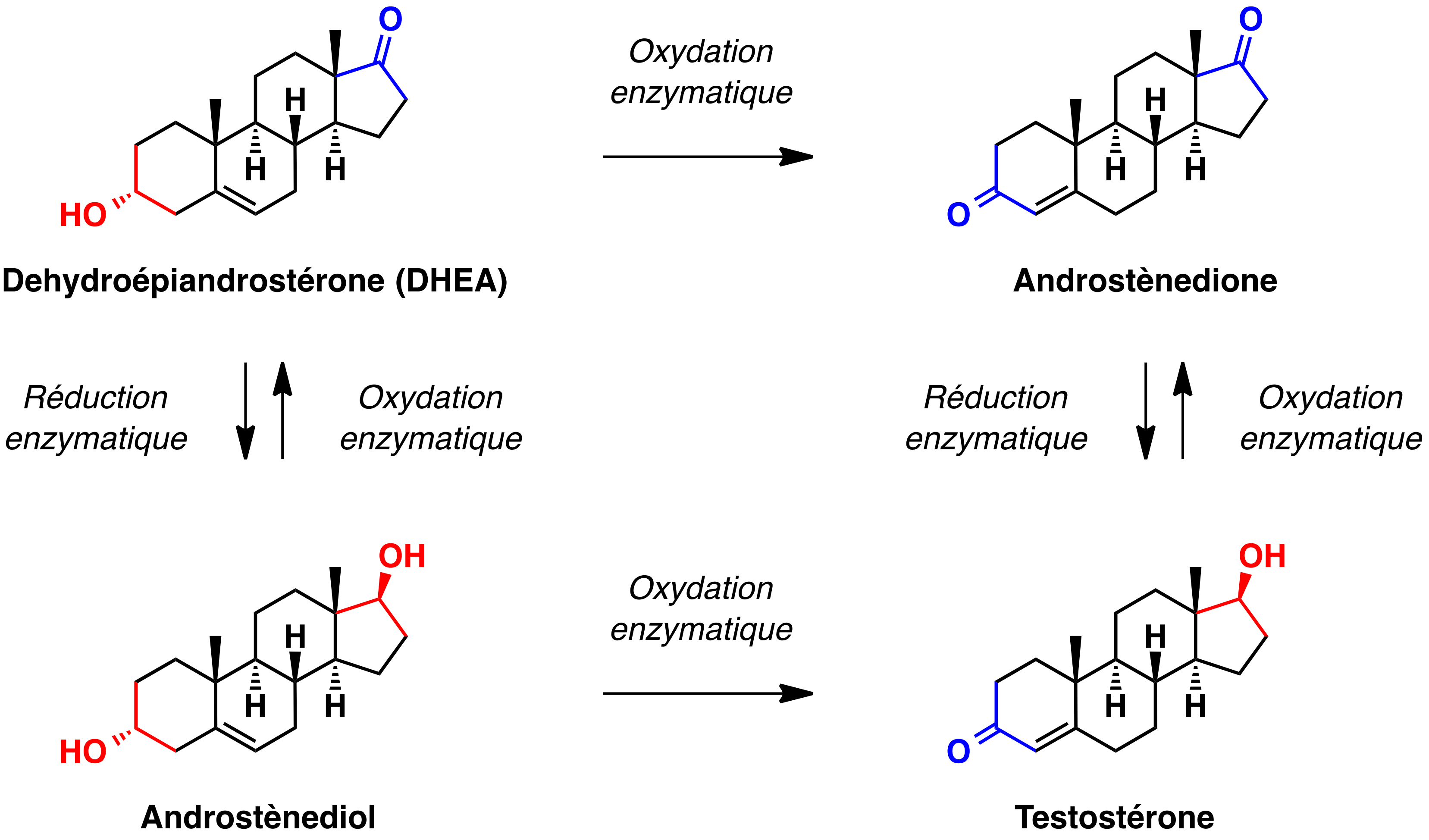


Cholestérol



Lovastatin

Les androgènes - stéroïdes sexuels



Dehydroépiandrostérone (DHEA)

Oxydation enzymatique

Androstènedione

Réduction enzymatique

Oxydation enzymatique

Réduction enzymatique

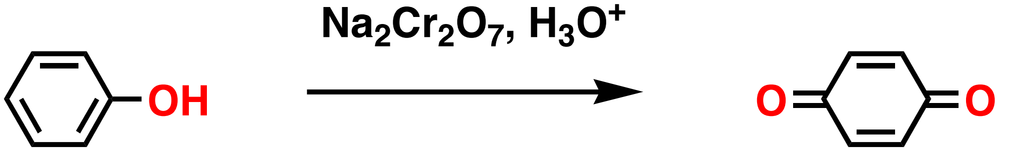
Oxydation enzymatique

Androstènediol

Oxydation enzymatique

Testostérone

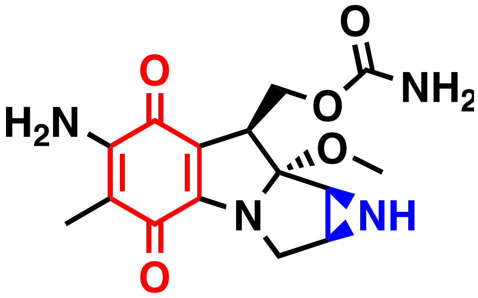
Oxydation des phénols - quinones



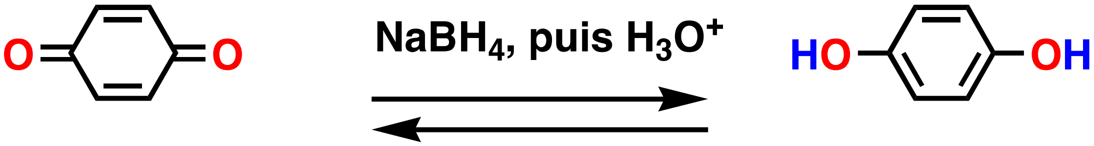
$Na_2Cr_2O_7$, H_3O^+

Phénol

Benzoquinone



Mitomycin C
(anticancéreux)

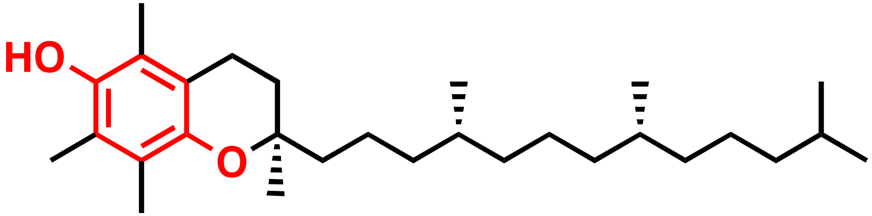


$NaBH_4$, puis H_3O^+

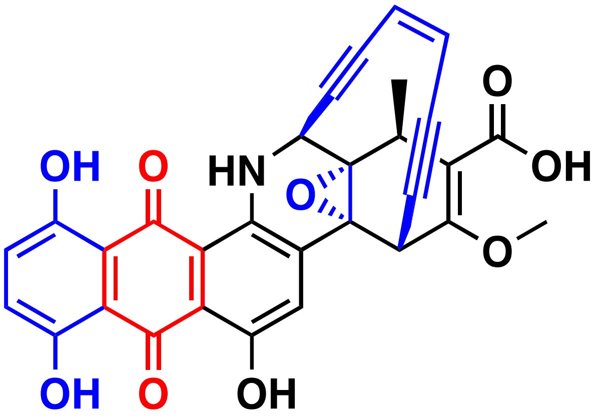
$Na_2Cr_2O_7$, H_3O^+

Benzoquinone

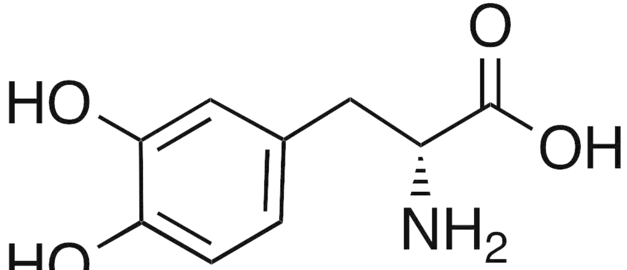
Hydroquinone



α-tocopherol (vitamin E)



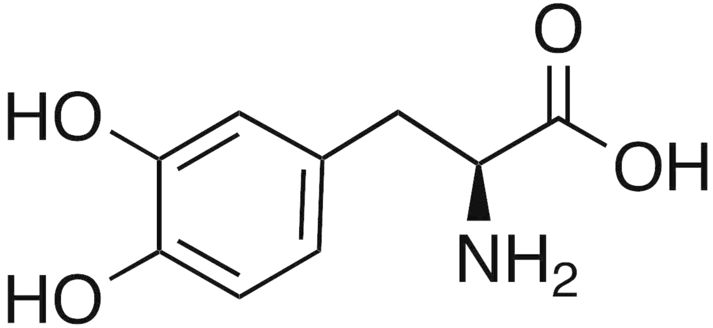
Dynémicine A
(anticancéreux)



D-Dopa
pas d'effet biologique (208)

1967
Hoffman-La Roche
Synthesis: William
Knowles, Monsanto,
prix Nobel 2001

N THE BEGINNING L-Dopa was first isolated rom *Vicia faba* seedlings. The aromatic amino acid is ommonly found in plants and animals.

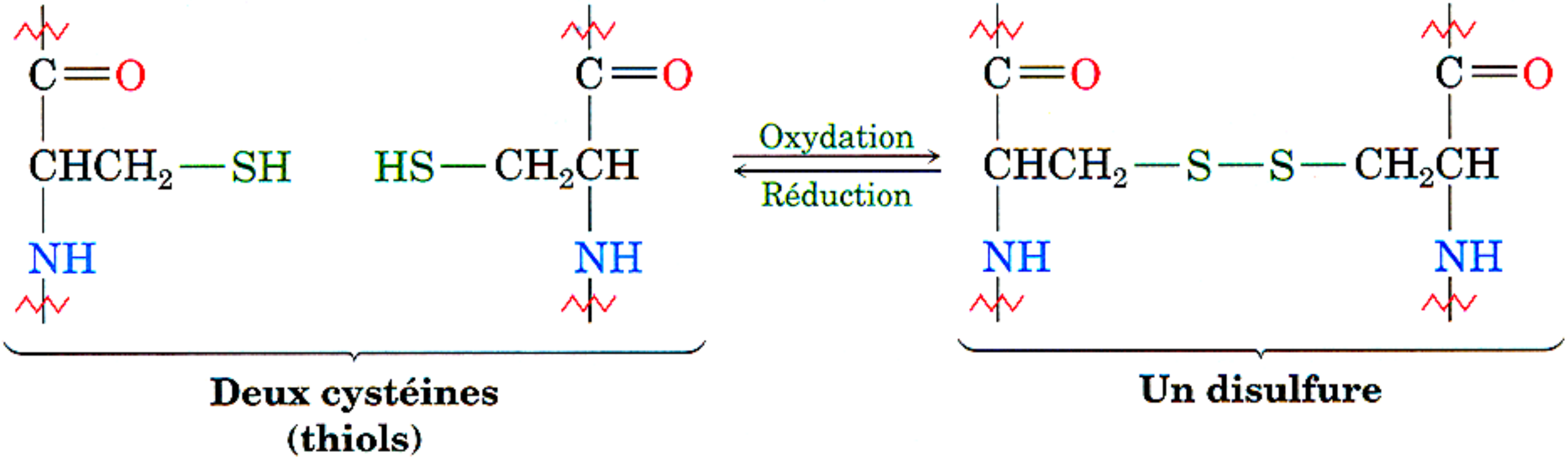


L-Dopa
(Levodopa)
Antiparkinson

520, 269

(271-2, 484)

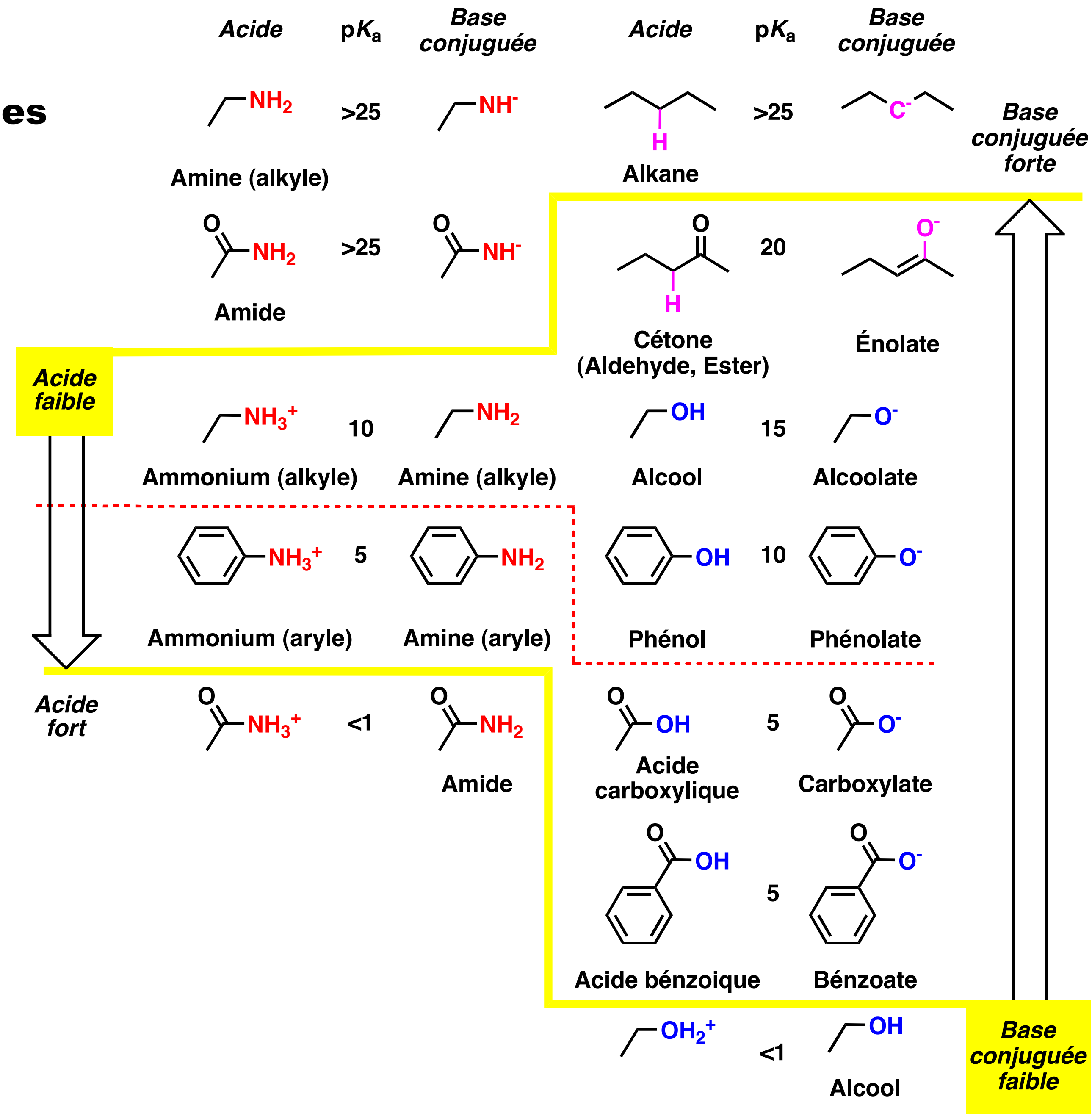
Oxydation des thiols - disulfures



$pK_a \sim 8$

Oxydation : Addition d’oxygène à une molécule ou retrait d’hydrogène (583)

Résumé acides et bases



Acide	pK_a	*Base conjuguée*
Amine (alkyle)	>25	
Amide	>25	
Ammonium (alkyle)	10	Amine (alkyle)
Ammonium (aryle)	5	Amine (aryle)
	<1	Amide

Acide	pK_a	*Base conjuguée*
Alkane	>25	
Cétone (Aldehyde, Ester)	20	Énolate
Alcool	15	Alcoolate
Phénol	10	Phénolate
Acide carboxylique	5	Carboxylate
Acide bénzoique	5	Bénzoate
	<1	Alcool

Base conjuguée forte

Acide faible

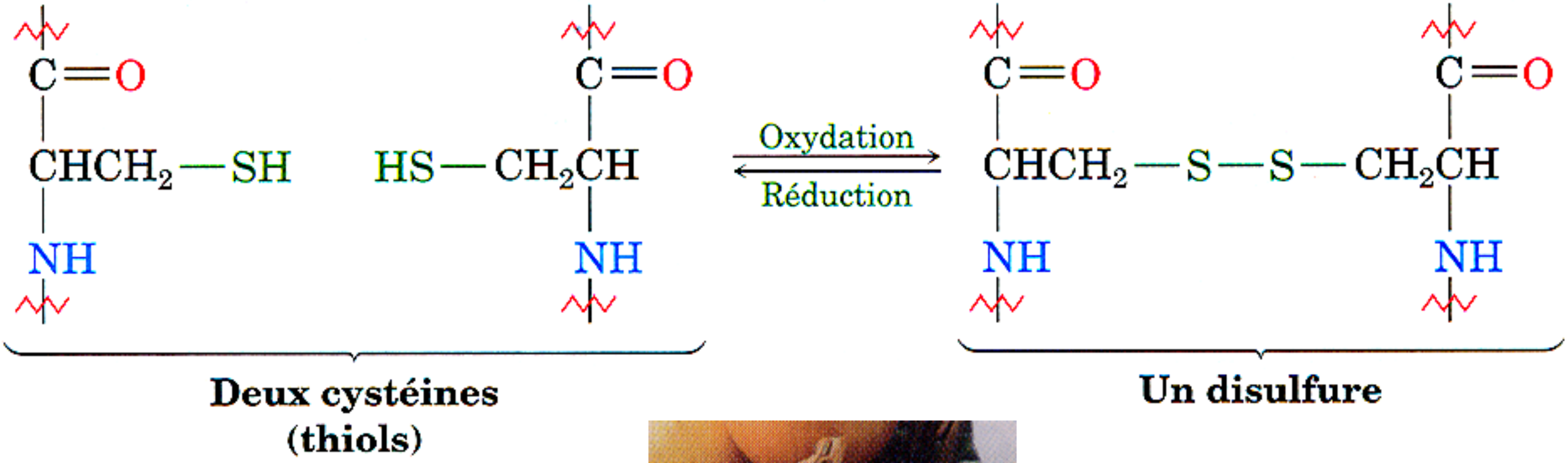
Acide fort

Base conjuguée faible

520, 269

(271-2, 484)

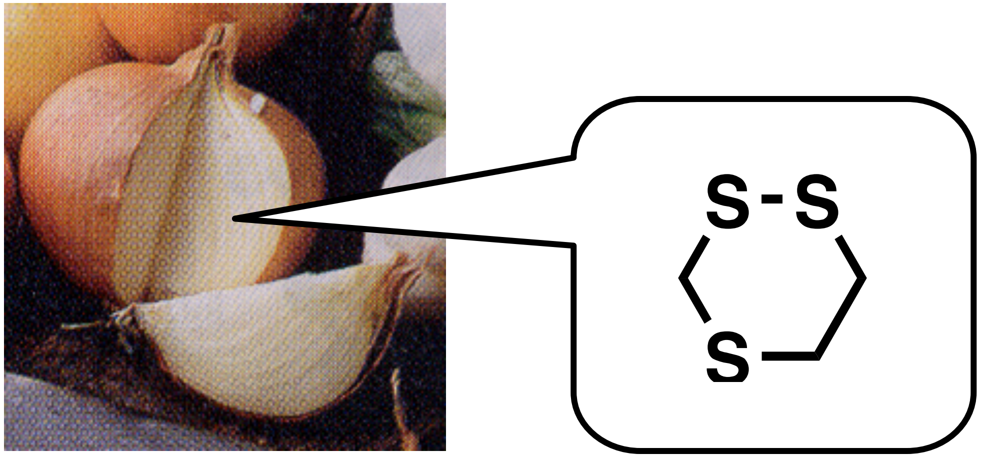
Oxydation des thiols - disulfures



p*K*$_a$ ~ 8

EN = 2.5

S–H = 1.34 Å

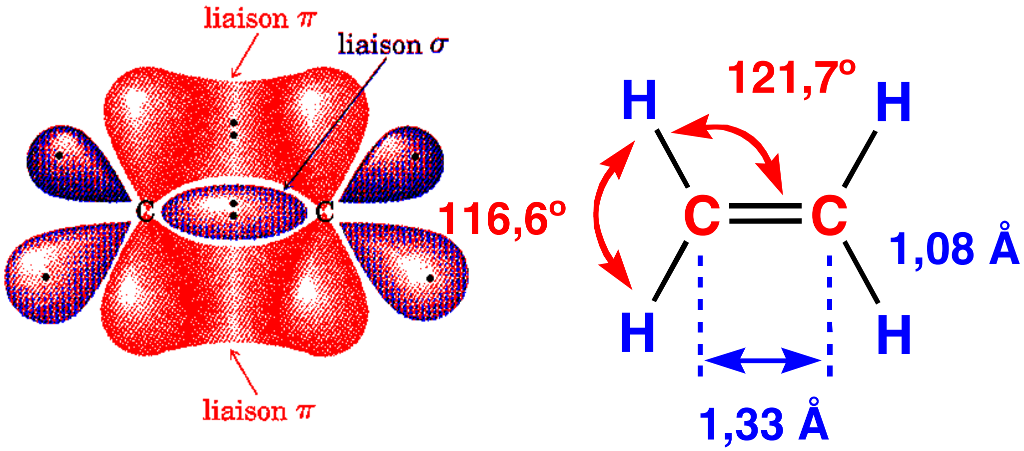


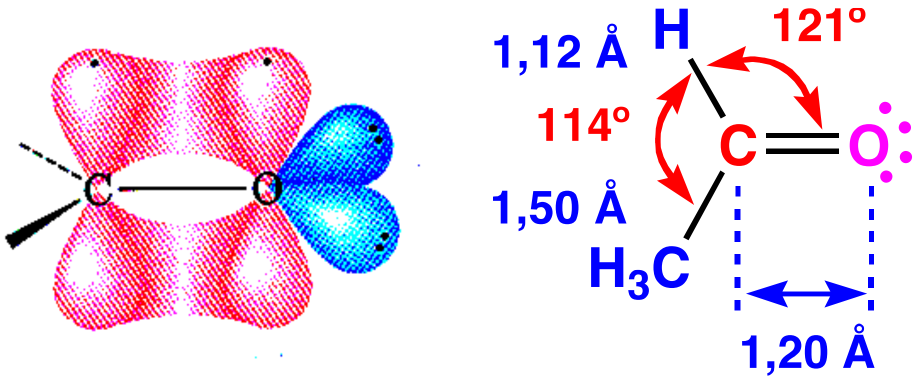
Oxydation : Addition d’oxygène à une molécule ou retrait d’hydrogène (583)

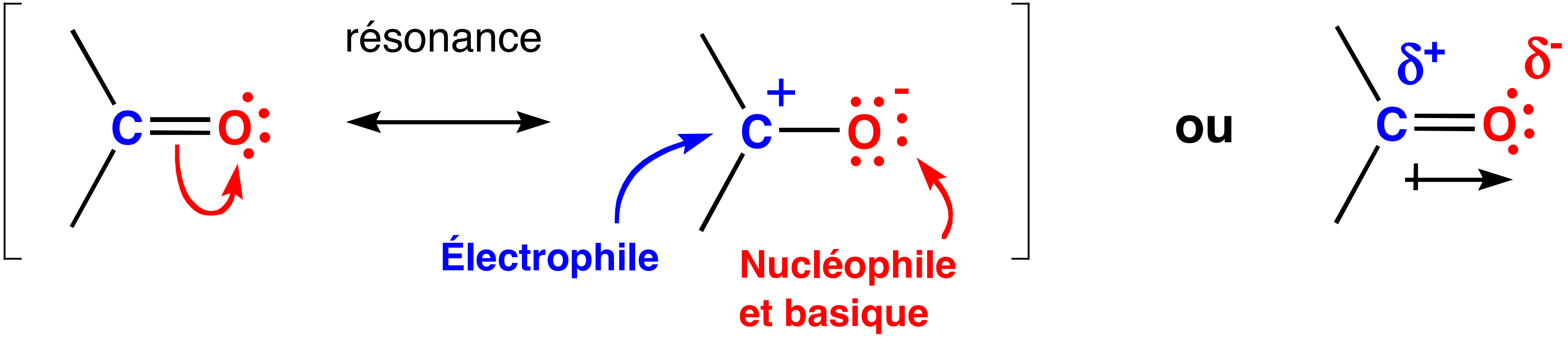
Résumé 4 (Alcools - phénols -)

- **liaison hydrogène :**
    - **donneur / accepteur - solubilité - points d'ébullition**
- **acides / bases :**
    - **donneur / accepteur H^+ (Brønsted) - conjugué - pK_a**
    - **acidité - résonance (alcool - phénol)**
- **oxydation / réduction :**
    - **alcool primaire : acide carboxylique**
        - **aldéhyde (PCC, rétinal) - ester, thioester (anti-cholestérol)**
    - **alcool secondaire : cétone (stéroïdes) - alcool tertiaire : -**
    - **phénol : quinone - hydroquinone - thiol : pK_a (antiviraux) - disulfure**

Le groupe carbonyle

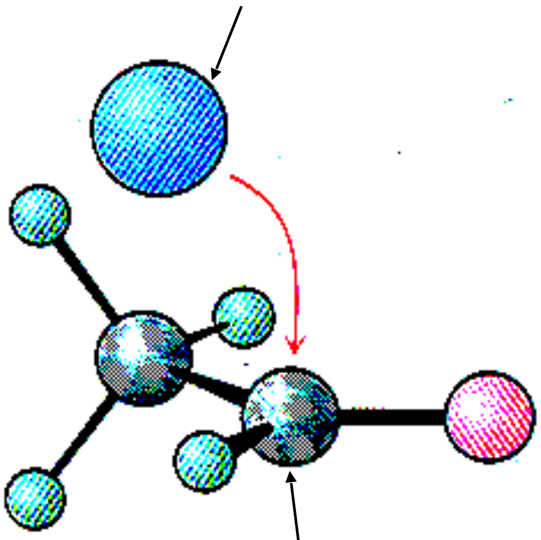


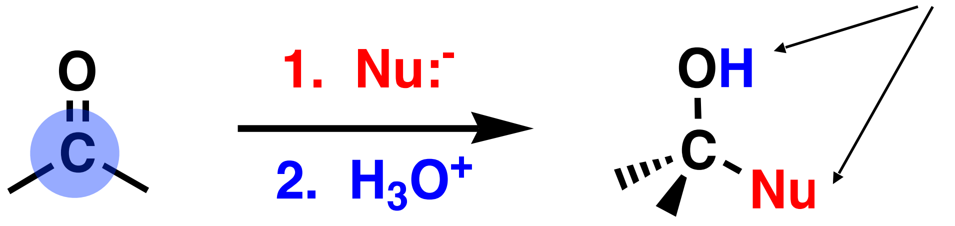




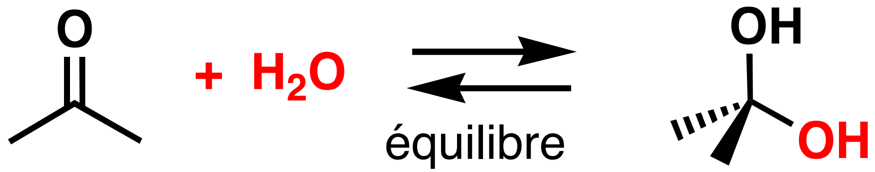
Addition nucléophile

288-293
(288-9)





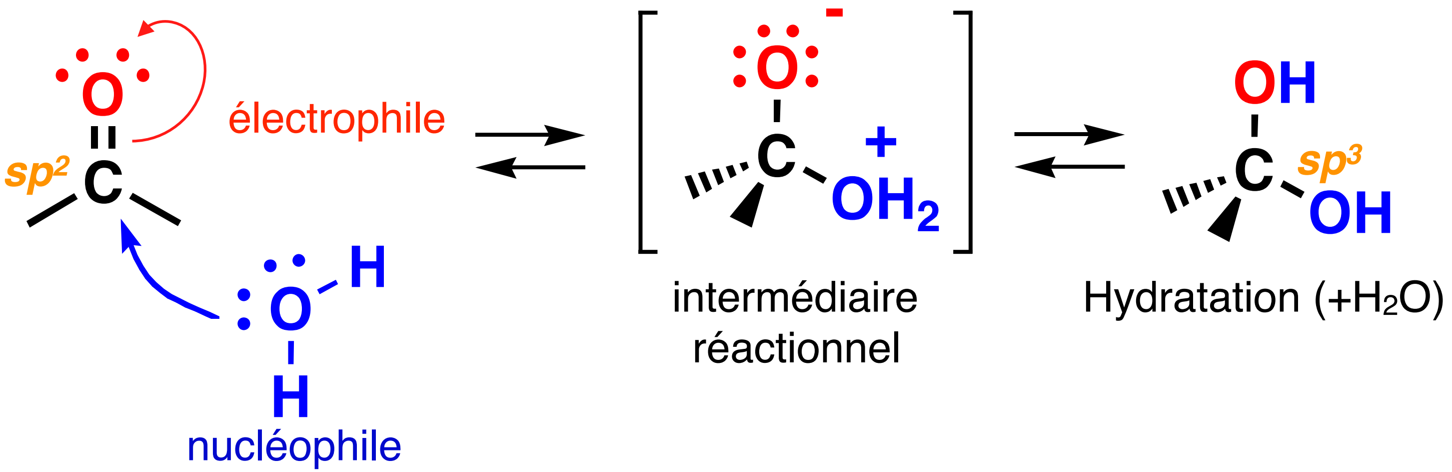
Hydratation



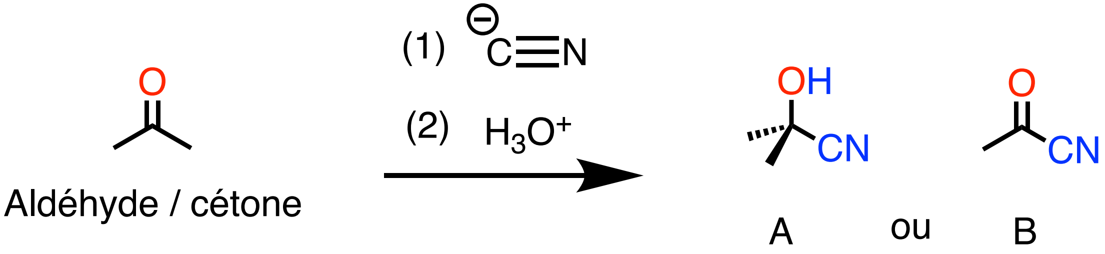
Addition nucléophile

288-293, 95-8

(290, 97-101)



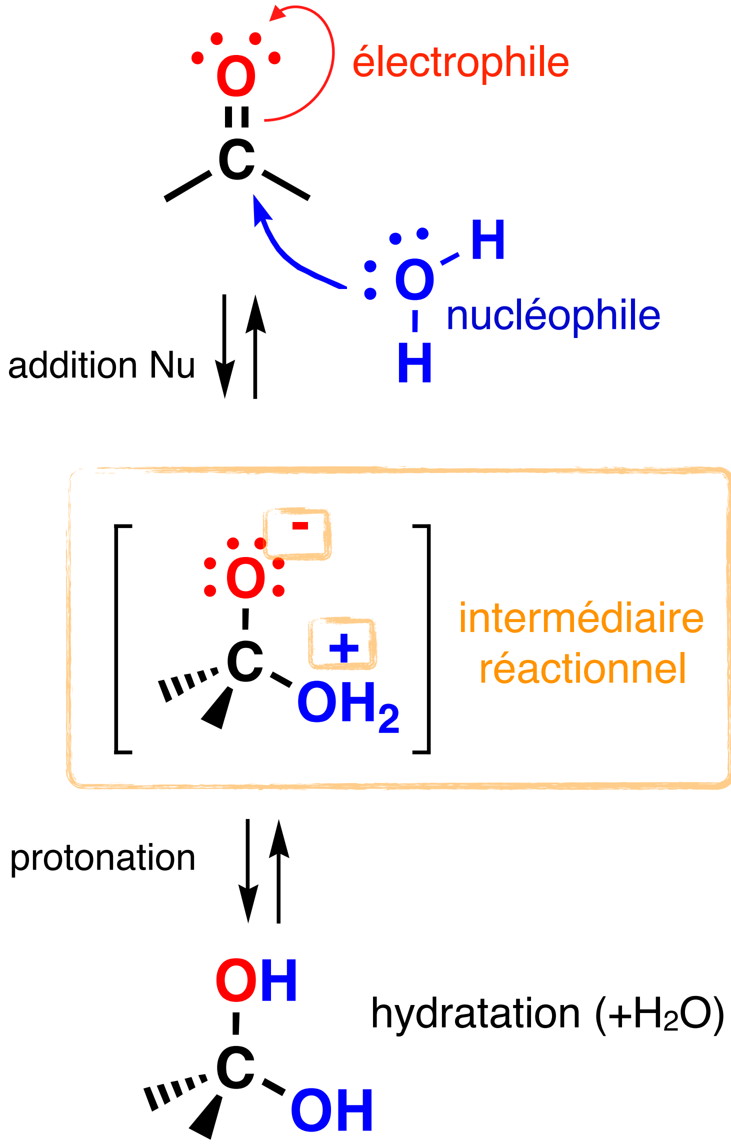
Quel produit obtiendrez vous lors de la réaction de l’ion cyanure avec l’acétone suivit d’une protonation de l’intermédiaire?

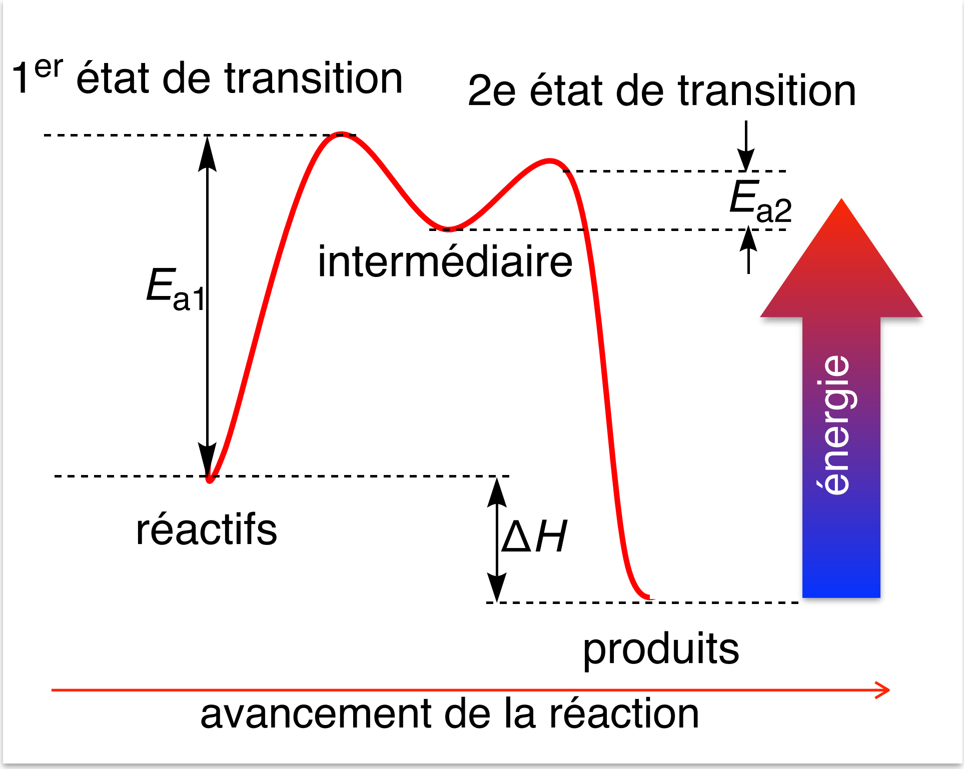


Addition nucléophile

288-293, 95-8

(290, 97-101)





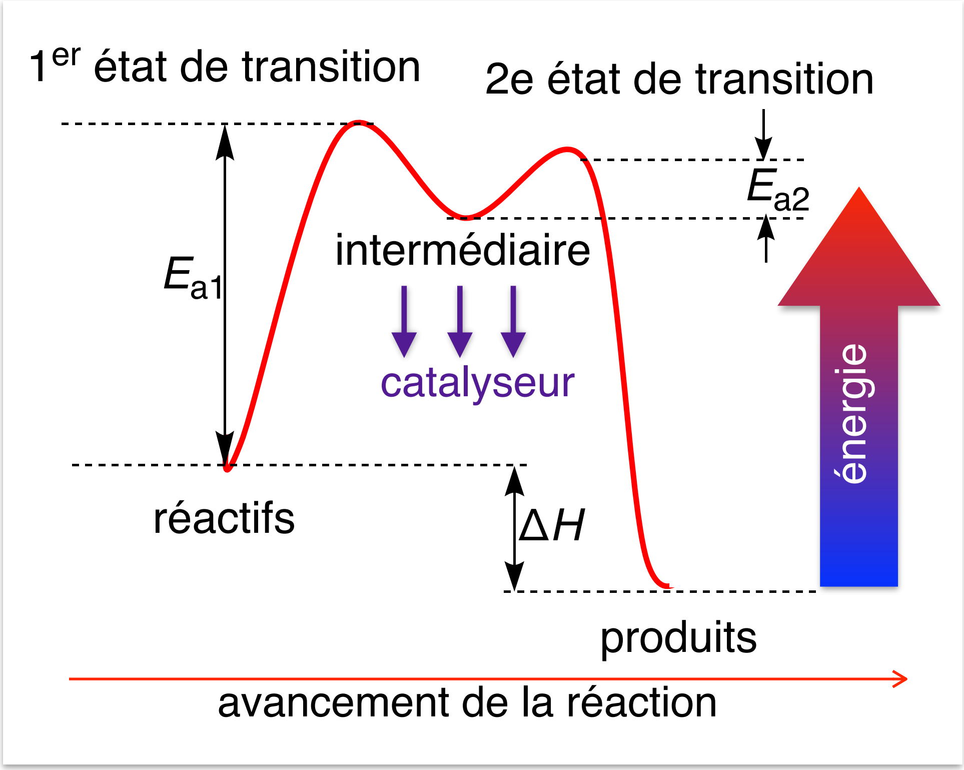
Quelques énergies

	kJ / mol		
E_a (température ambiante)	80	(99)	96
briser liaison C-C	380	(14)	13
Basculement cyclohexane	45	(65)	63
Rotation liaison C-C	12	(54)	54
Liaison hydrogène	20-40	(255)	

Catalyseur

288-293, 95-98

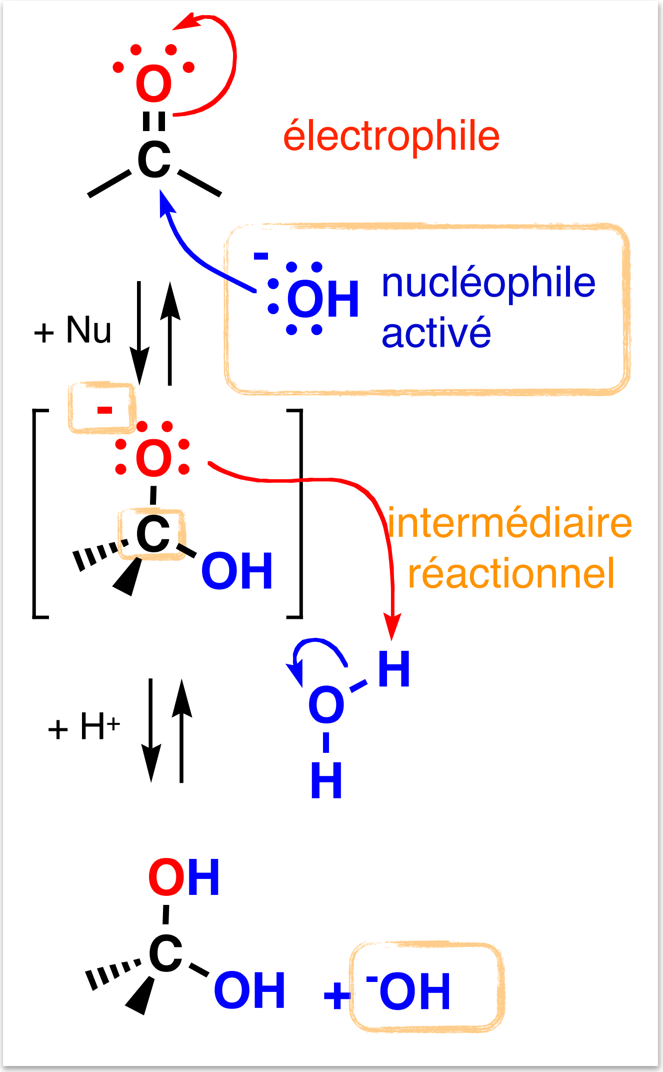
(290, 97-101)

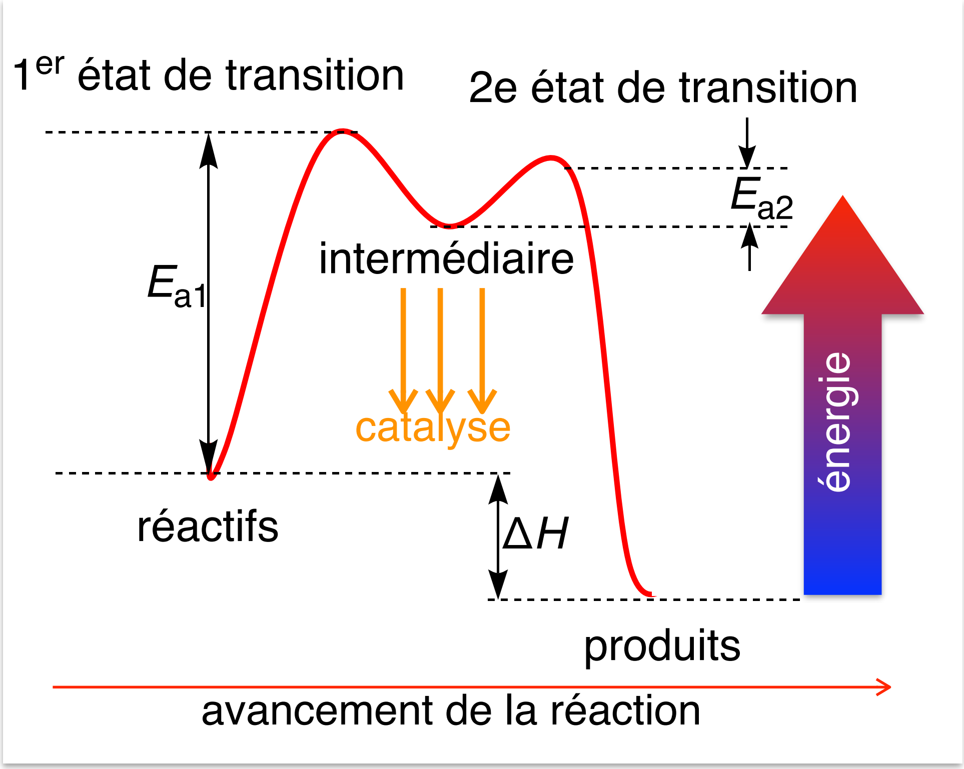


Catalyse basique

288-293, 95-98

(290, 97-101)

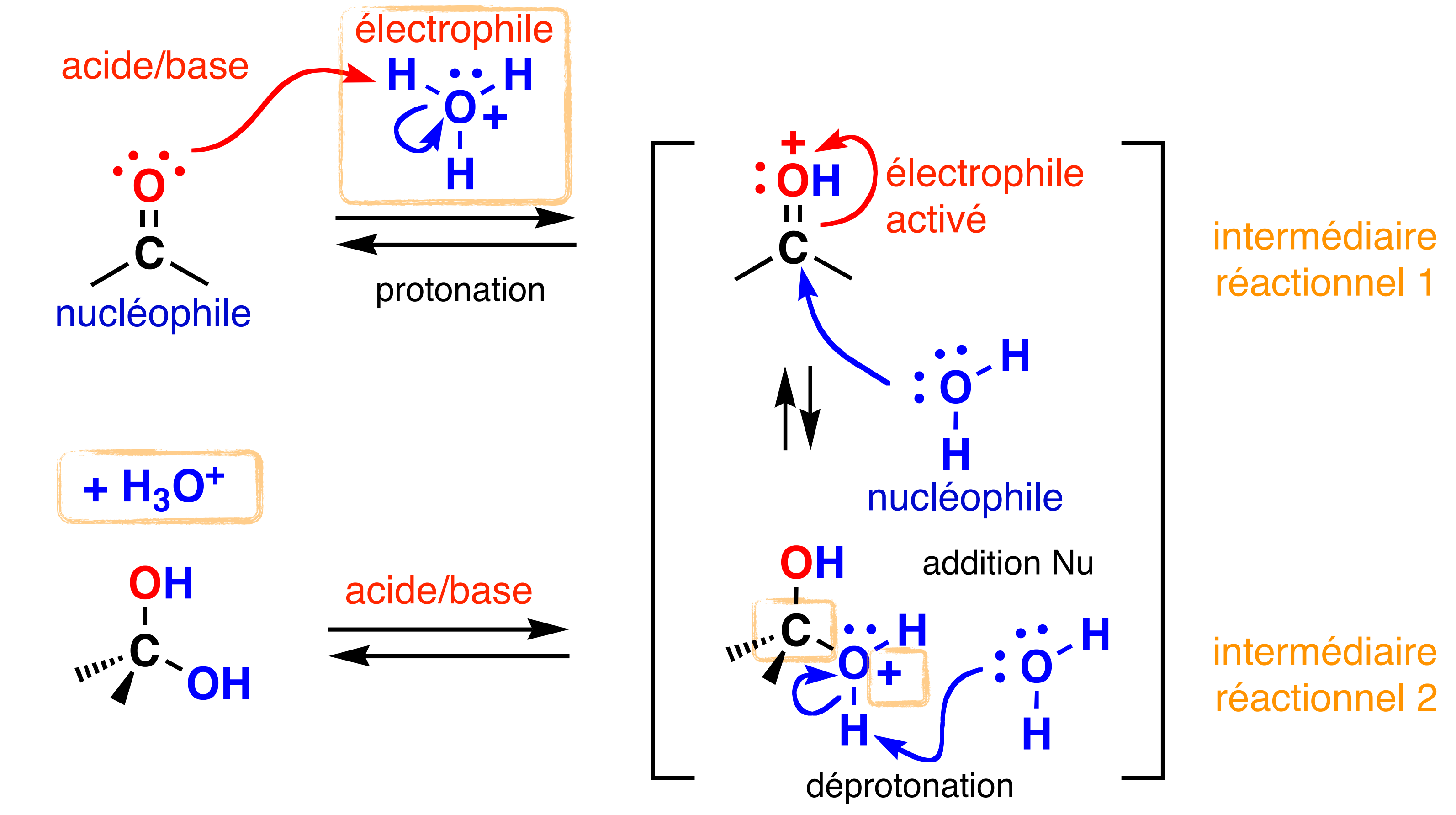




Catalyse acide

288-293, 95-98

(292)



Quelles affirmations sont exacts?

A. L’addition d’un nucléophile sur une cétone ou aldéhyde transforme le C sp^2 en C sp^3.

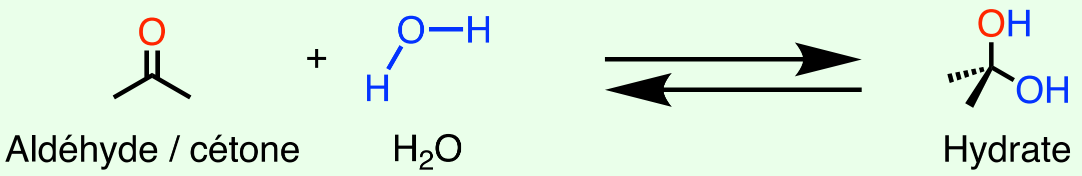
B. L’addition nucléophile sur un groupe cétone ou aldéhyde est toujours suivit d’une étape de protonation.

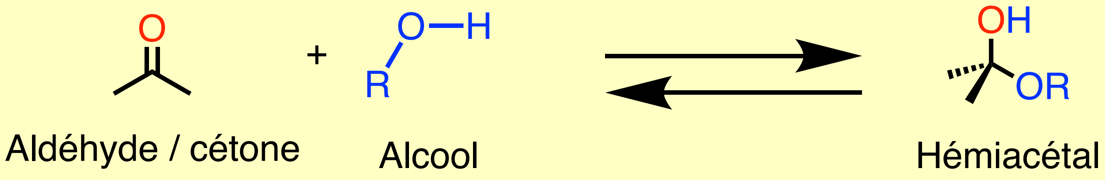
C. Une addition nucléophile peut être catalysée par un acide.

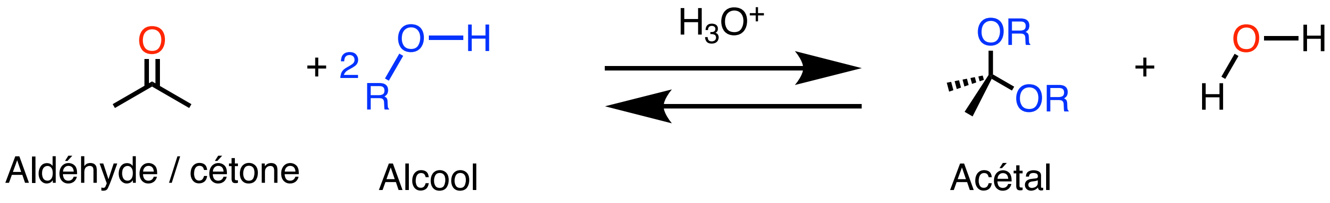
D. Les cétones possèdent un groupe C=O liés à deux alkyles.

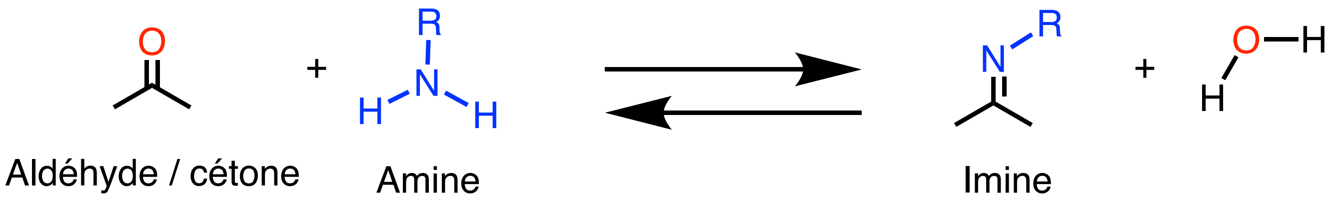
E. Les aldéhydes possèdent un group C=O lié à deux alkyles.

Résumé des réactions

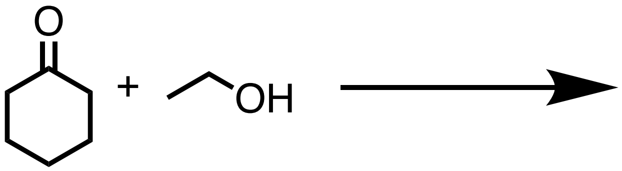


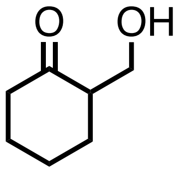






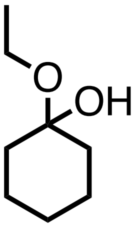
Quel est le produit lors de la réaction de la cyclohexanone avec l’éthanol?





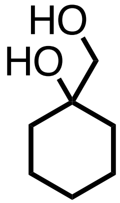
A

ou



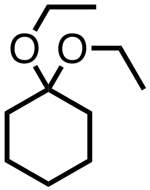
B

ou

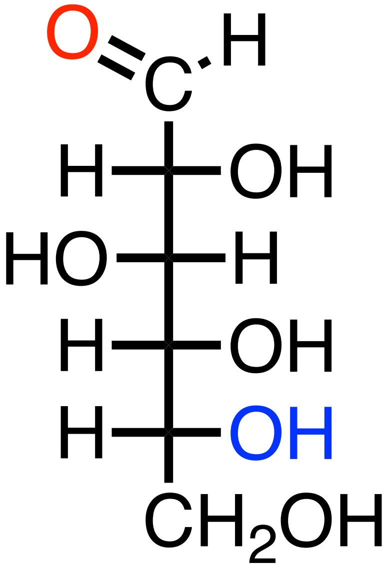


C

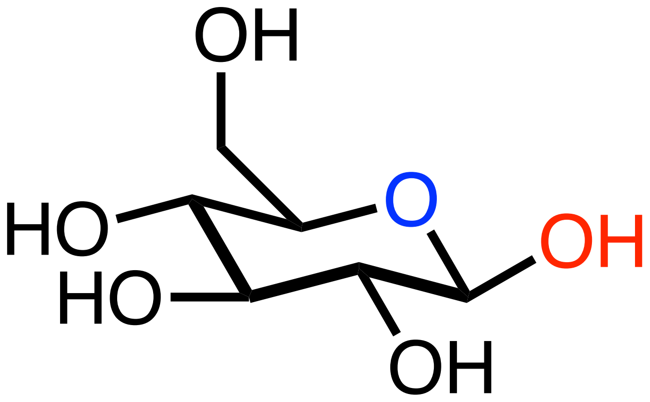
ou



D



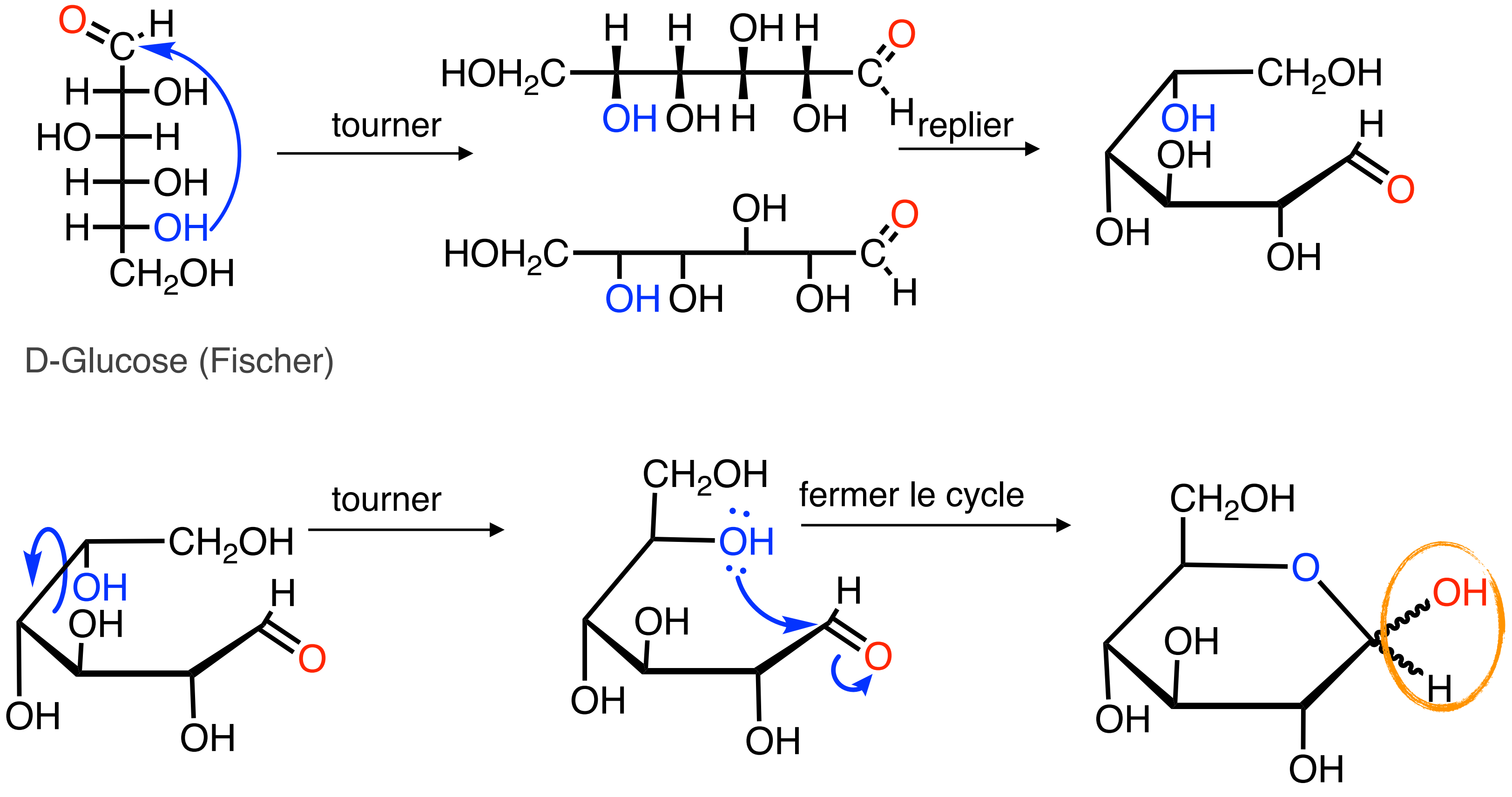
$\overset{?}{=}$



Addition nucléophile - aldohexoses

478-80

(451)



D-Glucose (Fischer)

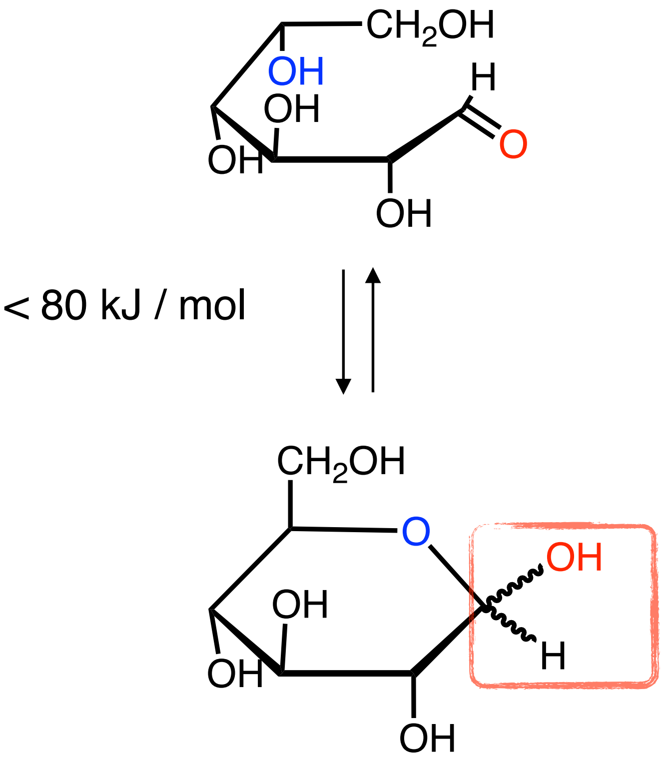
D-Glucose (Haworth)
hémiacétal

Addition nucléophile - aldohexoses

478-80

(451)

forme ouverte (aldéhyde)

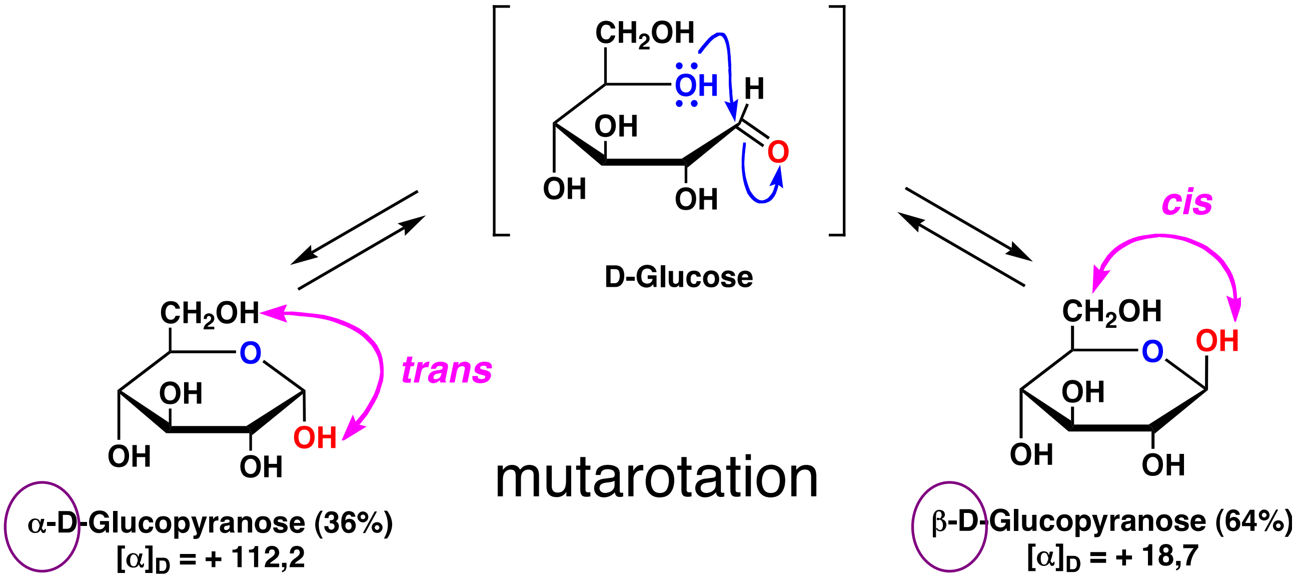


D-Glucose (Haworth)

hémiacétal

Anomères

480-481
(453, 455)



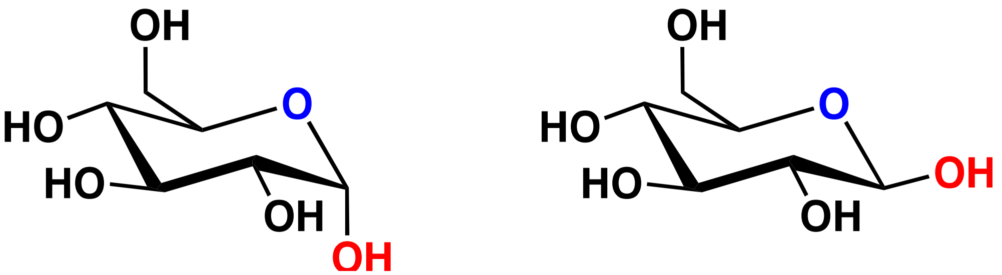
D-Glucose

α-D-Glucopyranose (36%)
$[\alpha]_D$ = + 112,2

β-D-Glucopyranose (64%)
$[\alpha]_D$ = + 18,7

mutarotation

+52,6



Glucides (carbohydrates, sucres)

$C_n(H_2O)_n$

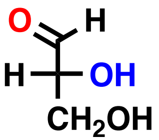
Aldoses *(Cétoses)*

Aldotriose

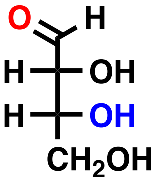
-tetroses

-pentoses

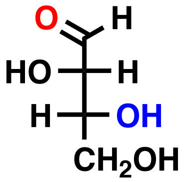
-hexoses



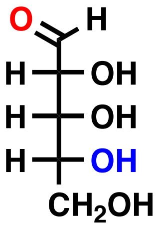
D-Glycéraldéhyde



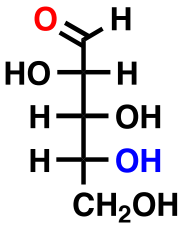
D-Érythrose



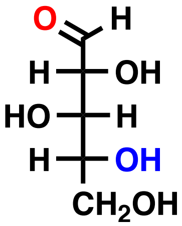
D-Thréose



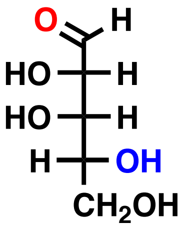
D-Ribose



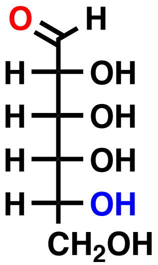
D-Arabinose



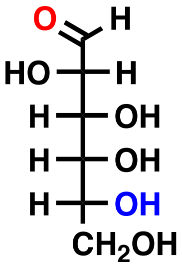
D-Xylose



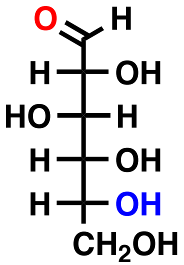
D-Lyxose



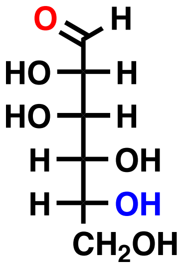
D-Allose



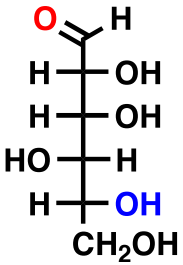
D-Altrose



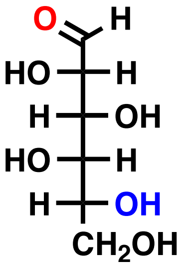
D-Glucose



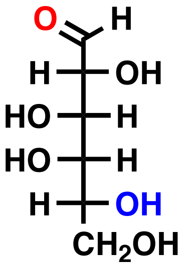
D-Mannose



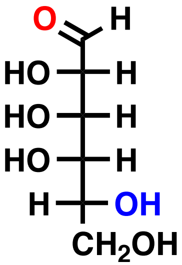
D-Gulose



D-Idose



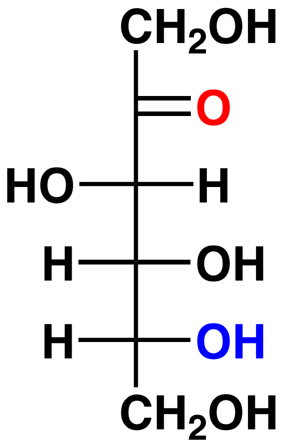
D-Galactose



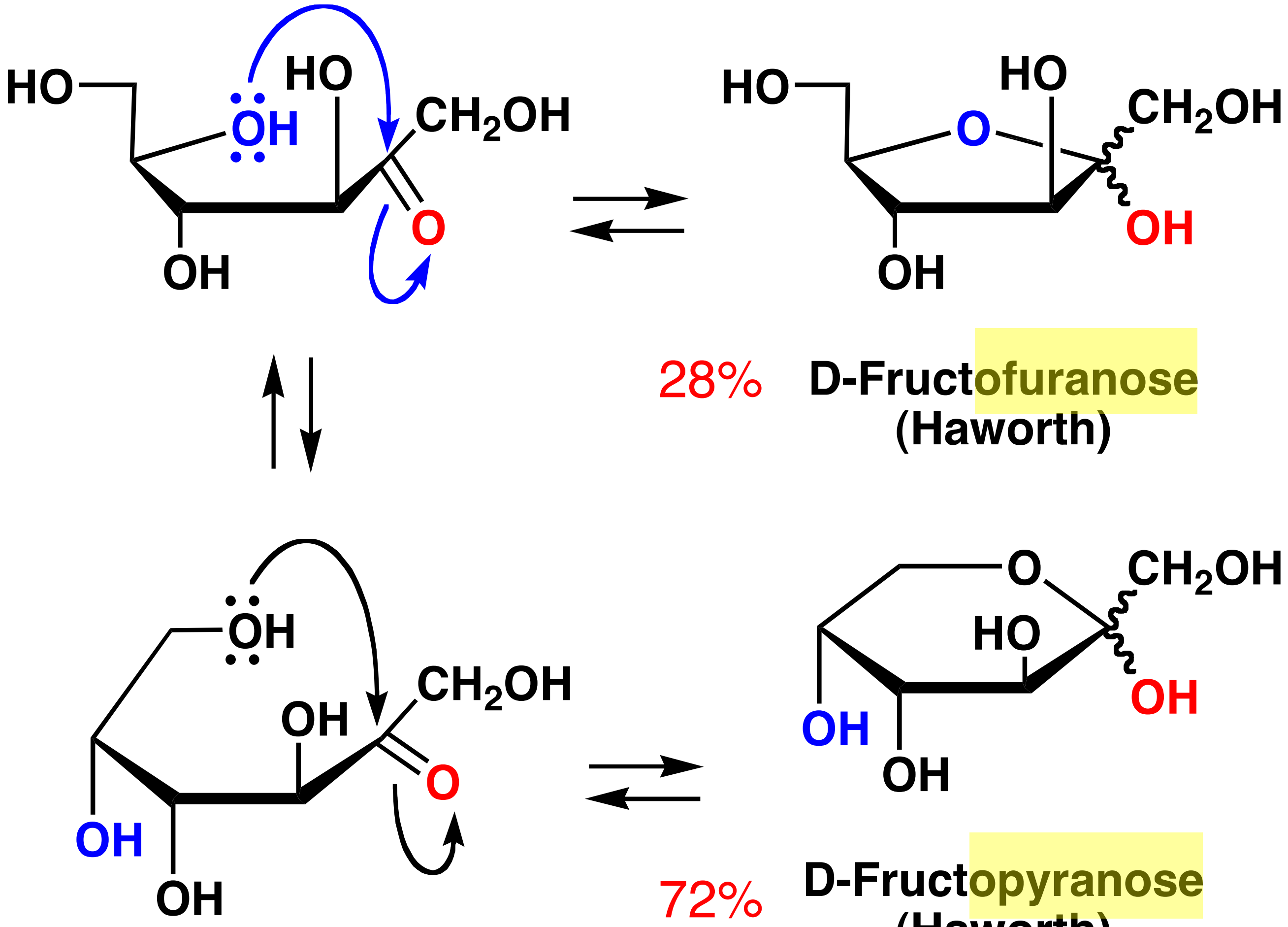
D-Talose

478-80
(450)

Addition nucléophile - cétohexoses

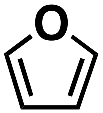


D-Fructose
(Fischer)

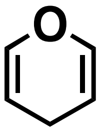


28% D-Fructofuranose
(Haworth)

72% D-Fructopyranose
(Haworth)

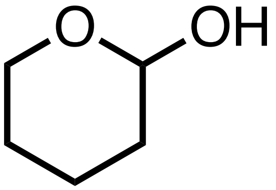


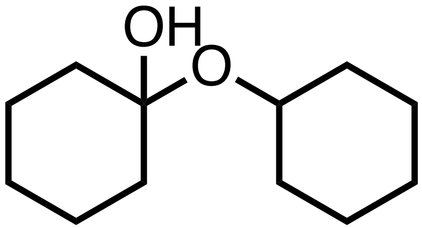
Furane

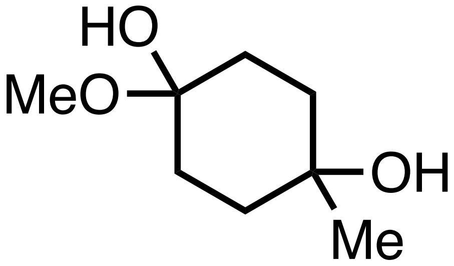


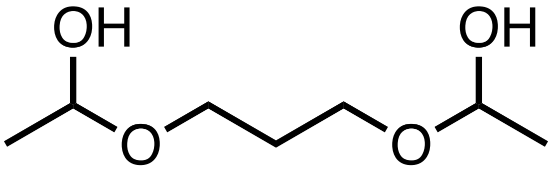
Pyrane

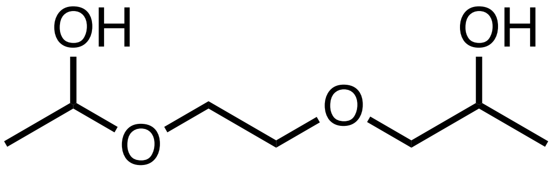
Chacun de ces composés est un hémiacétal et donc formé à partir d'un alcool et d'un composé carbonylé. Dans chaque cas, donnez la structure des molécules de départ.



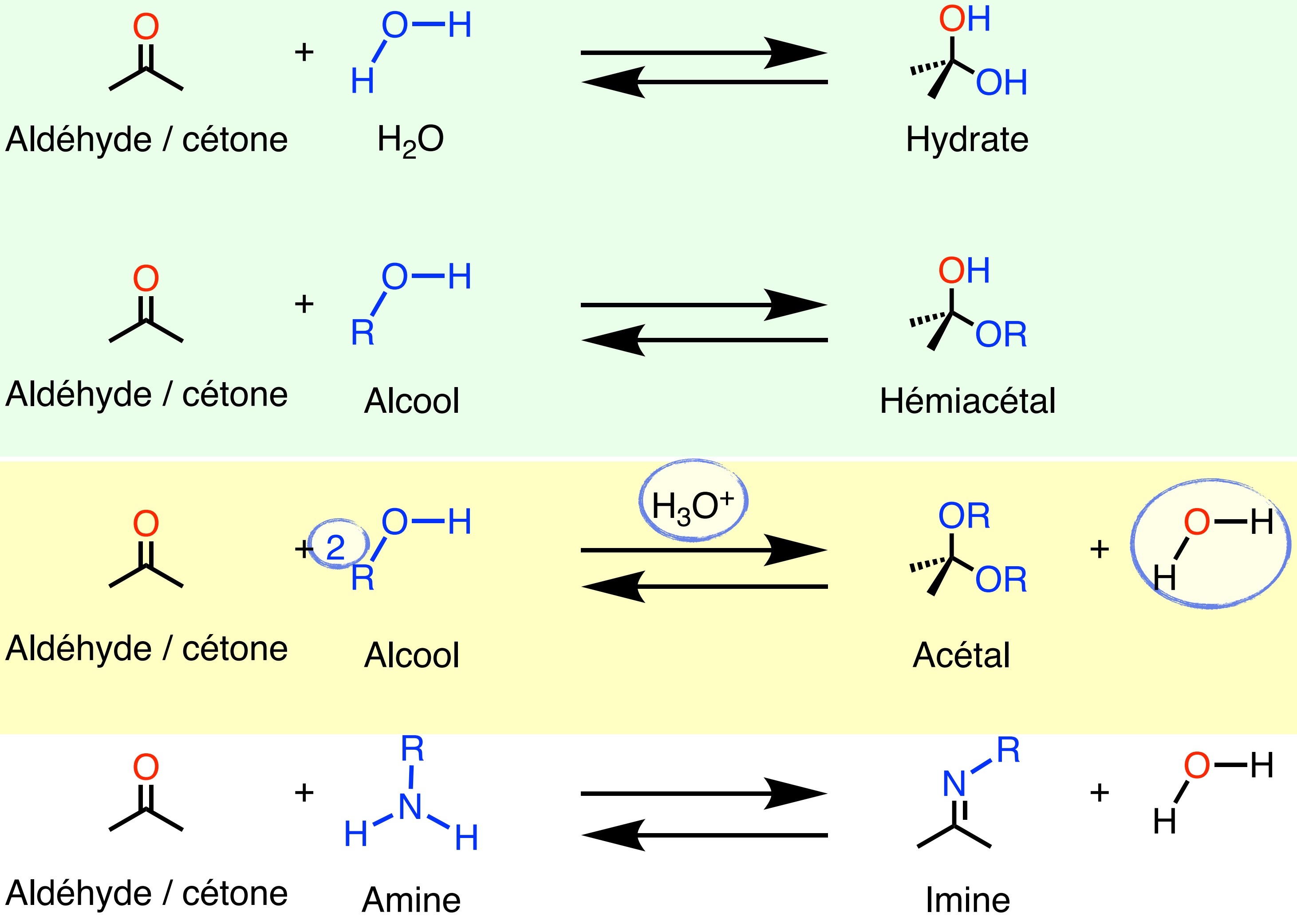








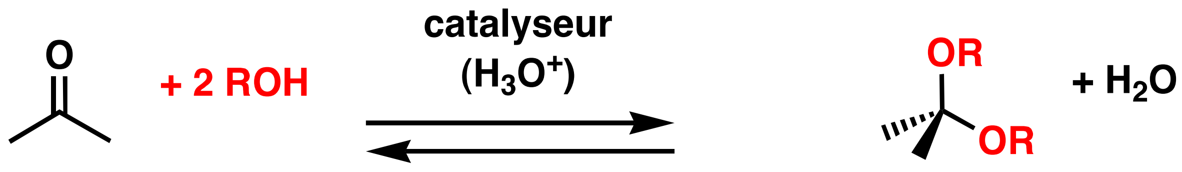
Résumé des réactions



293-6, 483-4, 488-90

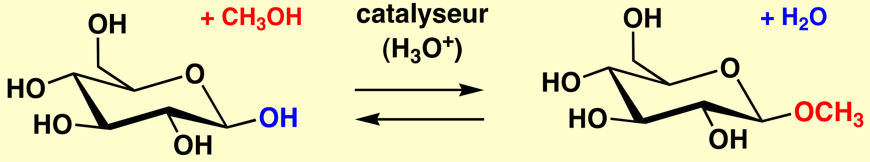
(493, 456)

Acétals - glycosides : substitution nucléophile



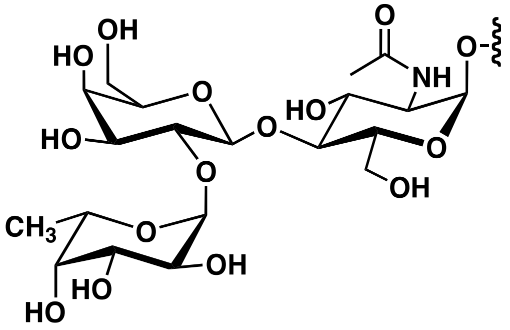
Aldéhyde /
Cétone

Acétal

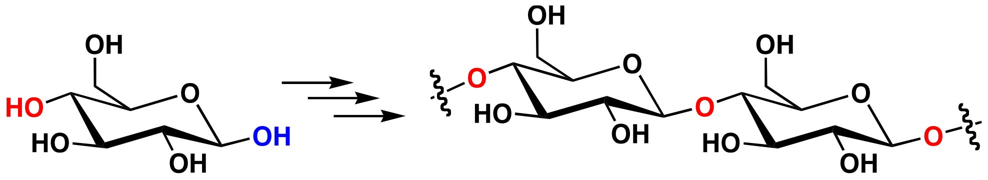


β-D-Glucopyranose
(hémiacétal)

β-D-Glucopyranoside
(acétal)



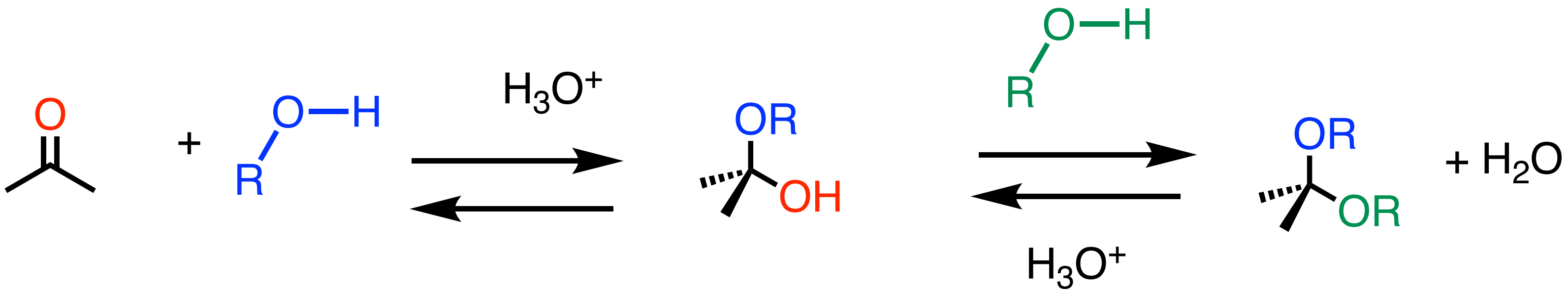
Groupe sanguin O
(trisaccharide, 466)

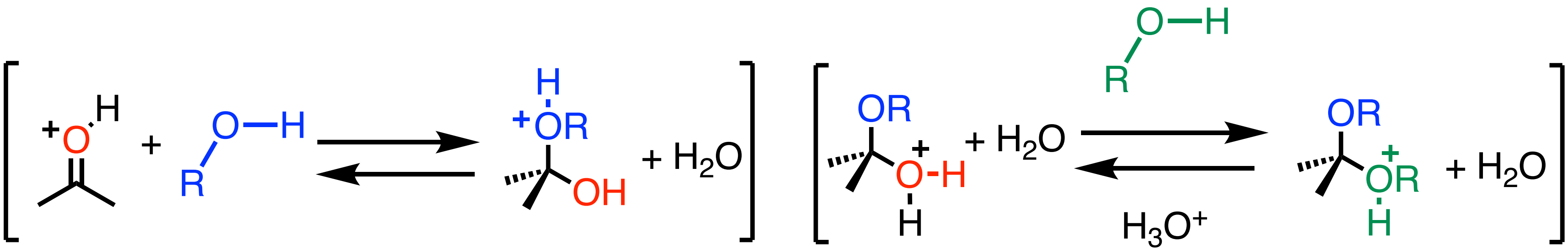


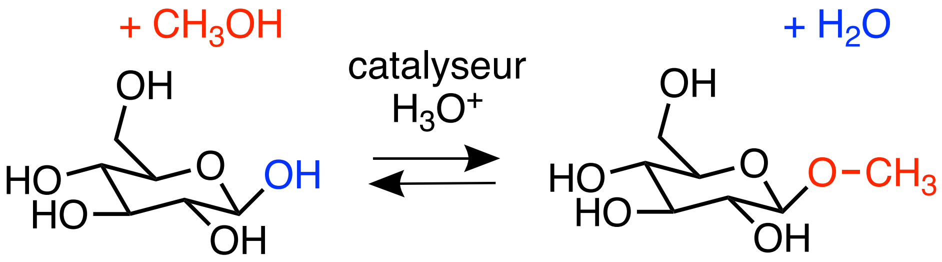
β-D-Glucopyranose
(hémiacétal)

Cellulose
(acétal, polysaccharide)

Addition nucléophile des alcools: formation d’acétals



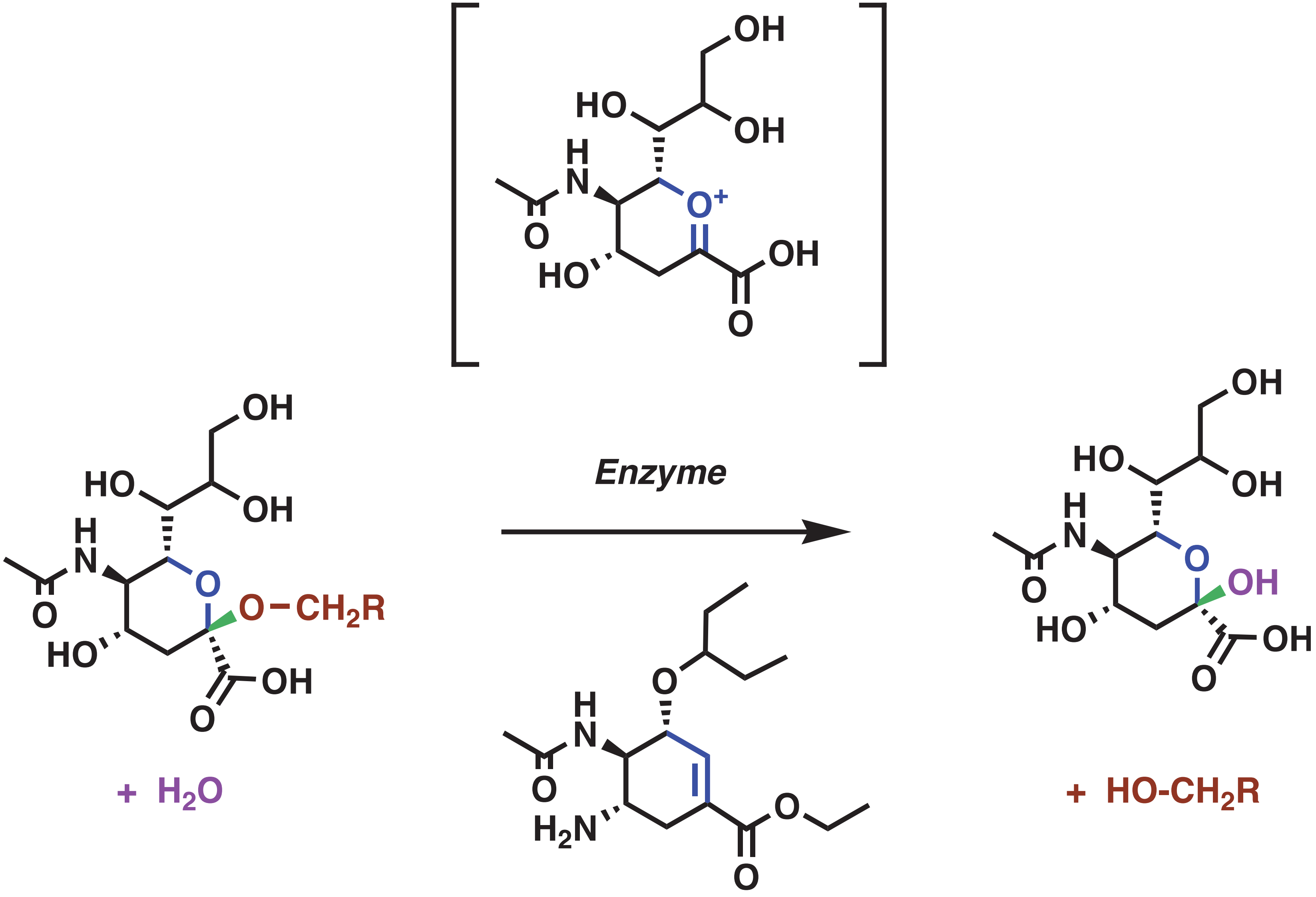



+ CH3OH
OH
HO
HO
O
OH
OH
catalyseur
H3O+
+ H2O
OH
HO
HO
O
O−CH3
OH

Tamiflu

293-6, 483-4, 488-90

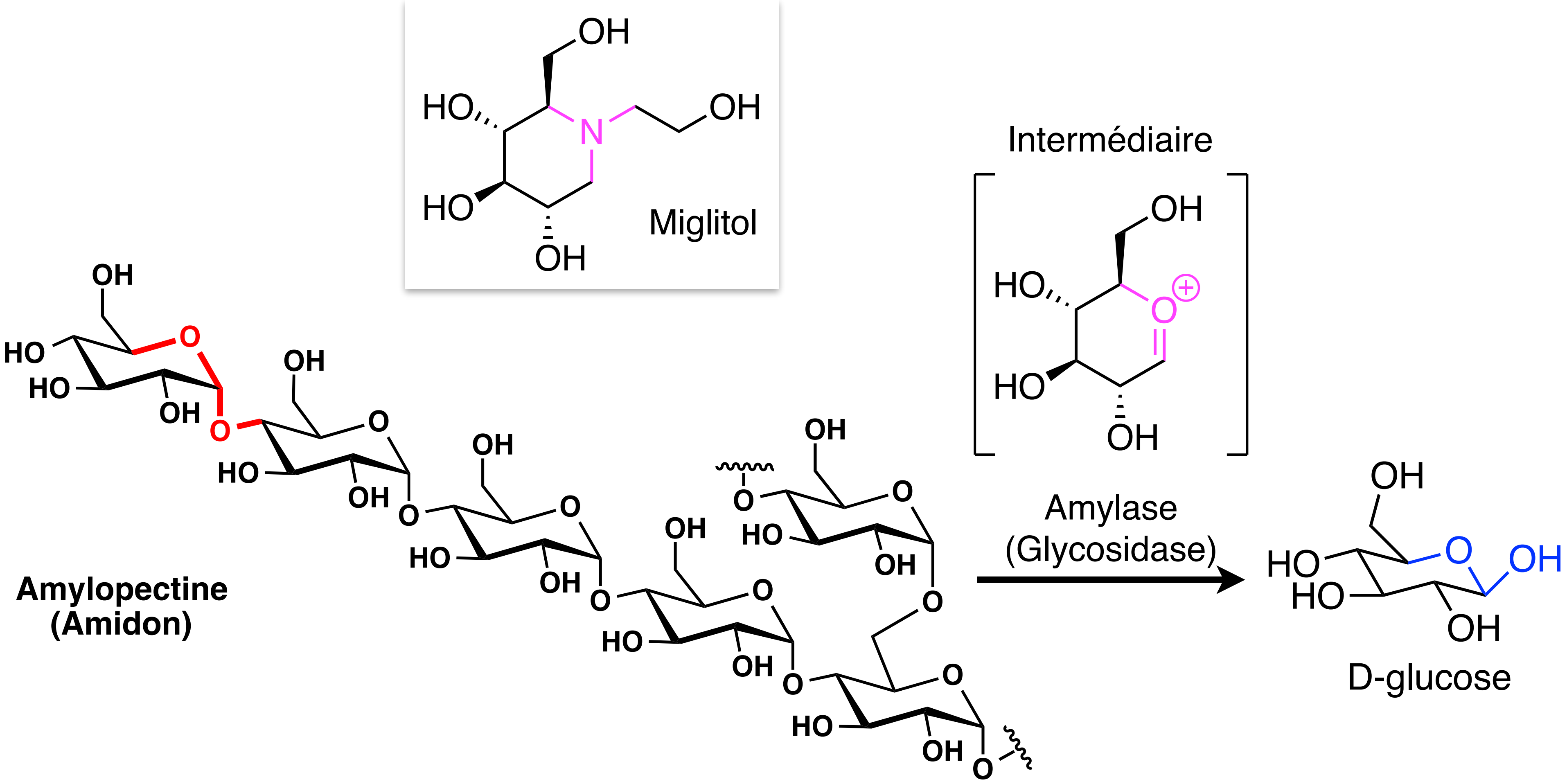
(493, 456)



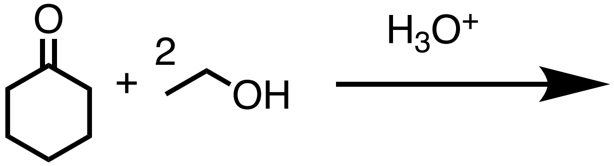
Tamiflu

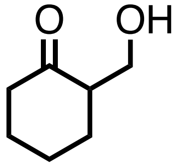
295, 489
(463, 456, 293)

Antidiabétiques



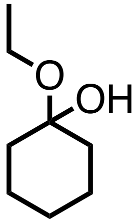
Quel est le produit obtenu lors de la réaction de la cyclohexanone avec l'éthanol catalysé par un acide?





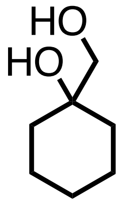
A

ou



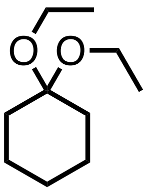
B

ou



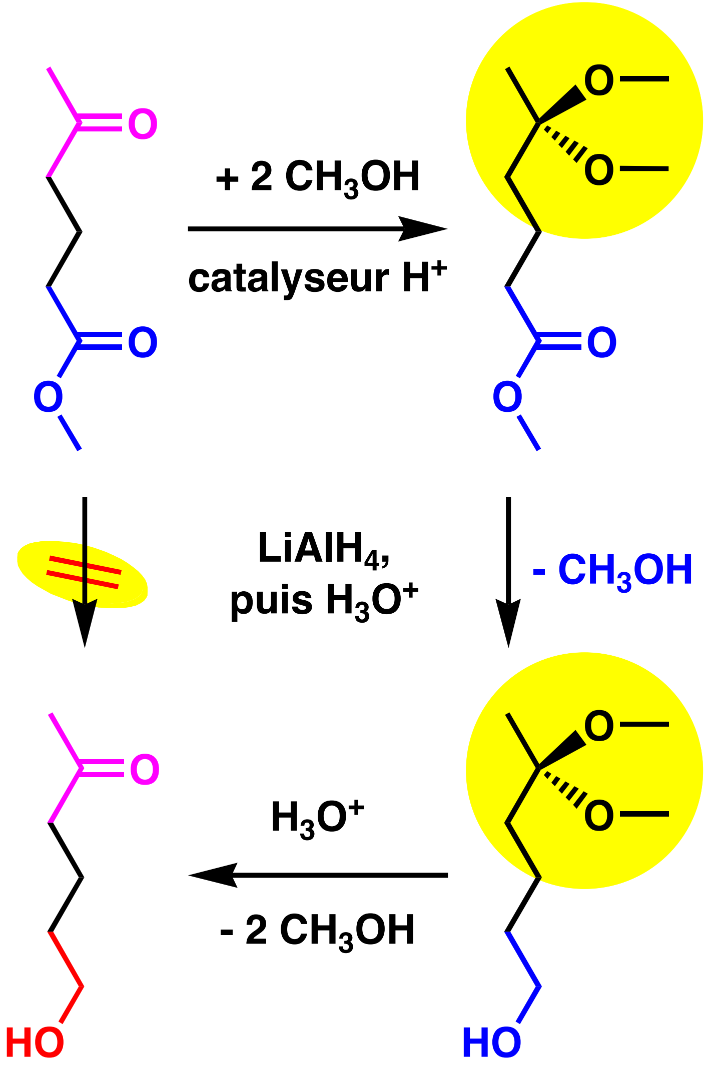
C

ou



D

Sélectivité, synthèse chimique et groupes protecteurs



+ 2 CH_3OH

catalyseur H^+

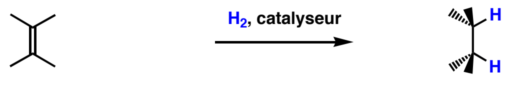
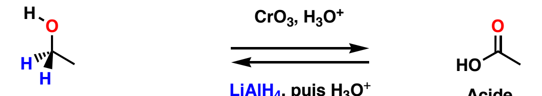
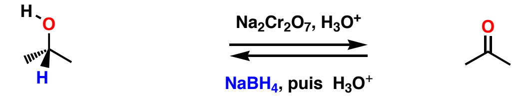
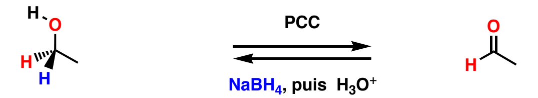
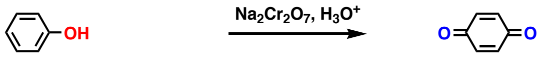
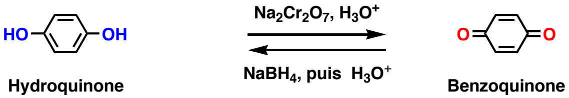
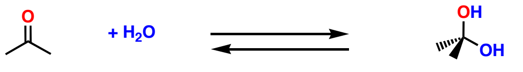
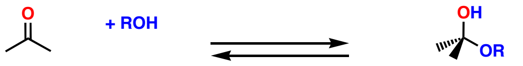
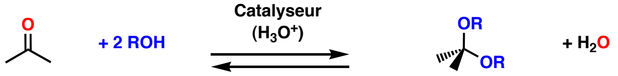
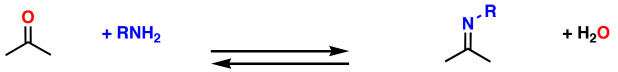
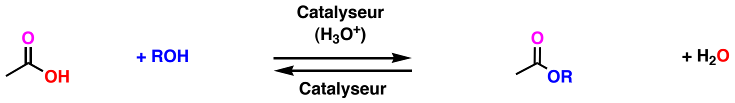
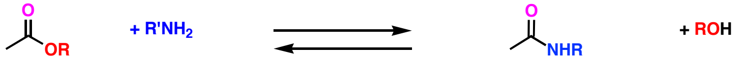
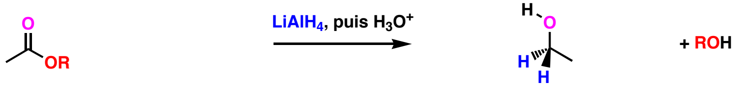
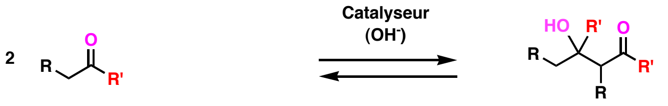
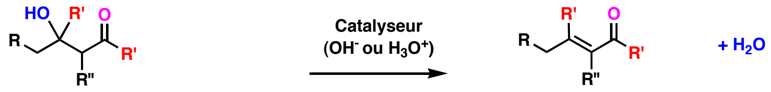
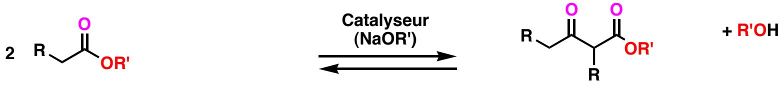
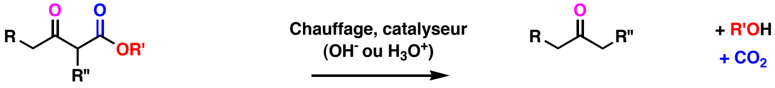
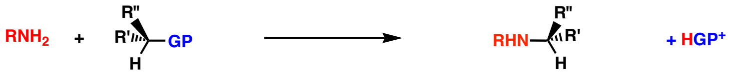
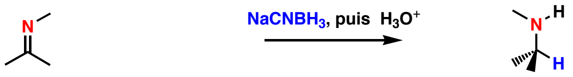
$LiAlH_4$,
puis H_3O^+

- CH_3OH

H_3O^+

- 2 CH_3OH

Résumé des réactions

Réaction	2007	2003
 Alcène → Alcane H_2, catalyseur	4.6	4.6
 Alcool primaire ⇄ Acide carboxylique CrO_3, H_3O^+ $LiAlH_4$, puis H_3O^+	8.5 8.4	8.7 8.5
 Alcool secondaire ⇄ Cétone $Na_2Cr_2O_7$, H_3O^+ $NaBH_4$, puis H_3O^+	8.5 8.4	8.7 8.5
 Alcool primaire ⇄ Aldéhyde PCC $NaBH_4$, puis H_3O^+	8.5 8.4	8.7 8.5
 Phénol → Benzoquinone $Na_2Cr_2O_7$, H_3O^+	8.6	8.8
 Hydroquinone ⇄ Benzoquinone $Na_2Cr_2O_7$, H_3O^+ $NaBH_4$, puis H_3O^+	8.6	8.8
 Aldéhyde / cétone + H_2O ⇄ Hydrate	9.7	9.7
 Aldéhyde / cétone + ROH (Alcool) ⇄ Hémiacétal	9.8 9.9 14.5 14.6	9.8 14.5 14.6
 Aldéhyde / cétone + 2 ROH (Alcool) ⇄ Acétal + H_2O Catalyseur (H_3O^+)	9.8 9.9 14.7	9.8 14.8
 Aldéhyde / cétone + RNH_2 (Amine) ⇄ Imine + H_2O	9.10	9.9
 Acide carboxylique + ROH (Alcool) ⇄ Ester + H_2O Catalyseur (H_3O^+) Catalyseur (OH^- ou H_3O^+)	10.8 10.11	10.6 10.9
 Ester + $R'NH_2$ (Amine) ⇄ Amide + ROH (Alcool) Chauffage, catalyseur (OH^- ou H_3O^+)	16.13 10.10	10.9 10.10
 Ester → Alcool primaire + ROH (Alcool) $LiAlH_4$, puis H_3O^+	10.11 8.4	10.9 8.5
 2 Aldéhyde / cétone ⇄ β-Hydroxycétone Catalyseur (OH^-)	11.9	11.8
 β-Hydroxycétone → Énone conjuguée + H_2O Catalyseur (OH^- ou H_3O^+)	11.10	11.9
 2 Ester ⇄ β-Cétoester + R'OH (Alcool) Catalyseur (NaOR')	11.11	11.10
 β-Cétoester → Cétone + R'OH + CO_2 Chauffage, catalyseur (OH^- ou H_3O^+)	17.4	17.4
 Amine + R''R'CH–GP → Alkylamine + HGP^+ GP = groupe partant	12.4 7.5	12.4 7.7 8.11
 Imine → Amine $NaCNBH_3$, puis H_3O^+	9.10	9.11