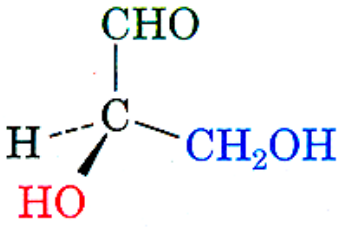
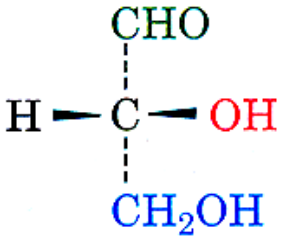
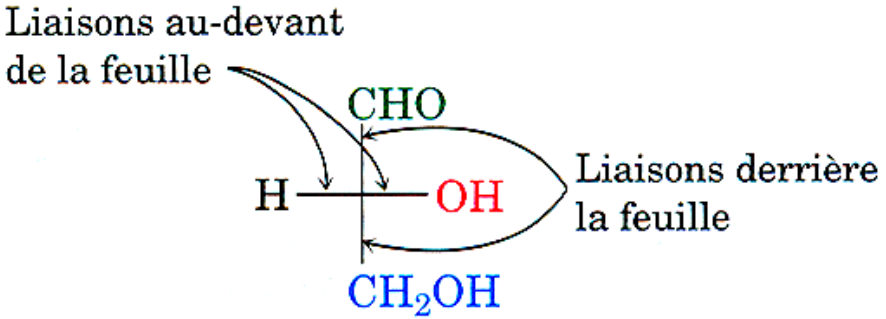
Projection de Fischer - chiralité

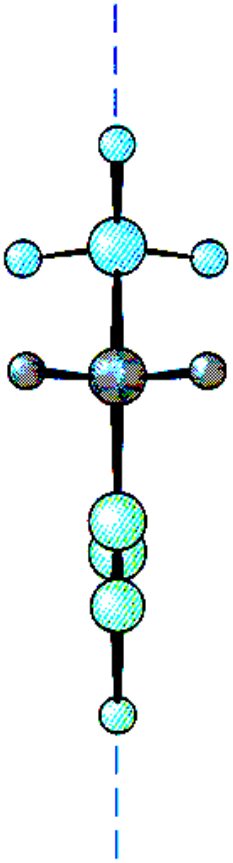


=

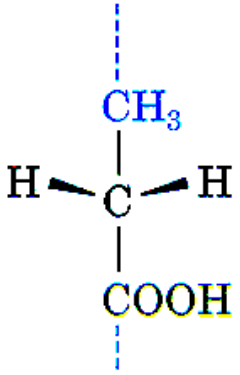




= Chiralité



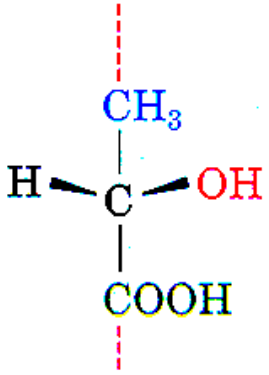
Plan
de symétrie

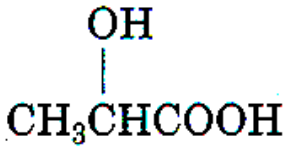


CH_3CH_2COOH

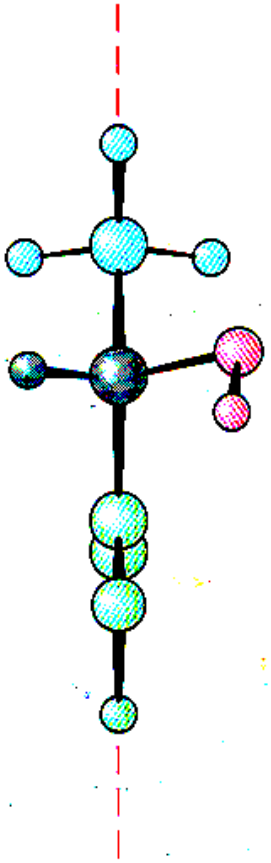
Acide propanoïque
(achiral)

Absence de plan
de symétrie

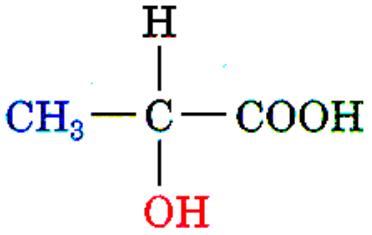


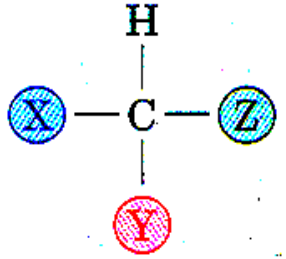


Acide lactique
(chiral)



Activité optique

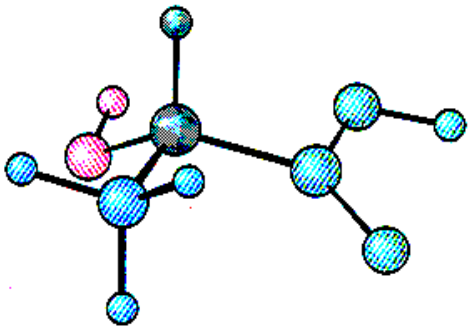


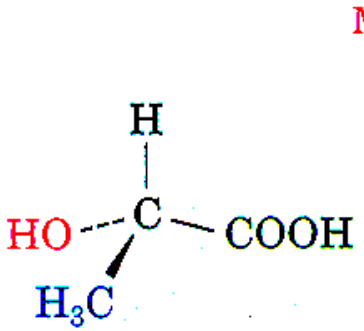


centre stéréogénique

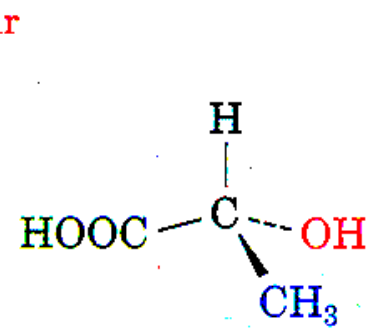
centre asymétrique

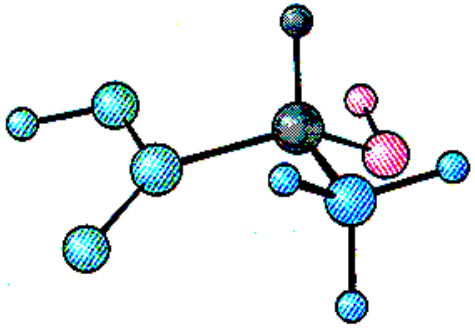
L'acide lactique : une molécule de formule générale CHXYZ





Miroir





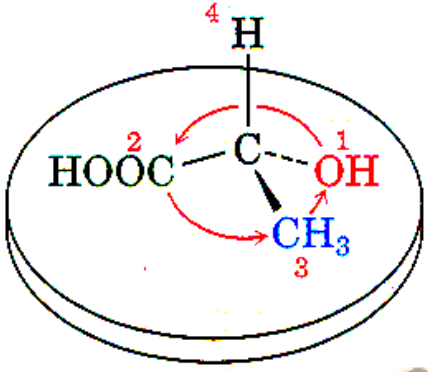
Acide-(+)-lactique
$[\alpha]_D = +3,82$

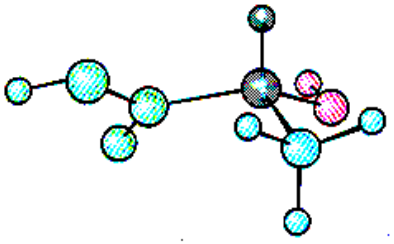
Acide-(−)-lactique
$[\alpha]_D = -3,82$

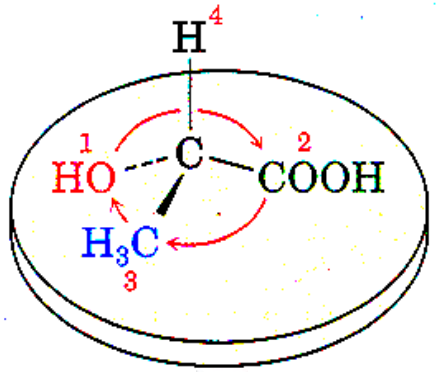
pouvoir rotatoire spécifique

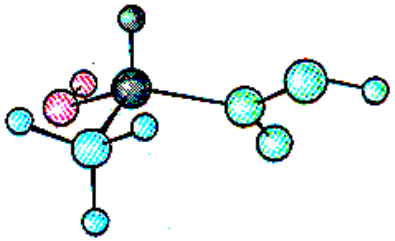
Capacité d'une molécule chirale en solution de faire tourner le plan de la lumière polarisée

Nomenclature







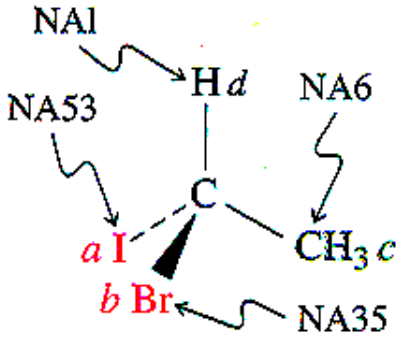


Configuration absolue

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

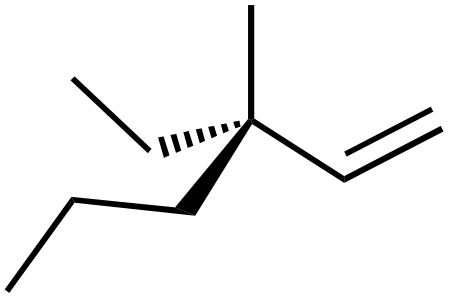
Règles séquencielles

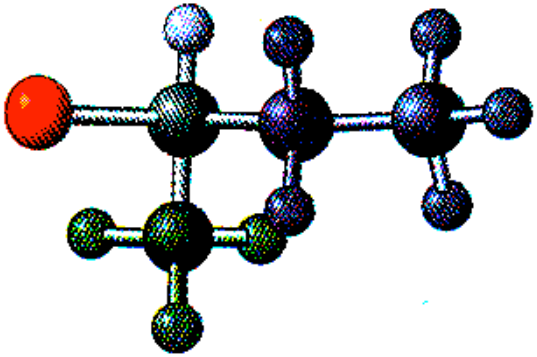
Br > Cl > O > N > C > H
35 17 8 7 6 1

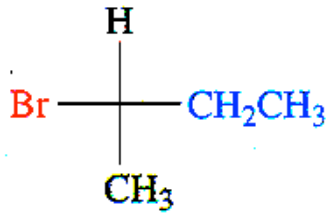


NA = numéro atomique

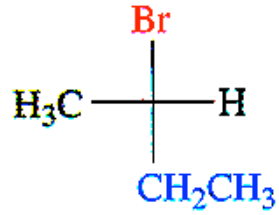
Acide (*S*)-(+)-lactique
(main gauche)

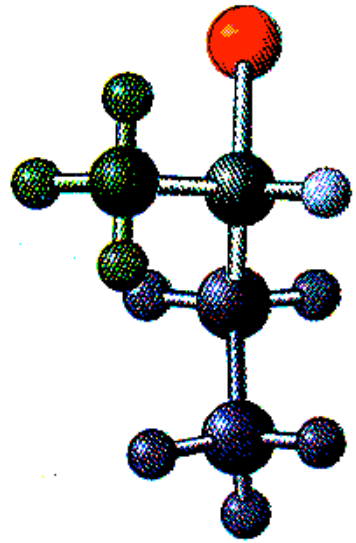




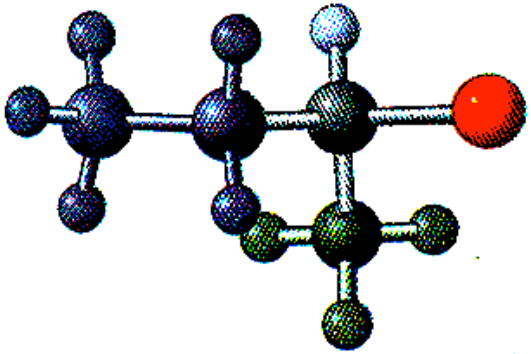


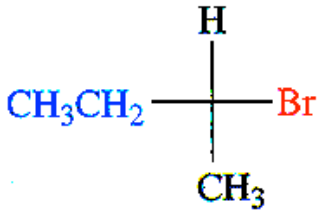
rotation de 90°



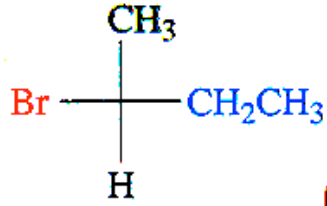


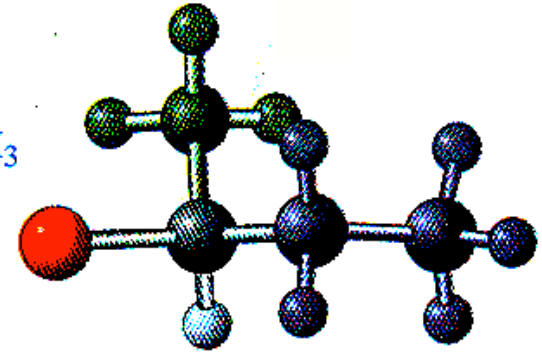
R



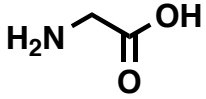


rotation de 180°

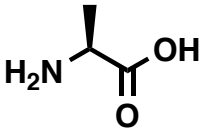




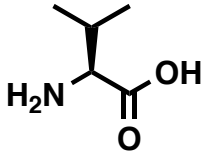
Les acides aminés



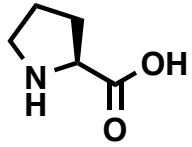
Glycine
(Gly, G)



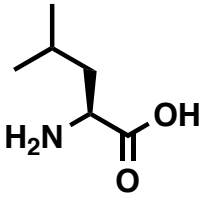
Alanine
(Ala, A)



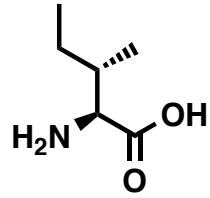
Valine
(Val, V)



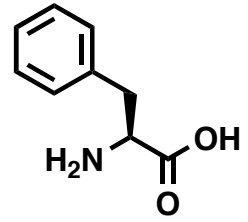
Proline
(Pro, P)



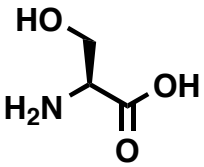
Leucine
(Leu, L)



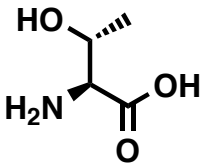
Isoleucine
(Ile, I)



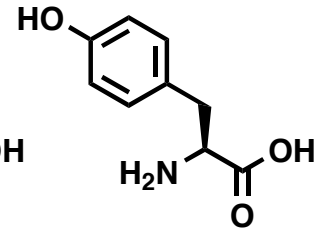
Phénylalanine
(Phe, F)



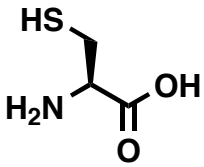
Sérine
(Ser, S)



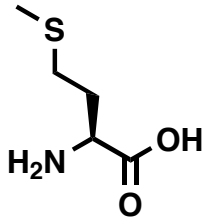
Thréonine
(Thr, T)



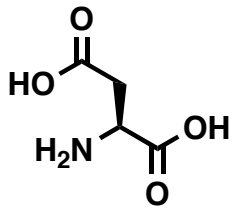
Tyrosine
(Tyr, Y)



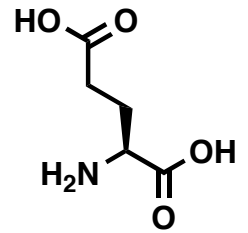
Cystéine
(Cys, C)



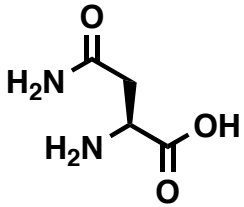
Méthionine
(Met, M)



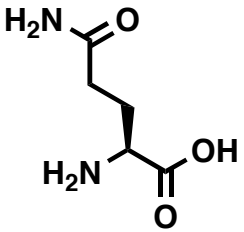
Acide aspartique
(Asp, D)



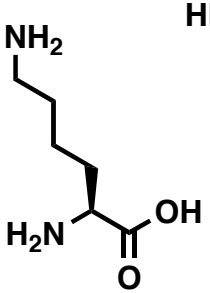
Acide glutamique
(Glu, E)



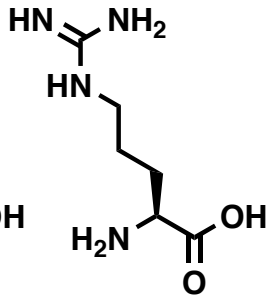
Asparagine
(Asn, N)



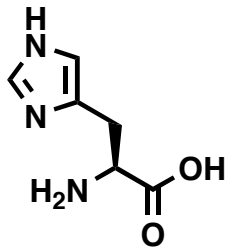
Glutamine
(Gln, Q)



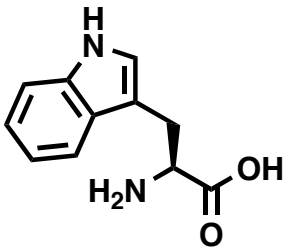
Lysine
(Lys, K)



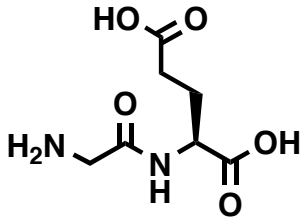
Arginine
(Arg, R)



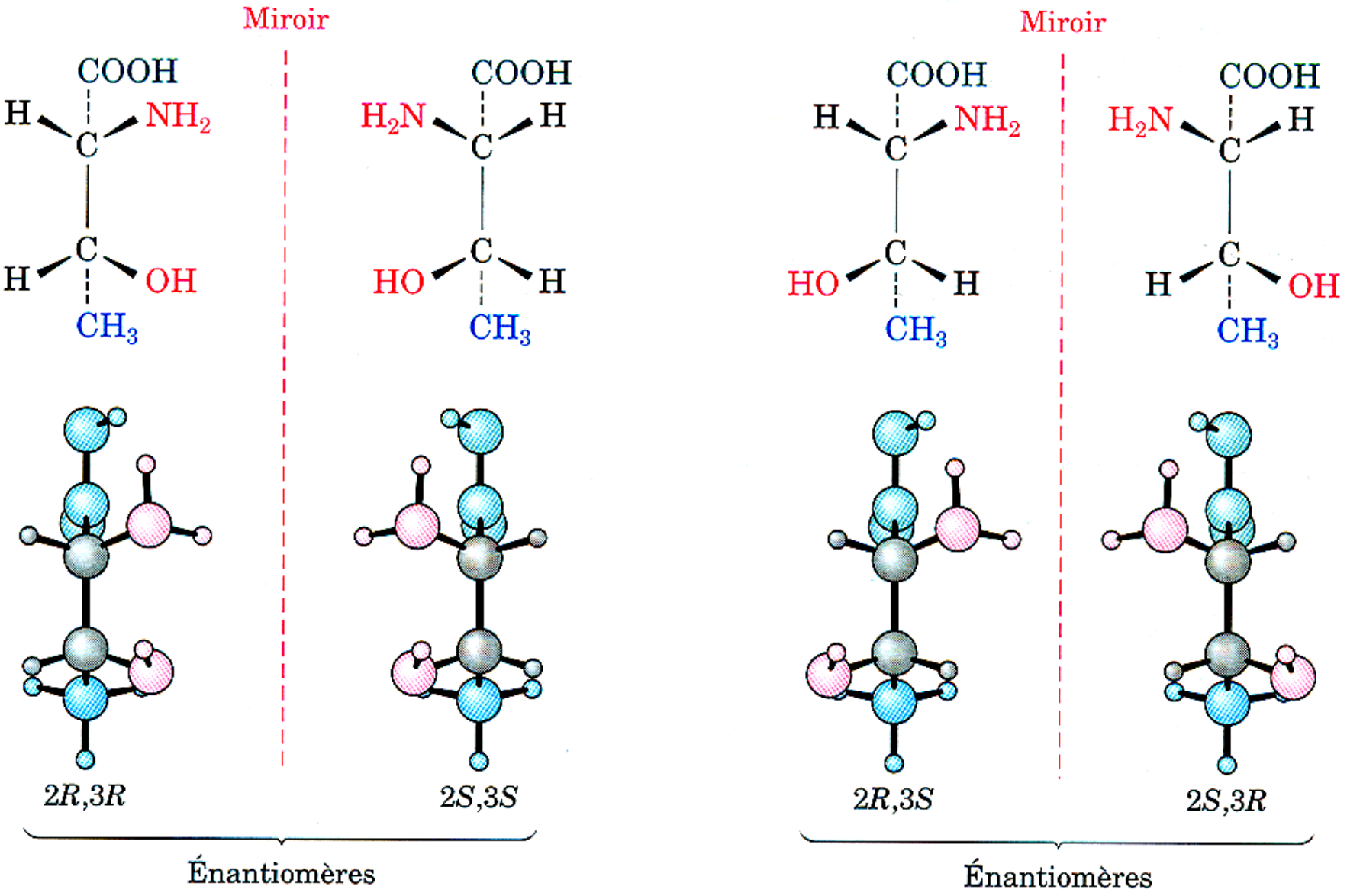
Histidine
(His, H)



Tryptophane
(Trp, W)

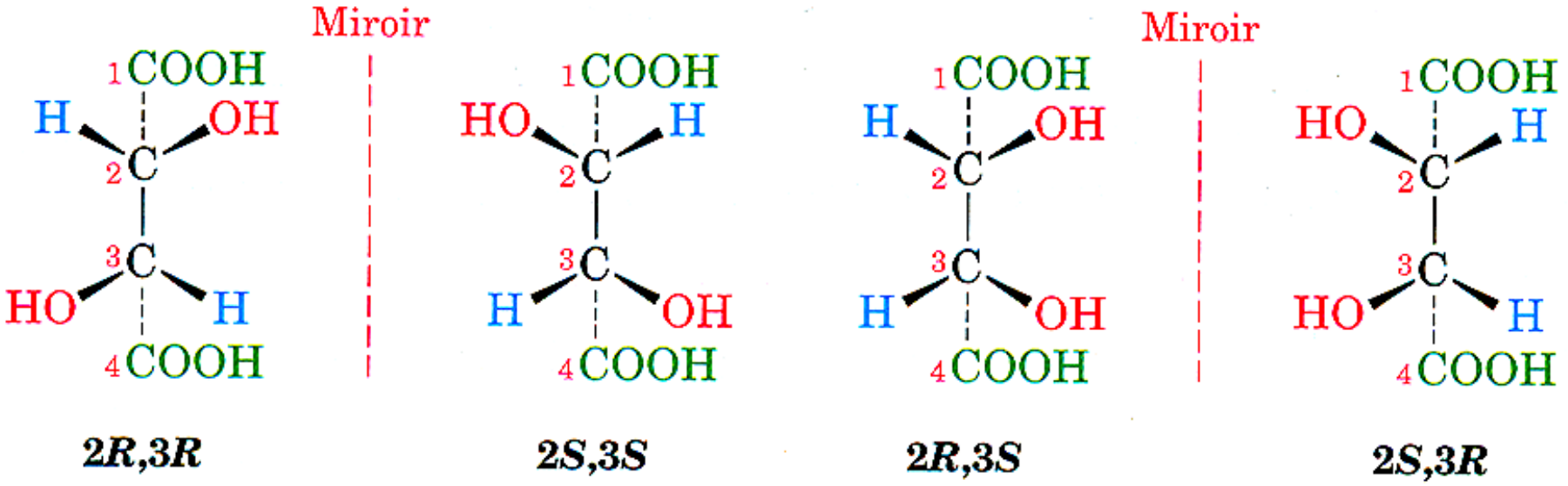


Diastéréoisomères - la thréonine



Composés méso - l'acide tartrique

(199, 205)



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)

$C_n(H_2O)_n$

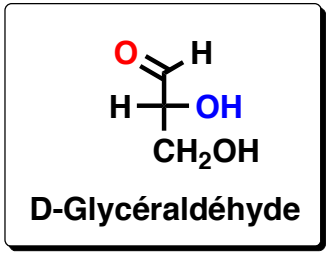
Aldoses (Cétoses)

Aldotriose

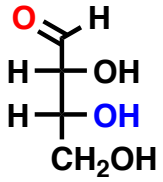
-tetroses

-pentoses

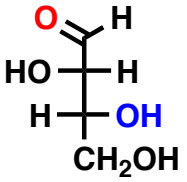
-hexoses



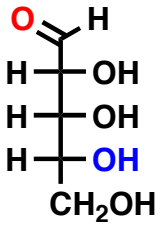
D-Glycéraldéhyde



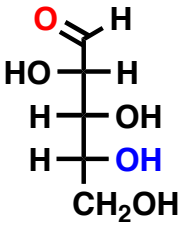
D-Érythrose



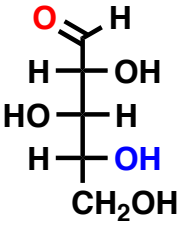
D-Thréose



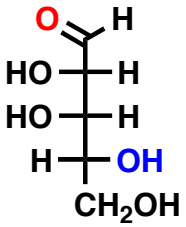
D-Ribose



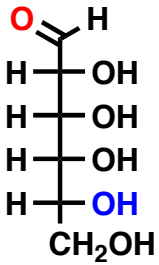
D-Arabinose



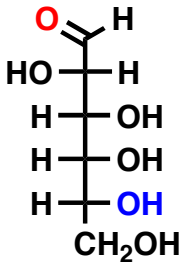
D-Xylose



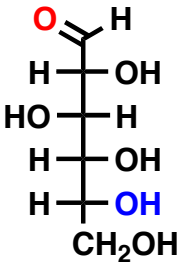
D-Lyxose



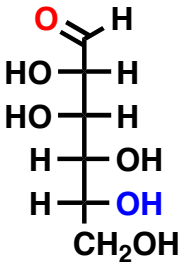
D-Allose



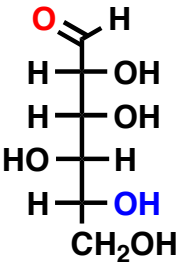
D-Altrose



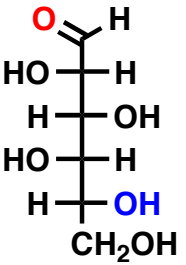
D-Glucose



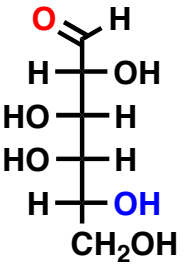
D-Mannose



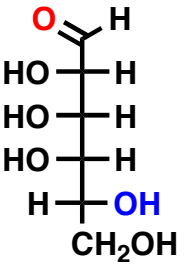
D-Gulose



D-Idose



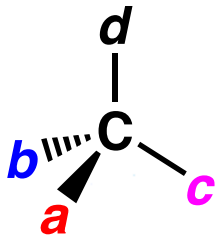
D-Galactose



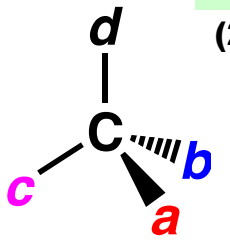
D-Talose

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

Configuration



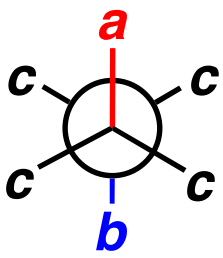
S



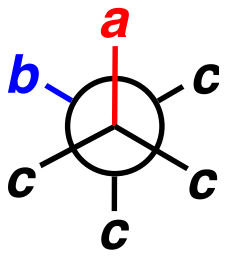
R

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

Conformation

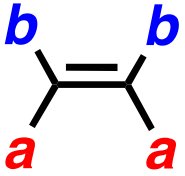


anti

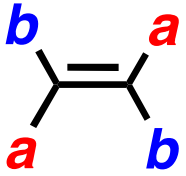


gauche

(décalées)



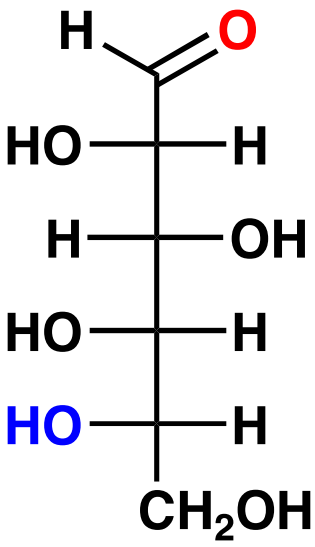
Z (cis)



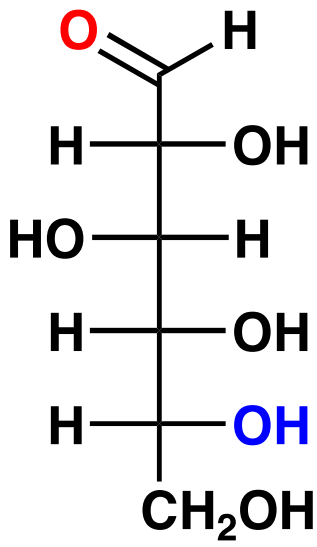
E (trans)

Plus de deux centres stéréogéniques

Miroir



L-Glucose
(composé non naturel)



D-Glucose

***n* centres**

$\leq 2^n$ stéréoisomères

$\leq 2^{n-1}$ couples d'énantiomères

Les glucides (carbohydrates, sucres)

$C_n(H_2O)_n$

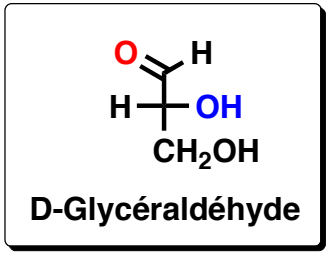
Aldoses (Cétoses)

Aldotriose

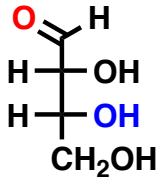
-tetroses

-pentoses

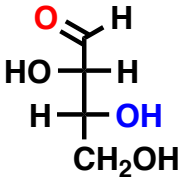
-hexoses



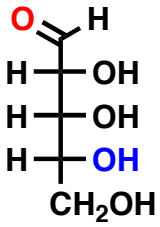
D-Glycéraldéhyde



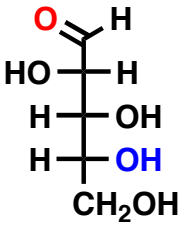
D-Érythrose



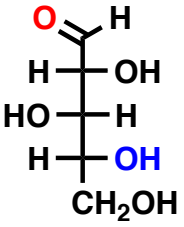
D-Thréose



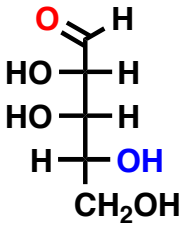
D-Ribose



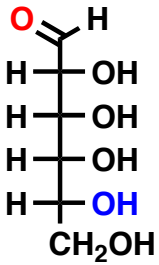
D-Arabinose



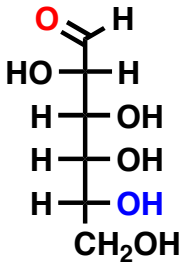
D-Xylose



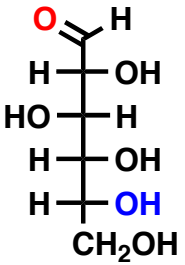
D-Lyxose



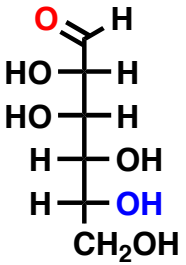
D-Allose



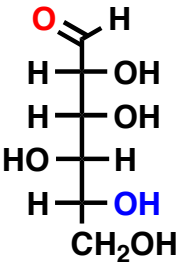
D-Altrose



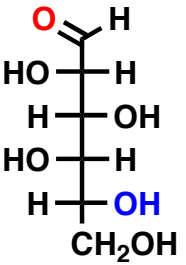
D-Glucose



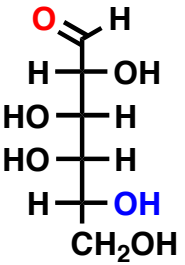
D-Mannose



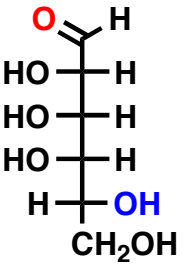
D-Gulose



D-Idose



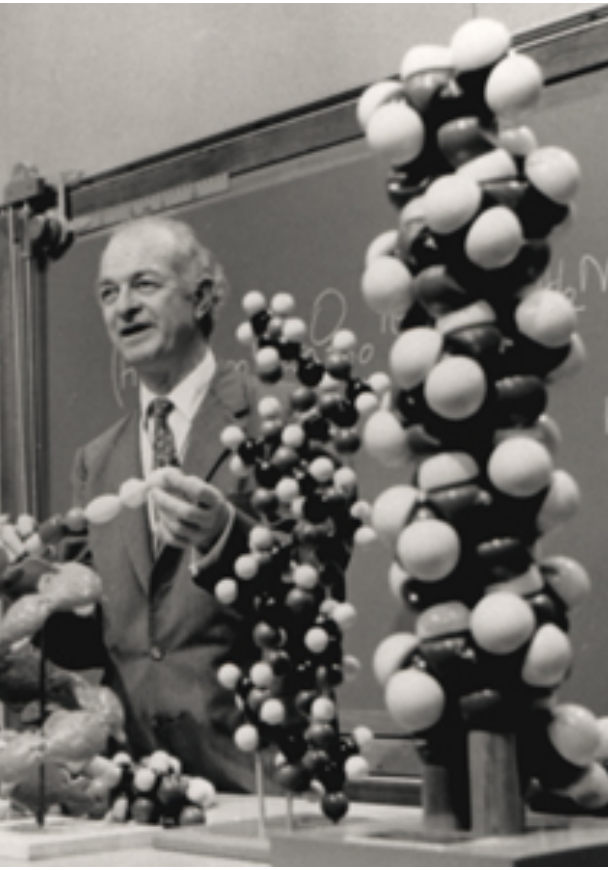
D-Galactose



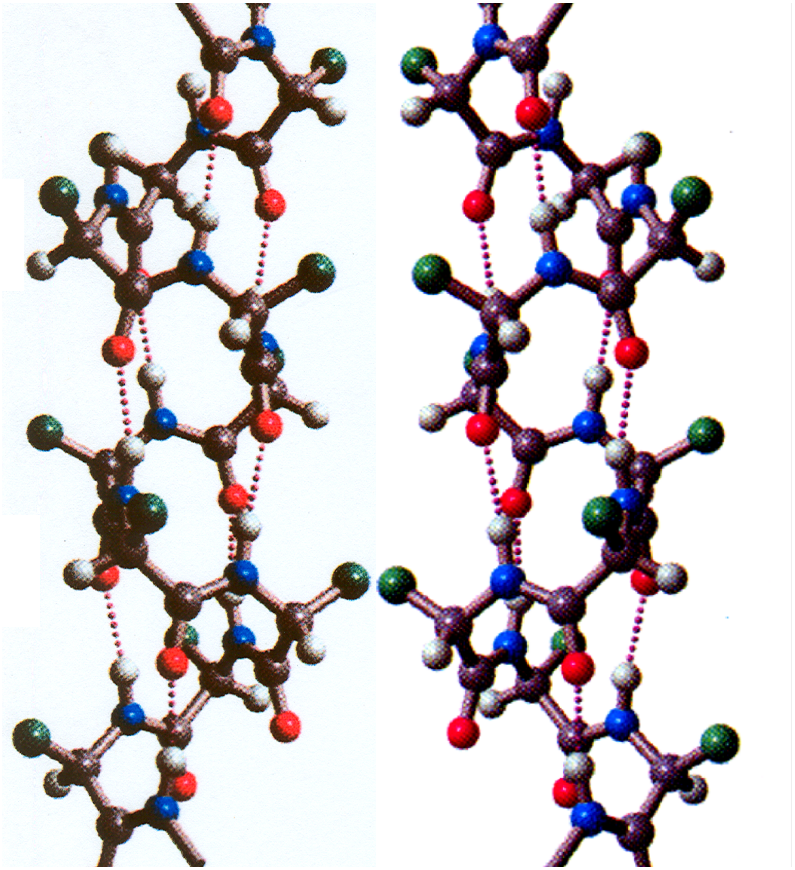
D-Talose

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

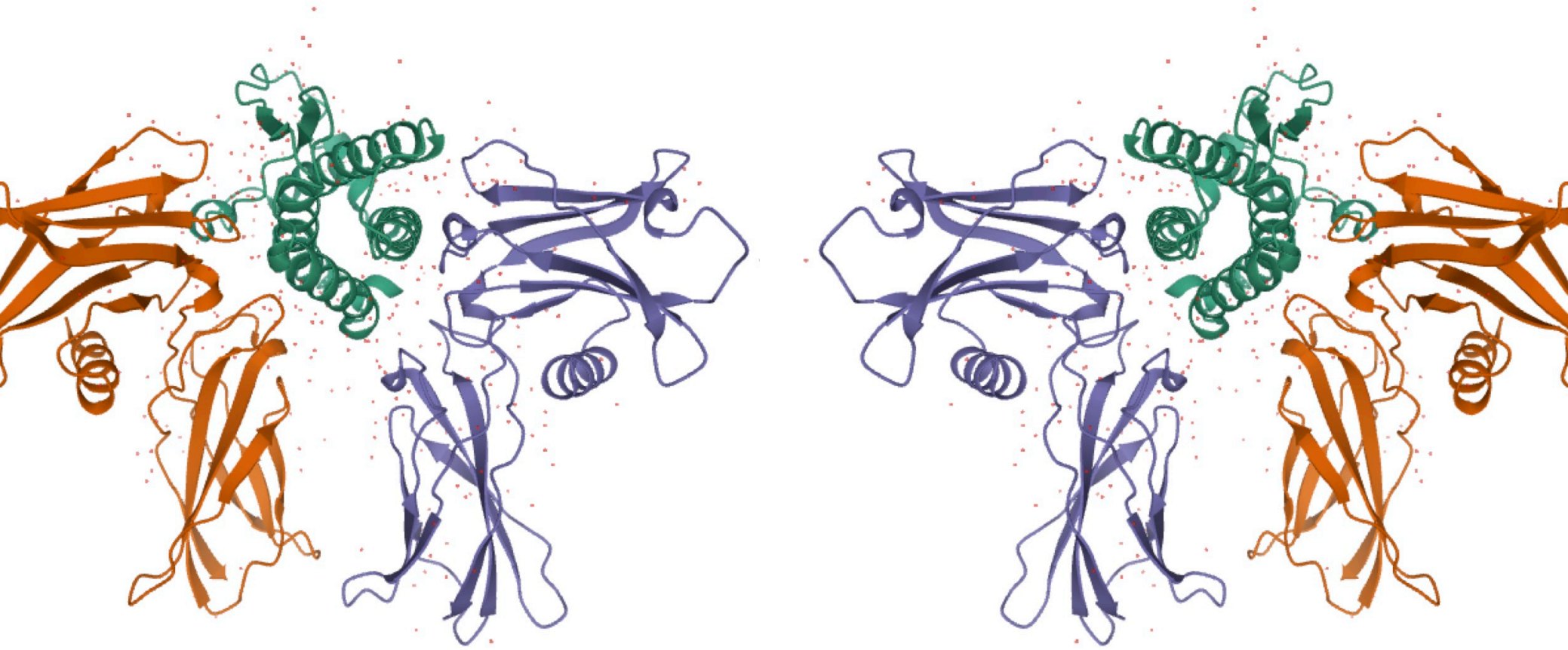
L'hélice α

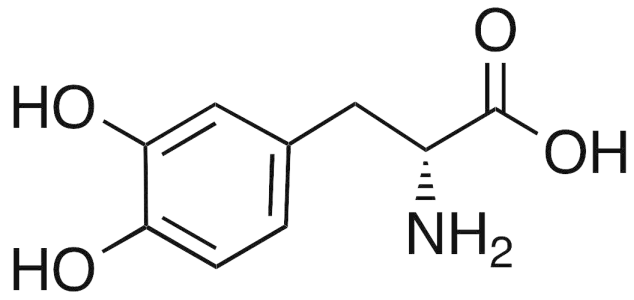


Linus Pauling
Prix Nobel, Chimie, 1954



McMurry

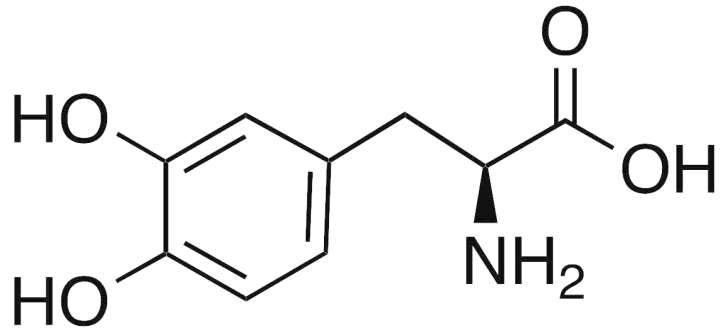




D-Dopa
pas d'effet biologique (208)

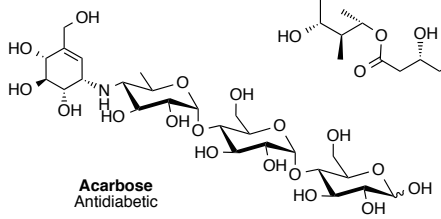
1967
Hoffman-La Roche
Synthesis: William Knowles, Monsanto, prix Nobel 2001

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

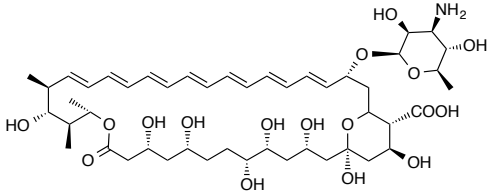


L-Dopa
(Levodopa)
Antiparkinson

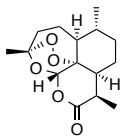
Molécules qui ont changé notre monde...



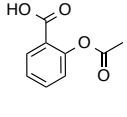
Acarbose
Antidiabetic



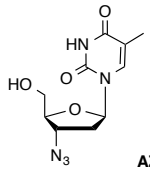
Amphotericin B
Antifungal



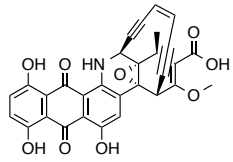
Artemisinin
Antimalarial



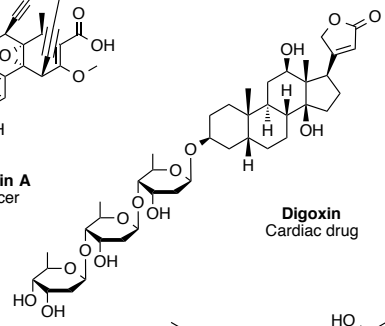
Aspirin
Analgesic



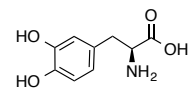
AZT
Antiviral (AIDS)



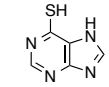
Dynemicin A
Anticancer



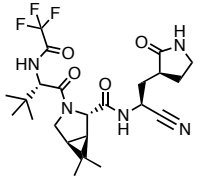
Digoxin
Cardiac drug



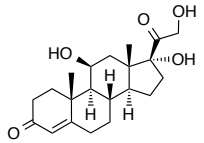
L-Dopa
Antiparkinson



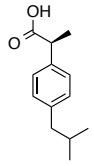
6-Mercaptopurine
Anticancer



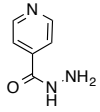
Paxlovid
Antiviral
(SARS-CoV-2)



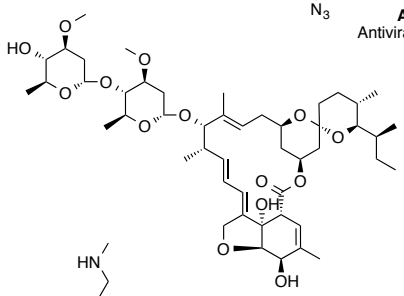
Hydrocortisone
Hormone



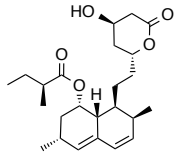
Ibuprofen
Analgesic



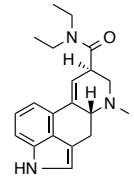
Isoniacid
Antibacterial
(Tuberculosis)



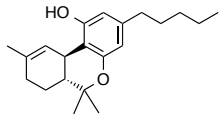
Ivermectin
Antiparasitic
(Onchocerciasis)



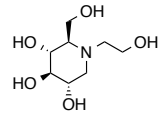
Lovastatin
Anti-cholesterol



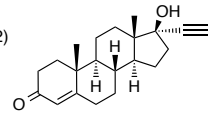
LSD
Psychedelic



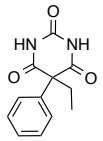
Marijuana
Antiemetic



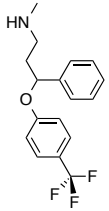
Miglitol
Antidiabetic



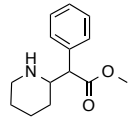
Norethindrone
Hormone
(oral contraceptive)



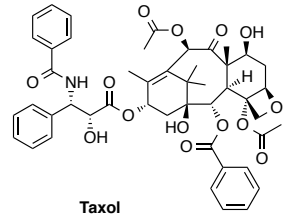
Phenobarbital
Anticonvulsant



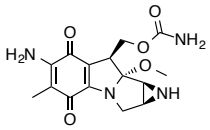
Prozac
Antidepressant



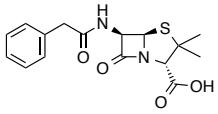
Ritalin
Stimulant



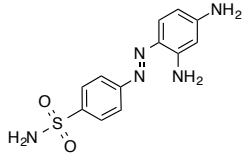
Taxol
Anticancer



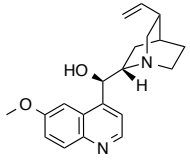
Mitomycin C
Anticancer



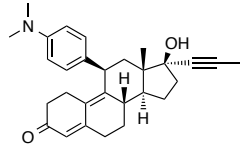
Penicillin
Antibacterial



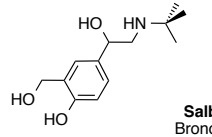
Prontosil
Antibacterial



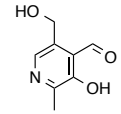
Quinine
Antimalarial



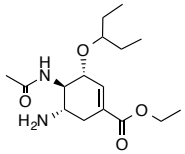
RU-486
Hormone
("abortion pill")



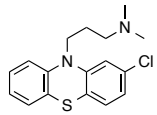
Salbutamol
Bronchodilator
(Asthma)



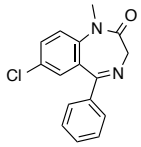
Vitamin B_6
Nutrient



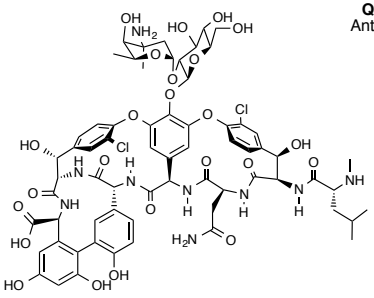
Tamiflu
Antiviral



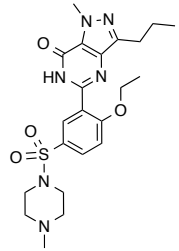
Thorazine
Antipsychotic
(Schizophrenia)



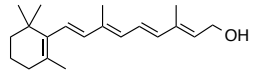
Valium
Tranquilizer



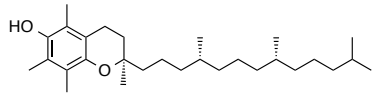
Vancomycin
Antibacterial



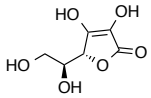
Viagra
Vasodilator



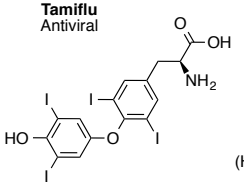
Vitamin A
Nutrient



Vitamin E
Nutrient



Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)

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

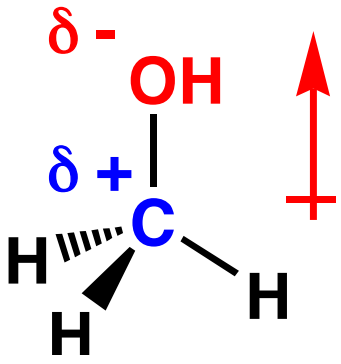
CONTENU	McMurry
1. Généralités	(1, 2, 15)
2. Lipides - stéroïdes - alcanes - alcènes - arènes -	(2 - 5, 16)
3. Glucides - stéréochimie -	(6, 14)
4. Alcools - éthers - phénols - hydroquinones - thiols - disulfures	(8, 16)
5. Glucides - aldéhydes - cétones - imines -	(9, 14)
6. Protéines - lipides - acides - esters - amides -	(10, 11, 15, 16)
7. Acides nucléiques - amines -	(12, 16)

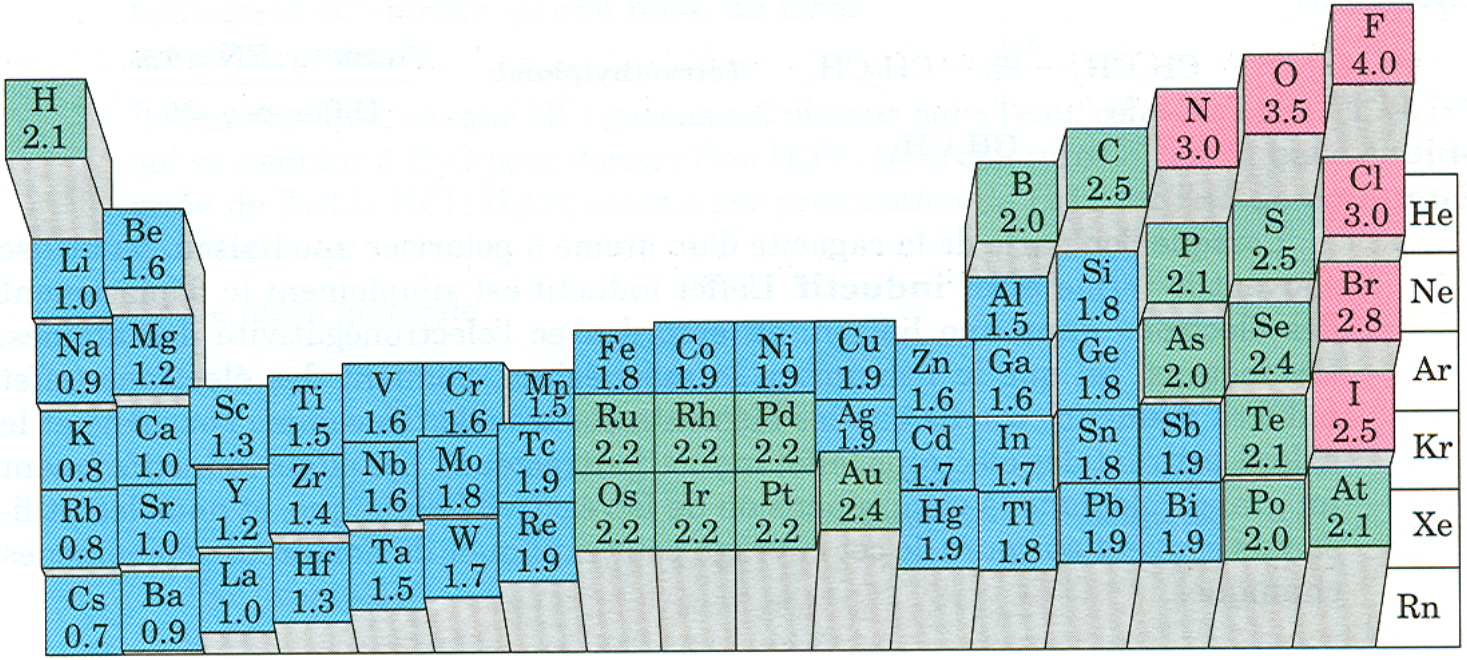
Caractère ionique → **Electronégativité**

Liaison covalente symétrique

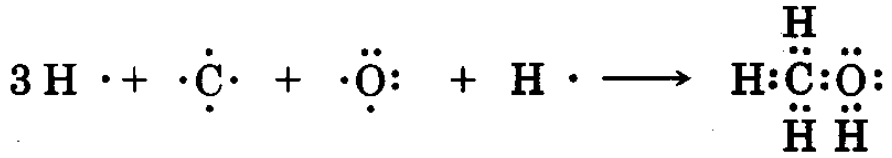
Liaison covalente polaire

Liaison ionique

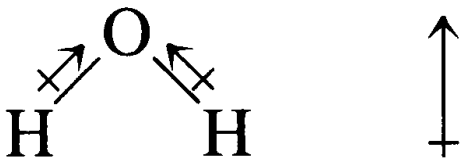




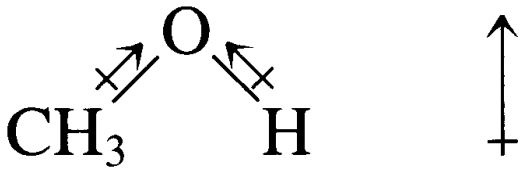
dipôle électrique



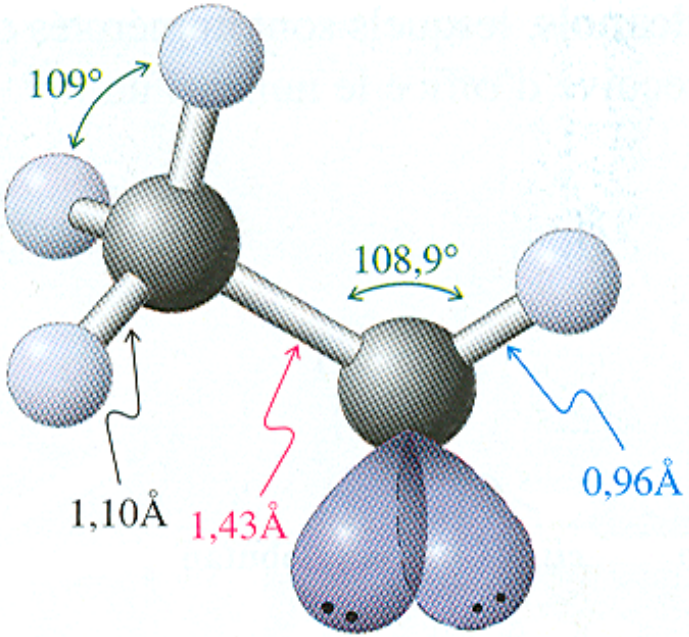
« L'oxygène sp^3 »



Moment dipolaire résultant

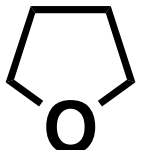


Moment dipolaire résultant



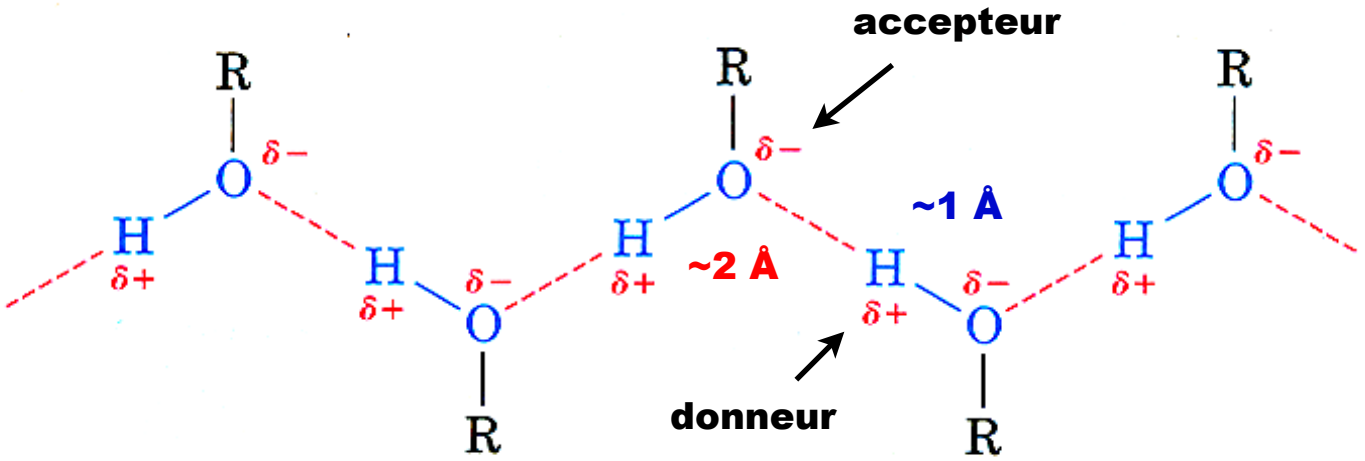
Méthanol

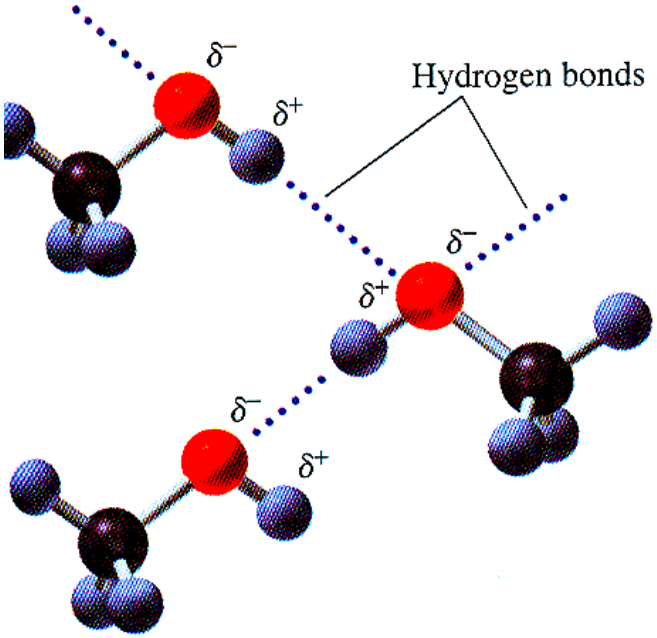
éther (linéaire)

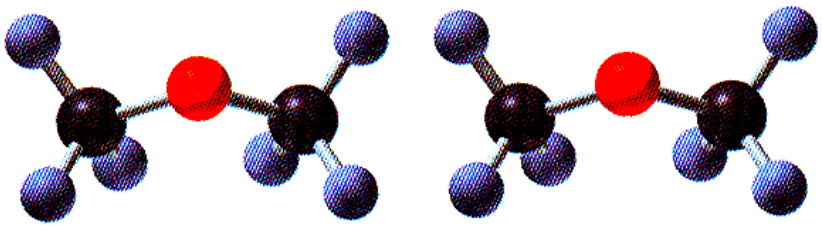


(cyclique)

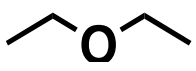
La liaison hydrogène

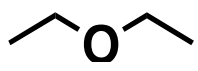


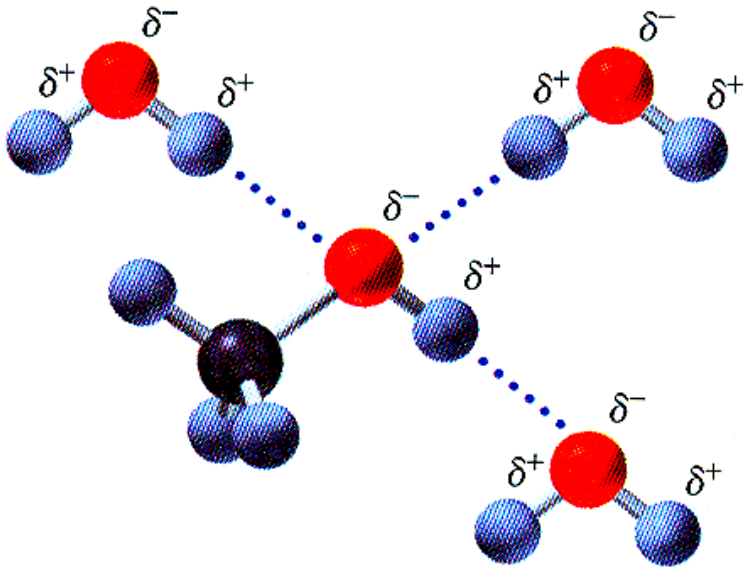


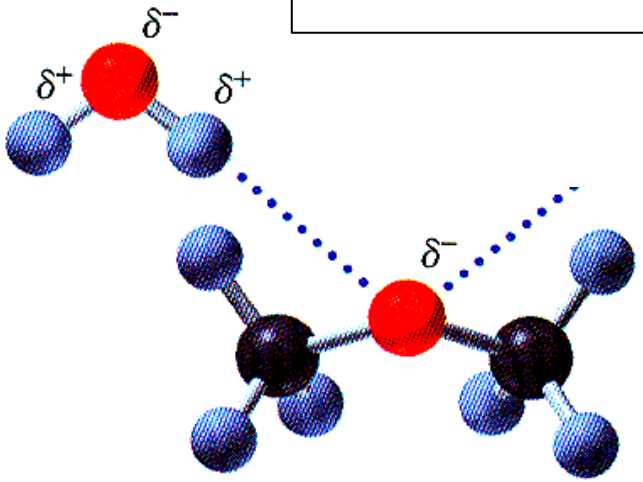


La liaison hydrogène

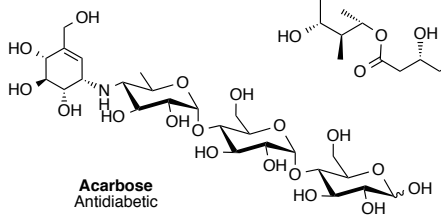
	Solubilité dans H_2O
CH_3CH_2OH	infinie (hydrophile)
CH_3CH_3	5 ml/100 ml (hydrophobe)
	

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

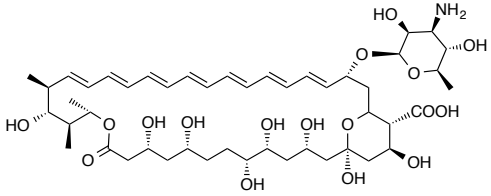




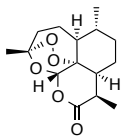
Molécules qui ont changé notre monde...



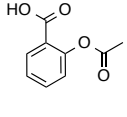
Acarbose
Antidiabetic



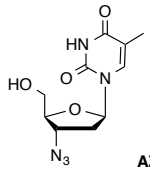
Amphotericin B
Antifungal



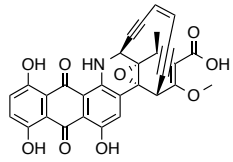
Artemisinin
Antimalarial



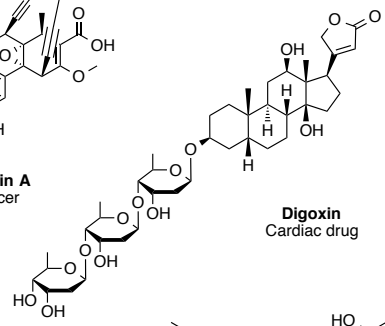
Aspirin
Analgesic



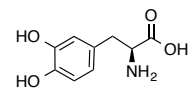
AZT
Antiviral (AIDS)



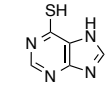
Dynemicin A
Anticancer



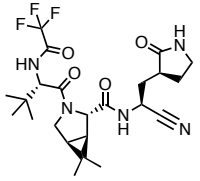
Digoxin
Cardiac drug



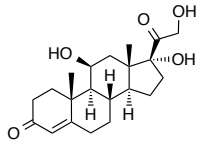
L-Dopa
Antiparkinson



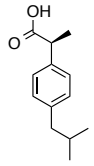
6-Mercaptopurine
Anticancer



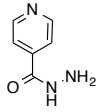
Paxlovid
Antiviral
(SARS-CoV-2)



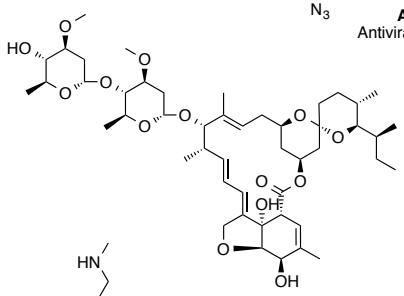
Hydrocortisone
Hormone



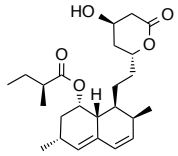
Ibuprofen
Analgesic



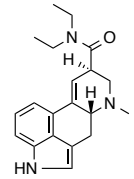
Isoniacid
Antibacterial
(Tuberculosis)



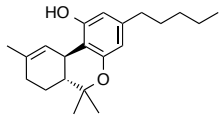
Ivermectin
Antiparasitic
(Onchocerciasis)



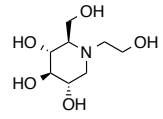
Lovastatin
Anti-cholesterol



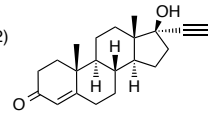
LSD
Psychedelic



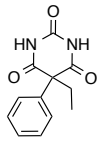
Marijuana
Antiemetic



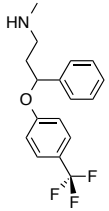
Miglitol
Antidiabetic



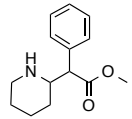
Norethindrone
Hormone
(oral contraceptive)



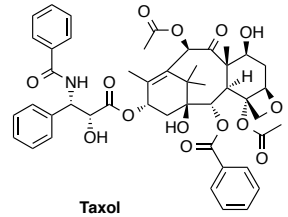
Phenobarbital
Anticonvulsant



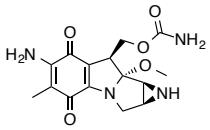
Prozac
Antidepressant



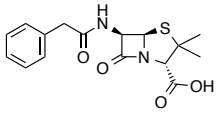
Ritalin
Stimulant



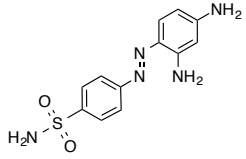
Taxol
Anticancer



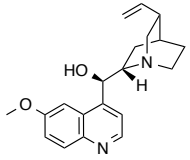
Mitomycin C
Anticancer



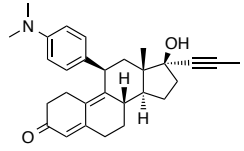
Penicillin
Antibacterial



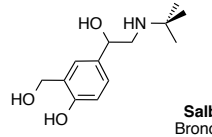
Prontosil
Antibacterial



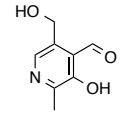
Quinine
Antimalarial



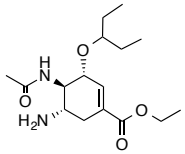
RU-486
Hormone
("abortion pill")



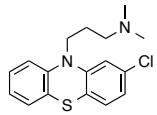
Salbutamol
Bronchodilator
(Asthma)



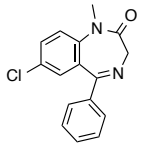
Vitamin B_6
Nutrient



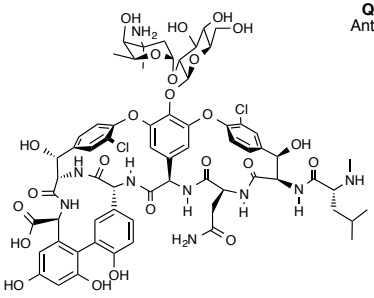
Tamiflu
Antiviral



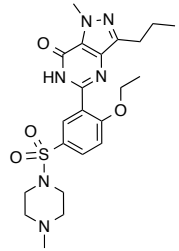
Thorazine
Antipsychotic
(Schizophrenia)



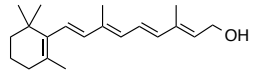
Valium
Tranquilizer



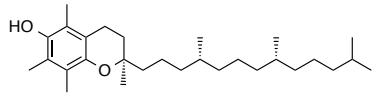
Vancomycin
Antibacterial



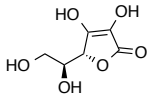
Viagra
Vasodilator



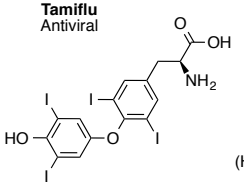
Vitamin A
Nutrient



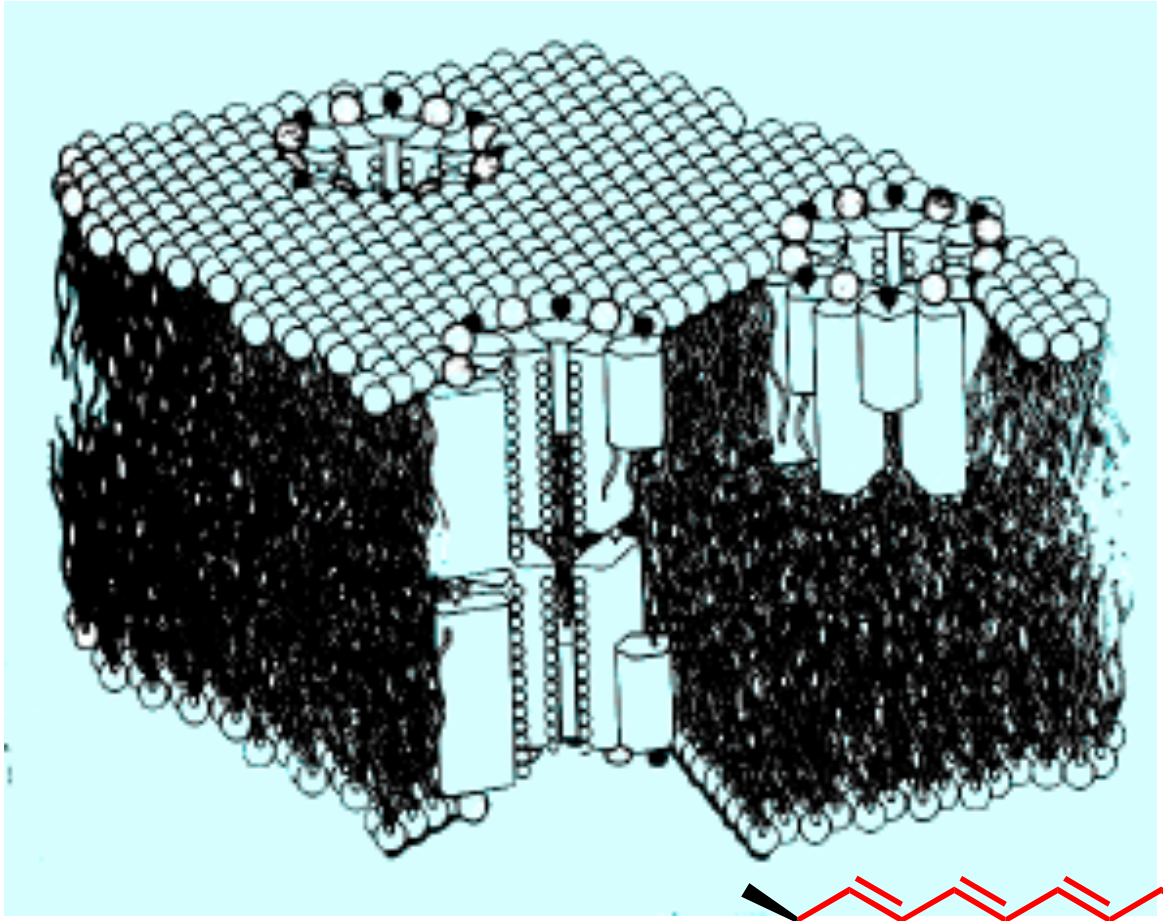
Vitamin E
Nutrient

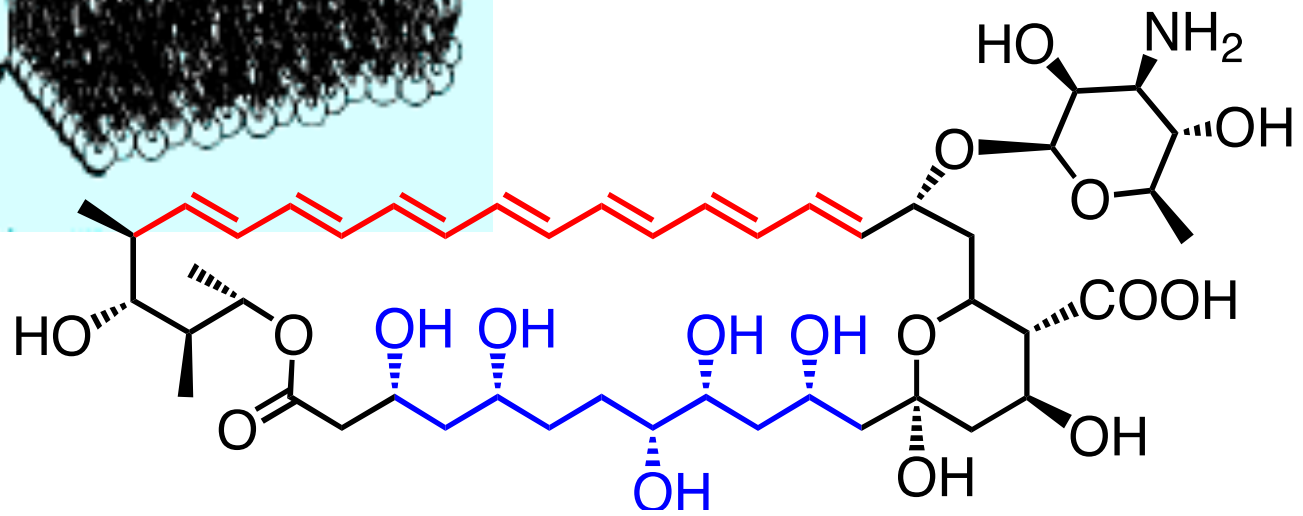


Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)

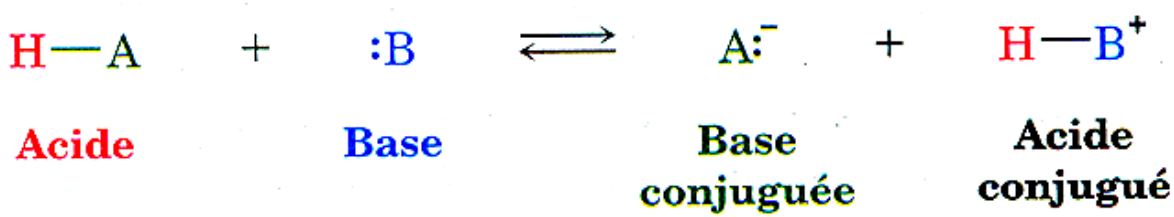




amphotericine B
antibiotique

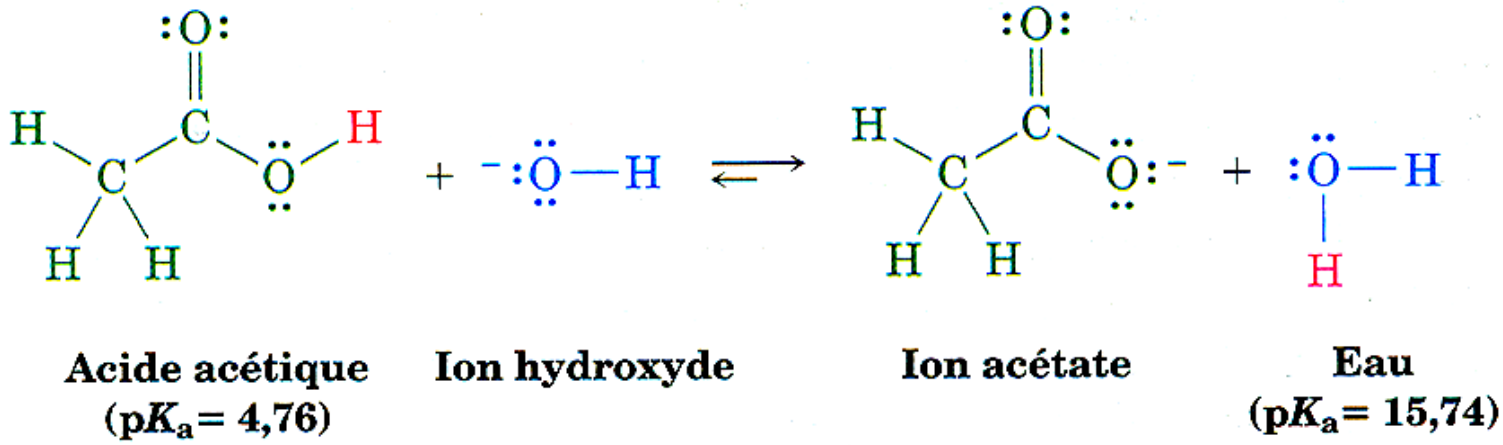
Acides et bases (Brønsted)

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



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

$$pK_a = -\log K_a$$



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

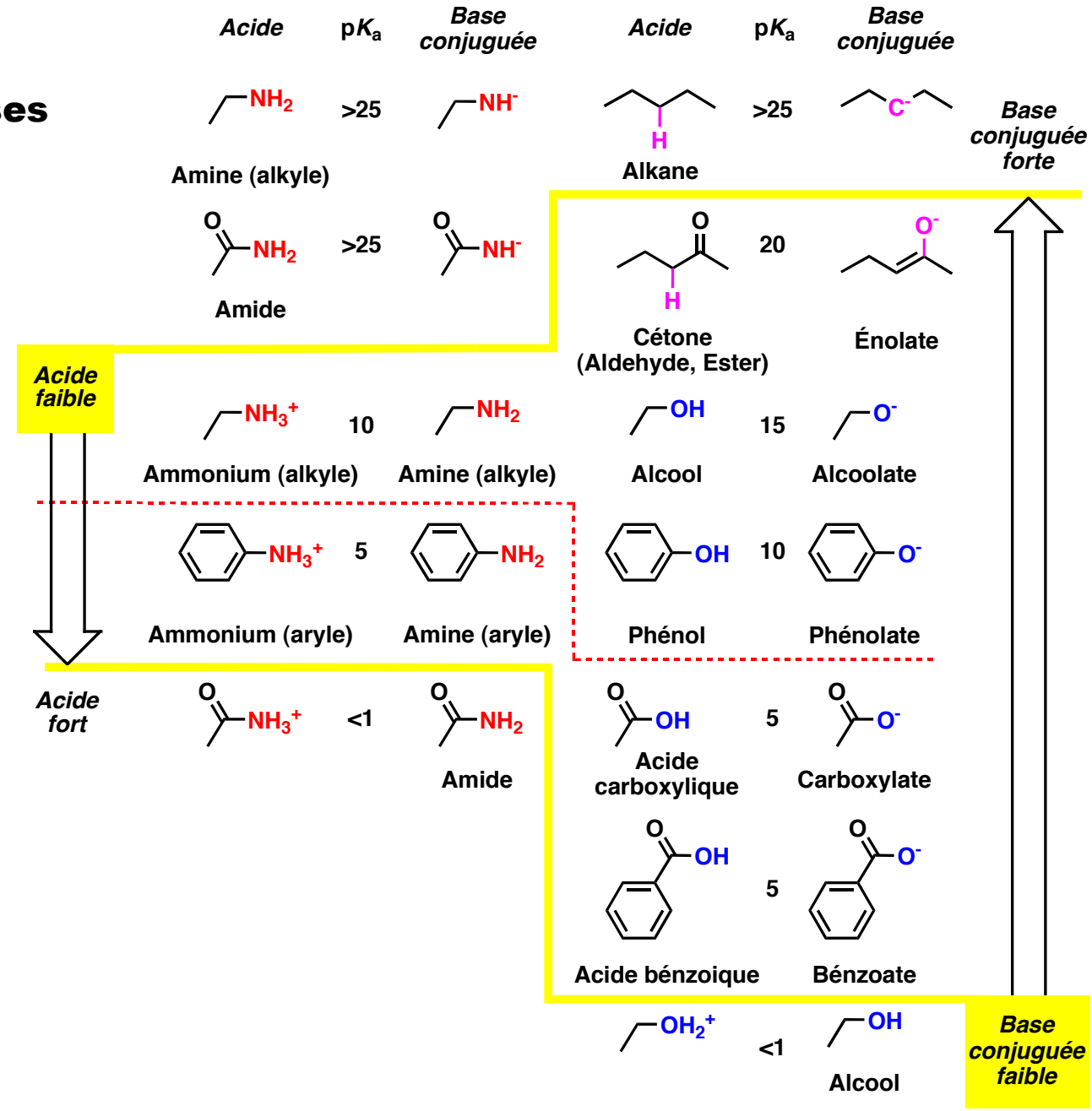
Acides et bases

Tableau 1.3 Acidité relative de certains acides courants

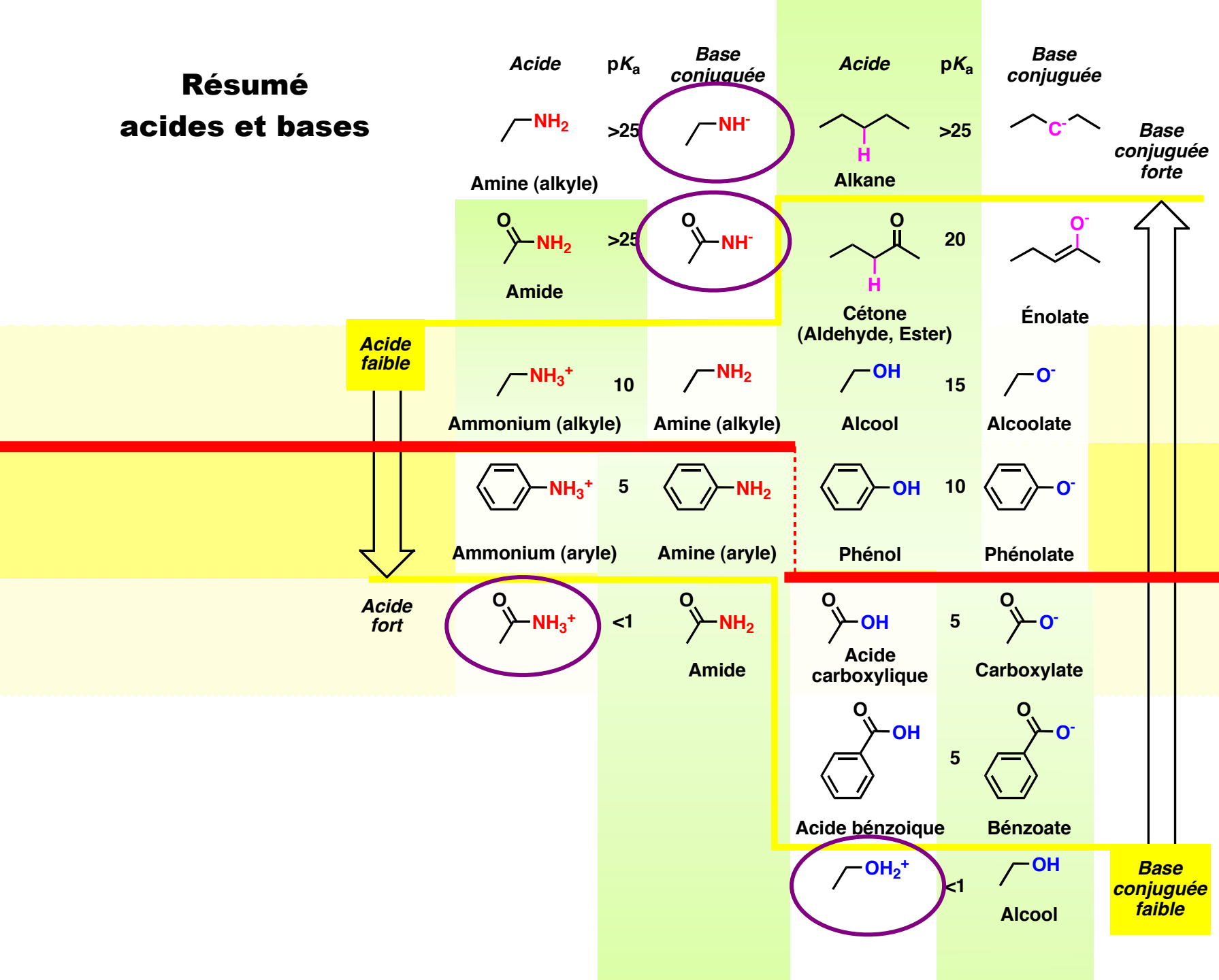
	Acide	*Nom*	pK_a	*Base conjuguée*	*Nom*	
Acide faible	CH_3CH_2OH	Éthanol	16	$CH_3CH_2O^-$	Éthanolate	Base forte
	H_2O	Eau	15,74	HO^-	Hydroxyde	
	HCN	Acide cyanhydrique	9,31	CN^-	Cyanure	
	CH_3COOH	Acide acétique	4,76	CH_3COO^-	Acétate	
	HF	Acide fluorhydrique	3,45	F^-	Fluorure	
	HNO_3	Acide nitrique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

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

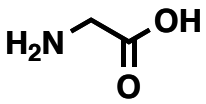
Résumé
acides et bases

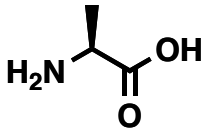


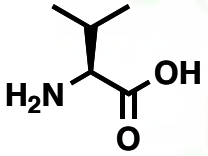
Résumé
acides et bases

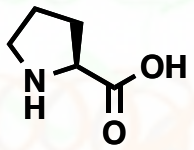


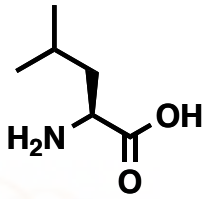
Les acides aminés

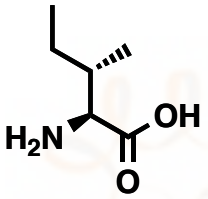

Glycine
(Gly, G)

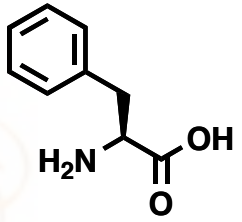

Alanine
(Ala, A)

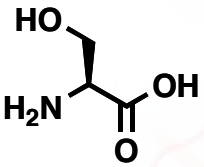

Valine
(Val, V)

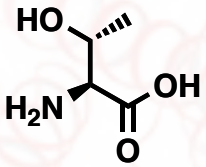

Proline
(Pro, P)

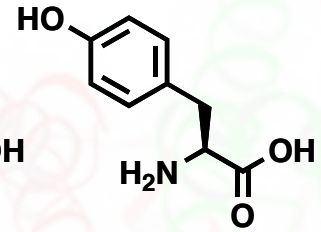

Leucine
(Leu, L)

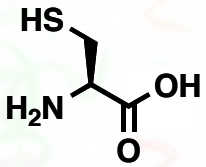

Isoleucine
(Ile, I)

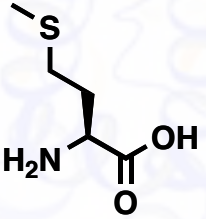

Phénylalanine
(Phe, F)

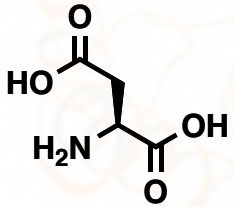

Sérine
(Ser, S)

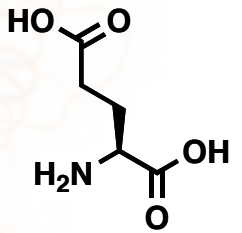

Thréonine
(Thr, T)

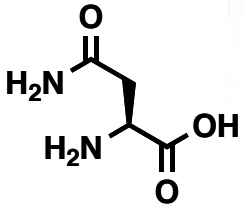

Tyrosine
(Tyr, Y)

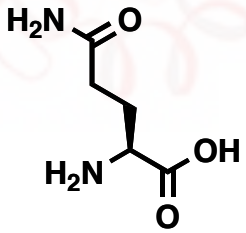

Cystéine
(Cys, C)

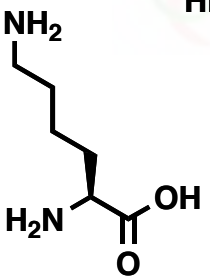

Méthionine
(Met, M)

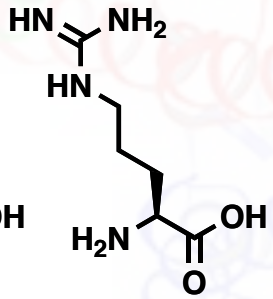

Acide aspartique
(Asp, D)

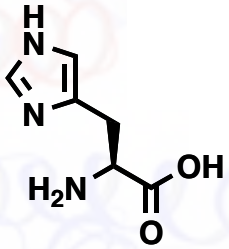

Acide glutamique
(Glu, E)

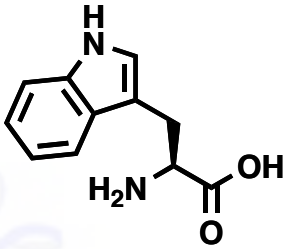

Asparagine
(Asn, N)

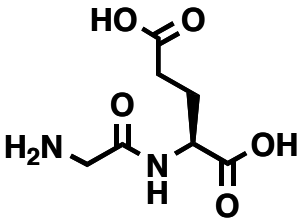

Glutamine
(Gln, Q)


Lysine
(Lys, K)

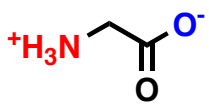

Arginine
(Arg, R)


Histidine
(His, H)

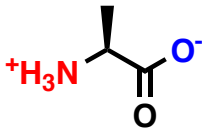

Tryptophane
(Trp, W)



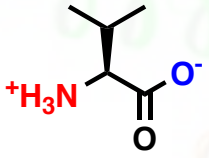
Les acides aminés (pH = 7)



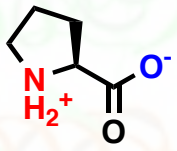
Glycine
(Gly, G)



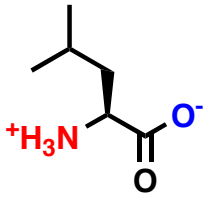
Alanine
(Ala, A)



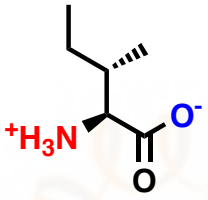
Valine
(Val, V)



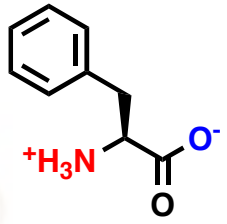
Proline
(Pro, P)



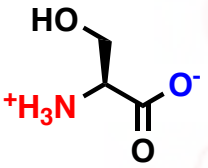
Leucine
(Leu, L)



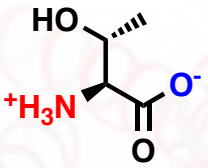
Isoleucine
(Ile, I)



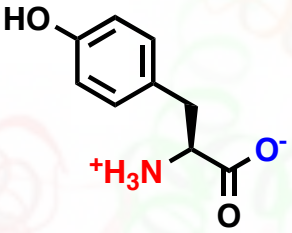
Phénylalanine
(Phe, F)



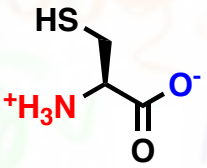
Sérine
(Ser, S)



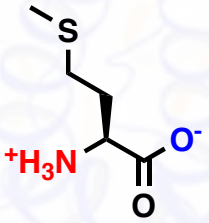
Thréonine
(Thr, T)



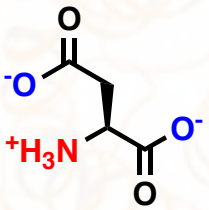
Tyrosine
(Tyr, Y)



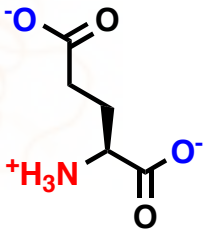
Cystéine
(Cys, C)



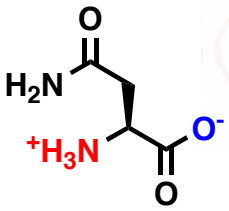
Méthionine
(Met, M)



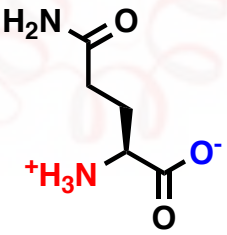
Acide aspartique
(Asp, D)



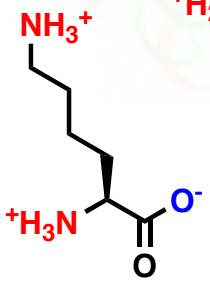
Acide glutamique
(Glu, E)



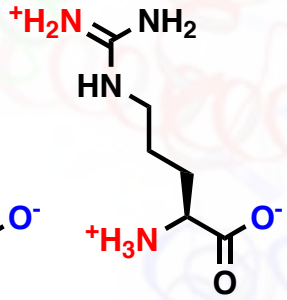
Asparagine
(Asn, N)



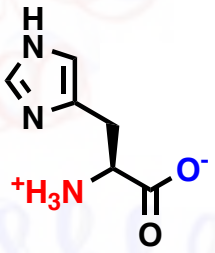
Glutamine
(Gln, Q)



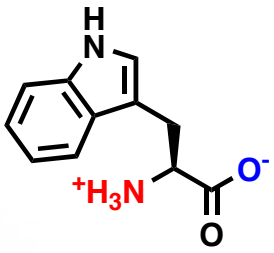
Lysine
(Lys, K)



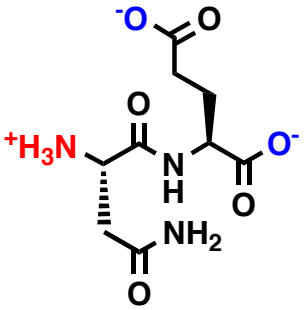
Arginine
(Arg, R)



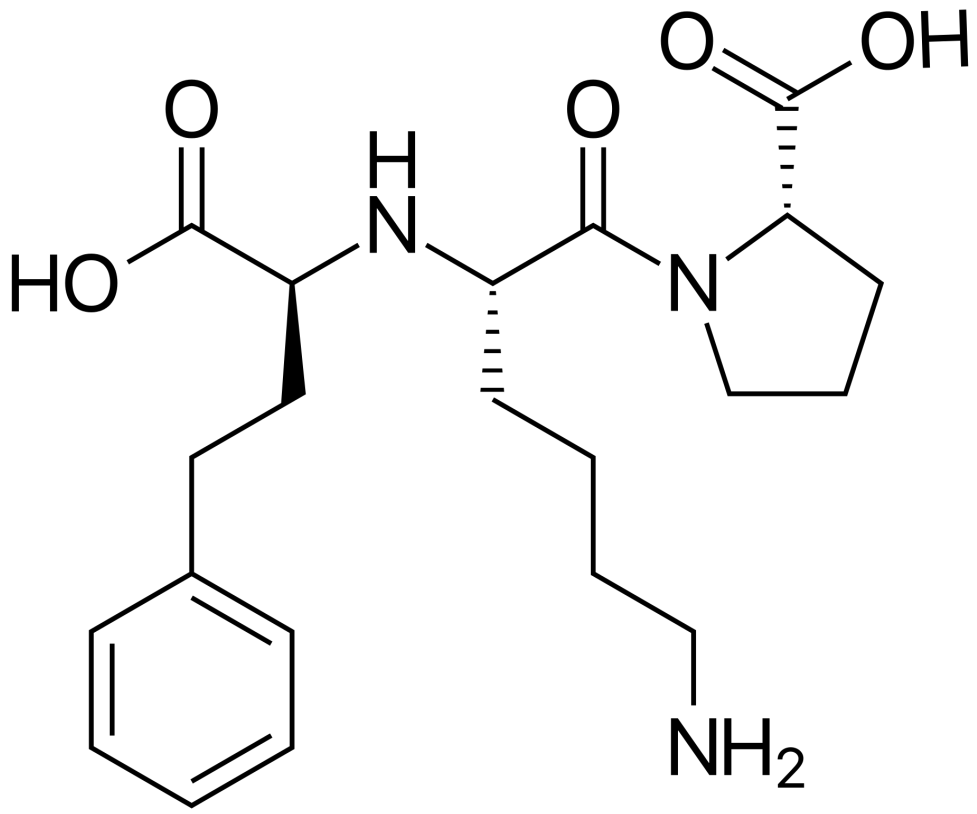
Histidine
(His, H)



Tryptophane
(Trp, W)



Lisitril (Lisinopril)



A **-2**

B **-1**

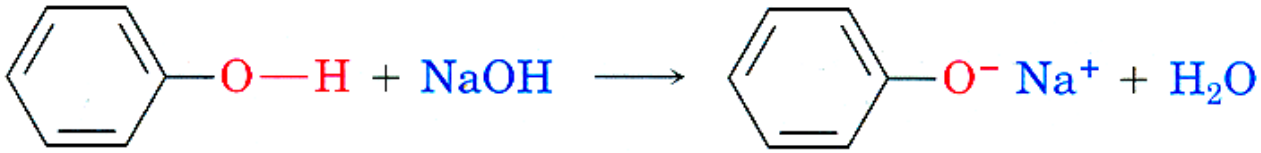
C **0**

D **+1**

E **+2**

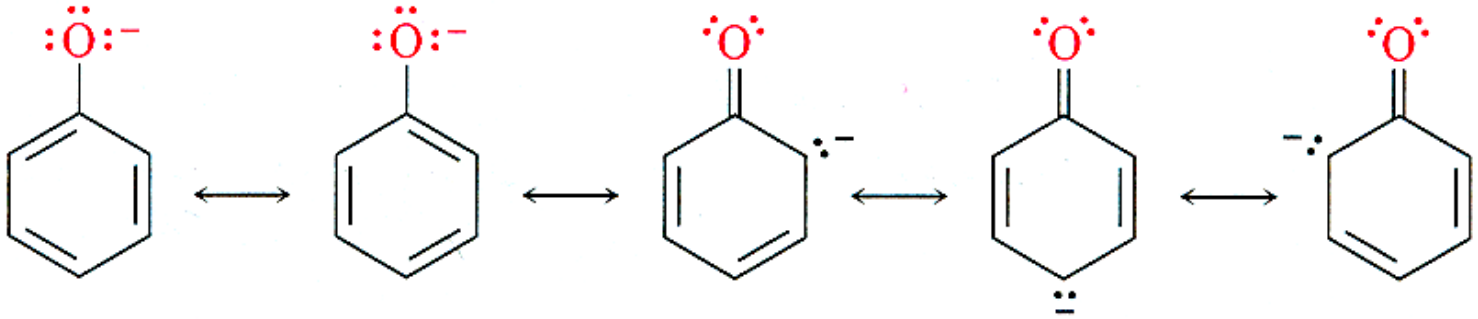
(hypertension, crises cardiaques)

Acidité et résonance

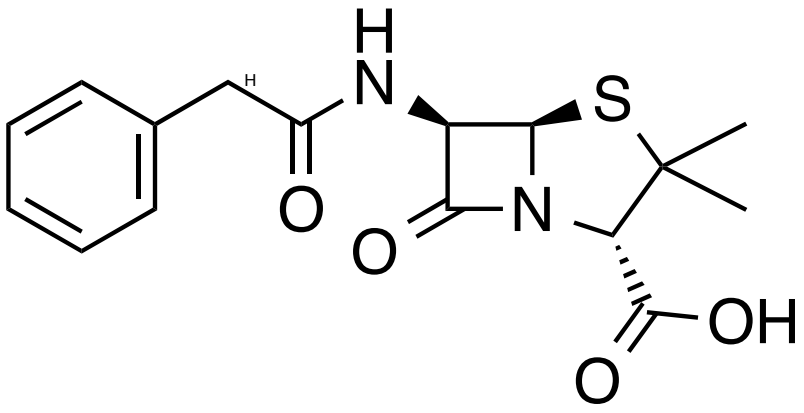


Phénol **Phénolate de sodium**

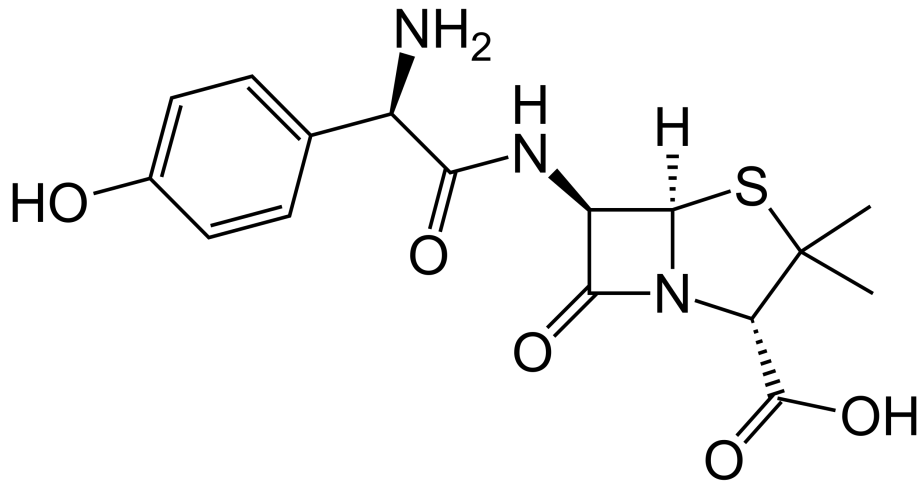
$pK_a \sim 10$



Amoxicilline

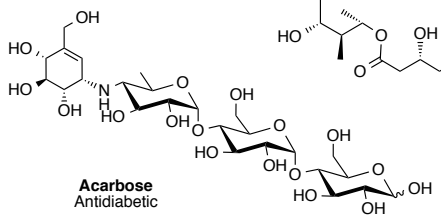


Penicillin
Antibacterial

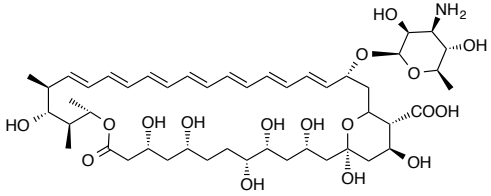


Amoxicillin

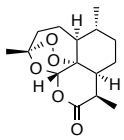
Molécules qui ont changé notre monde...



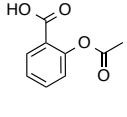
Acarbose
Antidiabetic



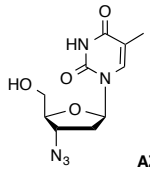
Amphotericin B
Antifungal



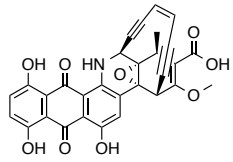
Artemisinin
Antimalarial



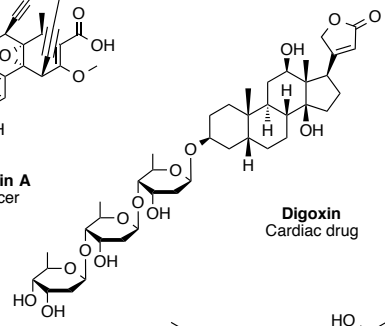
Aspirin
Analgesic



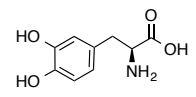
AZT
Antiviral (AIDS)



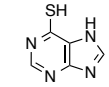
Dynemicin A
Anticancer



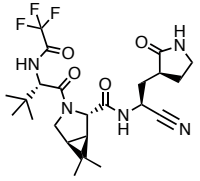
Digoxin
Cardiac drug



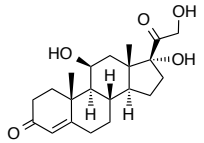
L-Dopa
Antiparkinson



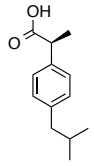
6-Mercaptopurine
Anticancer



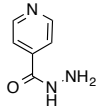
Paxlovid
Antiviral
(SARS-CoV-2)



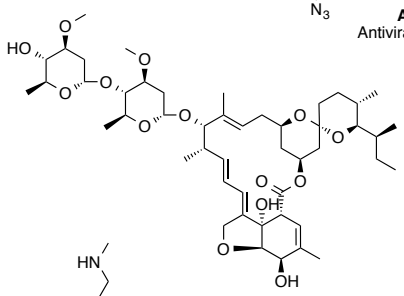
Hydrocortisone
Hormone



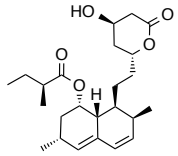
Ibuprofen
Analgesic



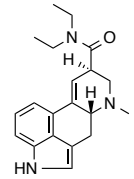
Isoniacid
Antibacterial
(Tuberculosis)



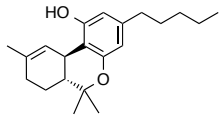
Ivermectin
Antiparasitic
(Onchocerciasis)



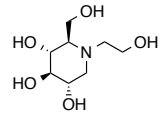
Lovastatin
Anti-cholesterol



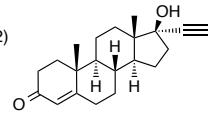
LSD
Psychedelic



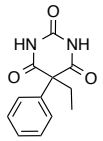
Marijuana
Antiemetic



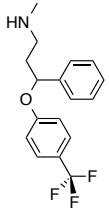
Miglitol
Antidiabetic



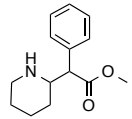
Norethindrone
Hormone
(oral contraceptive)



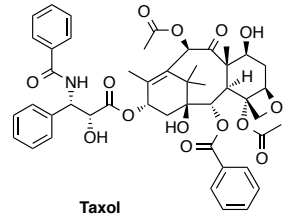
Phenobarbital
Anticonvulsant



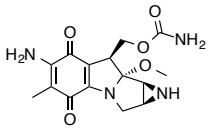
Prozac
Antidepressant



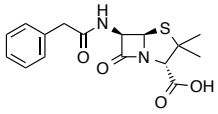
Ritalin
Stimulant



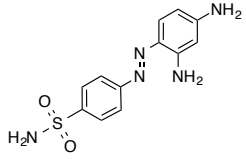
Taxol
Anticancer



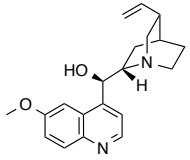
Mitomycin C
Anticancer



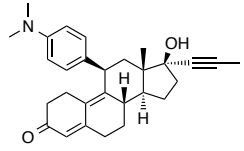
Penicillin
Antibacterial



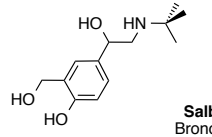
Prontosil
Antibacterial



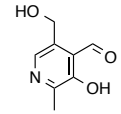
Quinine
Antimalarial



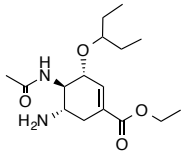
RU-486
Hormone
("abortion pill")



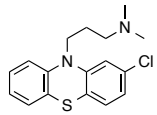
Salbutamol
Bronchodilator
(Asthma)



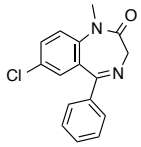
Vitamin B_6
Nutrient



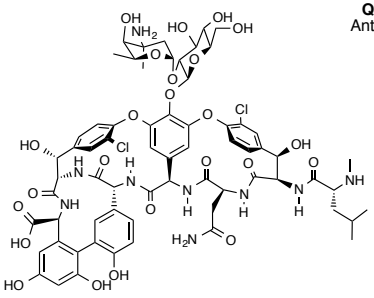
Tamiflu
Antiviral



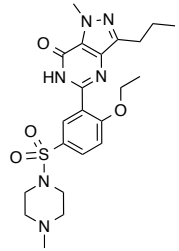
Thorazine
Antipsychotic
(Schizophrenia)



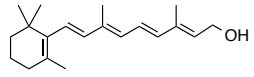
Valium
Tranquilizer



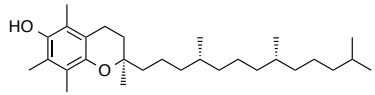
Vancomycin
Antibacterial



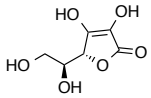
Viagra
Vasodilator



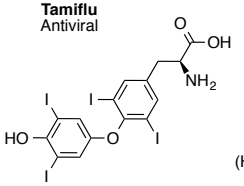
Vitamin A
Nutrient



Vitamin E
Nutrient

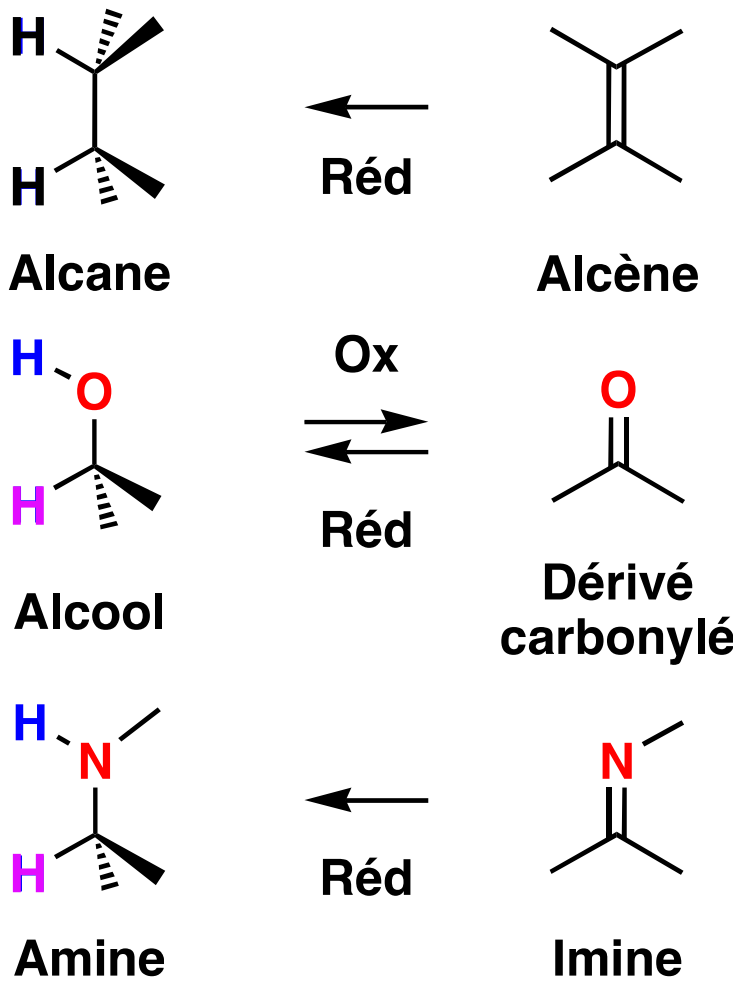


Vitamin C
Nutrient



Thyroxine
Hormone
(Hypothyroidism)

Oxydation - réduction



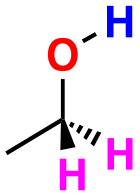
Oxydation : Addition d'oxygène à une molécule ou retrait d'hydrogène (583)

Résumé des réactions

	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 → Hémiacétal (Alcool)	9.8 9.9 14.5 14.6	9.8 14.5 14.6
Aldéhyde / cétone + 2 ROH → Acétal + H_2O (Alcool ; Catalyseur (H_3O^+))	9.8 9.9 14.7	9.8 14.8
Aldéhyde / cétone + RNH_2 → Imine + H_2O (Amine)	9.10	9.9
Acide carboxylique + ROH → Ester + H_2O (Alcool ; Catalyseur (H_3O^+) ; Catalyseur (OH^- ou H_3O^+))	10.8 10.11	10.6 10.9
Ester + $R'NH_2$ → Amide + ROH (Amine ; Chauffage, catalyseur (OH^- ou H_3O^+) ; Alcool)	16.13 10.10	10.9 10.10
Ester → Alcool primaire + ROH ($LiAlH_4$, puis H_3O^+ ; Alcool)	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 + ROH (Catalyseur (NaOR') ; Alcool)	11.11	11.10
β-Cétoester → Cétone + R'OH + CO_2 (Chauffage, catalyseur (OH^- ou H_3O^+))	17.4	17.4
RNH_2 + $R''R'CH$-GP → Alkylamine + HGP^+ (Amine ; GP = groupe partant)	12.4 7.5	12.4 7.7 8.11
Imine → Amine ($NaCNBH_3$, puis H_3O^+)	9.10	9.11

Oxydation - réduction

Réactif Catalyseur (Solvant)



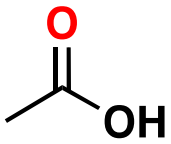
Alcool primaire

Substrat
(Réactant principale)

CrO_3, H_3O^+ (H_2O)

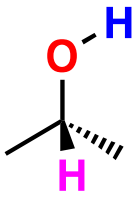
$LiAlH_4$, puis H_3O^+

éther Solvant



Acide carboxylique

Produit

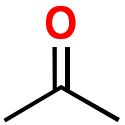


Alcool secondaire

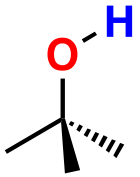
Chauffage

$Na_2Cr_2O_7$ (H_3O^+, Δ)

$NaBH_4$, puis H_3O^+



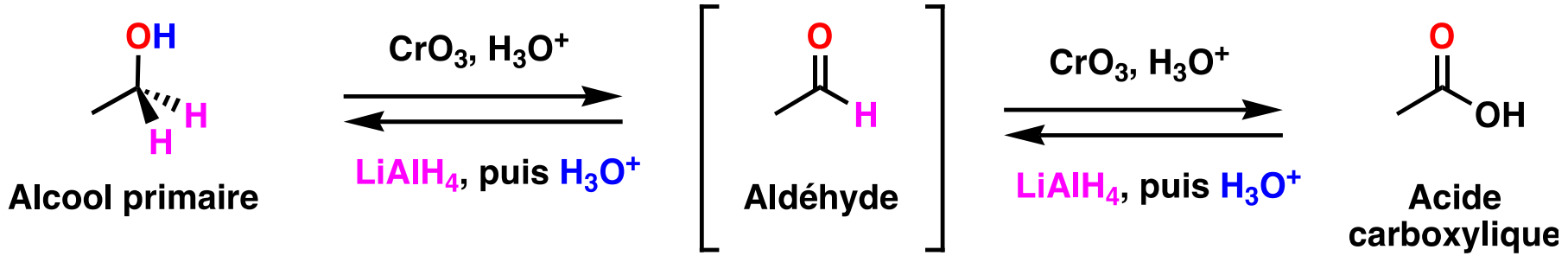
Cétone

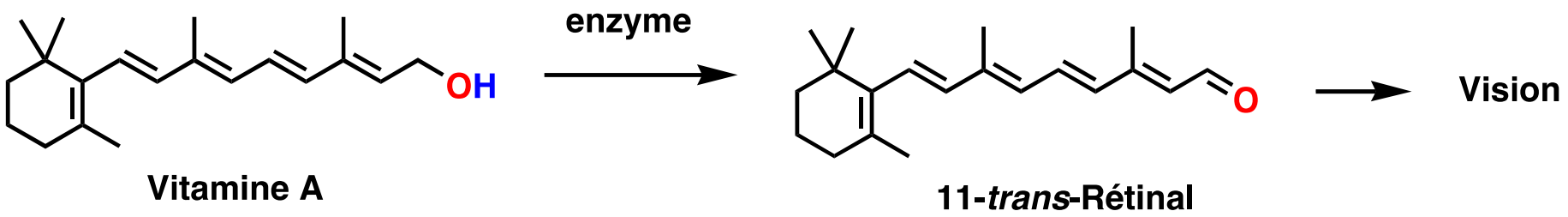


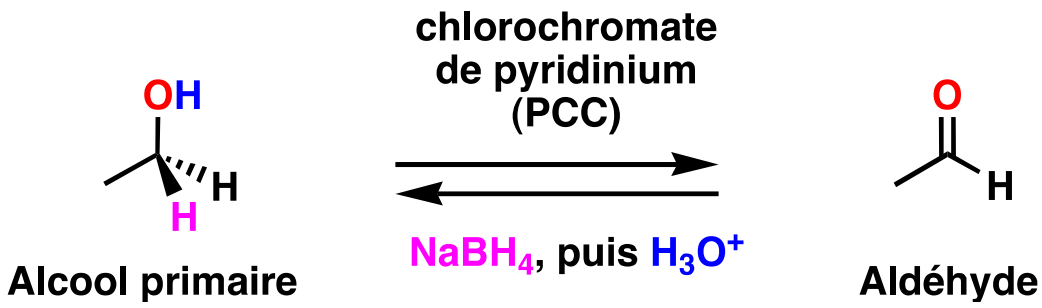
Alcool tertiaire

CrO_3, H_3O^+

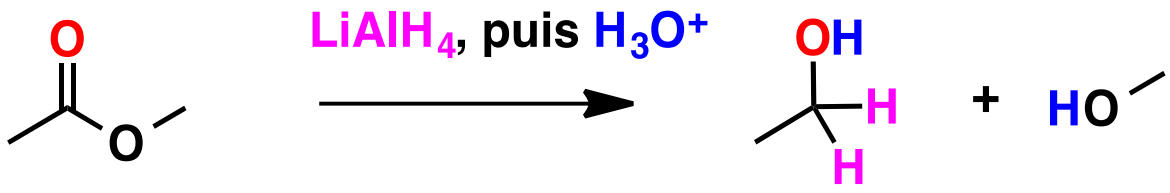
Oxydation des alcools - aldéhydes



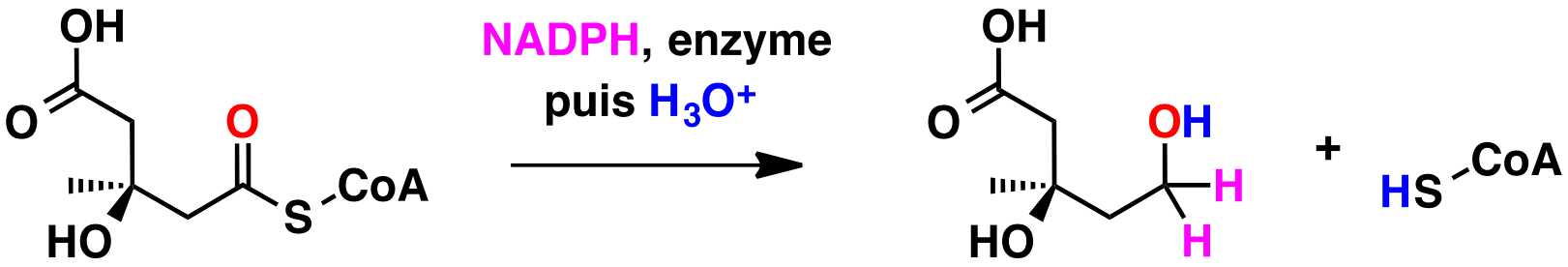




Réduction des esters



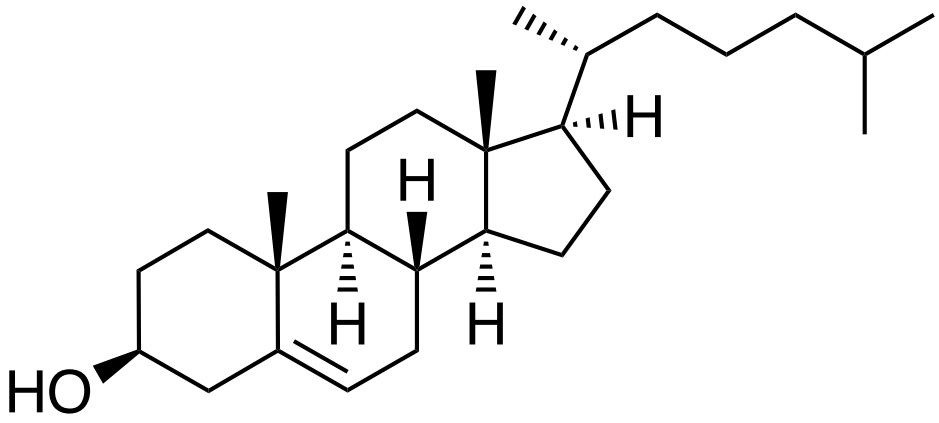
Thioesters, sélectivité



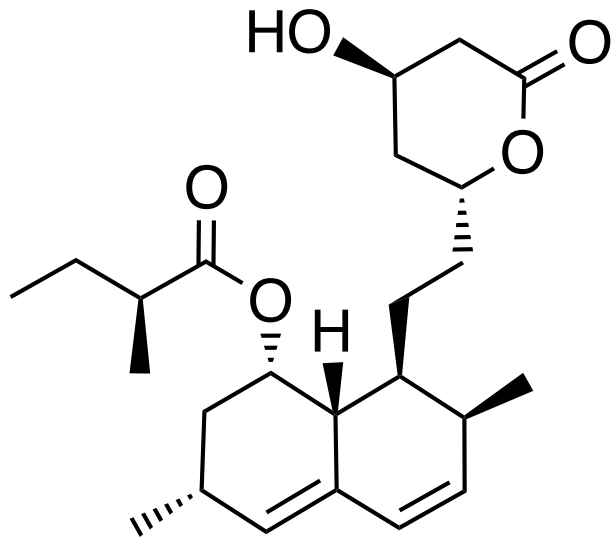
HMG-CoA

Mévalonate

La biosynthèse des stéroïdes
Médicaments anti-cholestérol

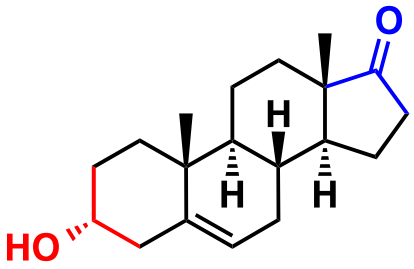


Cholestérol



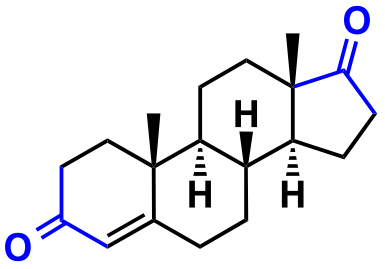
Lovastatin

Les androgènes - stéroïdes sexuels



Dehydroépiandrostérone (DHEA)

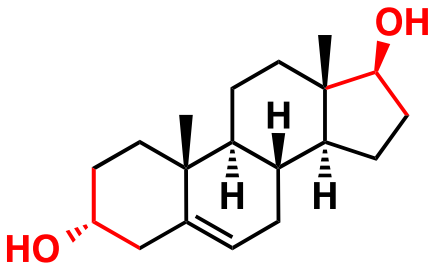
Oxydation enzymatique



Androstènedione

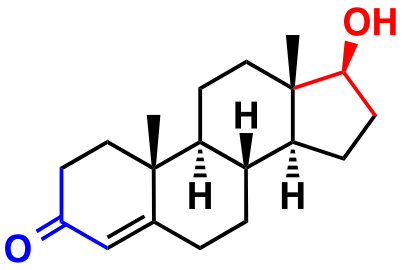
Réduction enzymatique ↓ ↑ *Oxydation enzymatique*

Réduction enzymatique ↓ ↑ *Oxydation enzymatique*



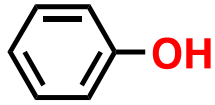
Androstènediol

Oxydation enzymatique



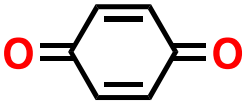
Testostérone

Oxydation des phénols - quinones



Phénol

$Na_2Cr_2O_7$, H_3O^+



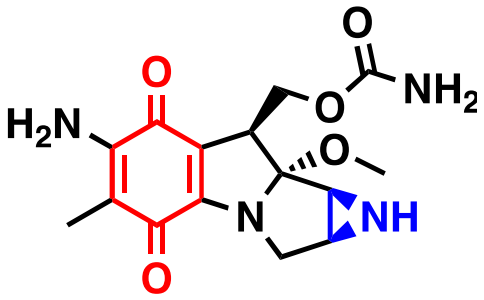
Benzoquinone

Benzoquinone

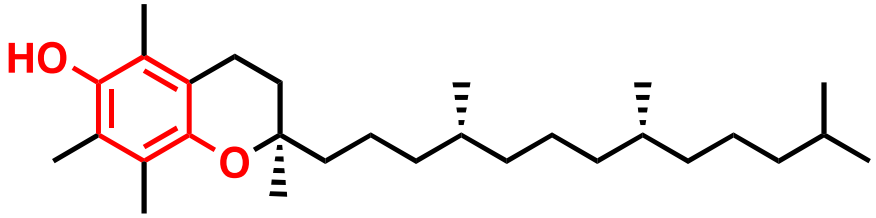
$NaBH_4$, puis H_3O^+

$Na_2Cr_2O_7$, H_3O^+

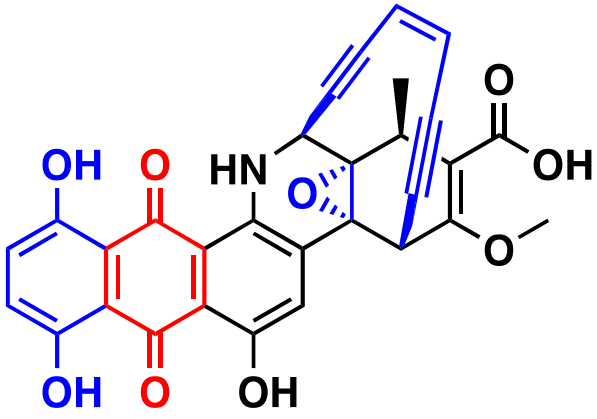
Hydroquinone



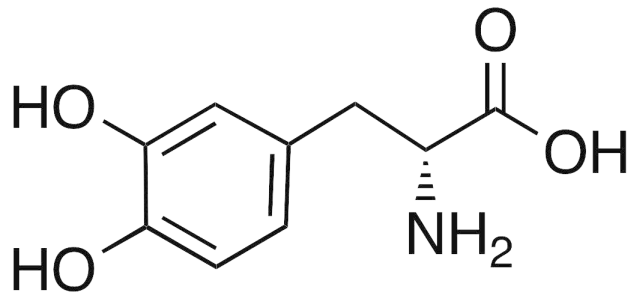
Mitomycin C
(anticancéreux)



α-tocopherol (vitamin E)



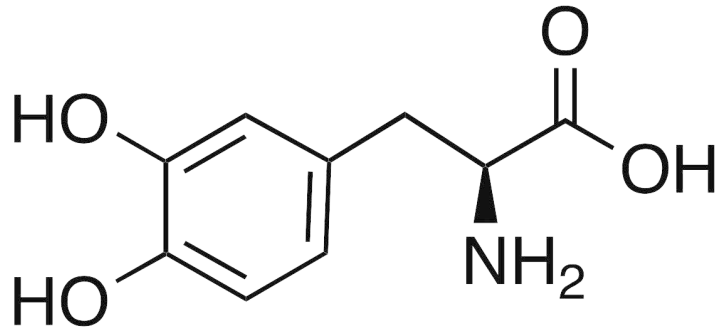
Dynémicine A
(anticancéreux)



D-Dopa
pas d'effet biologique (208)

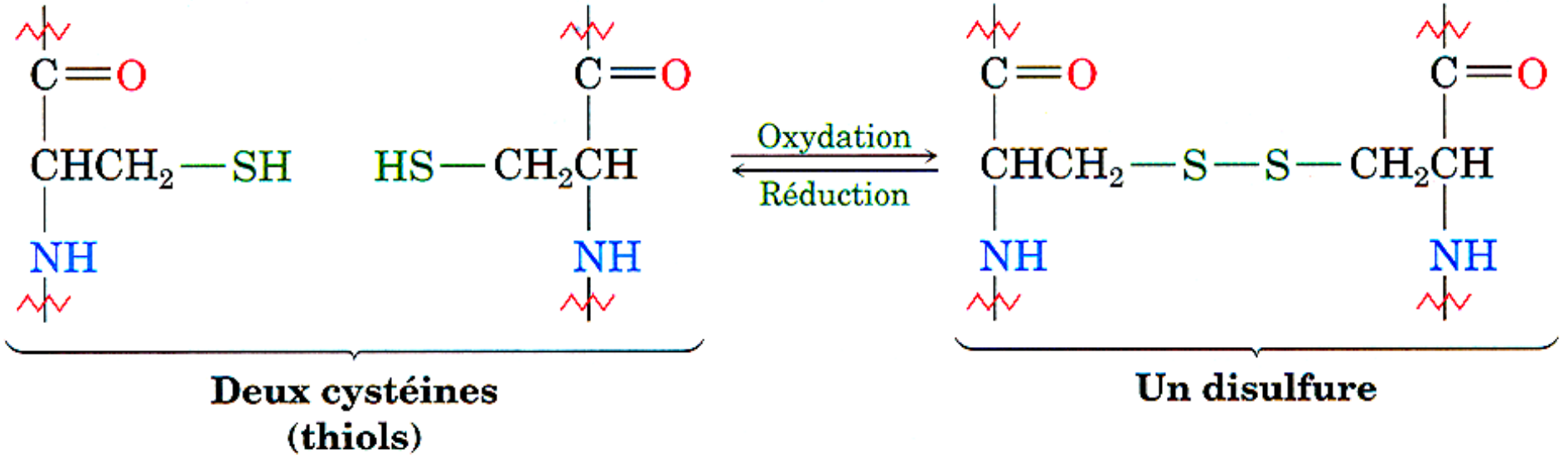
1967
Hoffman-La Roche
Synthesis: William Knowles, Monsanto, prix Nobel 2001

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

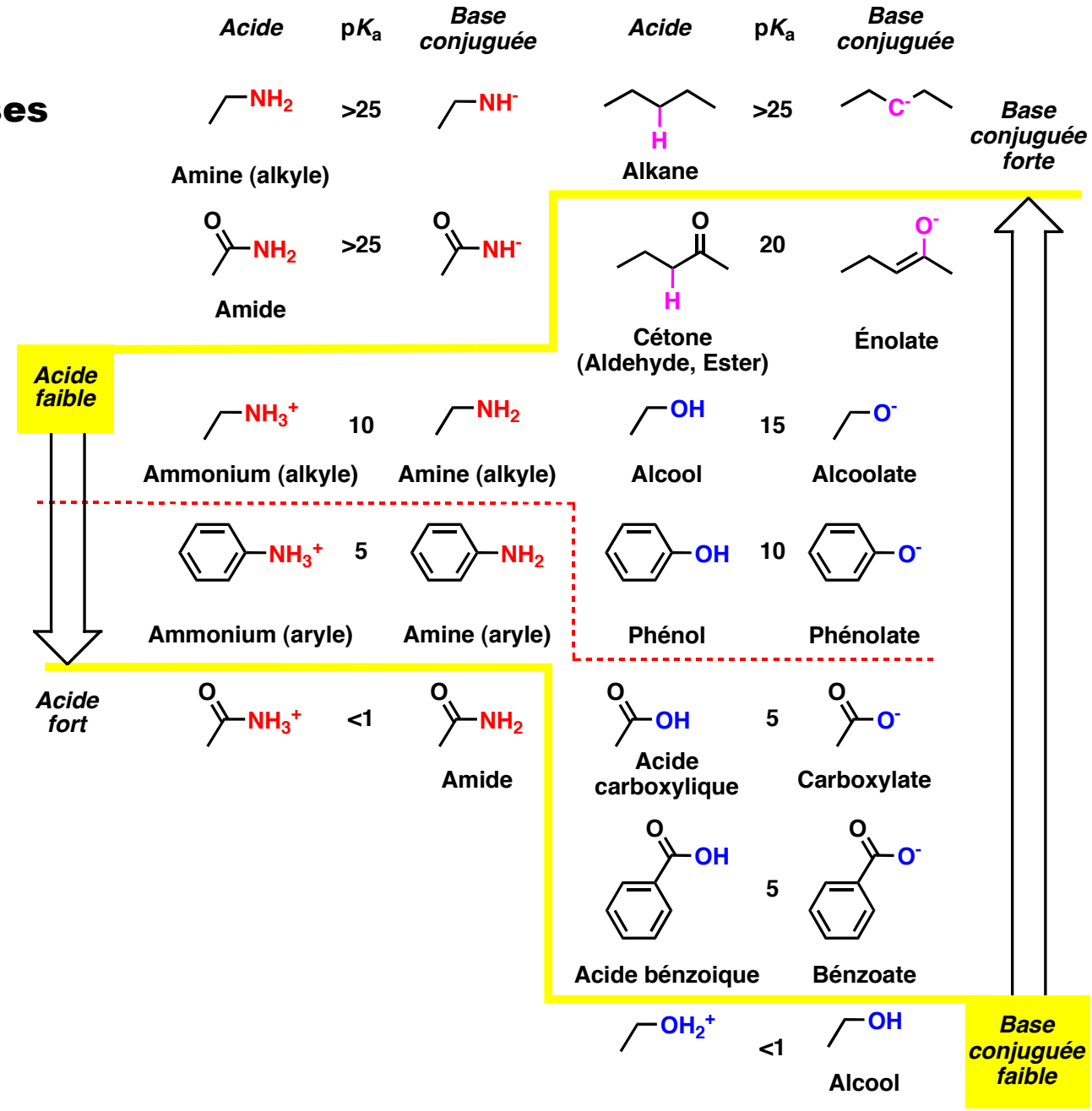
Oxydation des thiols - disulfures



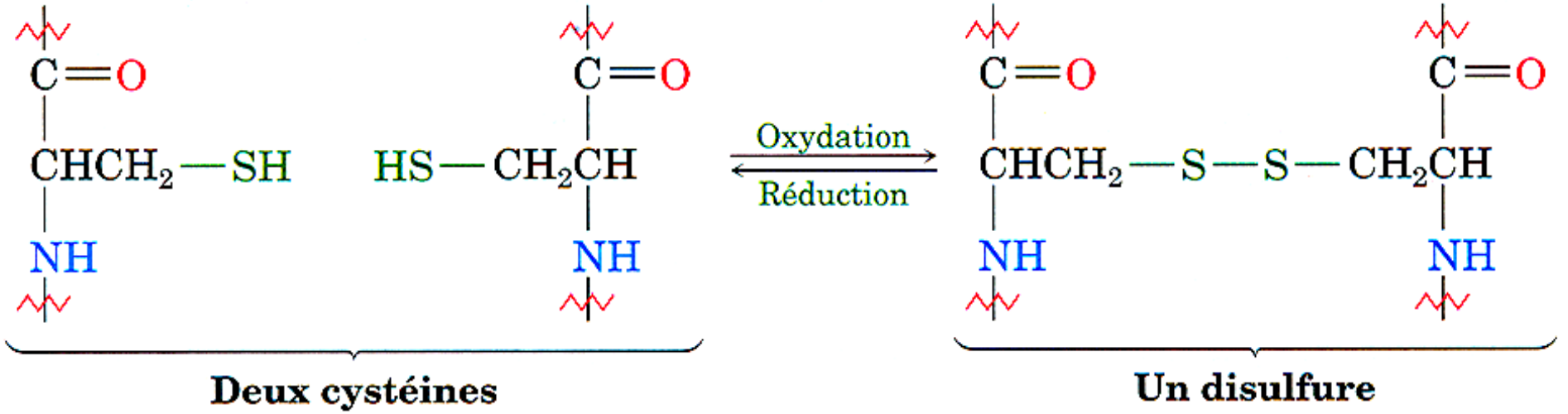
$pK_a \sim 8$

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

Résumé
acides et bases



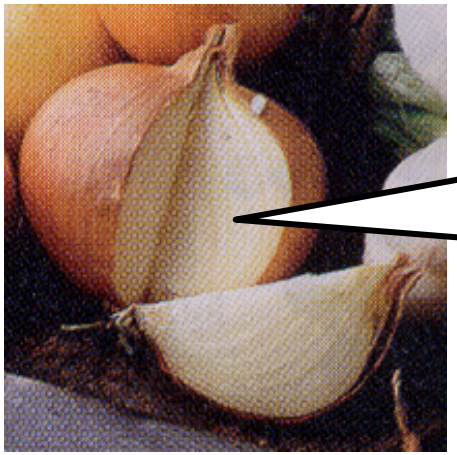
Oxydation des thiols - disulfures

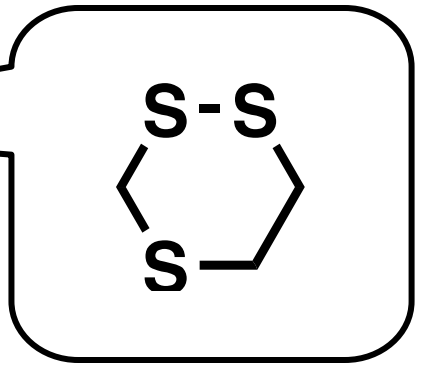


$pK_a \sim 8$

EN = 2.5

S–H = 1.34 Å





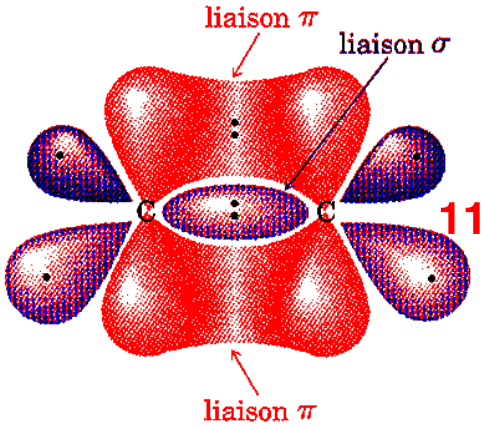
Oxydation : Addition d'oxygène à une molécule ou retrait d'hydrogène (583)

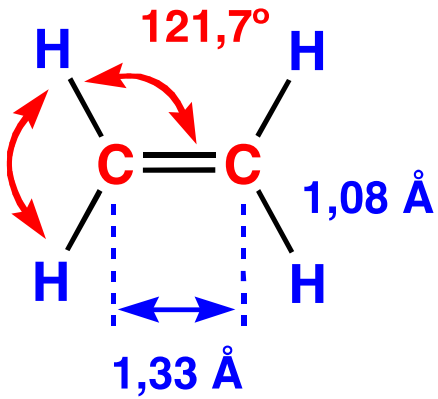
Résumé 4 (Alcools - phénols -)

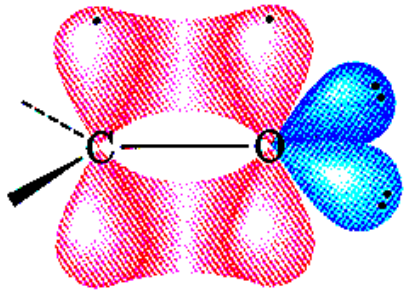
- liaison hydrogène :
  - donneur / accepteur - solubilité - points d'ébullition
- acides / bases :
  - donneur / accepteur H^+ (Brønsted) - conjugué - pK_a
  - acidité - résonance (alcool - phénol)
- oxydation / réduction :
  - alcool primaire : acide carboxylique
    - aldéhyde (PCC, rétinal) - ester,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

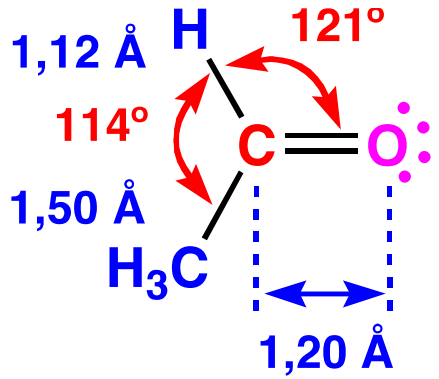
CONTENU	McMurry
1. Généralités	(1, 2, 15)
2. Lipides - stéroïdes - alcanes - alcènes - arènes -	(2 - 5, 16)
3. Glucides - stéréochimie -	(6, 14)
4. Alcools - éthers - phénols - hydroquinones - thiols - disulfures	(8, 16)
5. Glucides - aldéhydes - cétones - imines -	(9, 14)
6. Protéines - lipides - acides - esters - amides -	(10, 11, 15, 16)
7. Acides nucléiques - amines -	(12, 16)

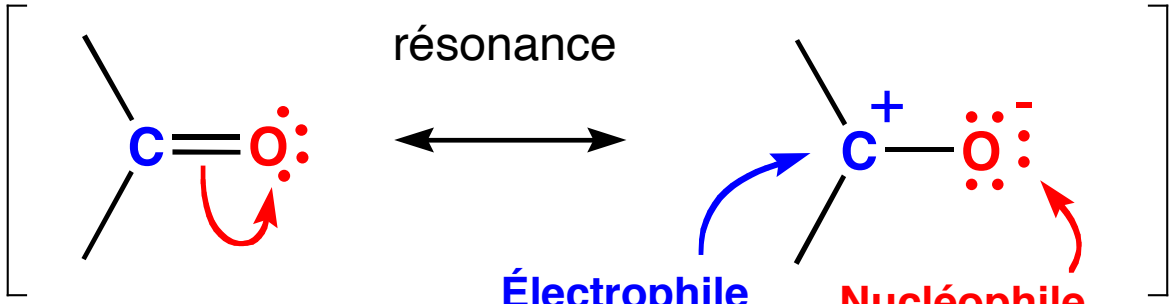
Le groupe carbonyle



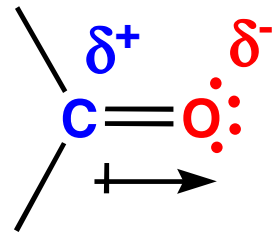




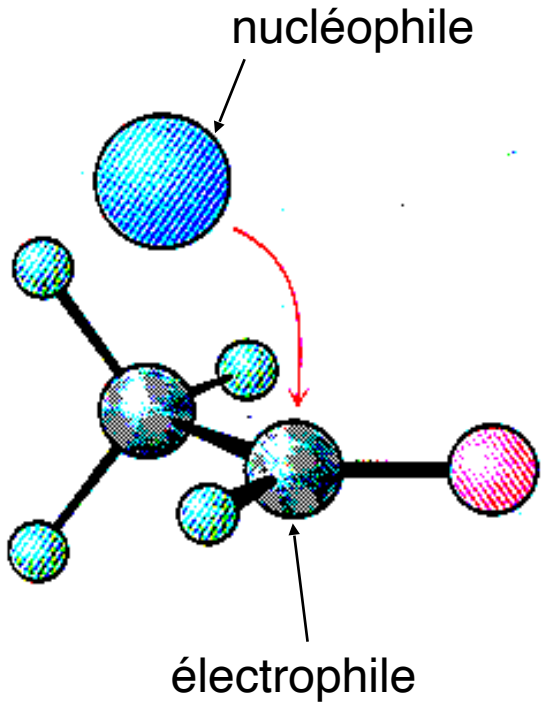




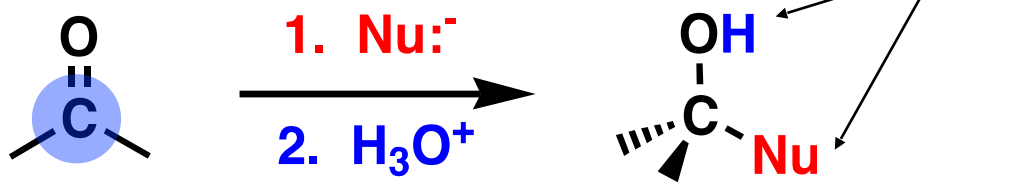
ou



Addition nucléophile

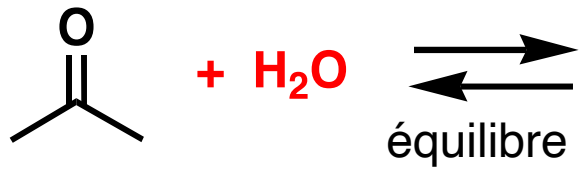


électrophile nucléophile



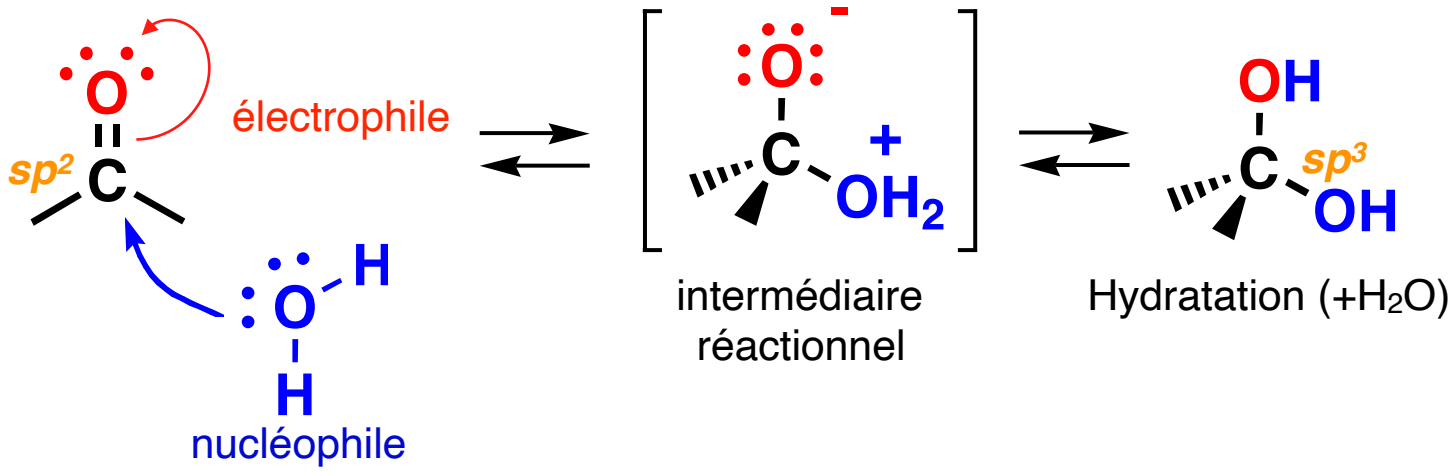
Hydratation

acétone

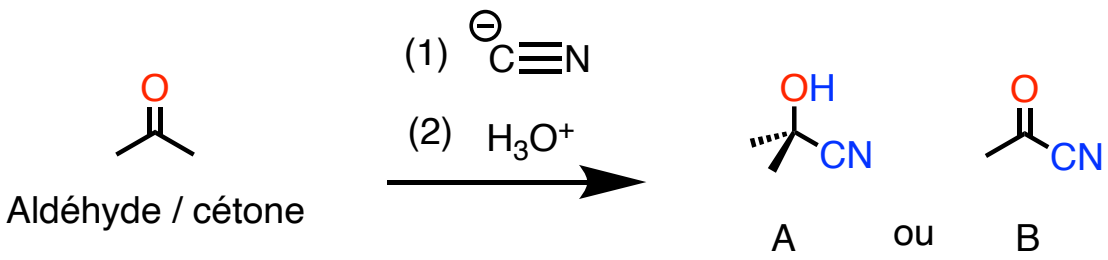


hydrate d'acétone
(un diol géminé)

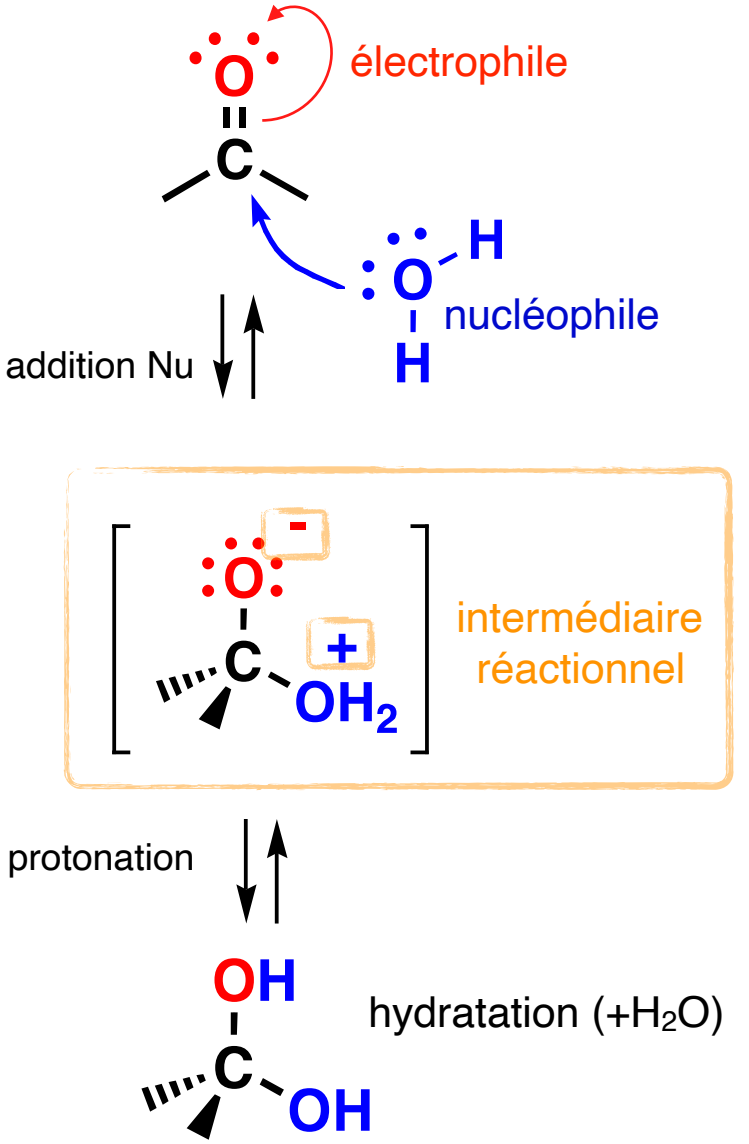
Addition nucléophile

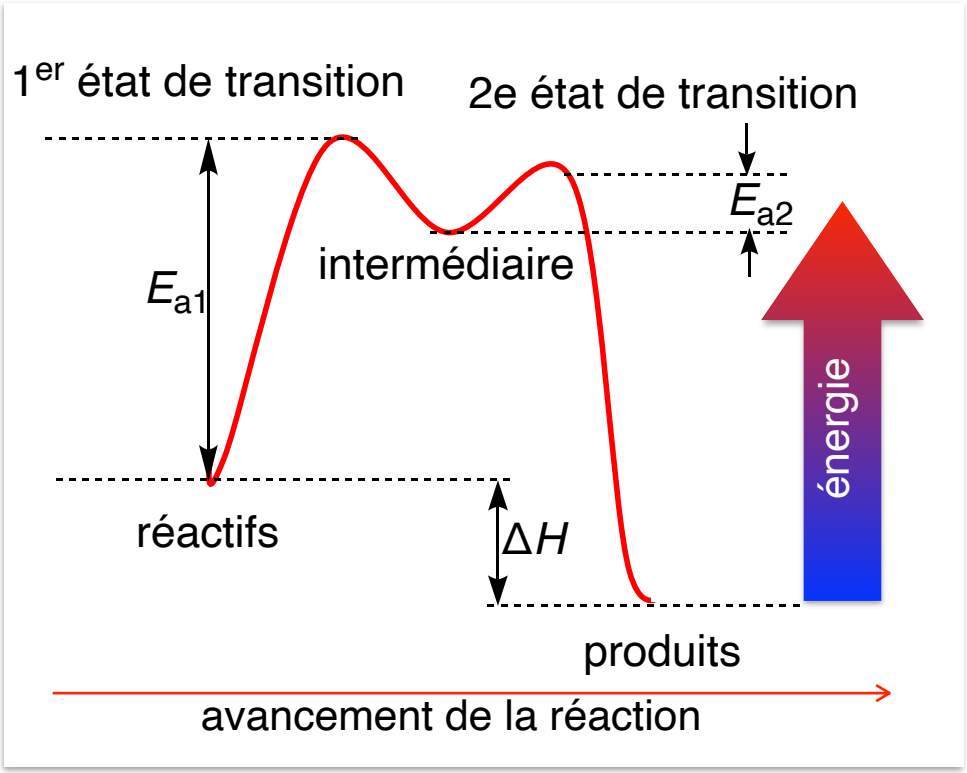


Quel produit obtiendrez vous lors de la réaction de l'ion cyanure avec l'acétone suivit d'une protonation de l'intermédiaire?



Addition nucléophile





Quelques énergies

	kJ / mol
E_a (température ambiante)	80
briser liaison C-C	380
Basculement cyclohexane	45
Rotation liaison C-C	12
Liaison hydrogène	20-40

(99) 96

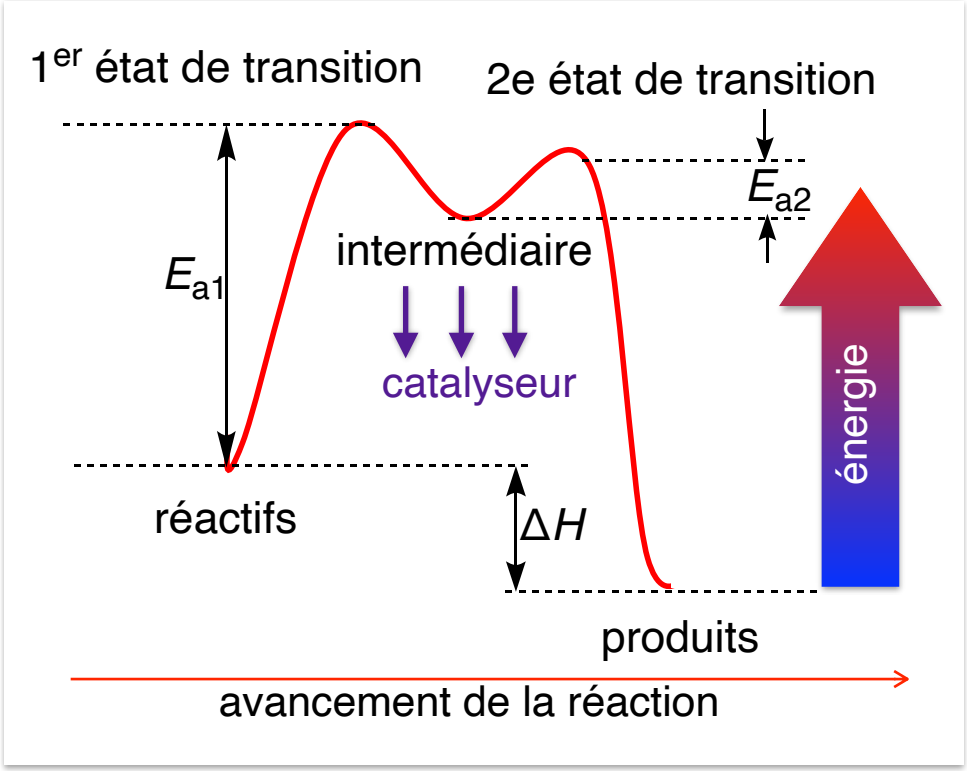
(14) 13

(65) 63

(54) 54

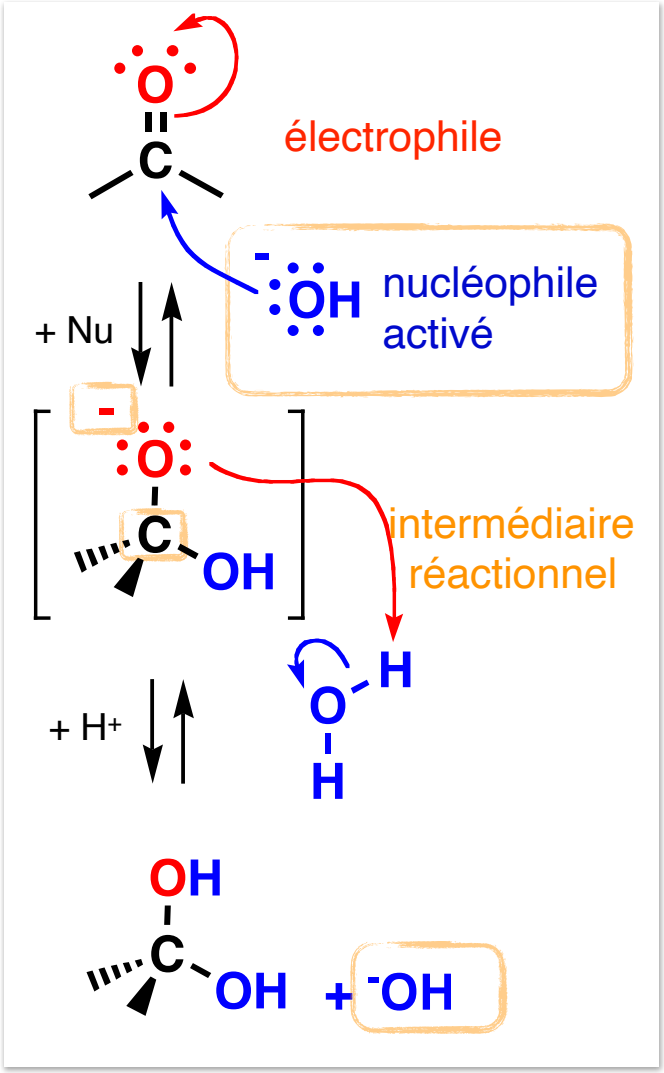
(255)

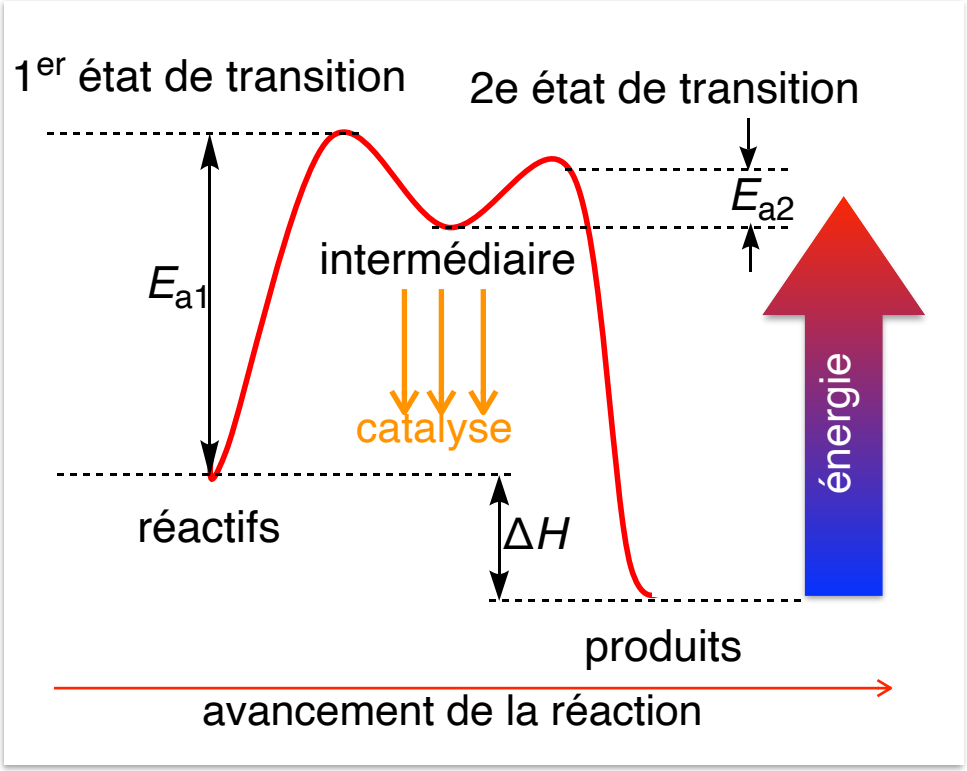
Catalyseur


1er état de transition
2e état de transition
Ea2
intermédiaire
Ea1
catalyseur
énergie
réactifs
ΔH
produits
avancement de la réaction

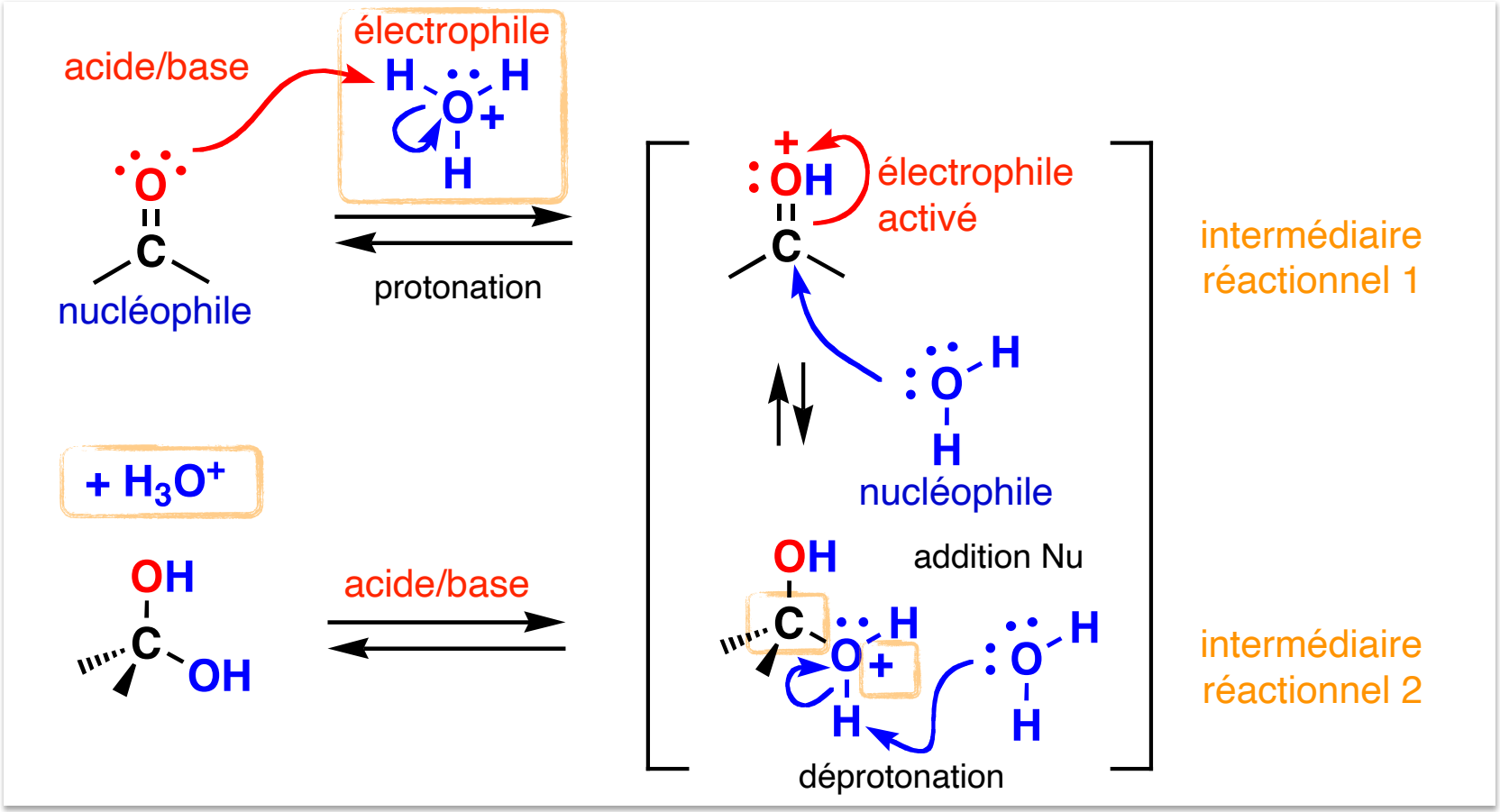
Catalyse basique

288-293, 95-98
(290, 97-101)





Catalyse acide



Quelles affirmations sont exacts?

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

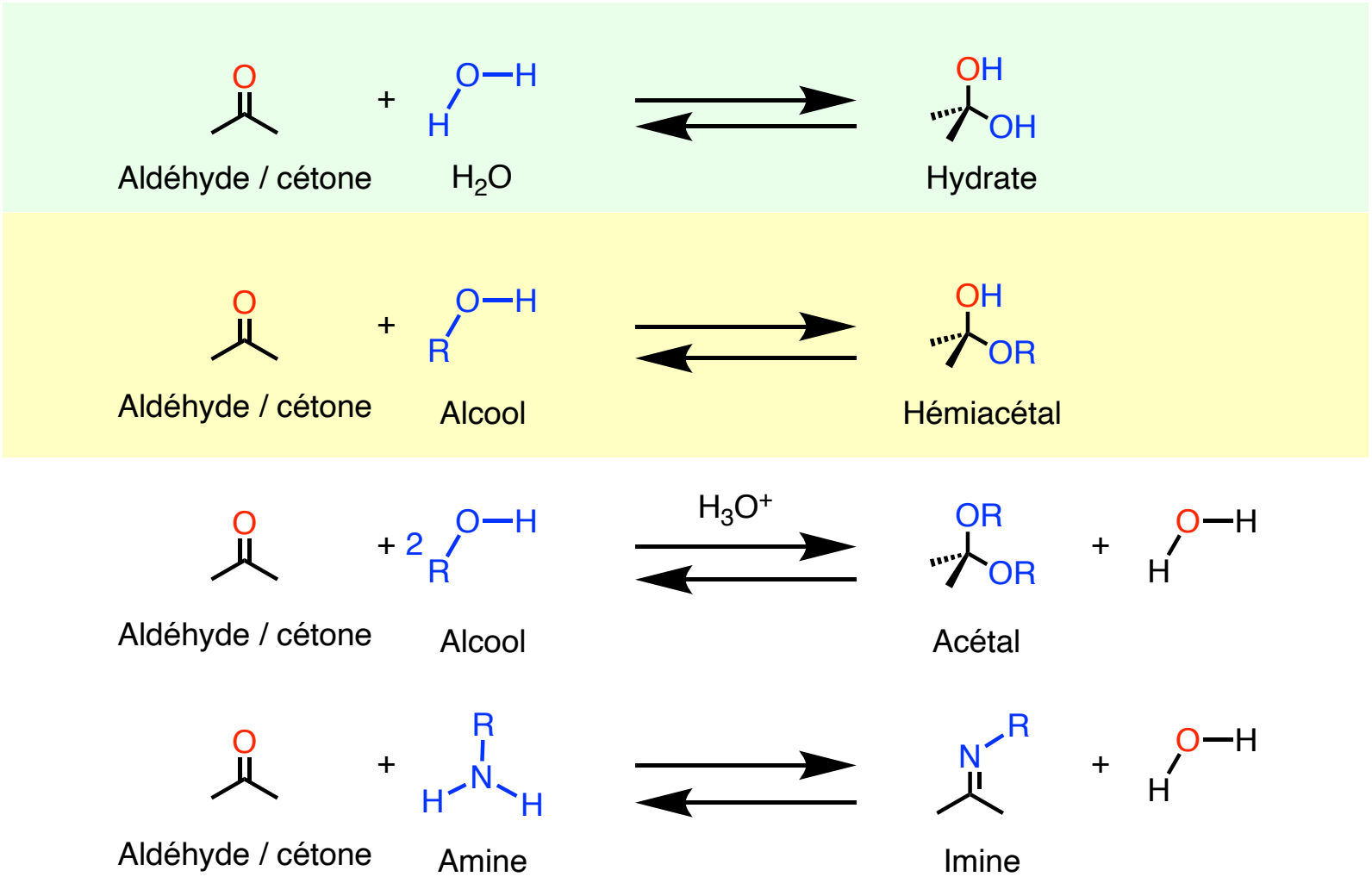
B. L'addition nucléophile sur un groupe cétone ou aldéhyde est toujours suivit d'une étape de protonation.

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

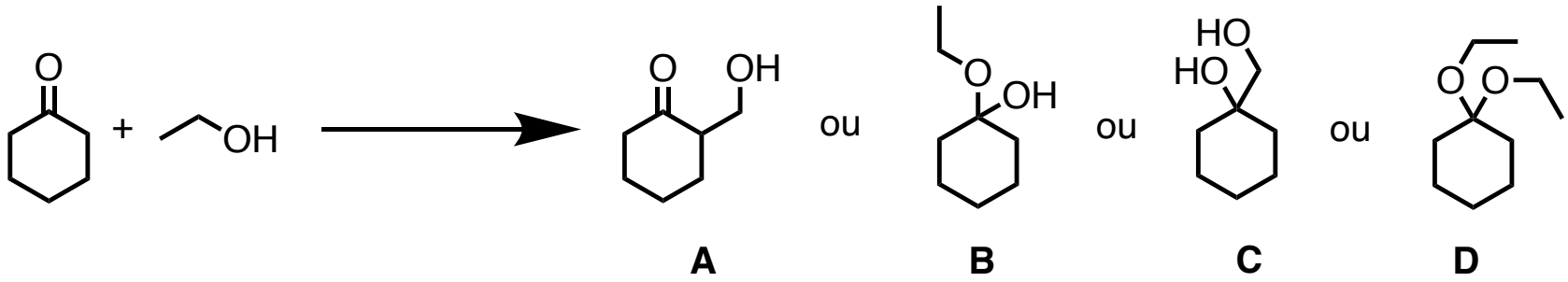
D. Les cétones possèdent un groupe C=O liés à deux alkyles.

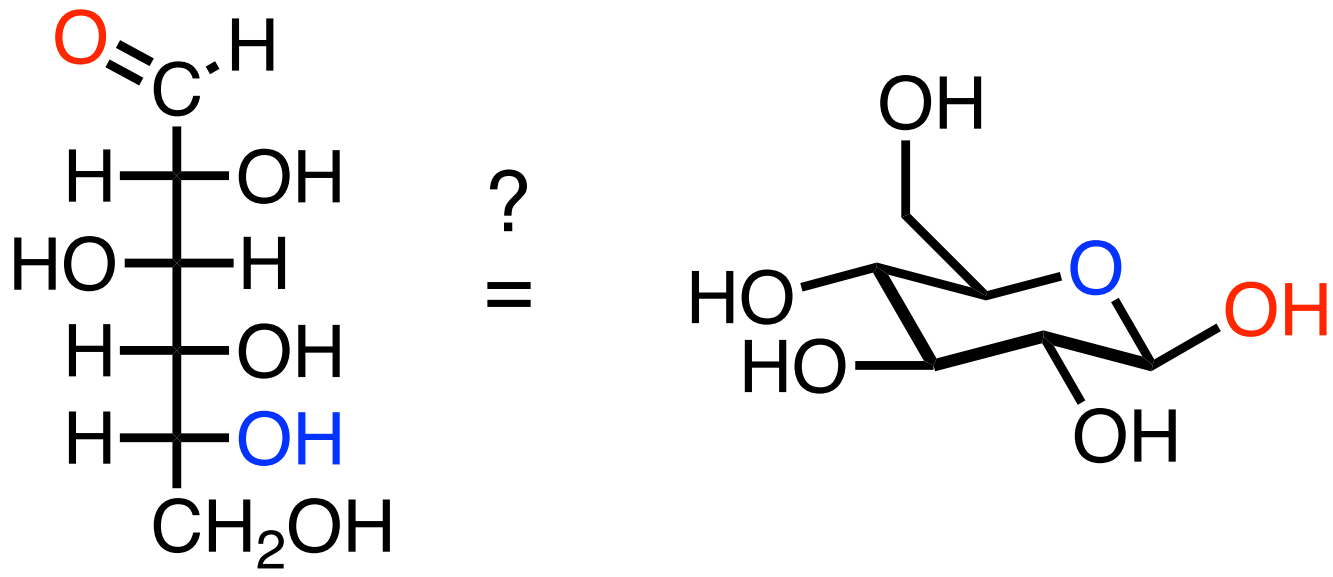
E. Les aldéhydes possèdent un group C=O lié à deux alkyles.

Résumé des réactions

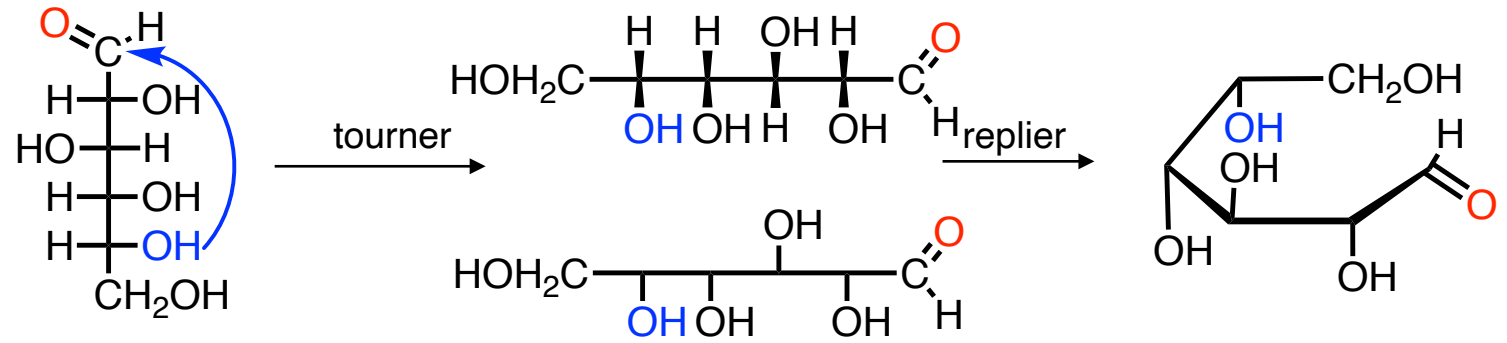


Quel est le produit lors de la réaction de la cyclohexanone avec l'éthanol?

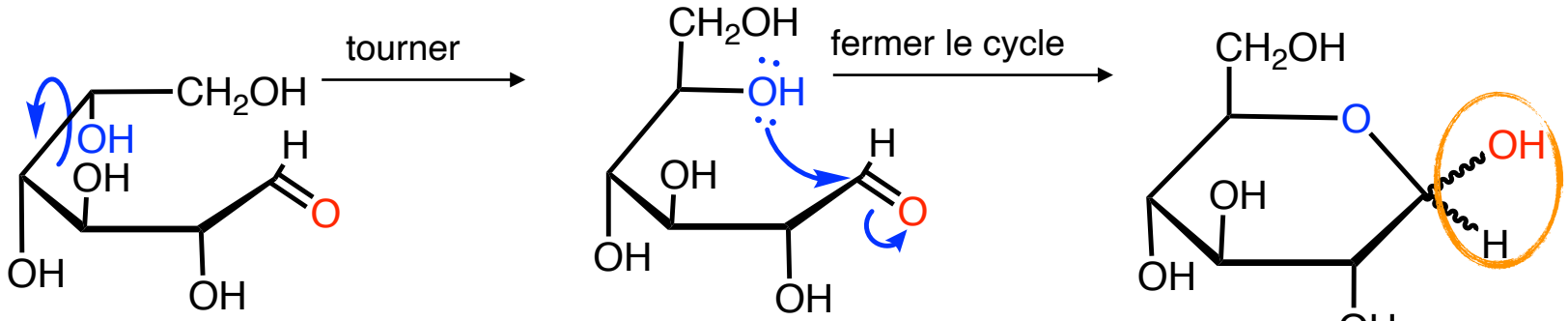



O
H
C
H
OH
HO
H
H
OH
H
OH
CH2OH
?
=
OH
O
HO
OH
HO
OH

Addition nucléophile - aldohexoses



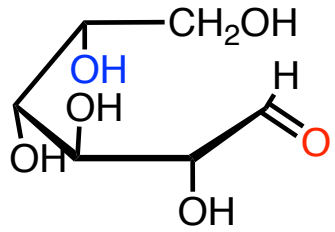
D-Glucose (Fischer)



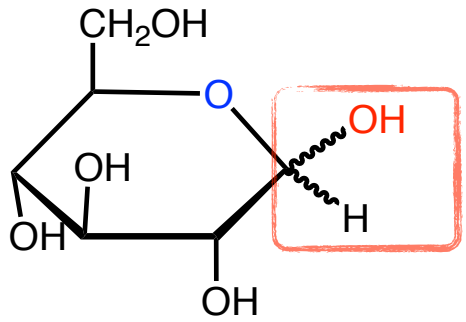
D-Glucose (Haworth)
hémiacétal

Addition nucléophile - aldohexoses

forme ouverte (aldéhyde)



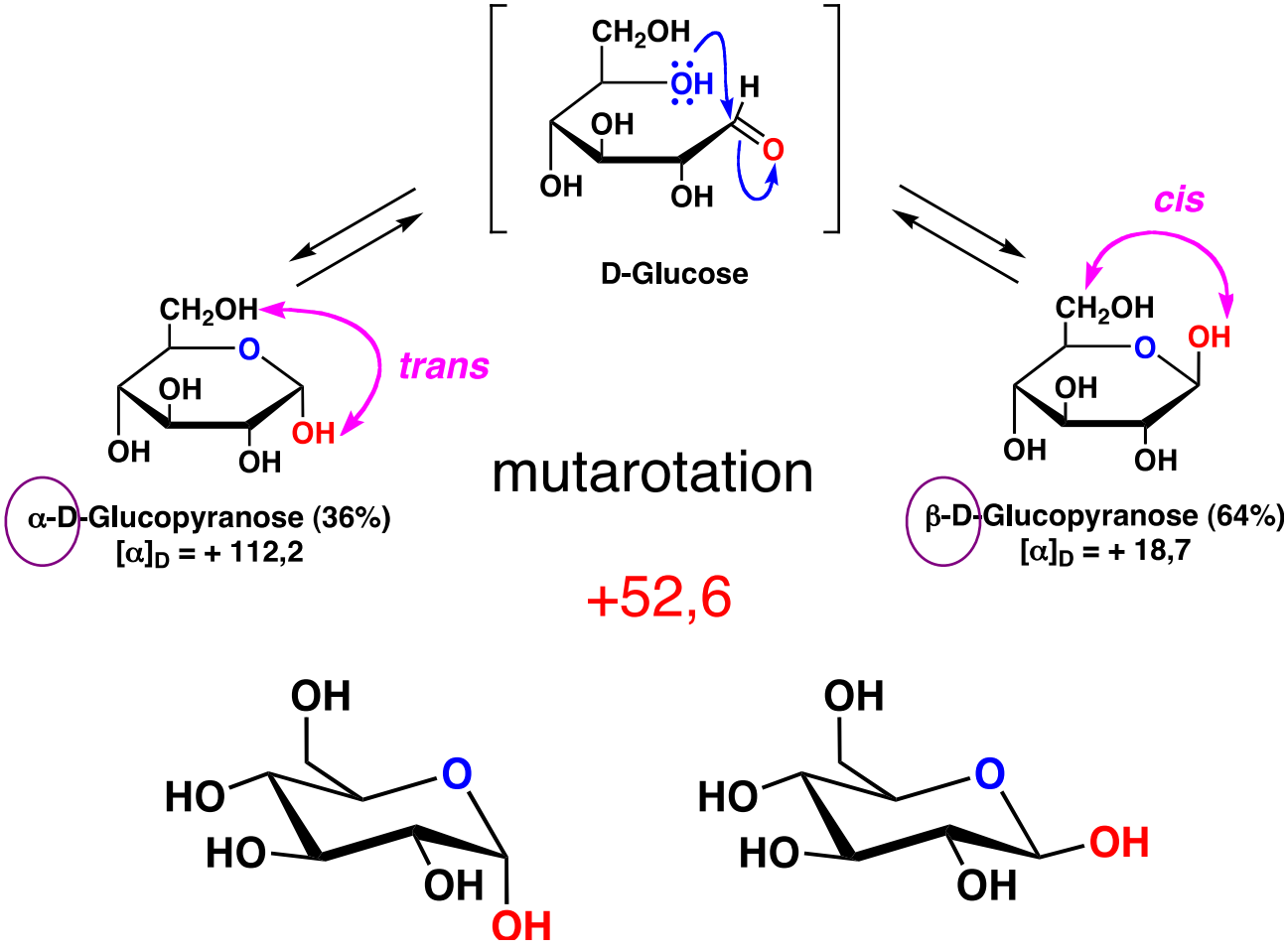
< 80 kJ / mol



D-Glucose (Haworth)

hémiacétal

Anomères


CH2OH
OH
H
OH
O
OH
OH
D-Glucose
cis
trans
CH2OH
O
OH
OH
OH
OH
CH2OH
O
OH
OH
OH
OH
α-D-Glucopyranose (36%)
[α]D = + 112,2
mutarotation
+52,6
β-D-Glucopyranose (64%)
[α]D = + 18,7
OH
HO
O
HO
OH
OH
OH
HO
O
HO
OH
OH

Glucides (carbohydrates, sucres)

$C_n(H_2O)_n$

(449)

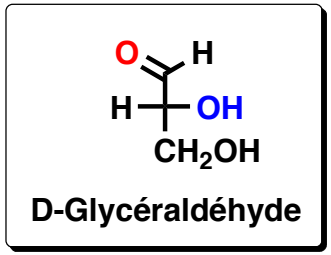
Aldoses (Cétoses)

Aldotriose

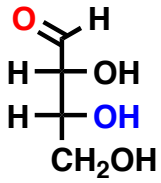
-tetroses

-pentoses

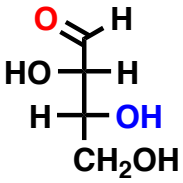
-hexoses



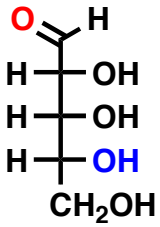
D-Glycéraldéhyde



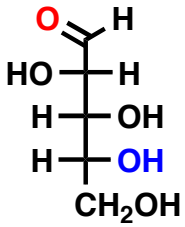
D-Érythrose



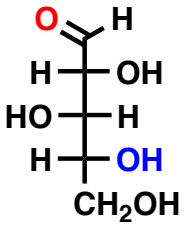
D-Thréose



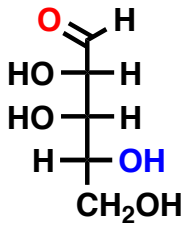
D-Ribose



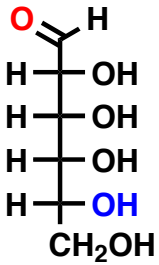
D-Arabinose



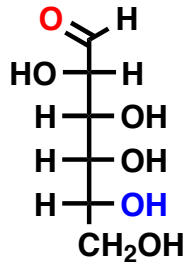
D-Xylose



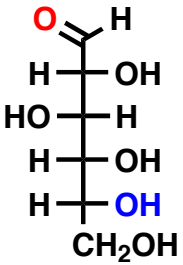
D-Lyxose



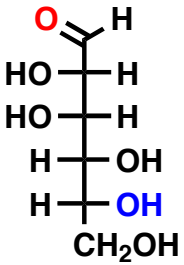
D-Allose



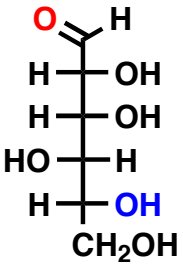
D-Altrose



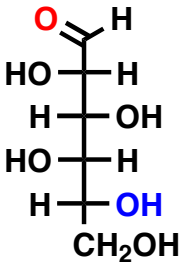
D-Glucose



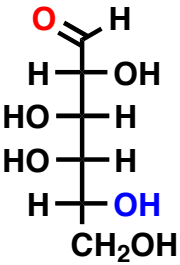
D-Mannose



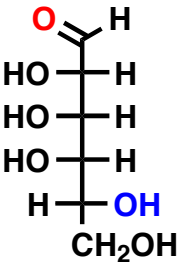
D-Gulose



D-Idose

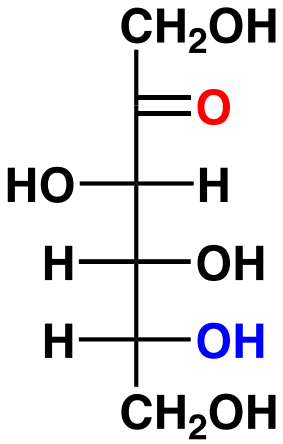


D-Galactose

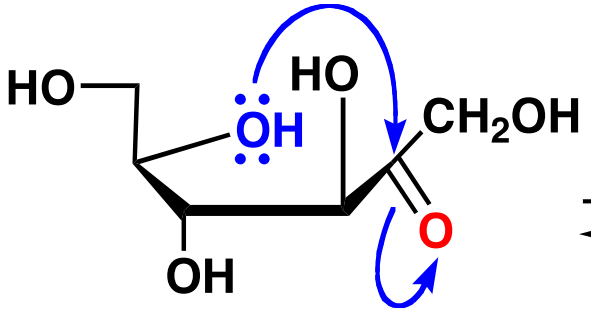


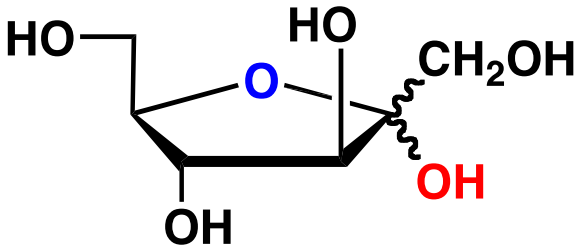
D-Talose

Addition nucléophile - cétohexoses

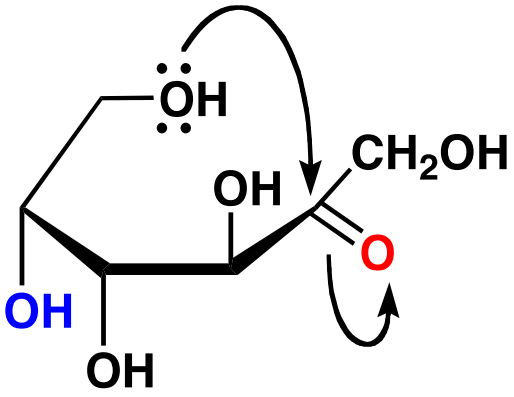


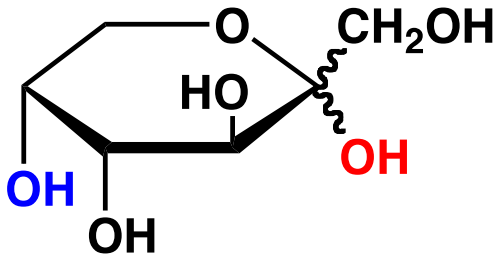
D-Fructose
(Fischer)



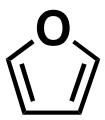


28% D-Fructofuranose
(Haworth)

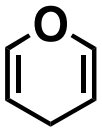




72% D-Fructopyranose
(Haworth)

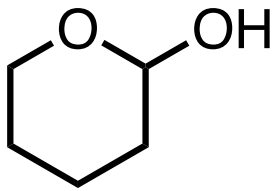


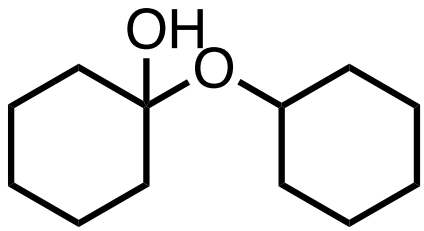
Furane

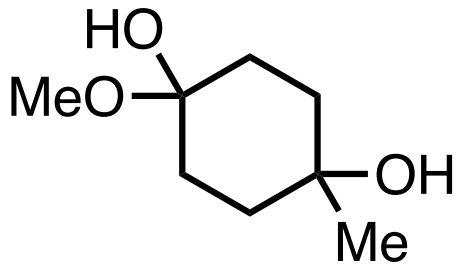


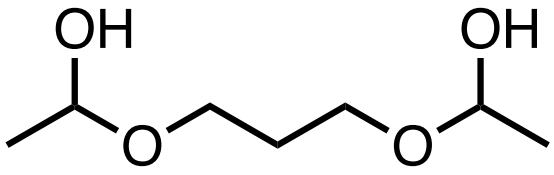
Pyrane

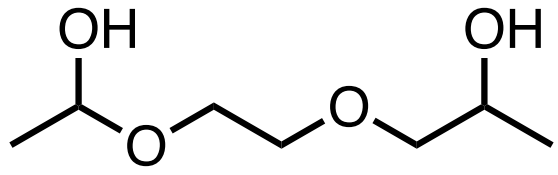
Chacun de ces composés est un hémiacétal et donc formé à partir d'un alcool et d'un composé carbonylé. Dans chaque cas, donnez la structure des molécules de départ.



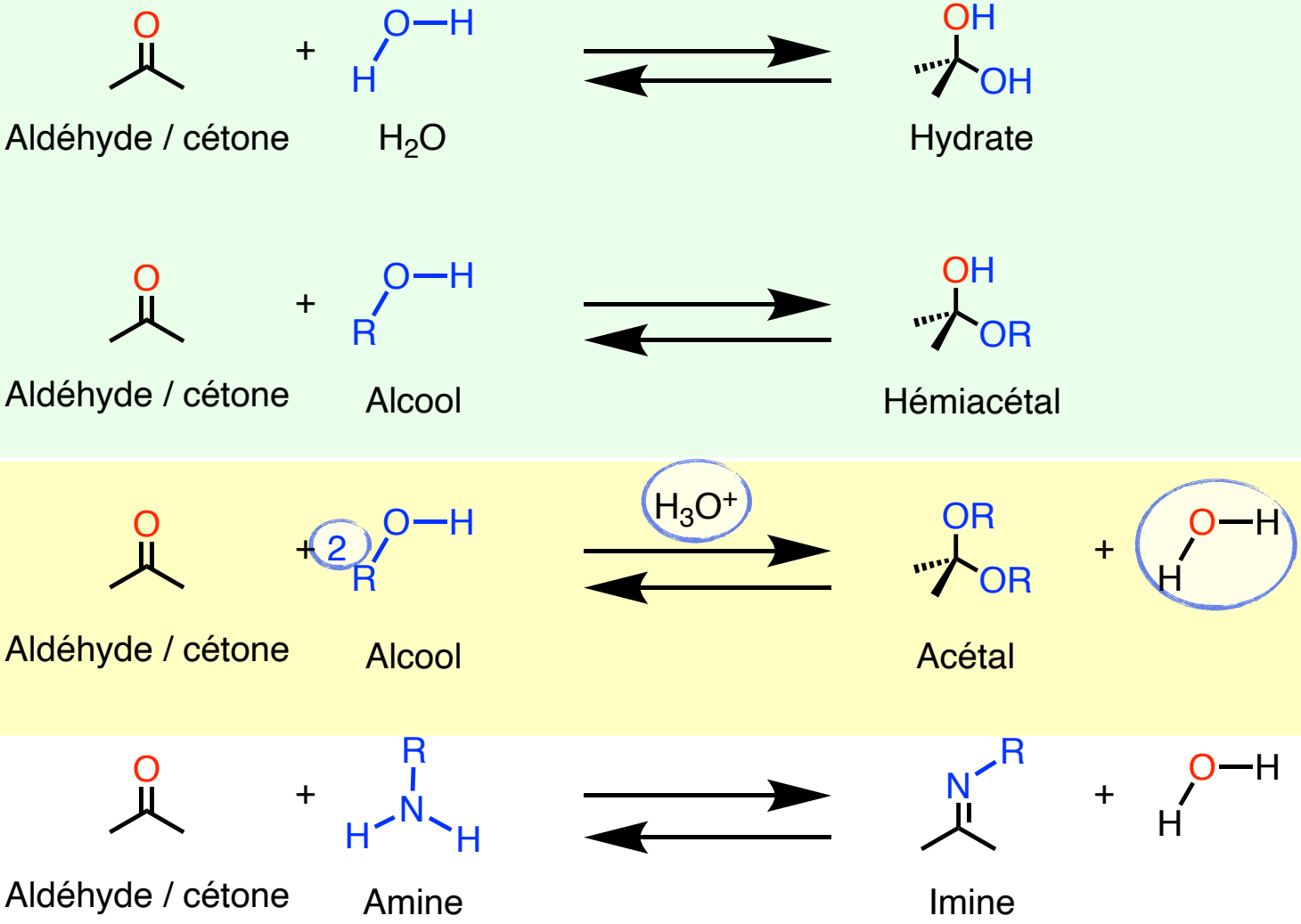




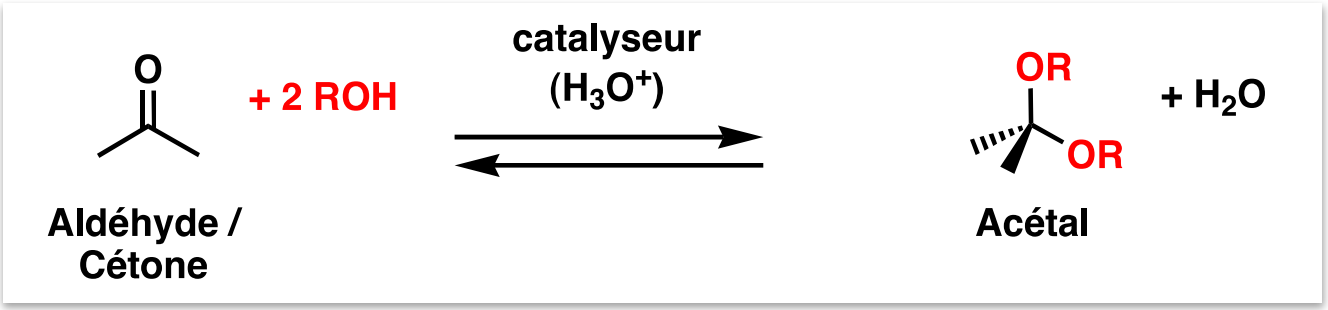


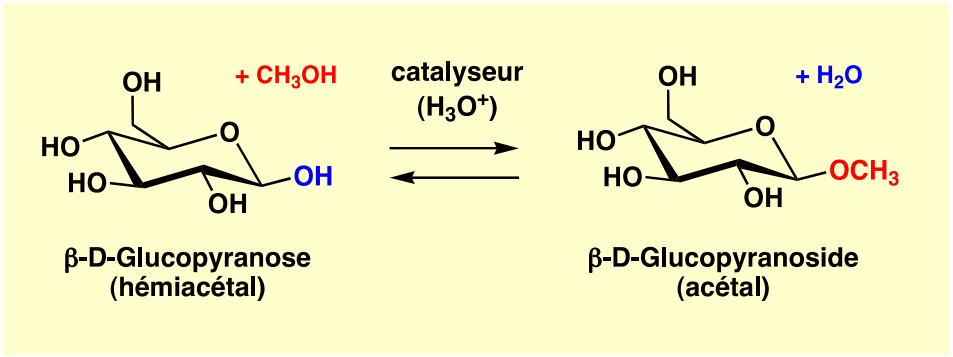


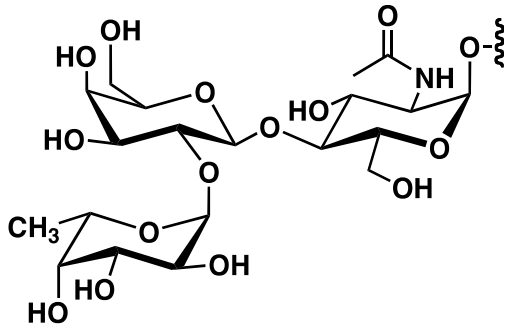
Résumé des réactions

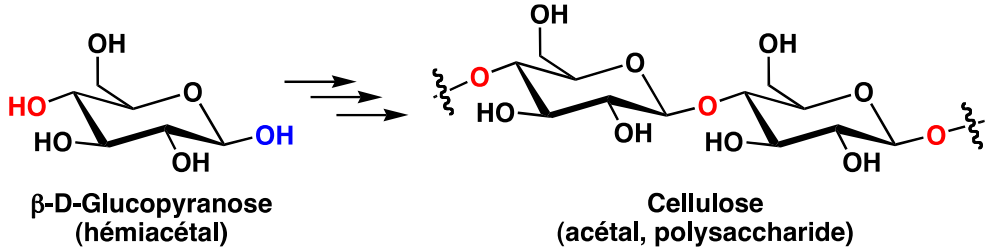


Acétals - glycosides : substitution nucléophile

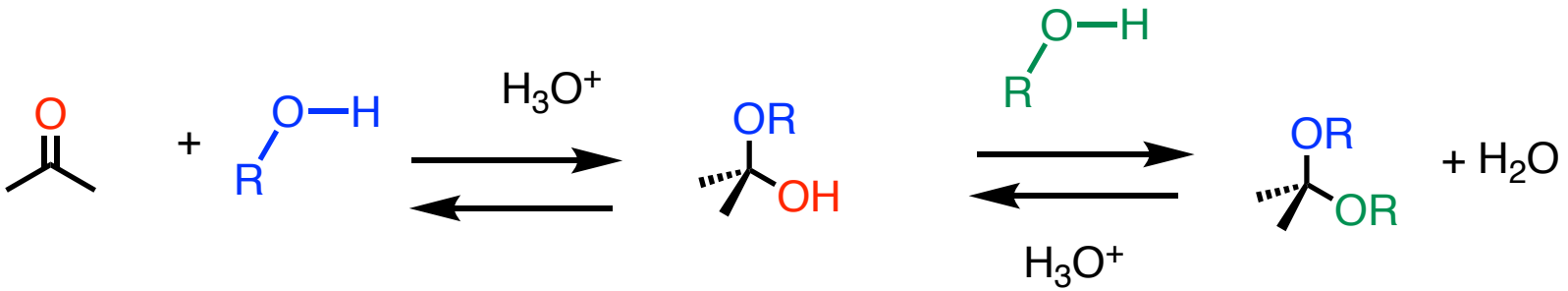


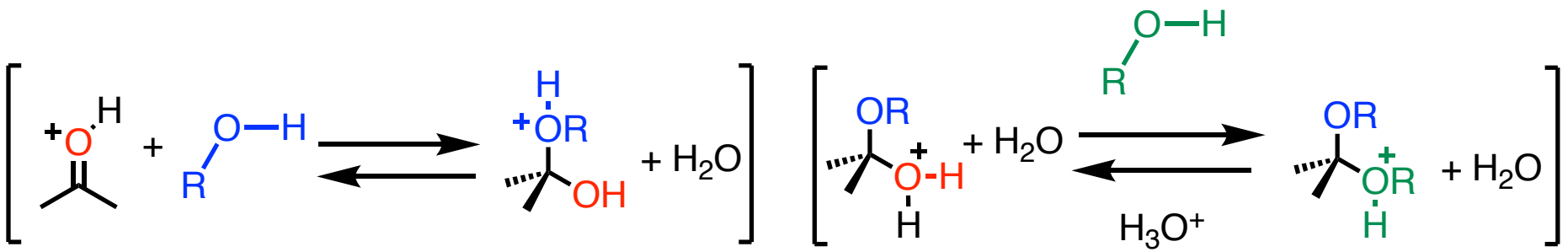


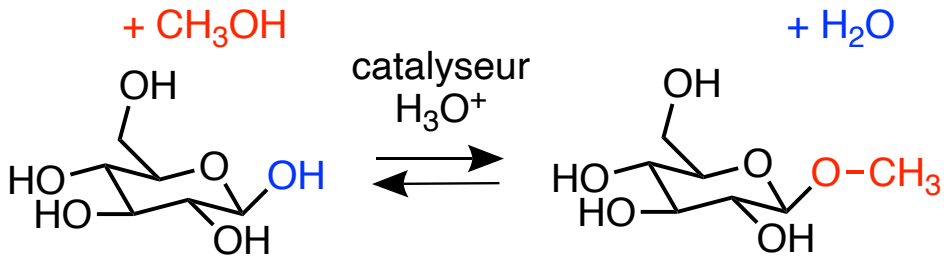




Addition nucléophile des alcools: formation d'acétals



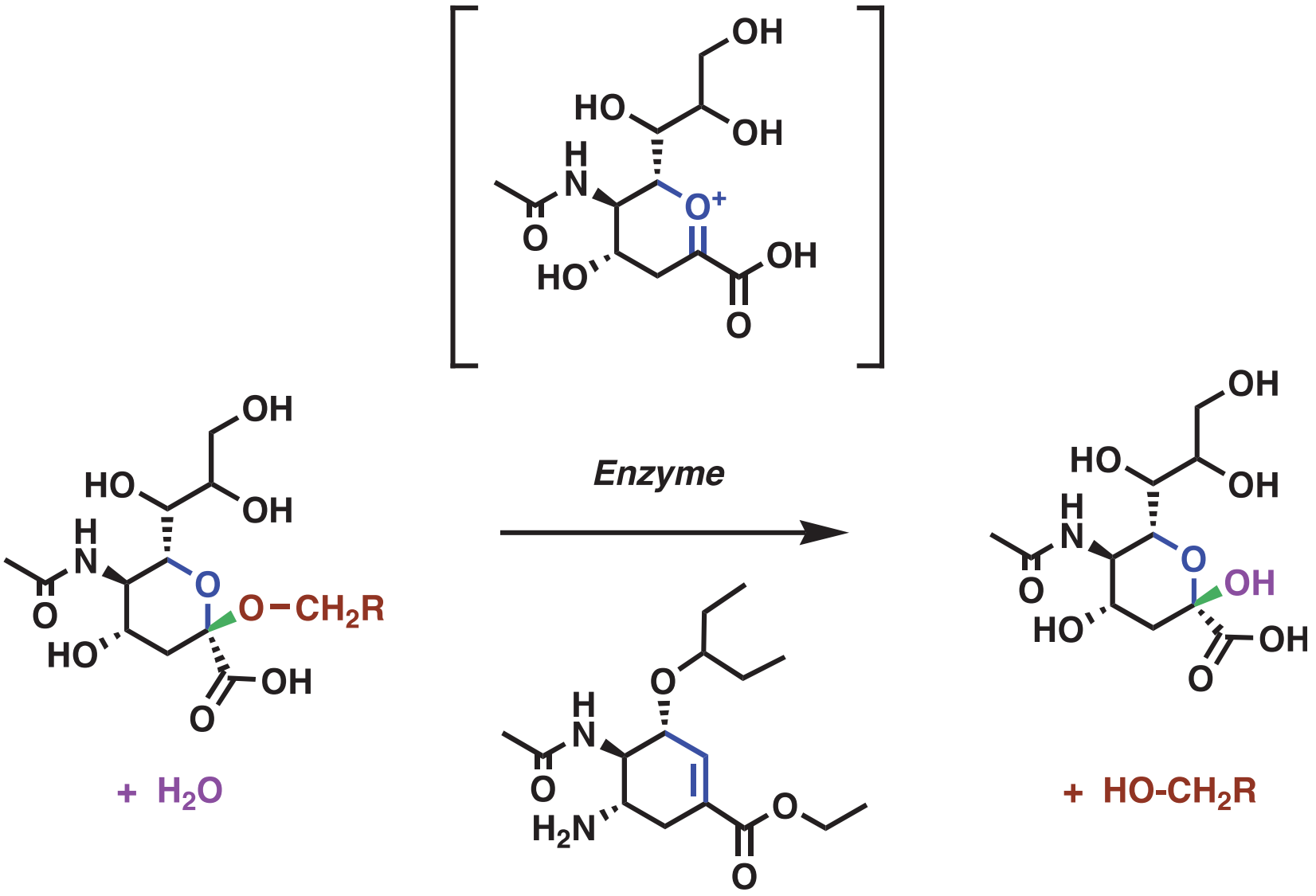



+ CH3OH
catalyseur
H3O+
+ H2O
OH
HO
HO
O
OH
OH
O–CH3

Tamiflu

293-6, 483-4, 488-90

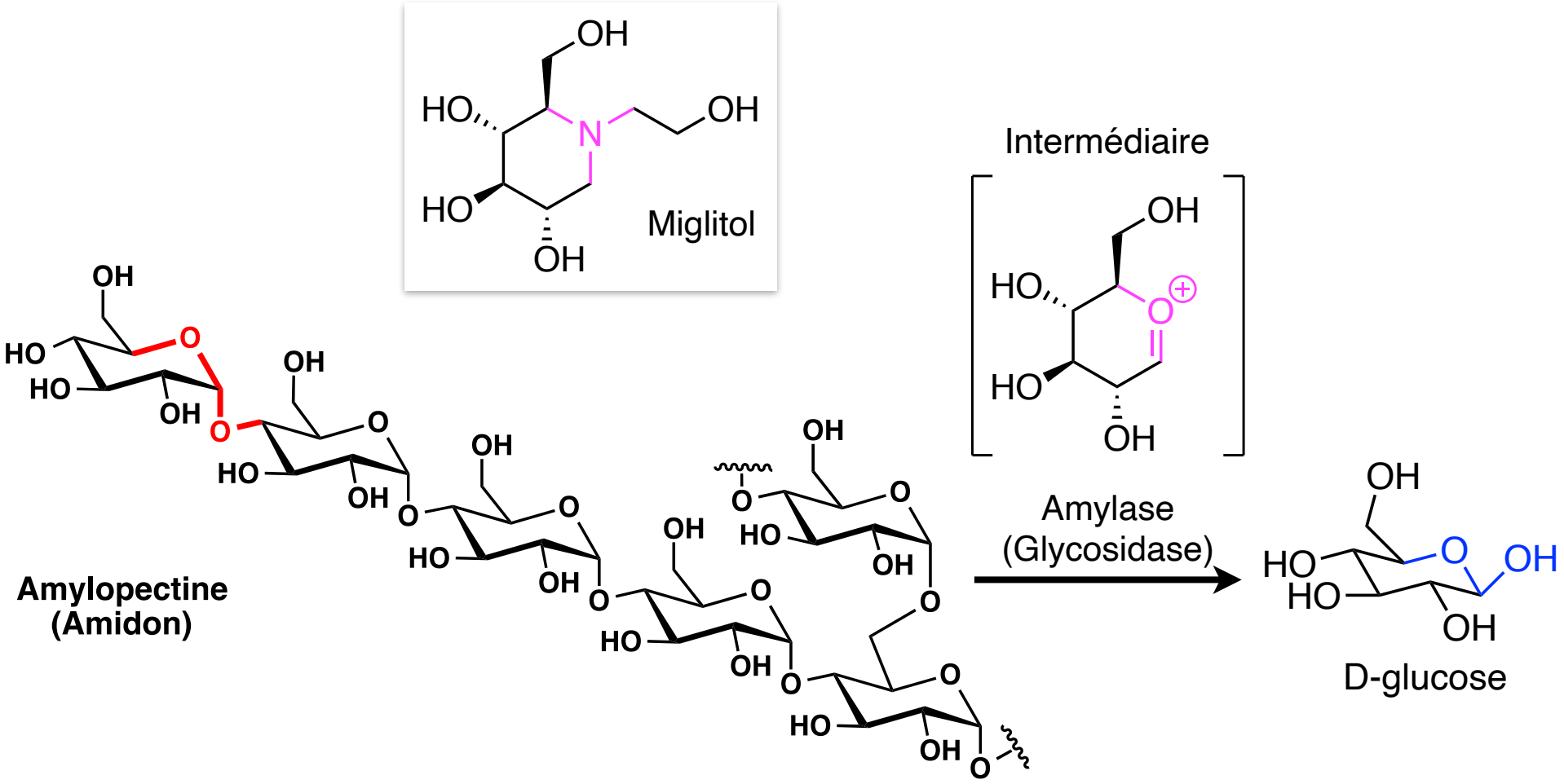
(493, 456)



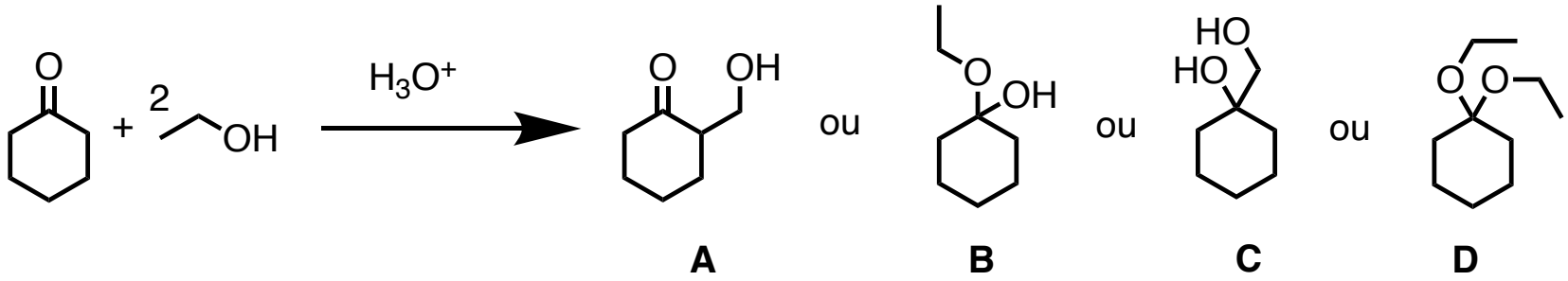
Tamiflu

Antidiabétiques

295, 489
(463, 456, 293)

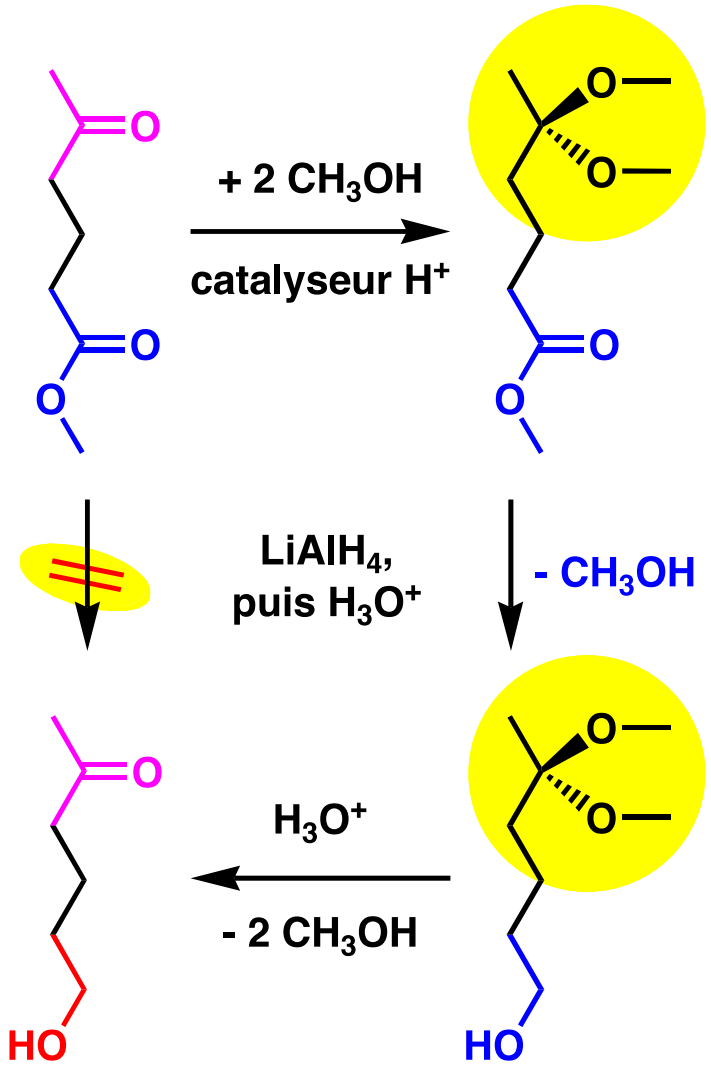


Quel est le produit obtenu lors de la réaction de la cyclohexanone avec l'éthanol catalysé par un acide?



A **B** **C** **D**

Sélectivité, synthèse chimique et groupes protecteurs



Résumé des réactions

		2007	2003
Alcène	H_2, catalyseur → Alcane	4.6	4.6
Alcool primaire	CrO_3, H_3O^+ ⇌ $LiAlH_4$, puis H_3O^+ → Acide carboxylique	8.5 8.4	8.7 8.5
Alcool secondaire	$Na_2Cr_2O_7$, H_3O^+ ⇌ $NaBH_4$, puis H_3O^+ → Cétone	8.5 8.4	8.7 8.5
Alcool primaire	PCC ⇌ $NaBH_4$, puis H_3O^+ → Aldéhyde	8.5 8.4	8.7 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^+) ⇌ Catalyseur (OH^- ou H_3O^+) Ester + H_2O	10.8 10.11	10.6 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 + 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