Chimie Biologique

Benoît MICHEL
Université de Nice Sophia Antipolis
Département de Chimie

benoit.michel@unice.fr
http://sondesfluorescentes.unice.fr/etudiants/L2SV/portail-l2sv.html

Facebook : L1SV Atomistique

La Chimie des sucres

Les sucres simples (oses)

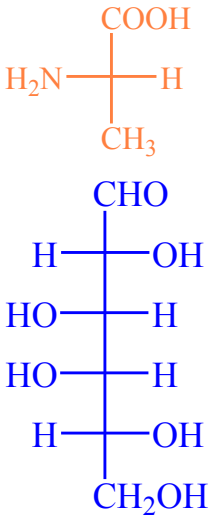
Les polysaccharides

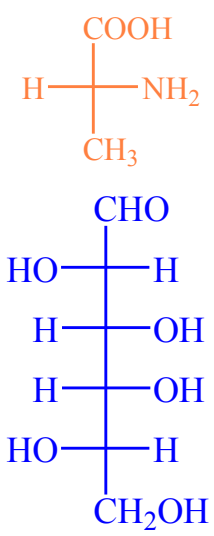
Catabolisme des sucres

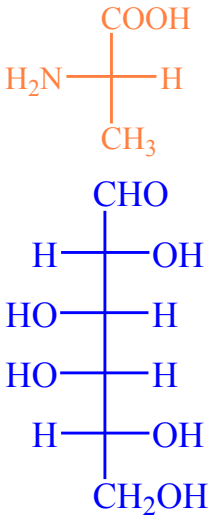
La chiralité des sucres...

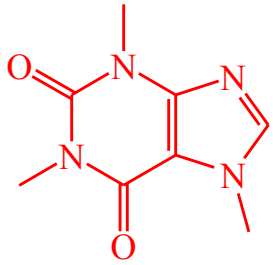
"How would you like to live in Looking-glass House, Kitty? I wonder if they'd give you milk, there? Perhaps Looking-glass milk isn't good to drink..."

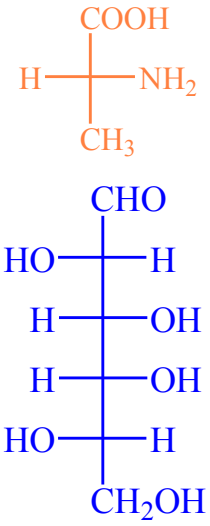
Lewis Carroll

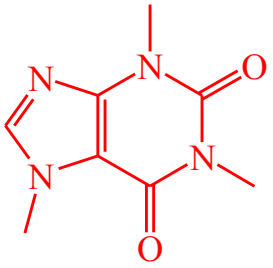

COOH
H2N
H
CH3
CHO
H
OH
HO
H
HO
H
H
OH
CH2OH

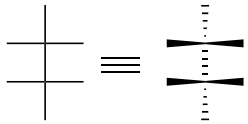

COOH
H
NH2
CH3
CHO
HO
H
H
OH
H
OH
HO
H
CH2OH

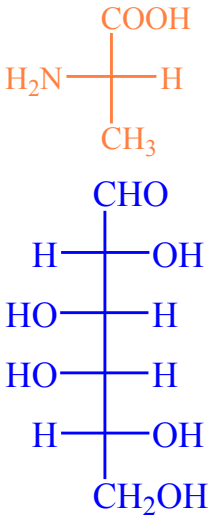

COOH
H2N
H
CH3
CHO
H
OH
HO
H
HO
H
H
OH
CH2OH

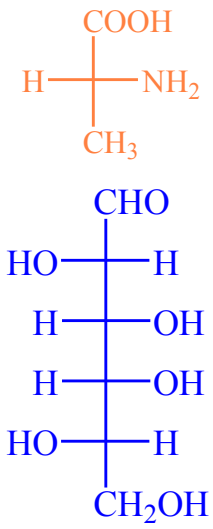

O
N
N
N
N
O


COOH
H
NH2
CH3
CHO
HO
H
H
OH
H
OH
HO
H
CH2OH

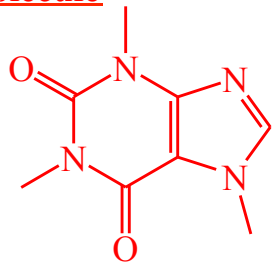

N
N
O
N
N
O

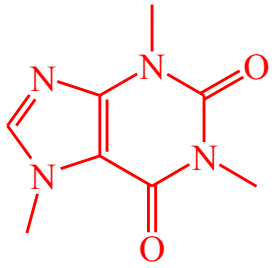


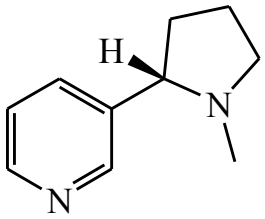




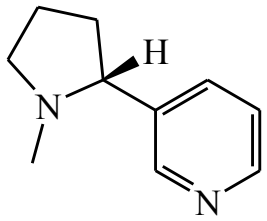
Même molécule







5 fois moins puissante



Nomenclature des composés chiraux :

(+)- = (dextrogyre : *d*-)

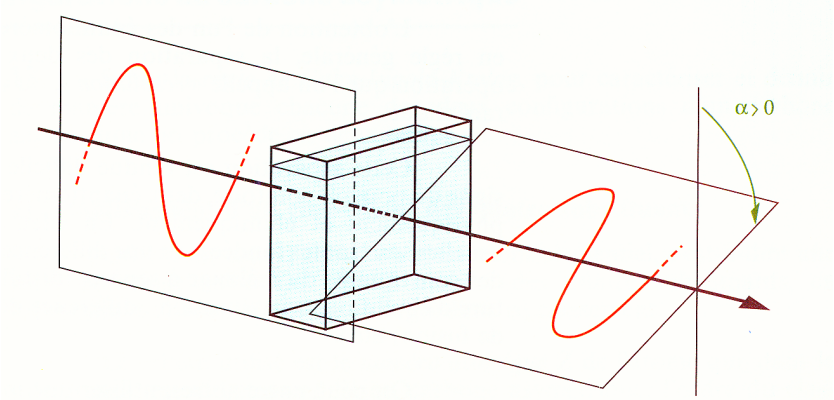
(-)- = (lévogyre : *l*-)

} **Activité optique**

Activité optique

La plupart des propriétés physiques et chimiques des énantiomères sont identiques (mêmes points d'ébullition & de fusion, réactivité chimique identique…). **Cependant ces composés agissent sur la lumière polarisée de façon opposée.**

Ce phénomène est appelé **activité optique ou pouvoir rotatoire**.



Un énantiomère qui déviera le plan polarisé de la lumière vers **la droite** avec une amplitude + α, sera appelé **dextrogyre (+)**

Son image dans un miroir (l'autre énantiomère ou *antipode optique*), qui déviera le plan polarisé de la lumière vers **la gauche (left)** avec une amplitude identique mais de signe opposé – α, sera appelé **lévogyre (-)**.

Nomenclature des composés chiraux :

(+)- = (dextrogyre : *d*-)

(-)- = (lévogyre : *l*-)

} **Activité optique**

R- = *rectus*

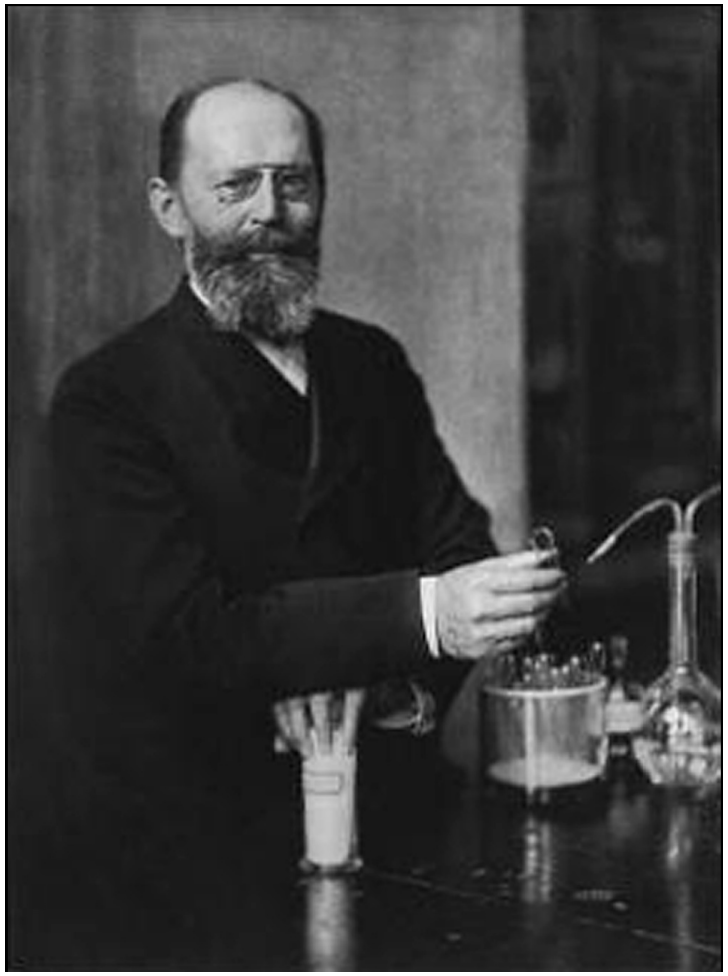
S- = *sinister*

} Configuration absolue du (des) centre(s) asymétrique(s) *

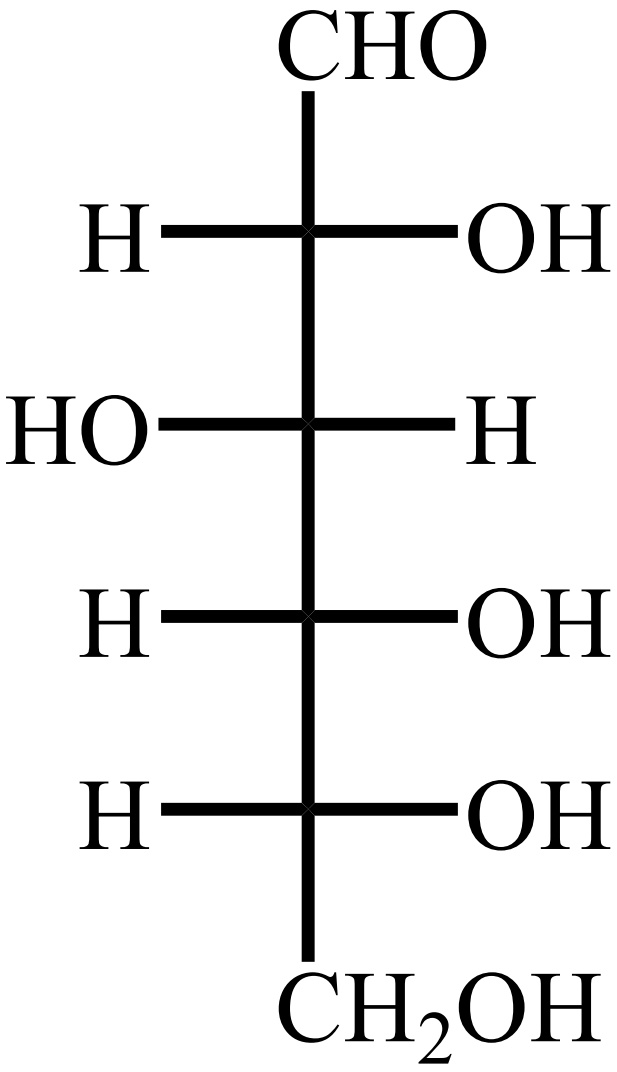
D-

L-

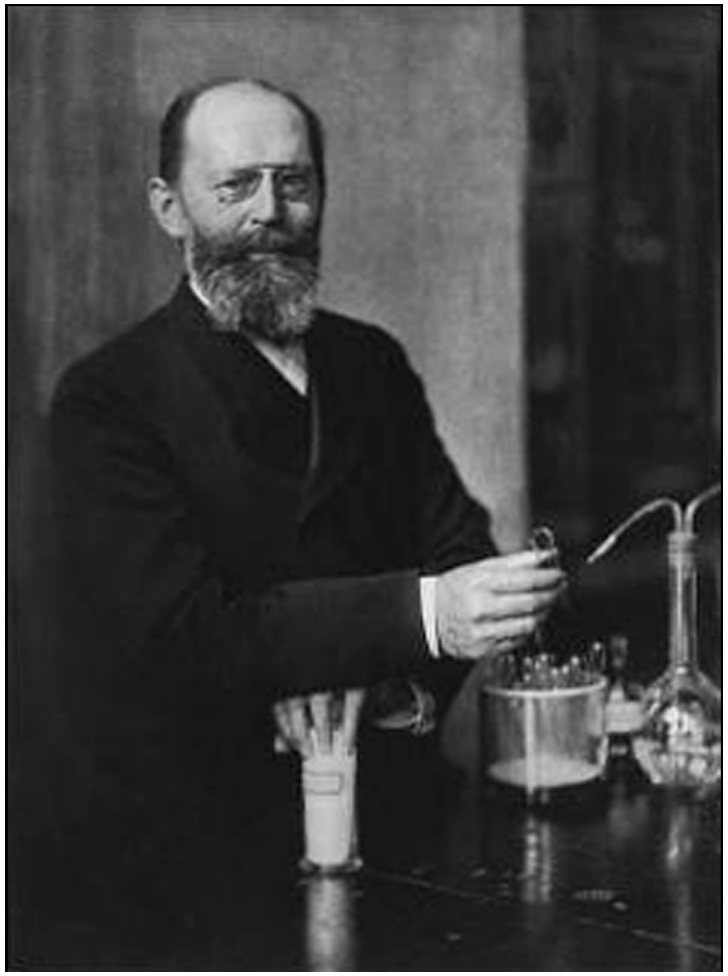
} Convention de Fischer



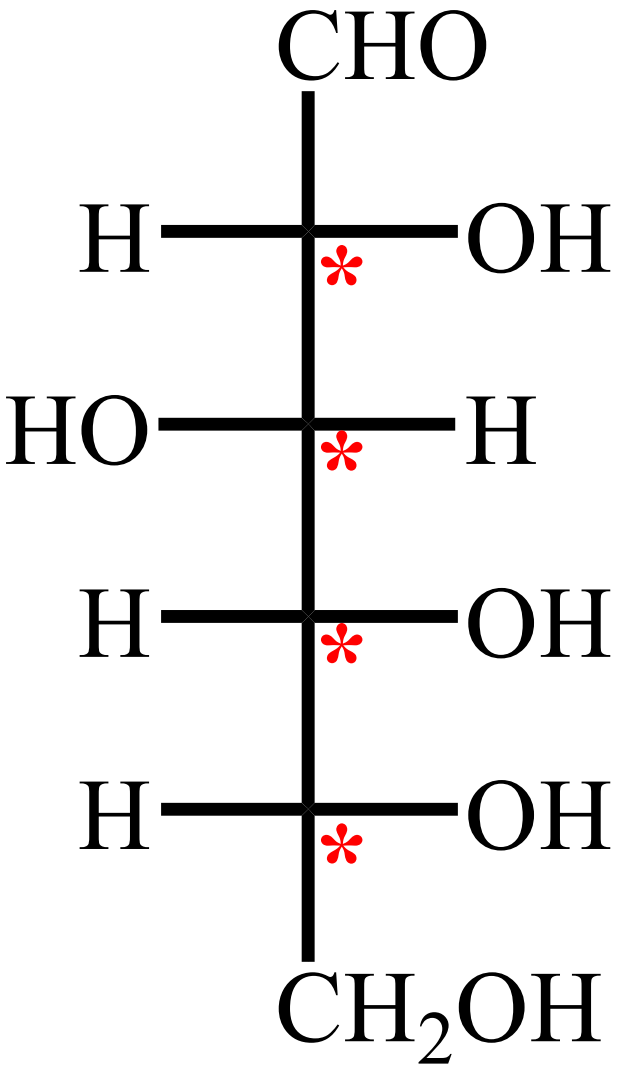
H.E. Fischer
(1852-1919)



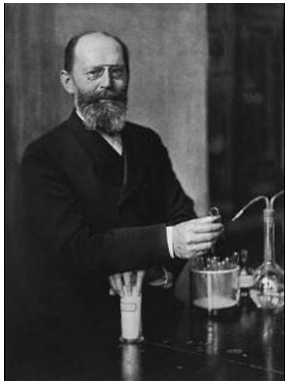
(+)-glucose



H.E. Fischer
(1852-1919)



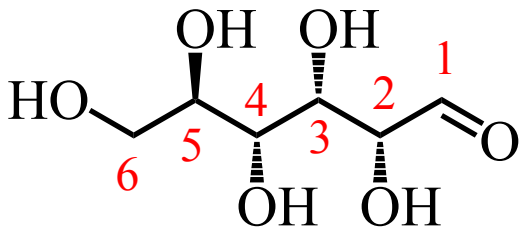
(+)-glucose



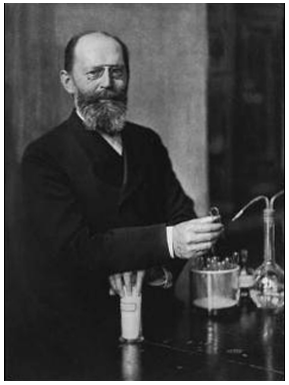
Dénomination de Fischer

1) Écrire la structure du composé en plaçant la chaîne principale verticalement, avec le carbone porteur de l'indice 1 en haut (i.e la fonction la plus oxydée = la fonction la plus prioritaire)

2,3,4,5,6-pentahydroxyhexanal

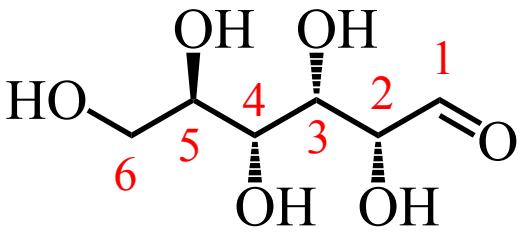


(+)-glucose (naturel)



Dénomination de Fischer

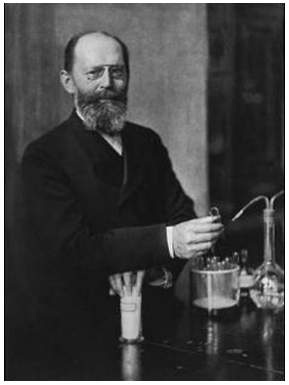
1) Écrire la structure du composé en plaçant la chaîne principale verticalement, avec le carbone porteur de l'indice 1 en haut (i.e la fonction la plus oxydée = la fonction la plus prioritaire)



(+)-glucose (naturel)

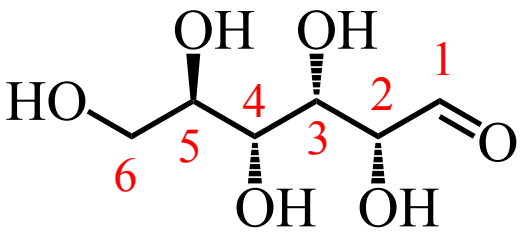
≡

CHO
CHOH
CHOH
CHOH
CHOH
CHOH
CH_2OH



Dénomination de Fischer

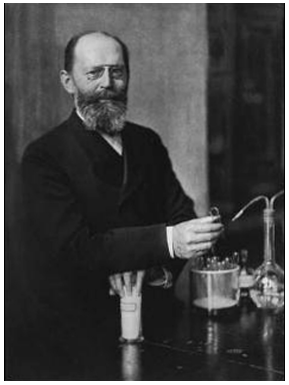
2) Les 4 liaisons du carbone sont dessinées sous forme de croix.



(+)-glucose (naturel)

≡

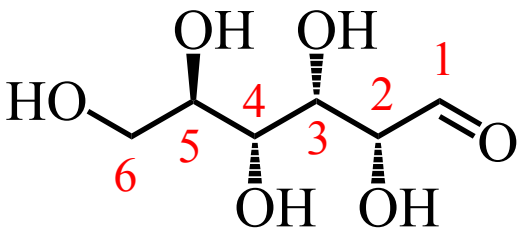
CHO
|
CHOH
|
CHOH
|
CHOH
|
CHOH
|
CH_2OH



Dénomination de Fischer

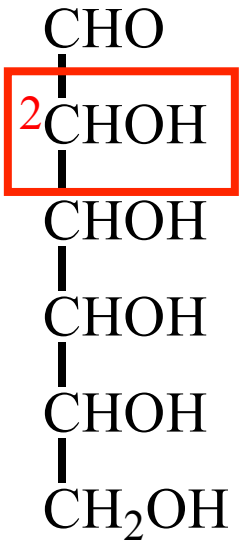
2) Les 4 liaisons du carbone sont dessinées sous forme de croix.

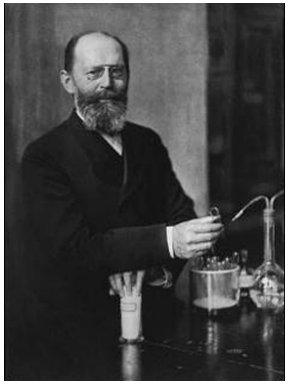
On prend ici l'exemple du C2 du (+)-glucose.



(+)-glucose (naturel)

≡

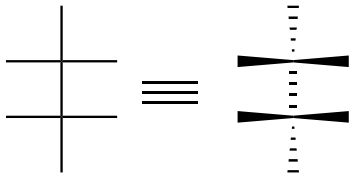


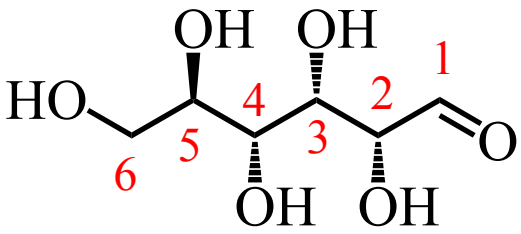


Dénomination de Fischer

2) Les liaisons verticales pointent vers l'arrière et les liaisons horizontales vers l'avant.

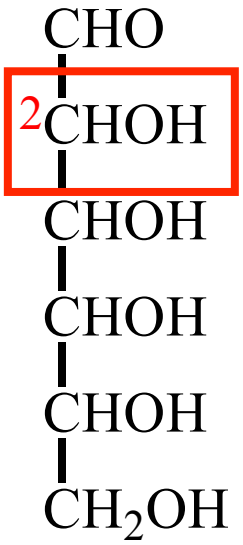
Pour simplifier l'écriture, on ne représente pas le carbone, celui-ci se trouve implicitement au centre de la croix.

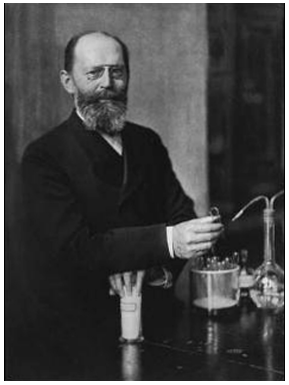




(+)-glucose (naturel)

≡

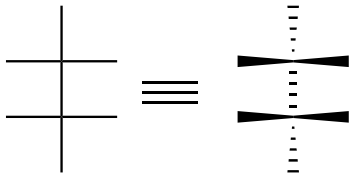


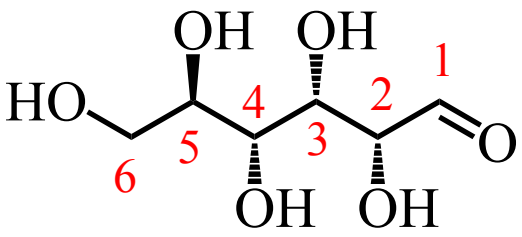


Dénomination de Fischer

2) Les liaisons verticales pointent vers l'arrière et les liaisons horizontales vers l'avant.

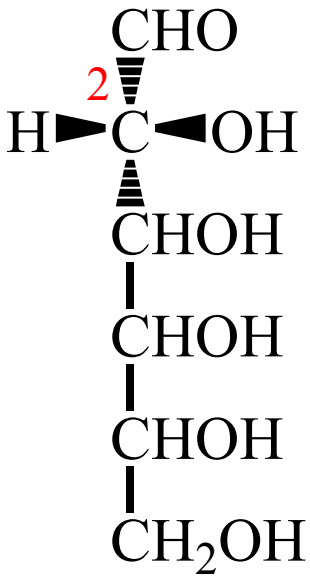
Pour simplifier l'écriture, on ne représente pas le carbone, celui-ci se trouve implicitement au centre de la croix.

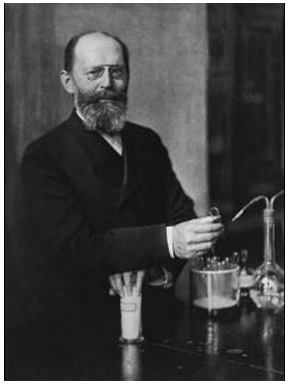




(+)-glucose (naturel)

≡

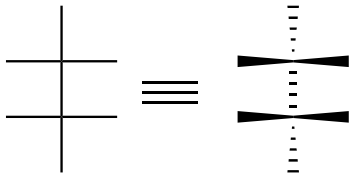


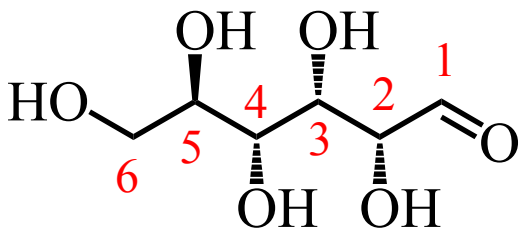


Dénomination de Fischer

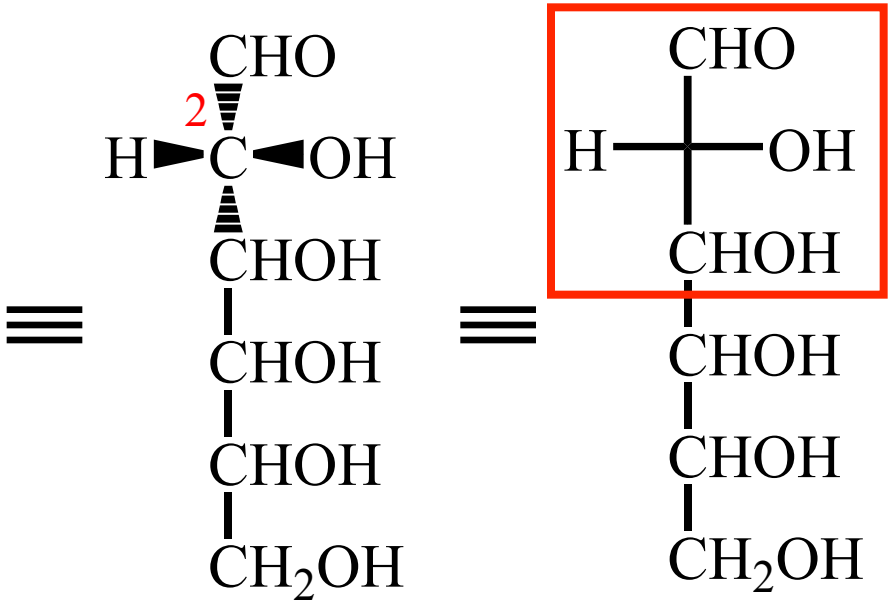
2) Les liaisons verticales pointent vers l'arrière et les liaisons horizontales vers l'avant.

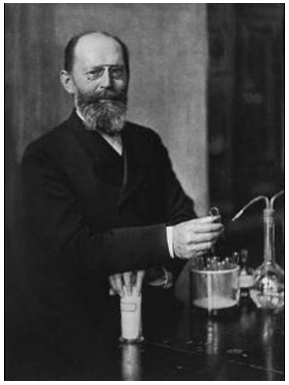
Pour simplifier l'écriture, on ne représente pas le carbone, celui-ci se trouve implicitement au centre de la croix.





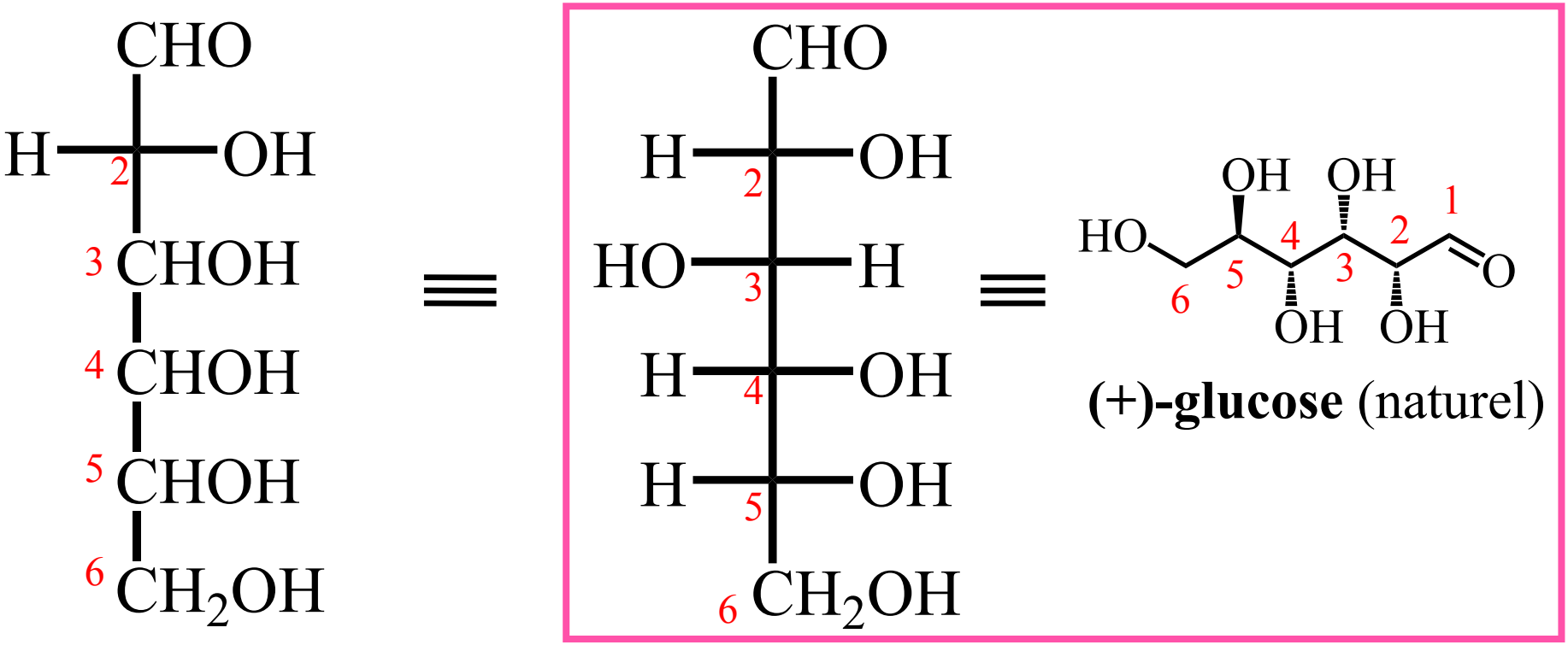
(+)-glucose (naturel)

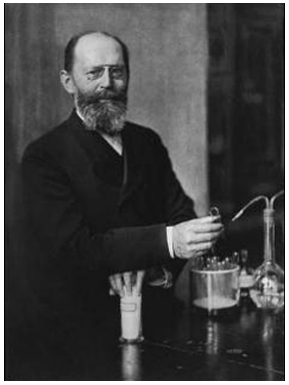




Dénomination de Fischer

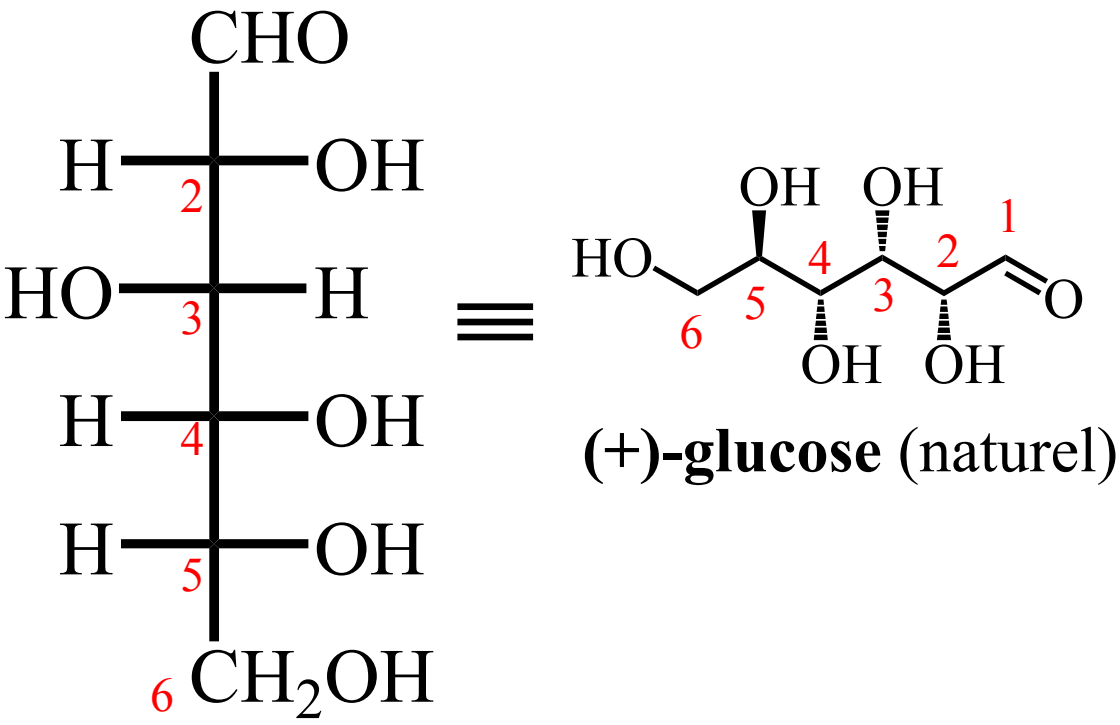
2) On généralise cette écriture aux autres carbones de la chaîne.

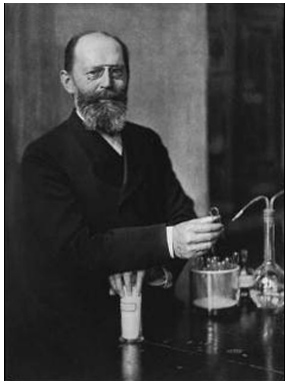




Dénomination de Fischer

3) On examine alors la représentation du carbone chiral portant l'indice le plus élevé.

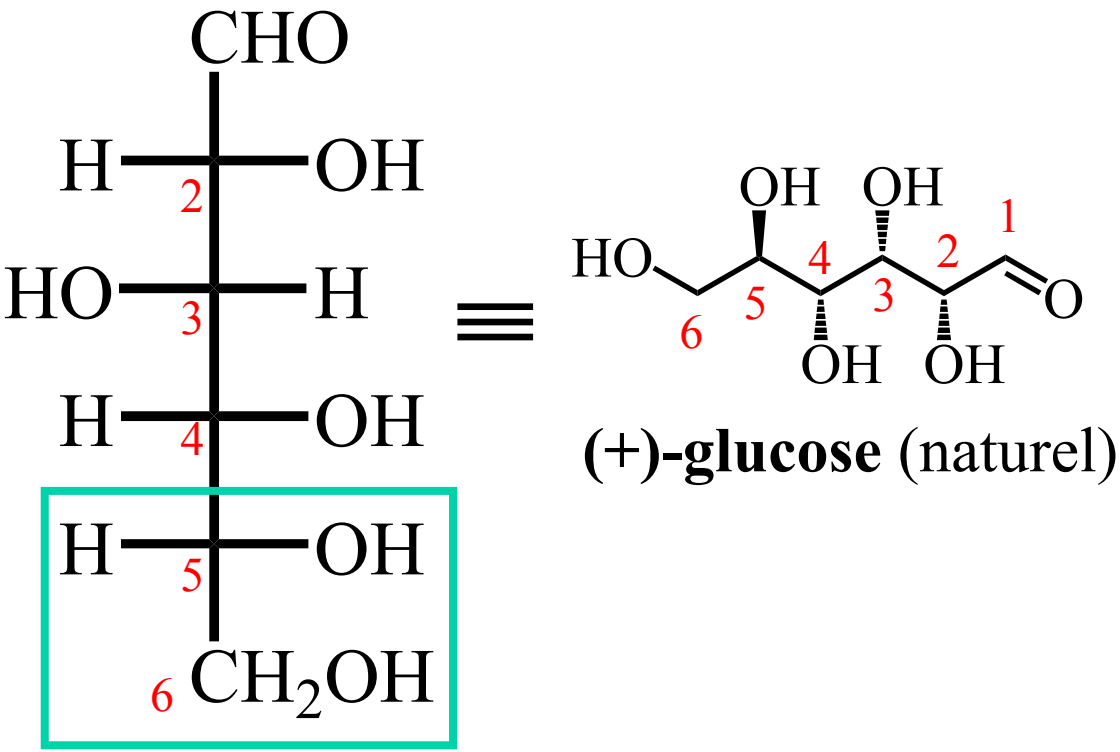




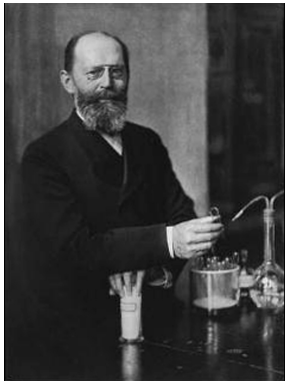
Dénomination de Fischer

3) On examine alors la représentation du carbone chiral portant l'indice le plus élevé.

Dans l'exemple du (+)-glucose, il s'agit du C5.

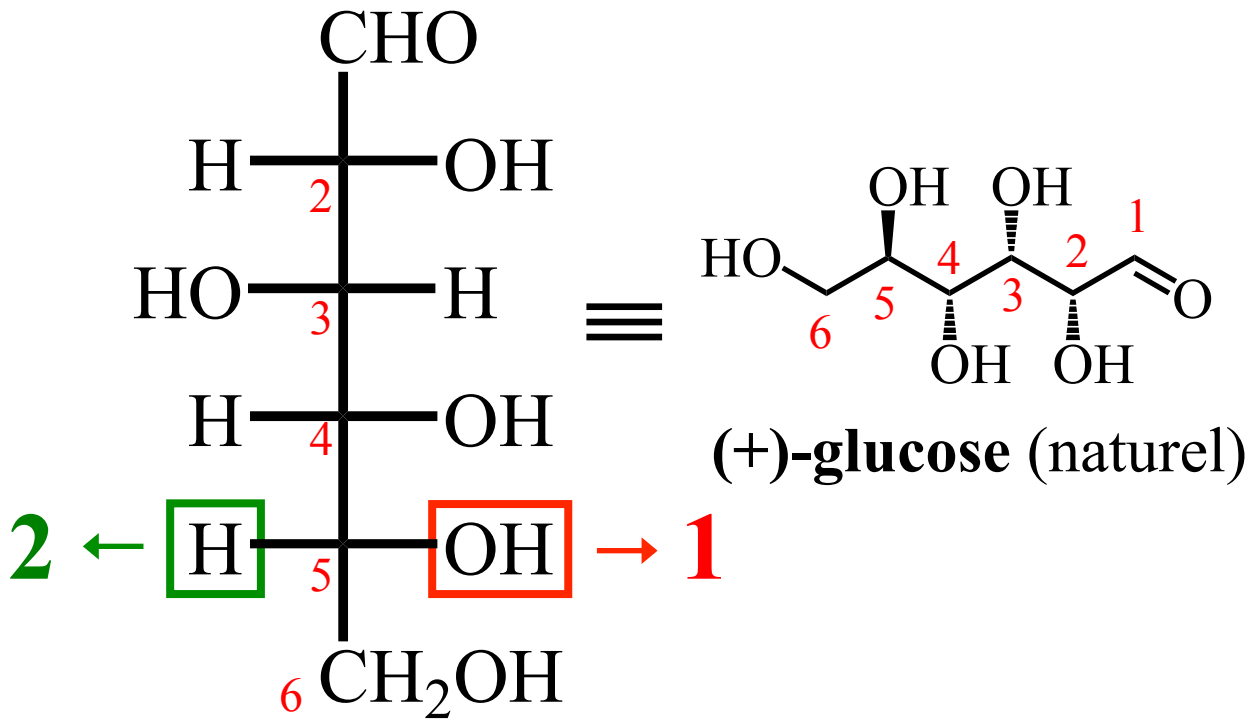


(+)-glucose (naturel)

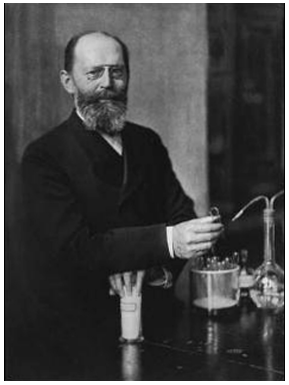


Dénomination de Fischer

3) On attribue alors des indices de priorité aux 2 substituants horizontaux, selon la convention de Cahn-Ingold-Prelog.

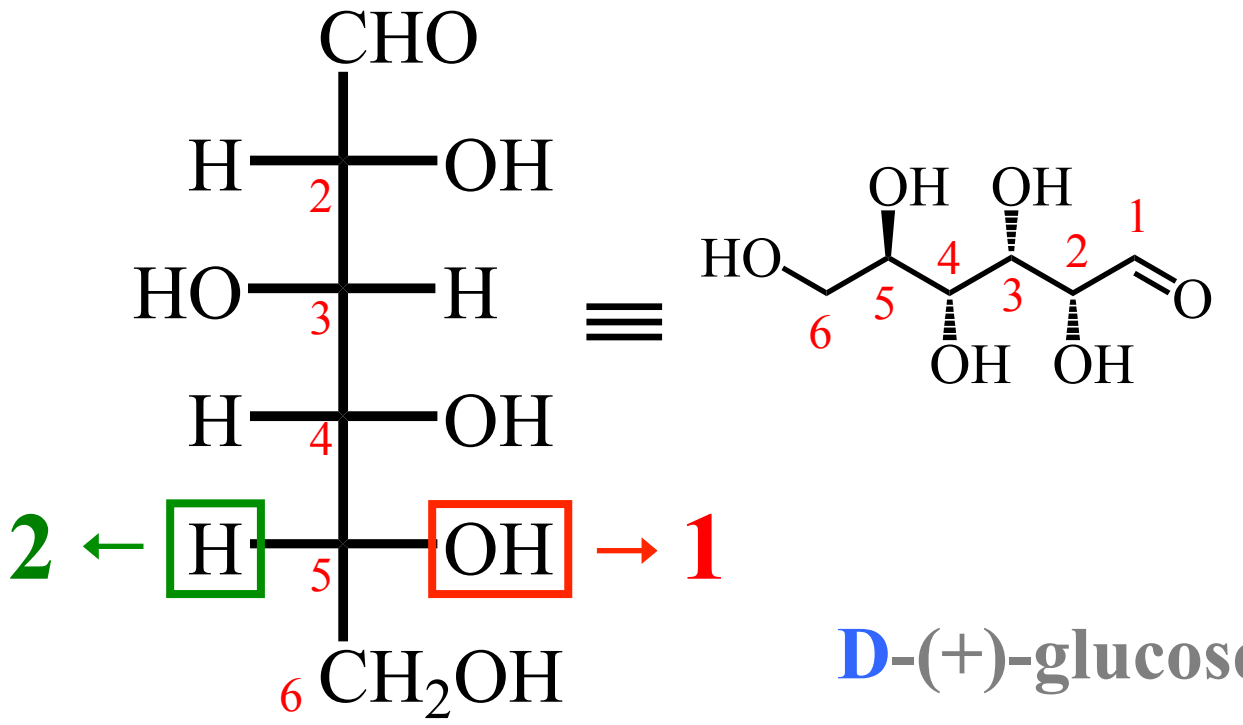


(+)-glucose (naturel)

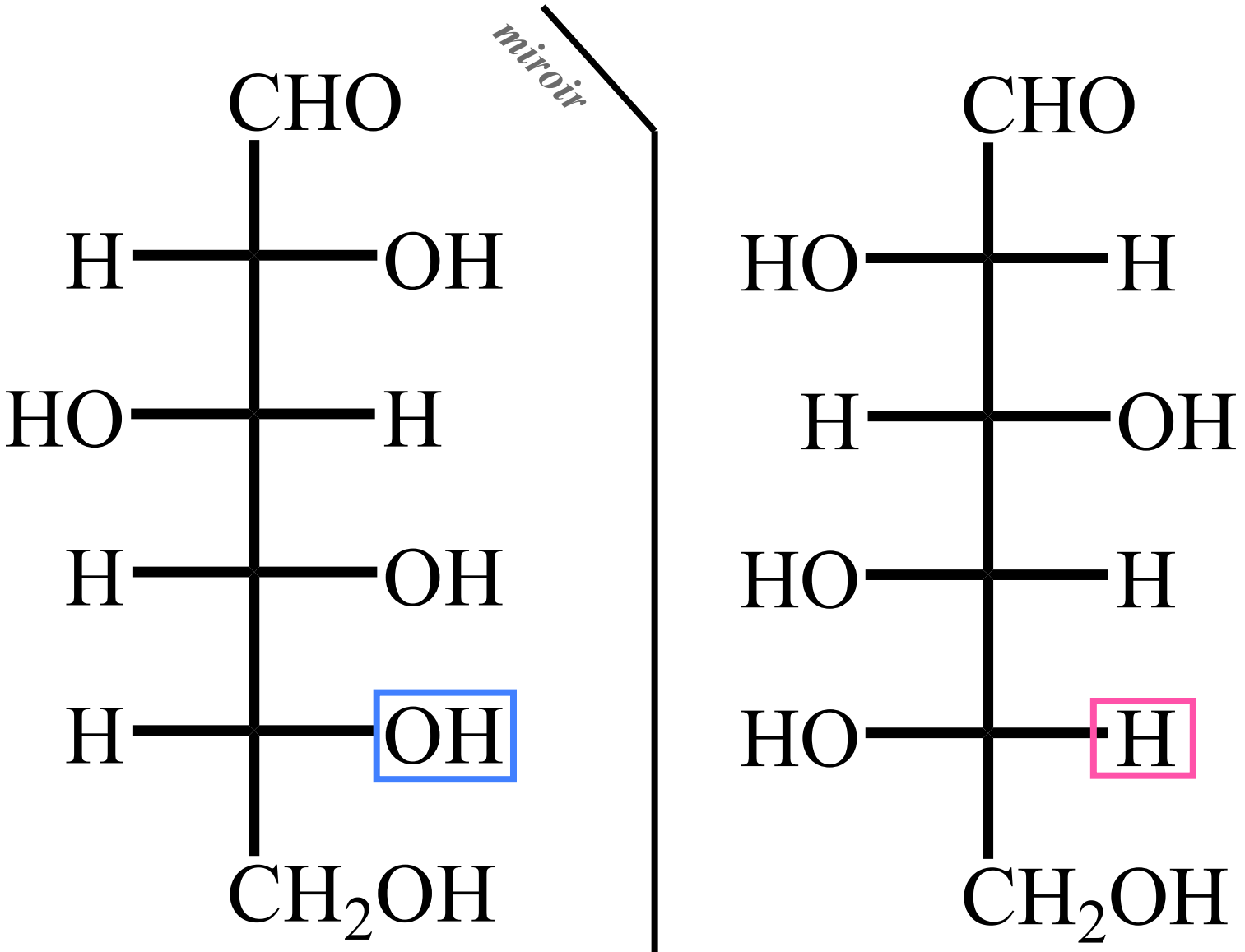


Dénomination de Fischer

3) Si le substituant prioritaire se trouve à droite, on a alors la configuration D (comme dans l'exemple ci-dessous). S'il est à gauche, on a la configuration L.

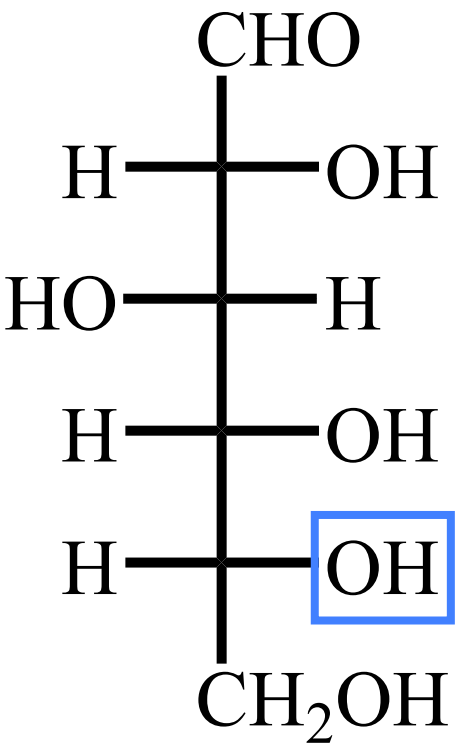


D-(+)-glucose

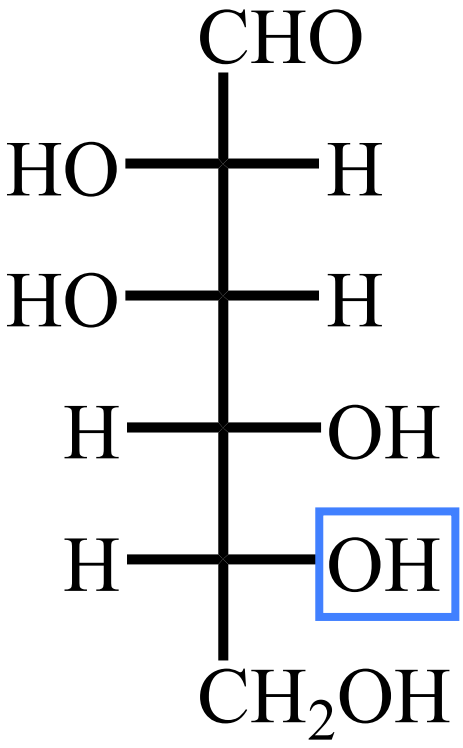


D-(+)-glucose **L-(-)-glucose**

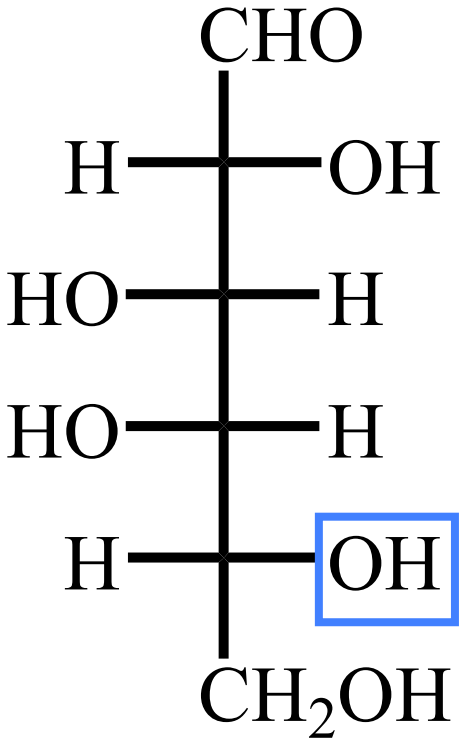
Exemples de structures



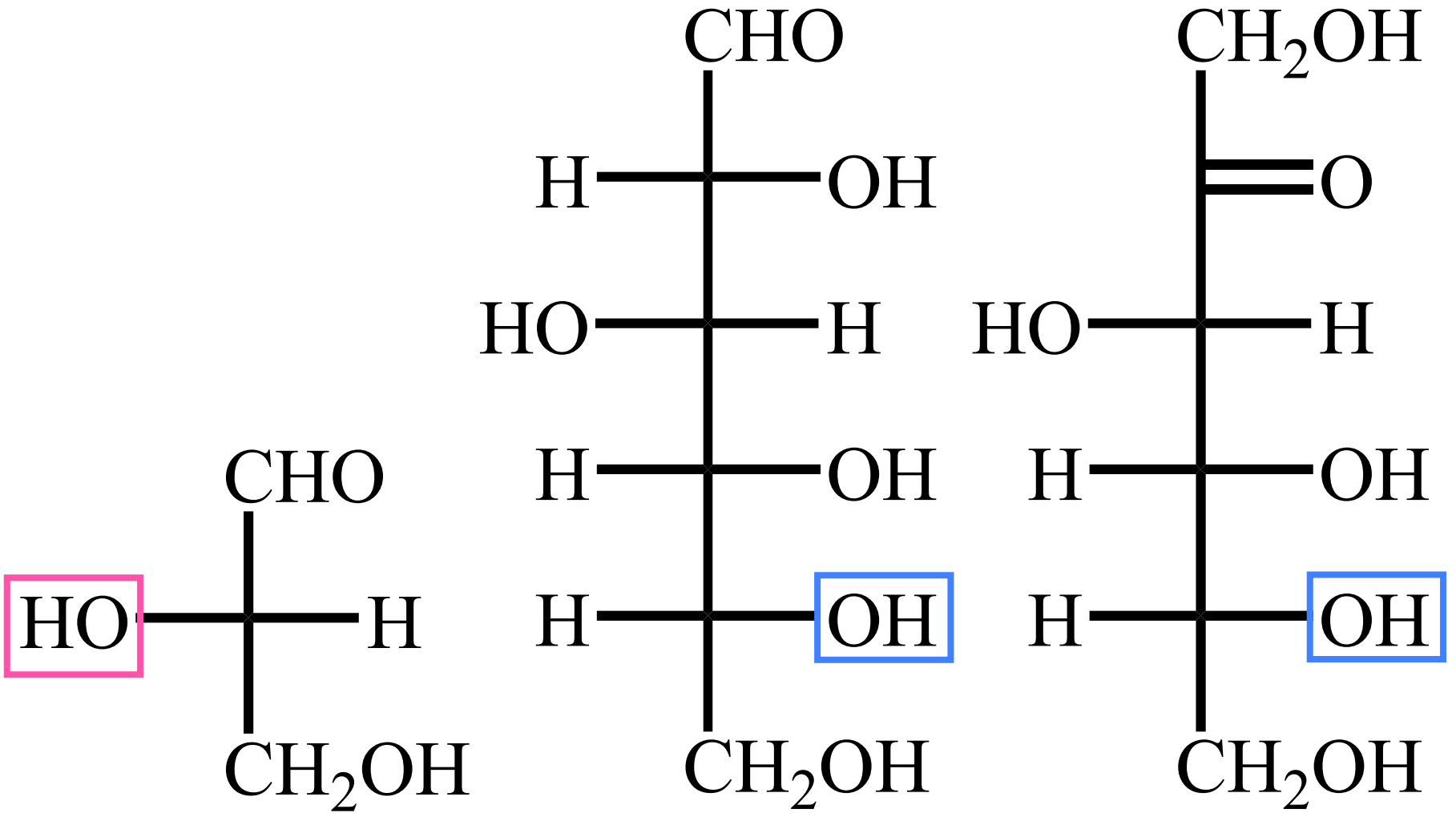
D-(+)-glucose



D-(+)-mannose



D-(+)-galactose

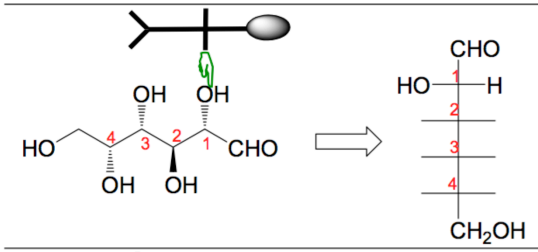


L-(-)-glycéraldéhyde **D**-(+)-glucose **D**-(-)-fructose

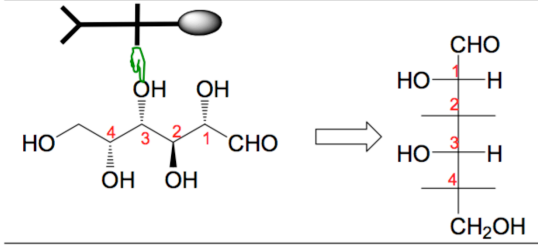
De Cram en Fischer - Technique du petit bonhomme

(*Technique du hérisson développée au tableau*)

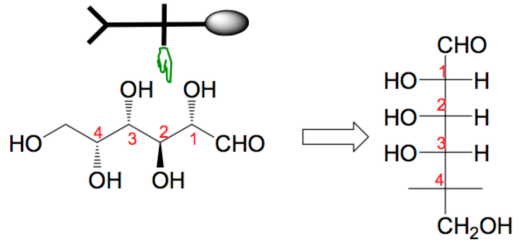
Notre exemple consiste à représenter le D-Talose en projection de Fischer depuis une représentation de Cram. Pour cela, il suffit de s'imaginer un petit bonhomme qui, au dessus de la molécule, regarde celle-ci. Sa main droite est représentée en vert. La tête de notre bonhomme doit **toujours** être orienté vers la fonction la plus oxydée (ici l'aldéhyde).



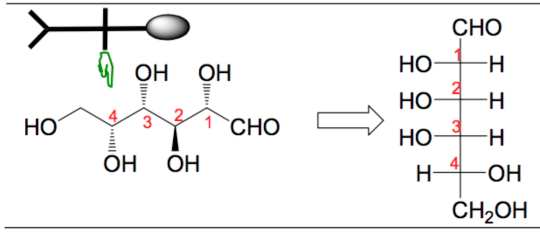
Si l'on regarde le carbone 1, on constate que le groupement hydroxyle (en représentation de Cram) est vers l'arrière, c'est-à-dire du coté la main gauche de notre bonhomme. Donc en projection de Fischer, ce groupement hydroxyle sera du coté gauche.



Dés lors, il apparaît clairement que, le groupement hydroxyle en position 3 est dans le même cas de figure que celui en position 1. On peut donc placer cet hydroxyle lui aussi à gauche sur la projection de Fischer.

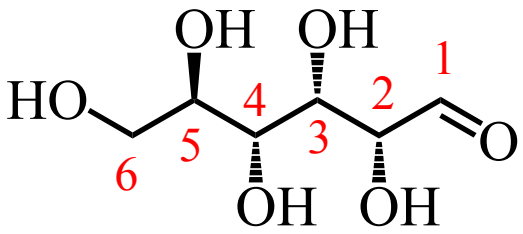


Concernant la position 2, la situation est inverse. En effet, pour notre bonhomme, ce carbone est plus loin que les carbones 1 et 3. On applique donc une règle complètement différente. **Tous ce qui, en représentation de Cram, se trouve du coté de la main droite de notre bonhomme, sera à gauche en projection de Fischer**. Ainsi le groupement hydroxyle en C_2 est en avant du plan et donc du coté de la main droite de notre bonhomme (en représentation de Cram), il sera donc à gauche sur la projection de Fischer.



Exactement la même situation se produit concernant le carbone C_4. Dans ce cas l'hydroxyle est vers l'arrière, donc du coté de la main gauche, d'où on le retrouve à droite en projection de Fischer, ce qui va parfaitement avec la notation D du D-Talose.

Passage d'un anomère à un autre

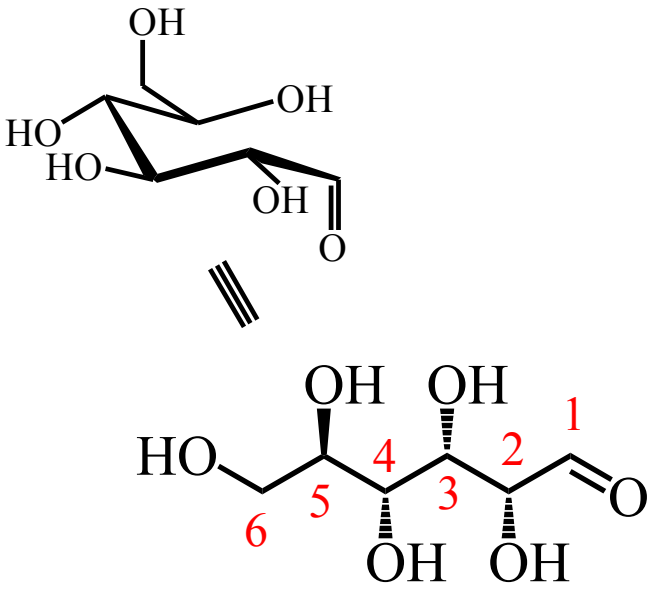


D-(+)-glucose

Passage d'un anomère à un autre

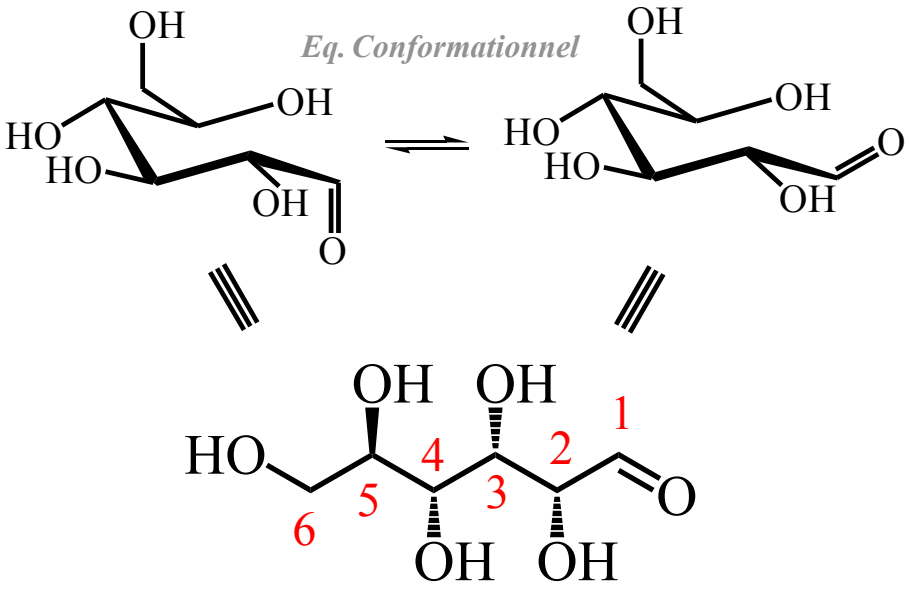
Représentation en

Perspective cavalière



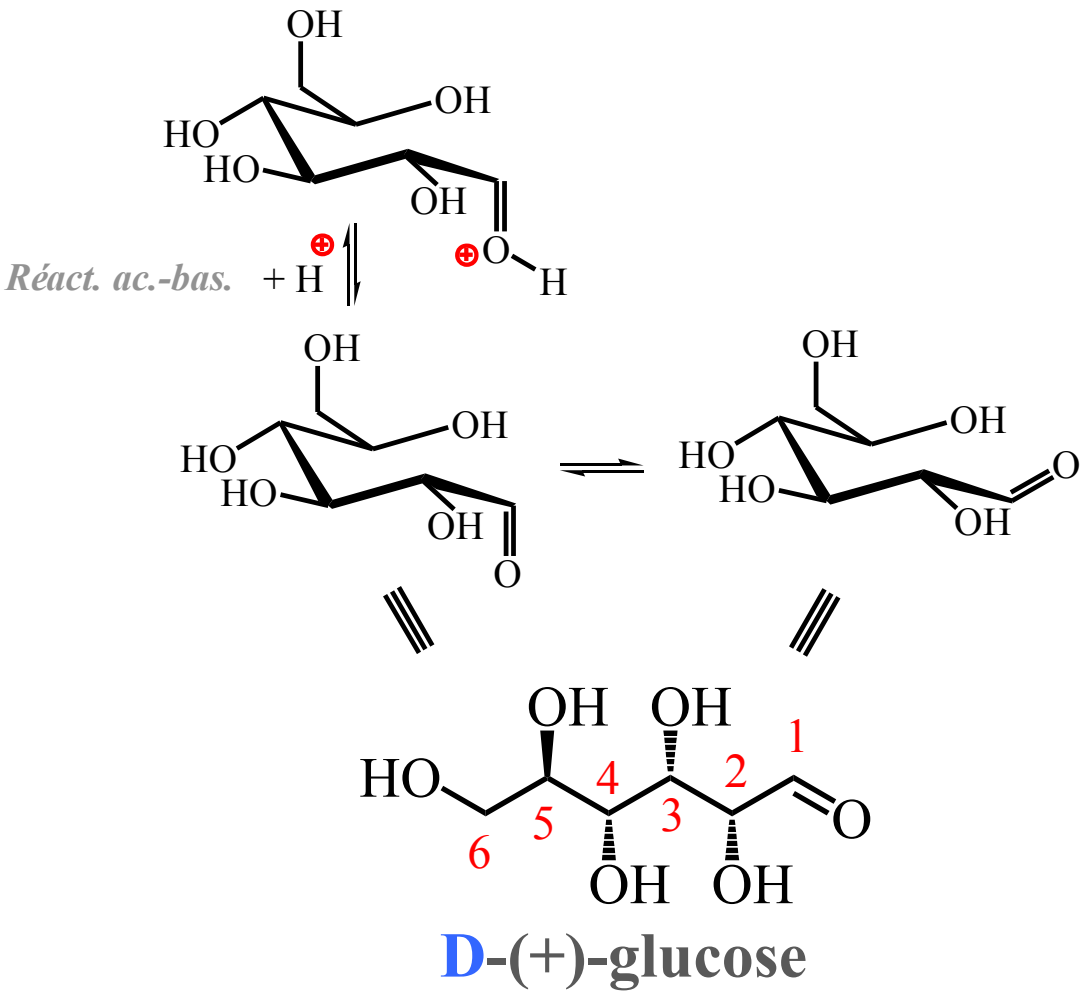
D-(+)-glucose

Passage d'un anomère à un autre



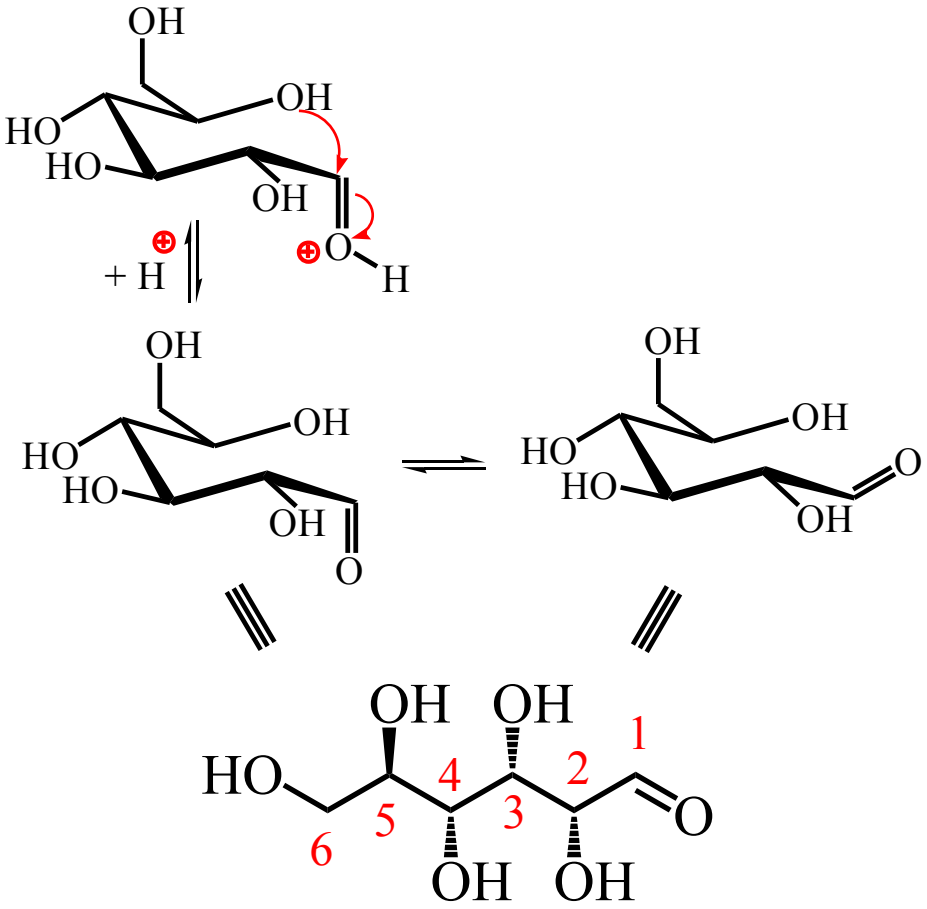
D-(+)-glucose

Passage d'un anomère à un autre



D-(+)-glucose

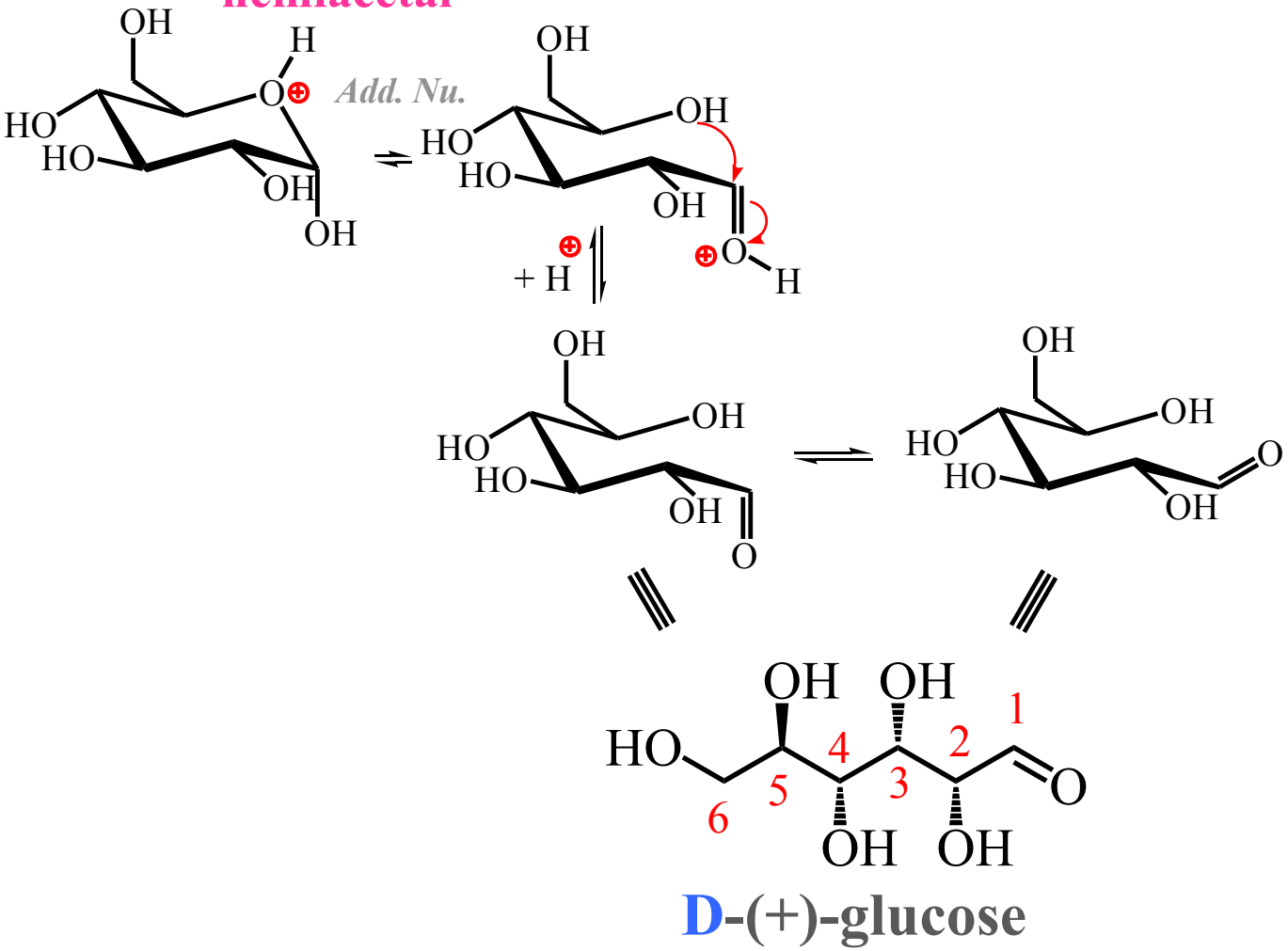
Passage d'un anomère à un autre



D-(+)-glucose

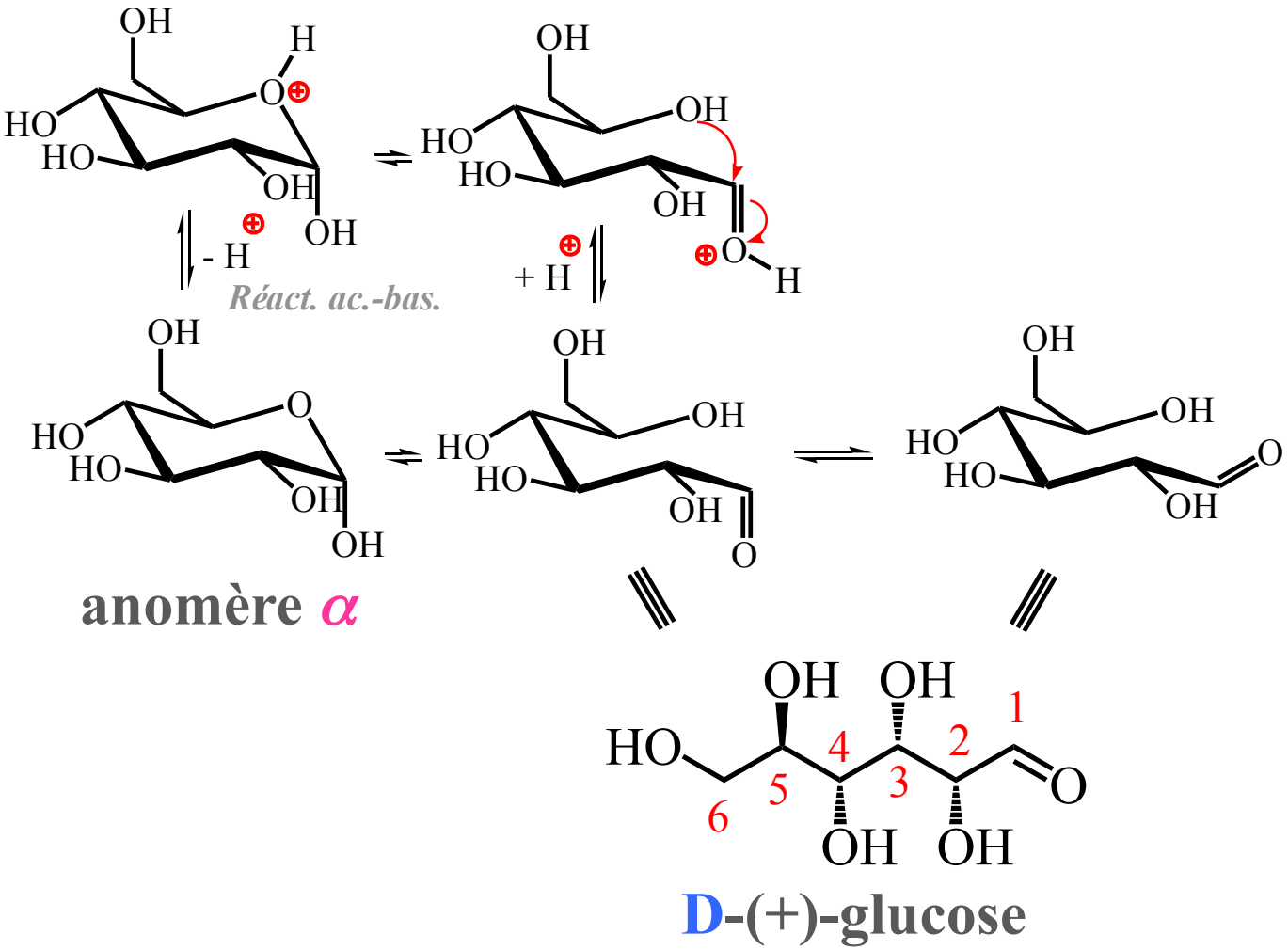
Passage d'un anomère à un autre

Formation d'un hémiacétal

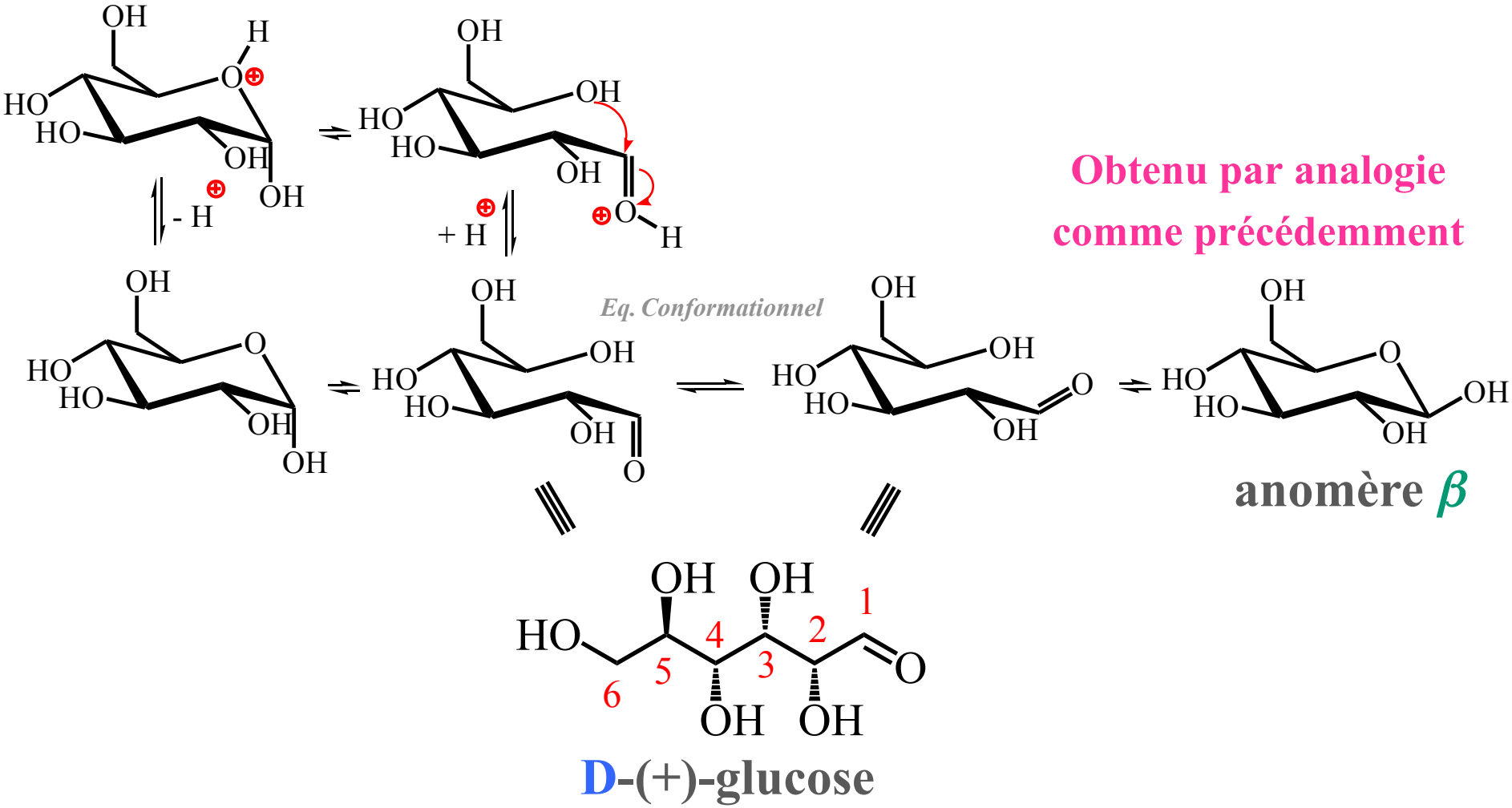


D-(+)-glucose

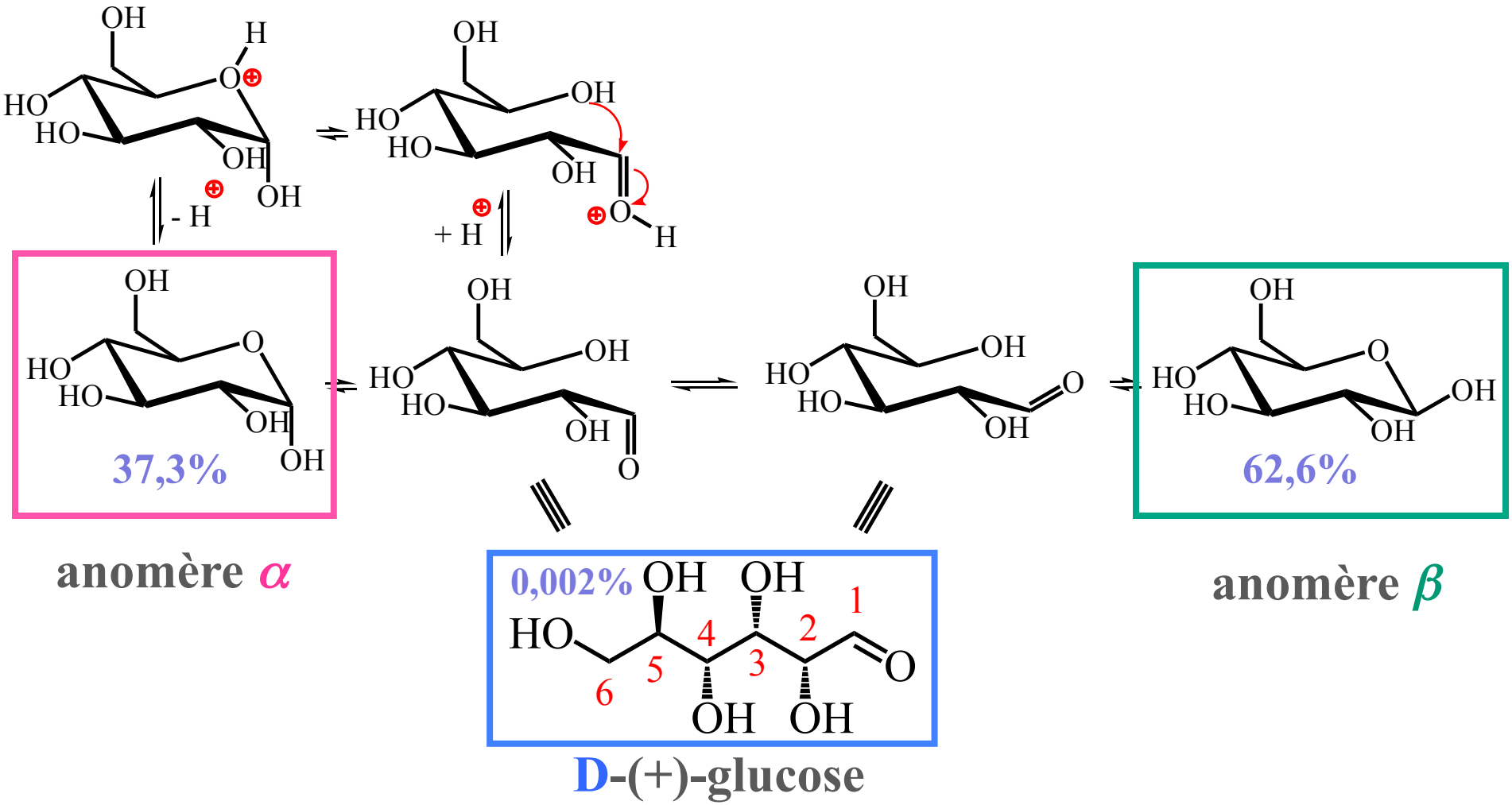
Passage d'un anomère à un autre



Passage d'un anomère à un autre



Passage d'un anomère à un autre



Le Catabolisme des Sucres

1) L'hydrolyse des polysaccharides

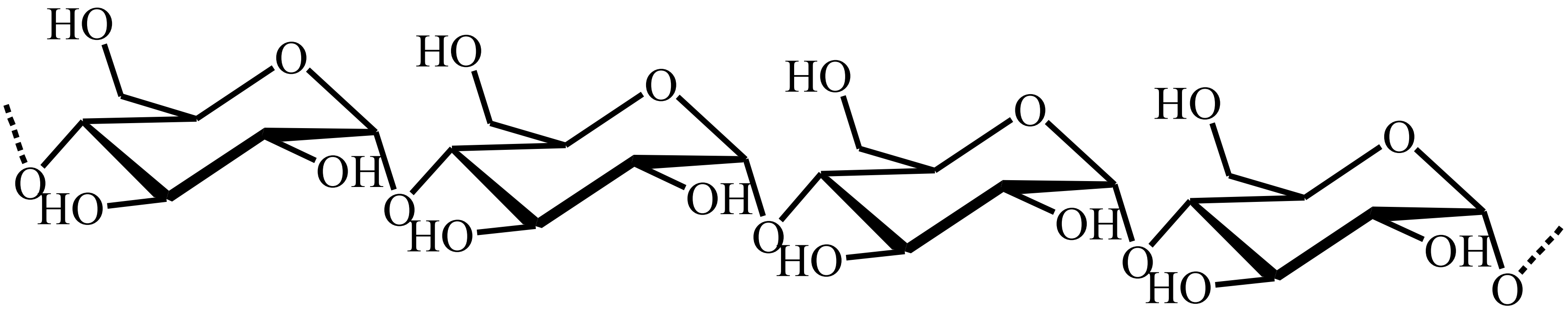
2) La glycolyse (Ose → Pyruvate)

3) Transformation du Pyruvate :

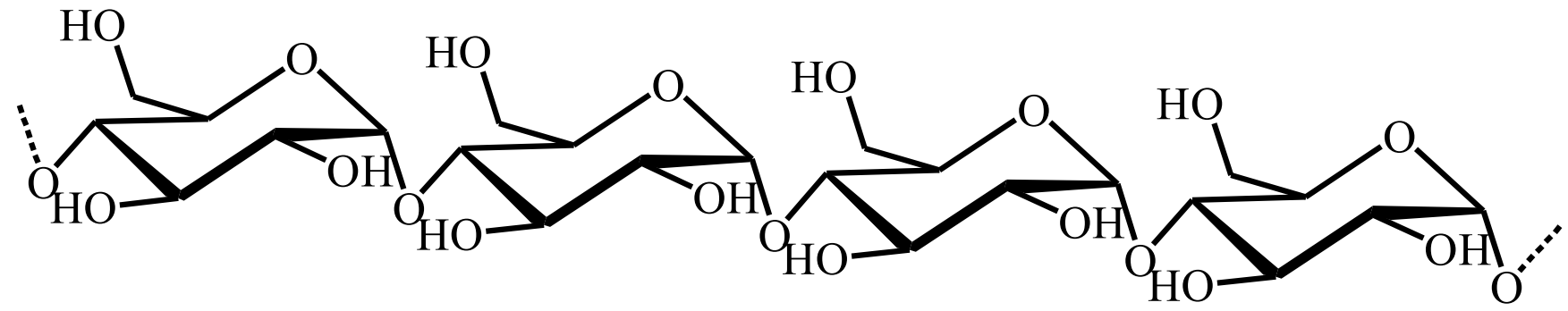
→ Lactate (anaérobie)

→ Ethanol (anaérobie / levures)

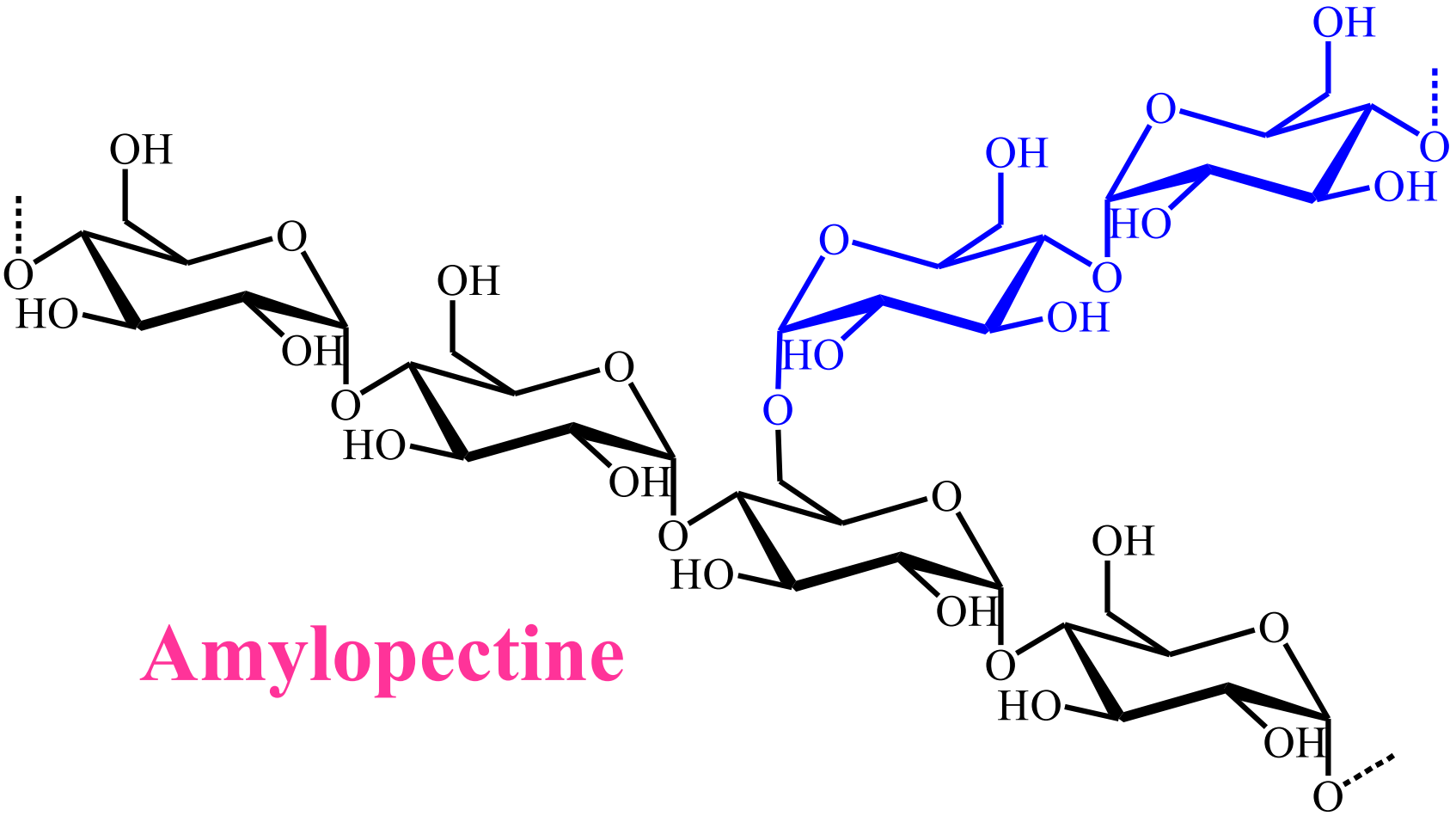
→ acétylCoA (aérobie)



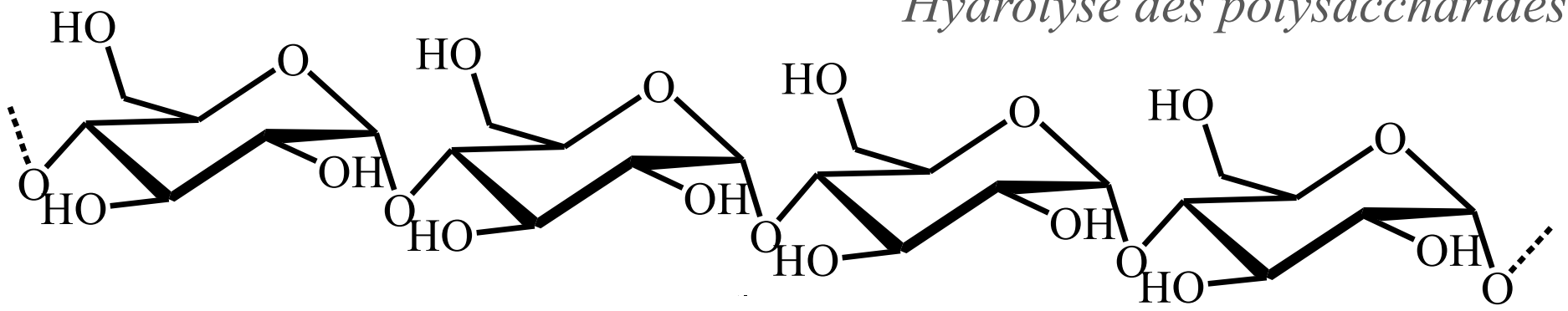
Amylose

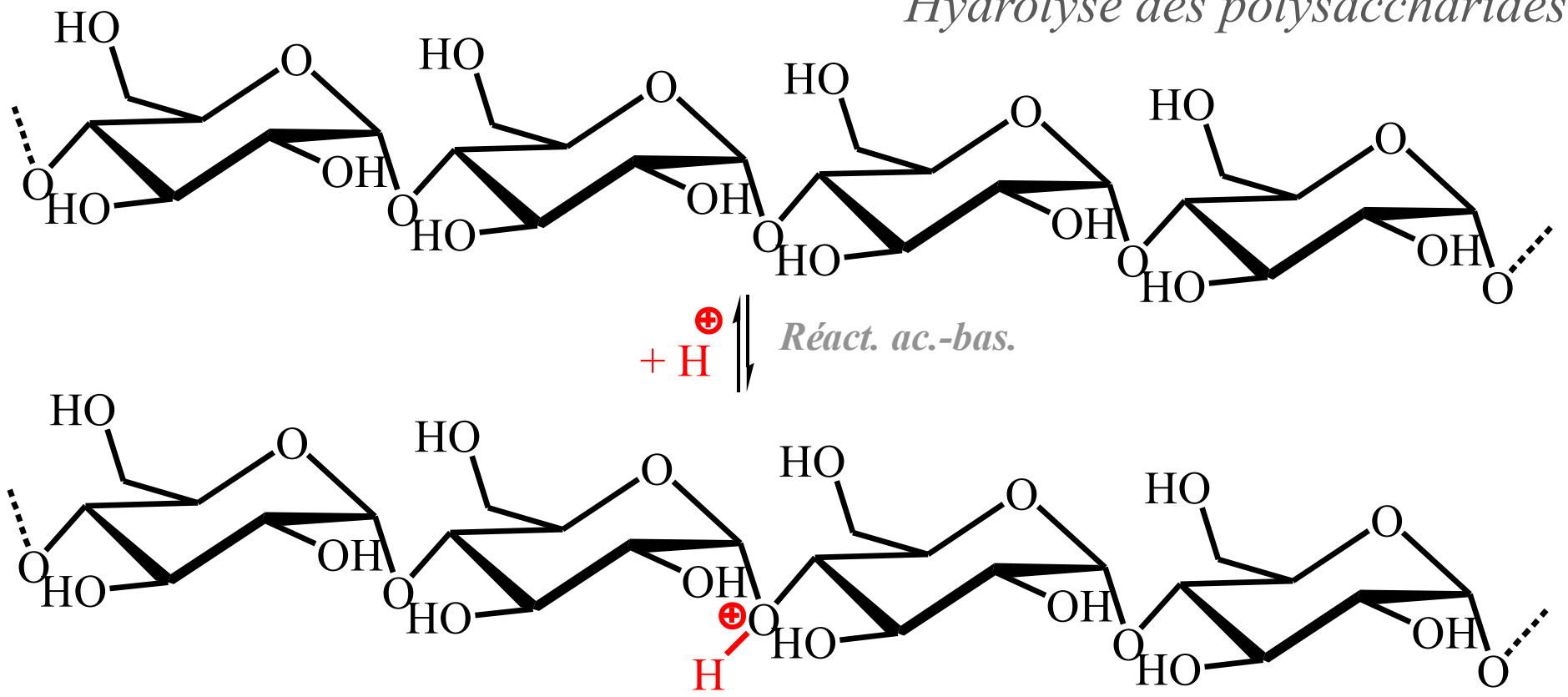


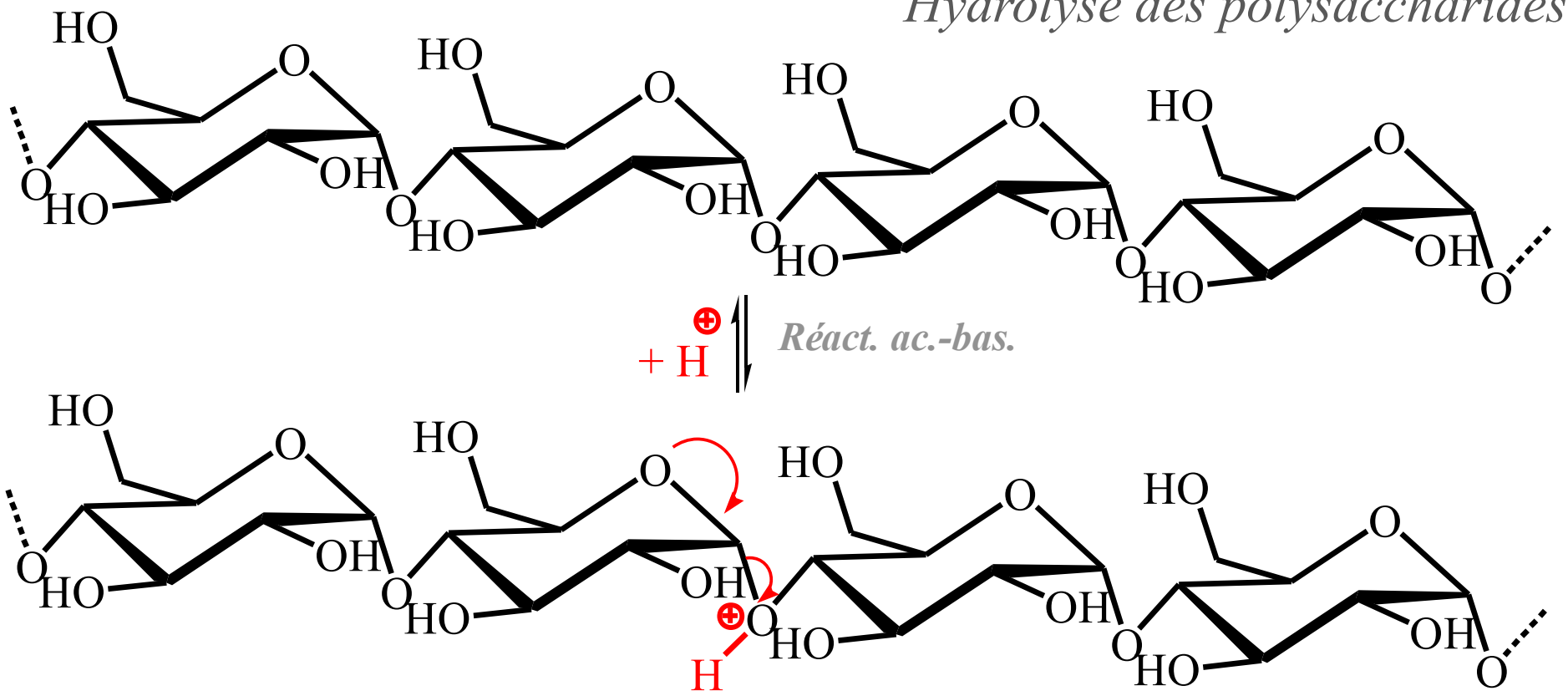
Amylose

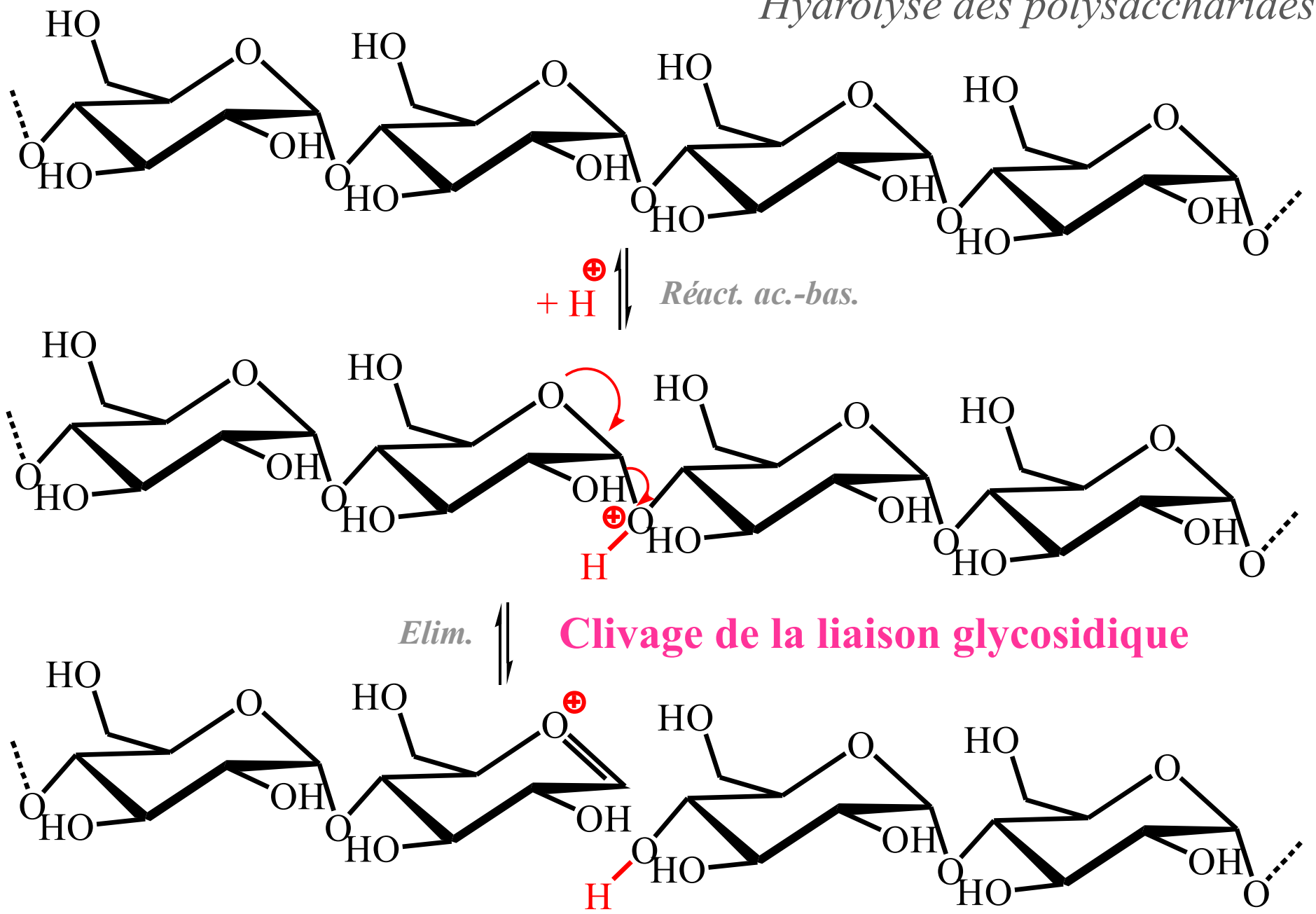


Amylopectine

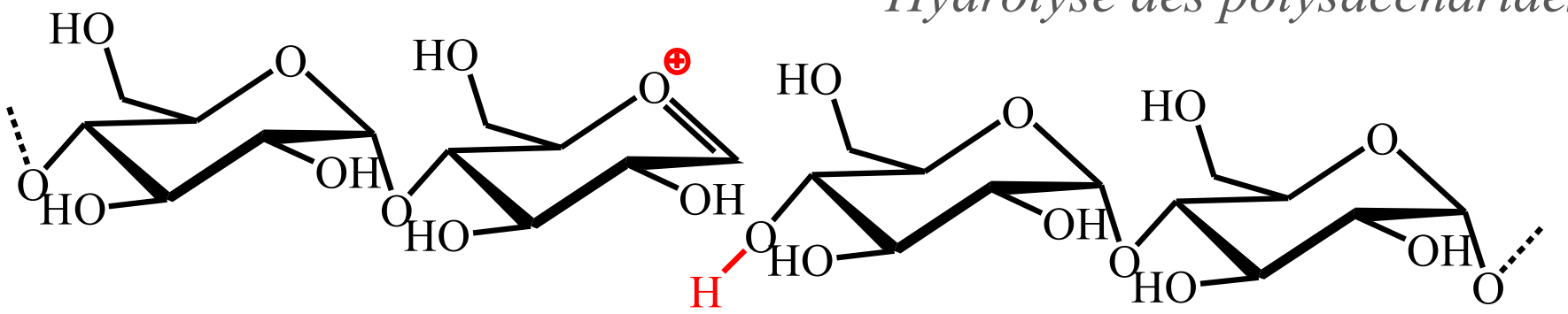

HO
O
HO
O
OH
HO
O
HO
O
OH
HO
O
HO
O
OH
HO
O
HO
O
OH
O


HO
O
OH
HO
+ H
Réact. ac.-bas.
H

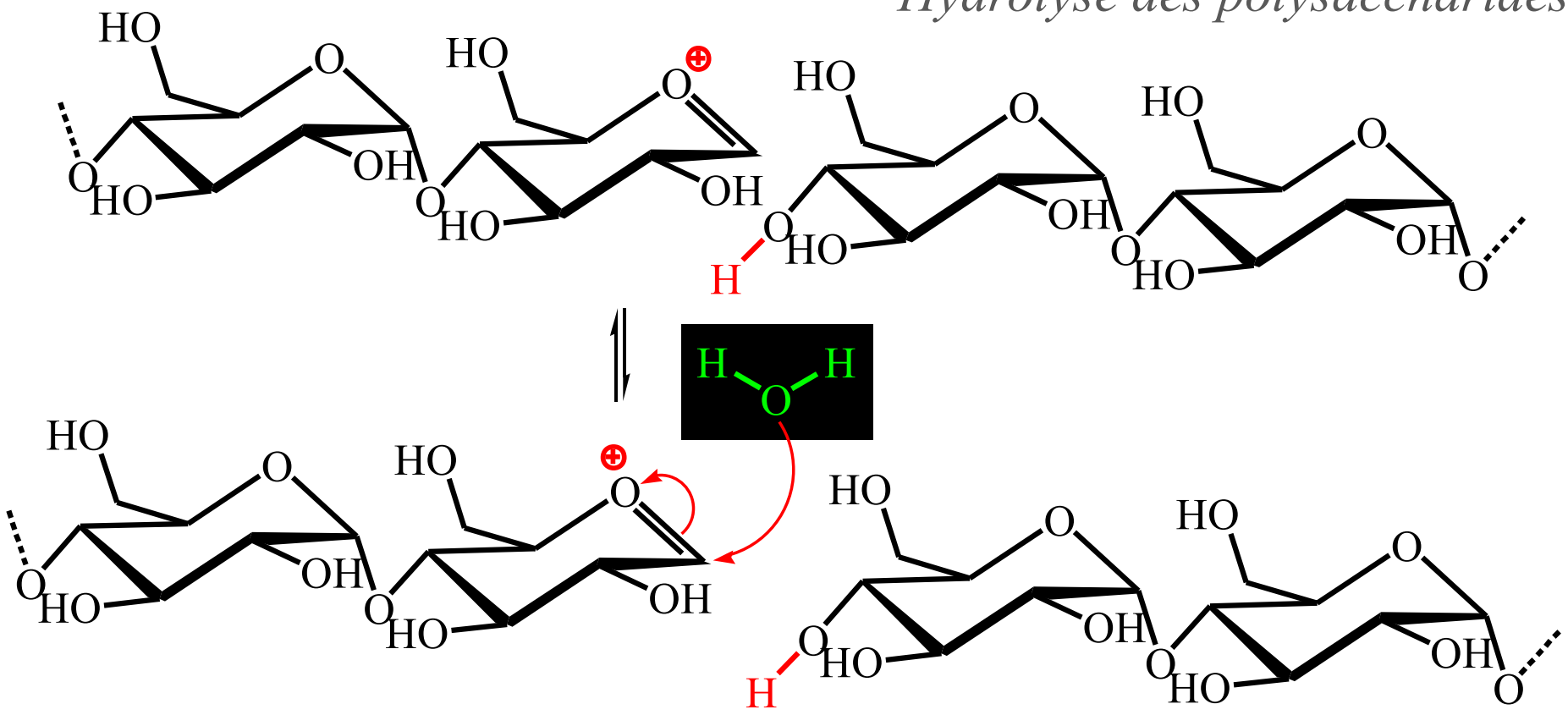

HO
O
OH
HO
+ H
Réact. ac.-bas.
H

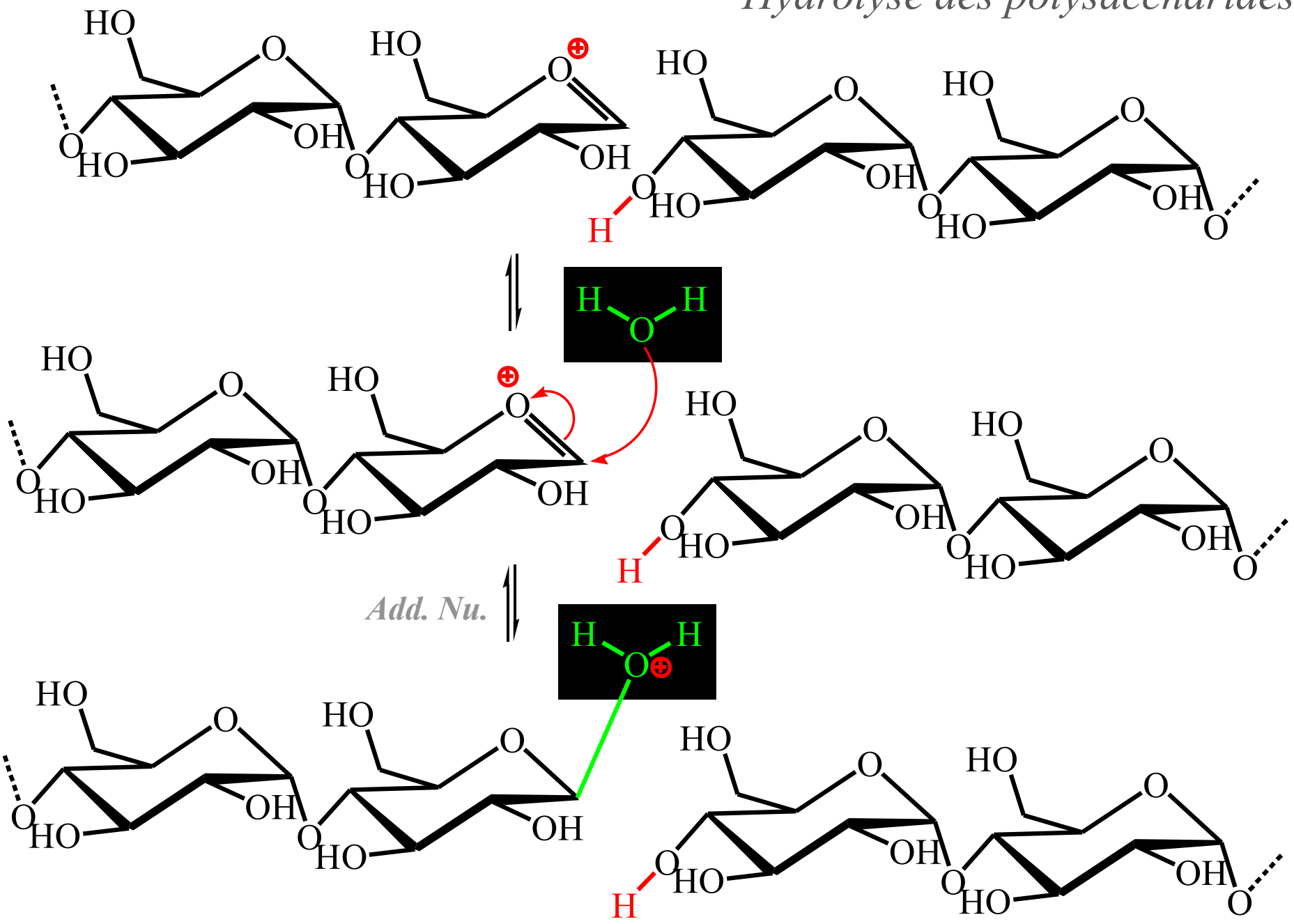


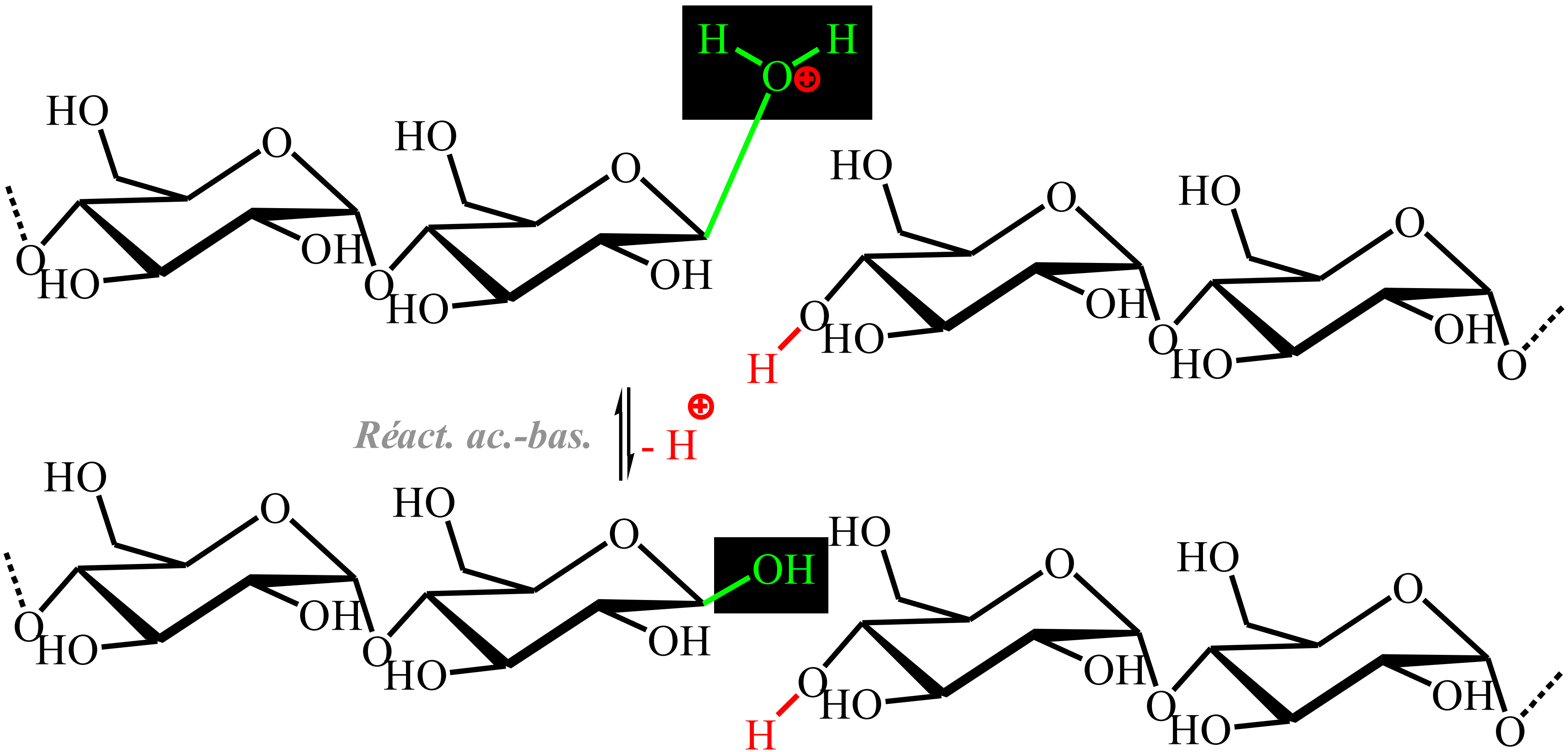
Formation d'un Oxocarbenium


HO
O
OH
HO
O
HO
O
OH
HO
O
H
HO
O
OH
HO
O
HO
O
OH
HO
O

Hydrolyse des polysaccharides

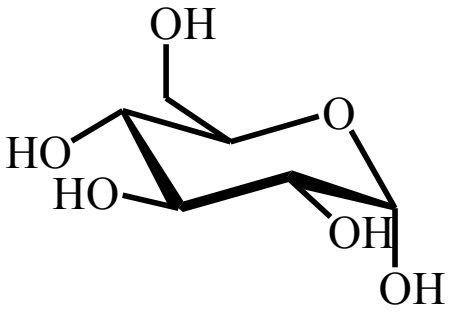



Add. Nu.

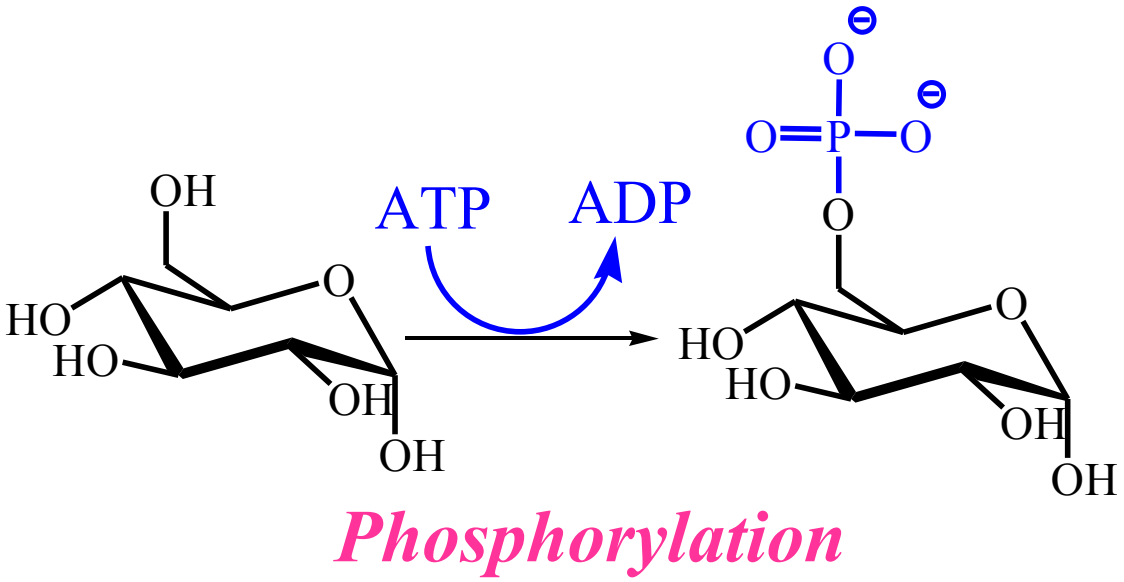


HO
O
OH
H
O⊕
Réact. ac.-bas.
- H⊕
OH

La glycolyse

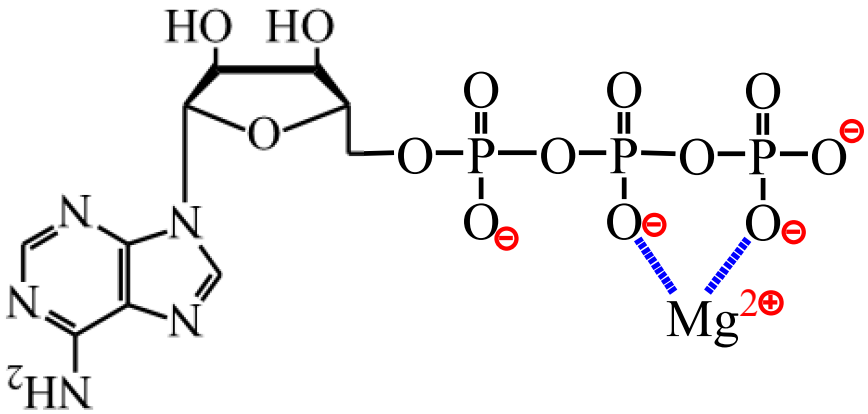


La glycolyse

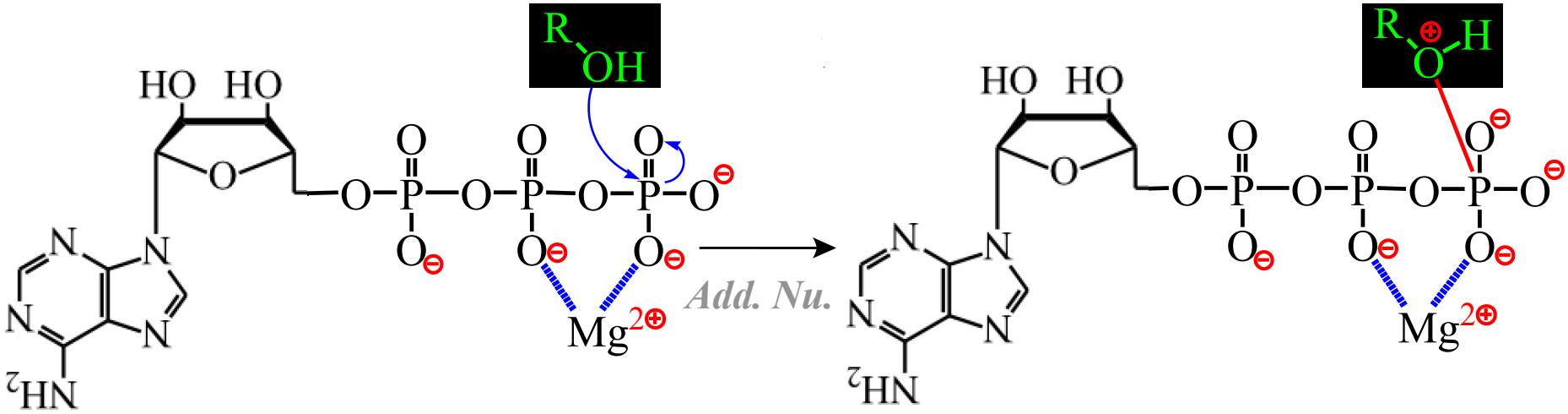


Phosphorylation

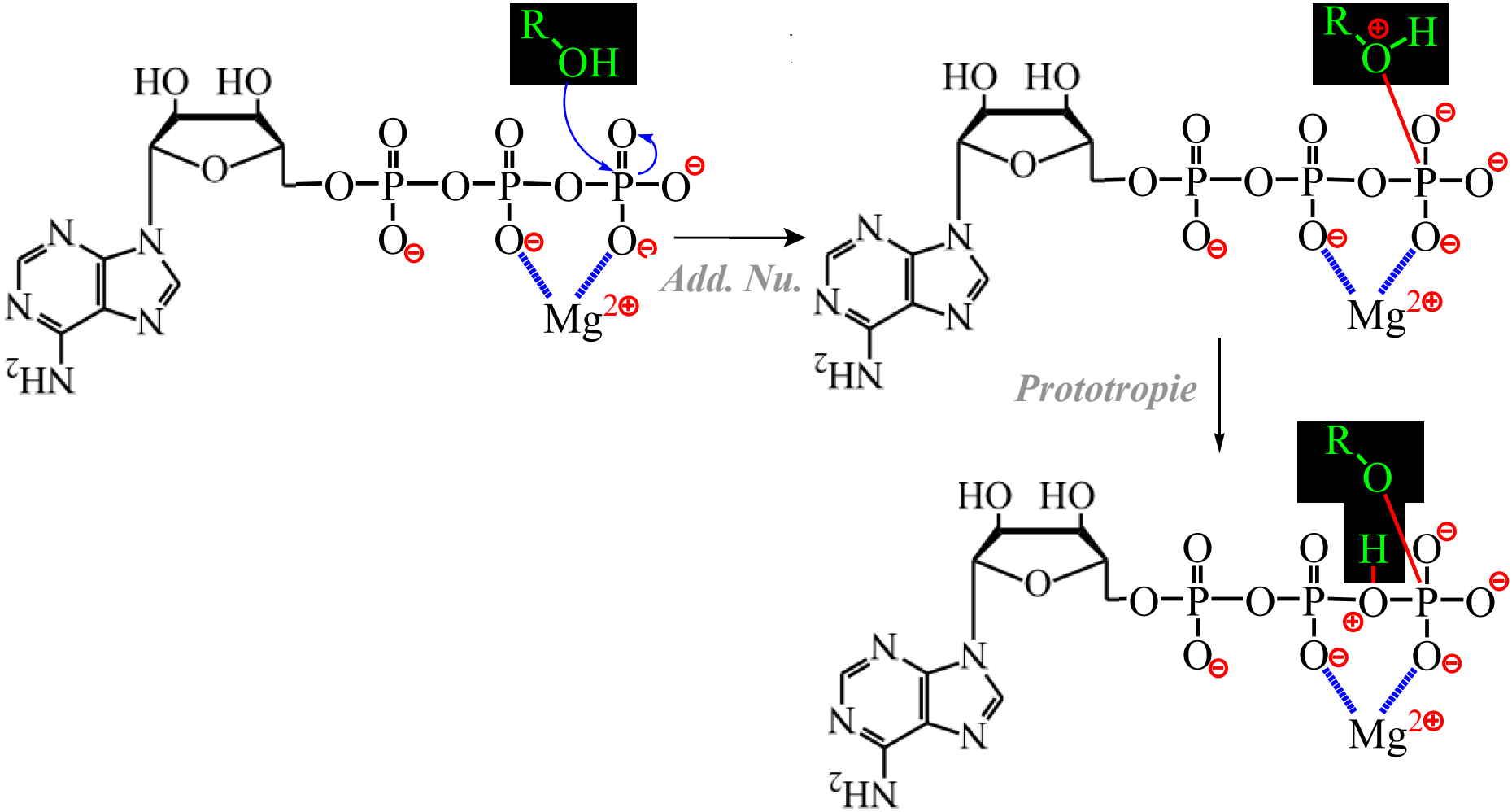
Mécanisme Phosphorylation



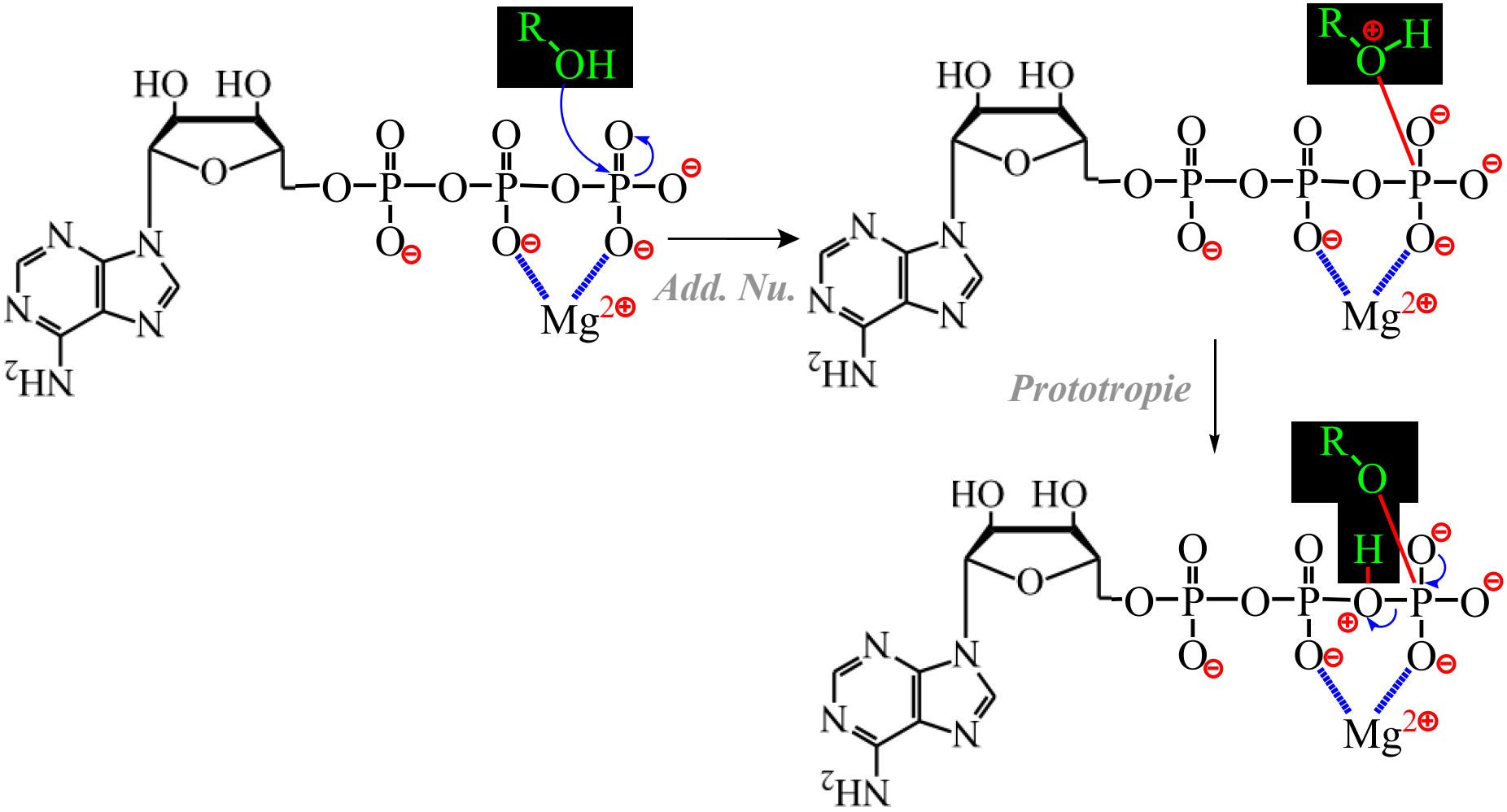
Mécanisme Phosphorylation



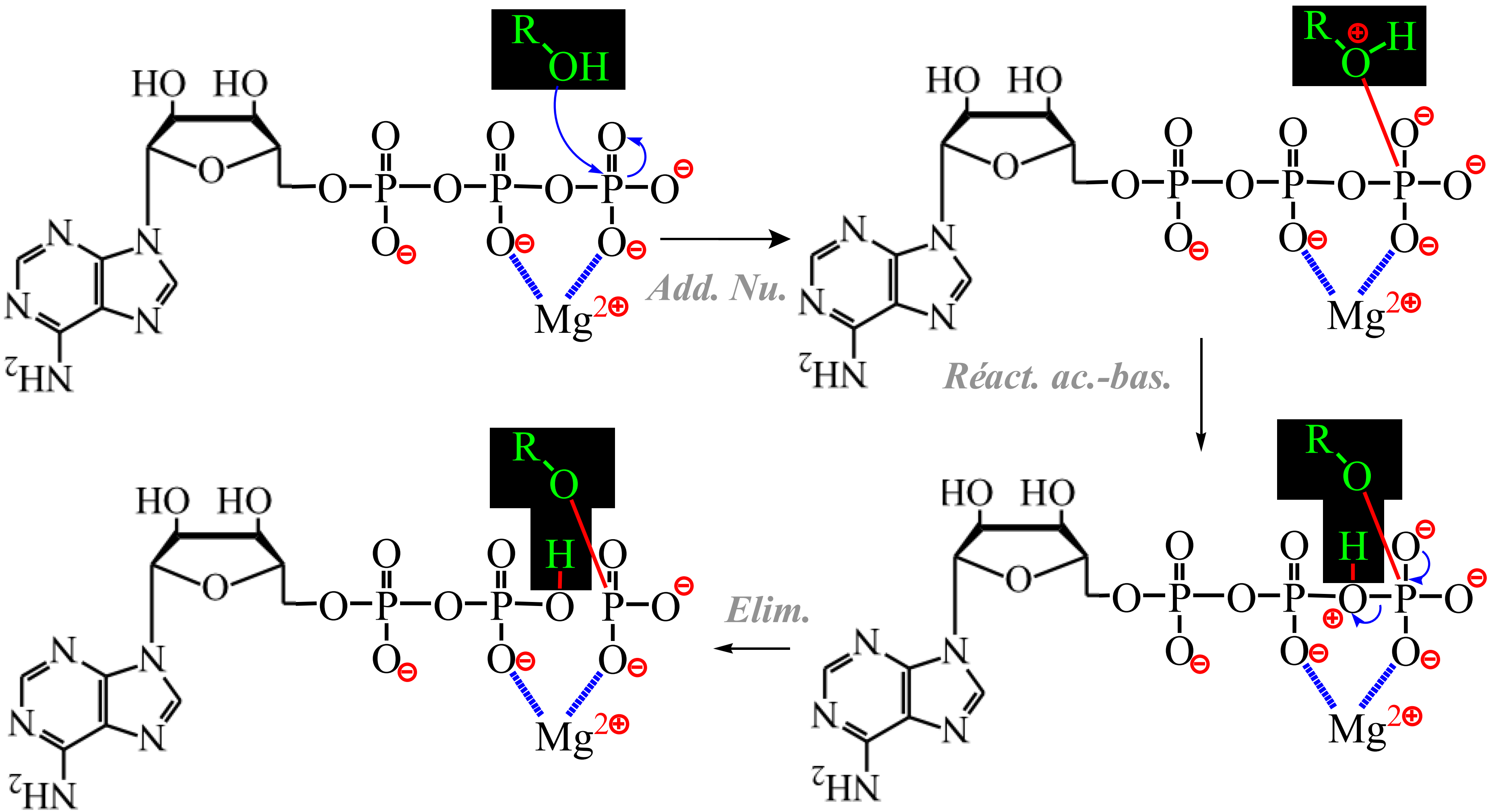
Mécanisme Phosphorylation



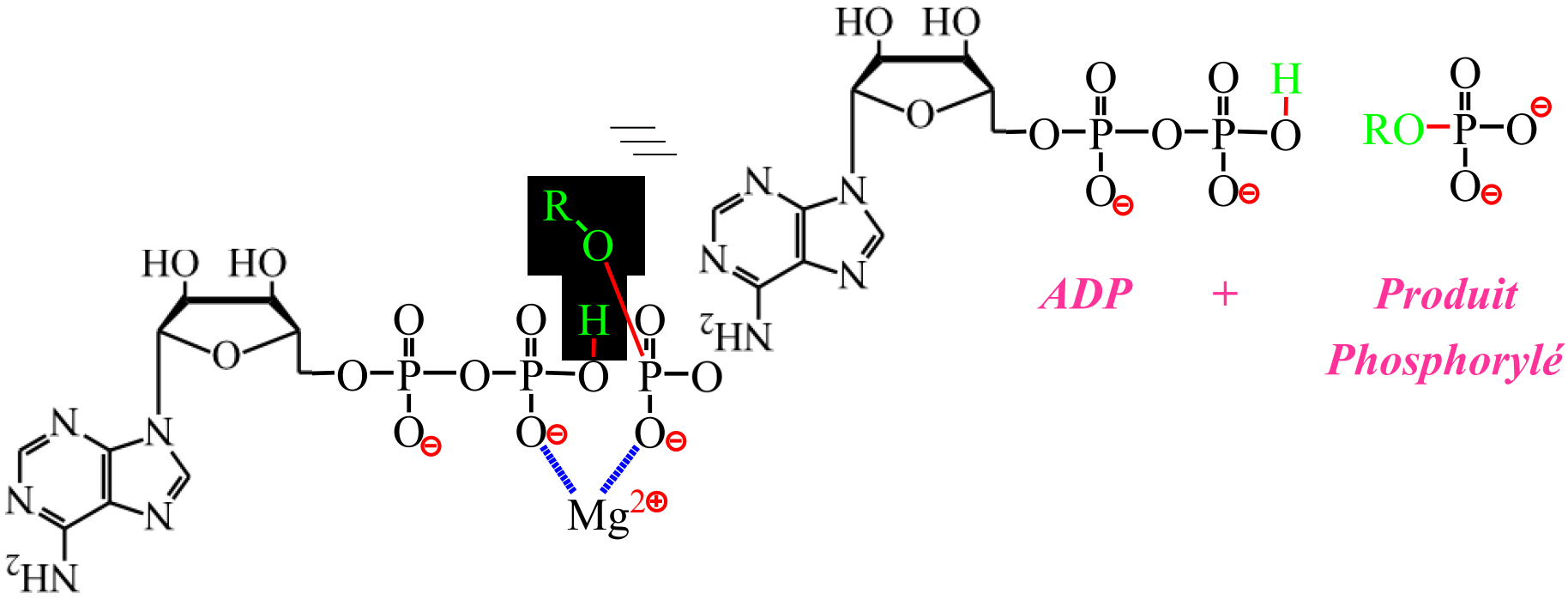
Mécanisme Phosphorylation



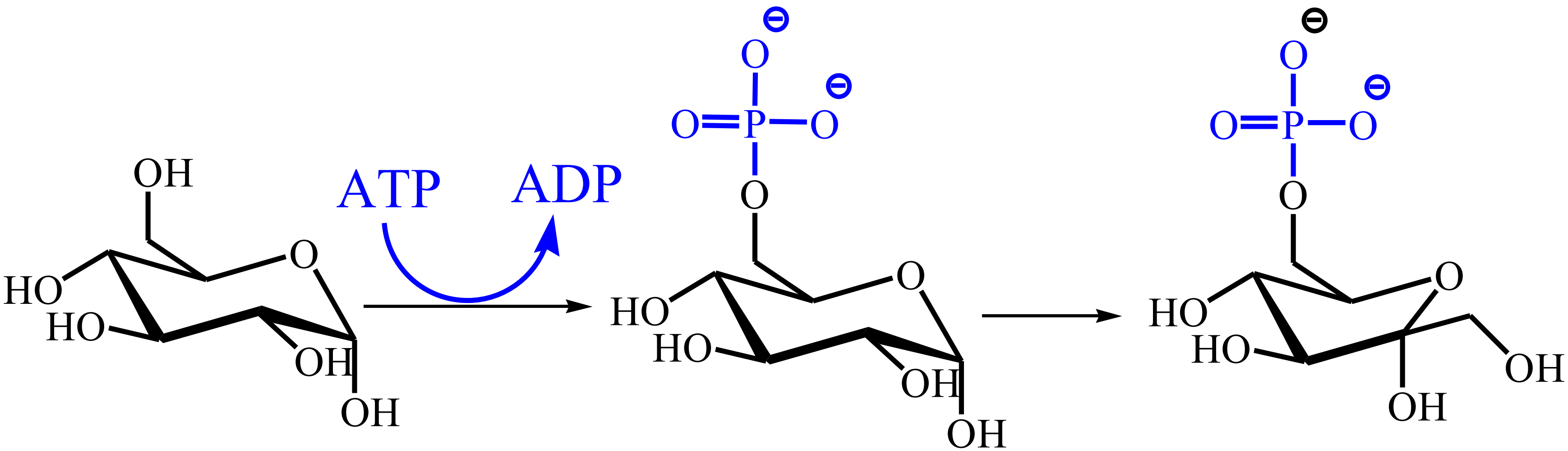
Mécanisme Phosphorylation



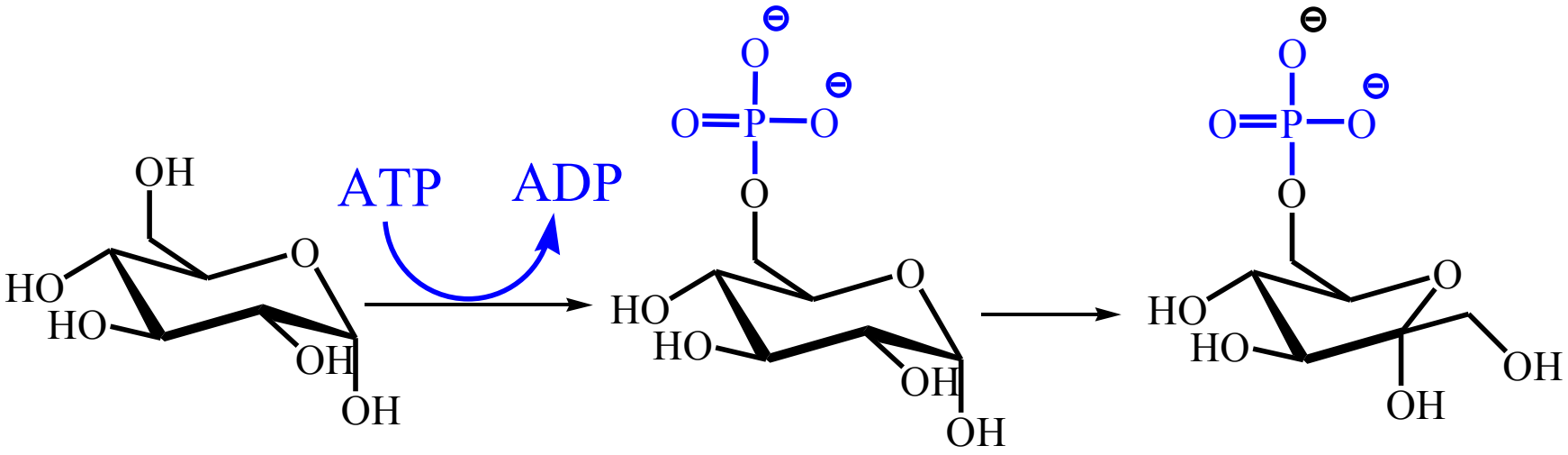
Mécanisme Phosphorylation



La glycolyse



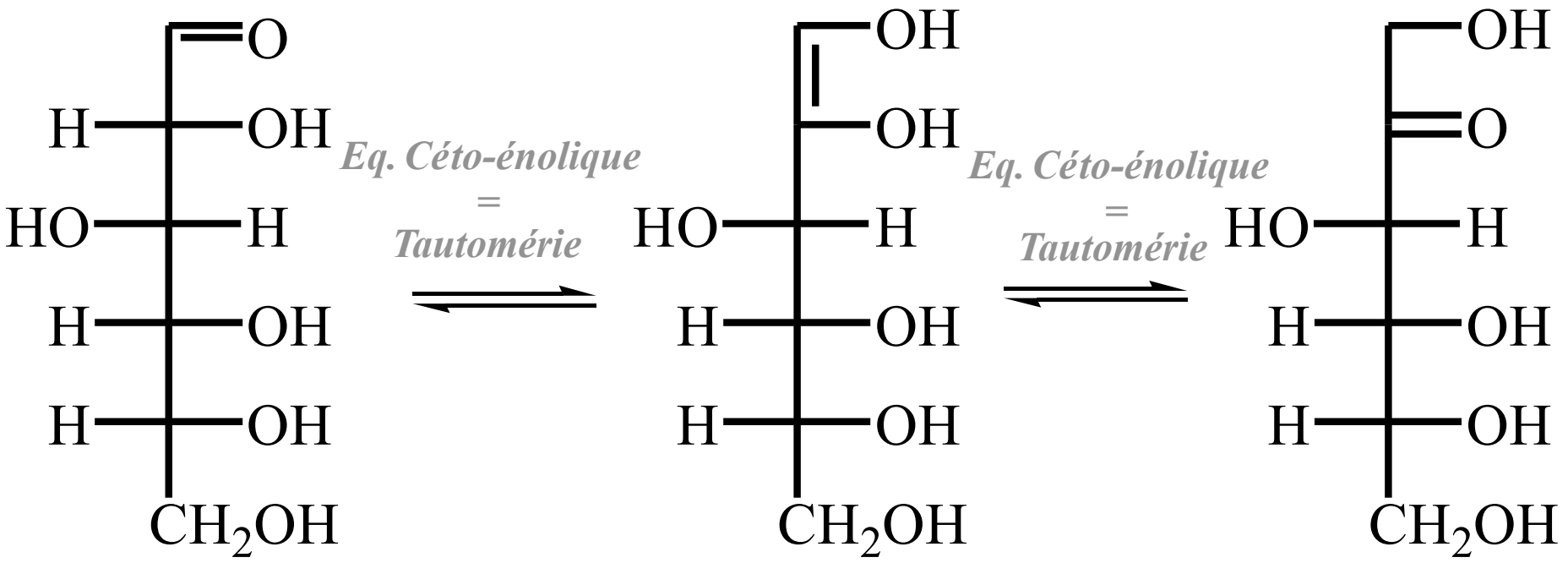
La glycolyse



1) *Ouverture (méca. Tableau)*
2) *Tautomérisation*
3) *Cyclisation (méca. Tableau)*

La Tautomérisation

Glucose → Fructose

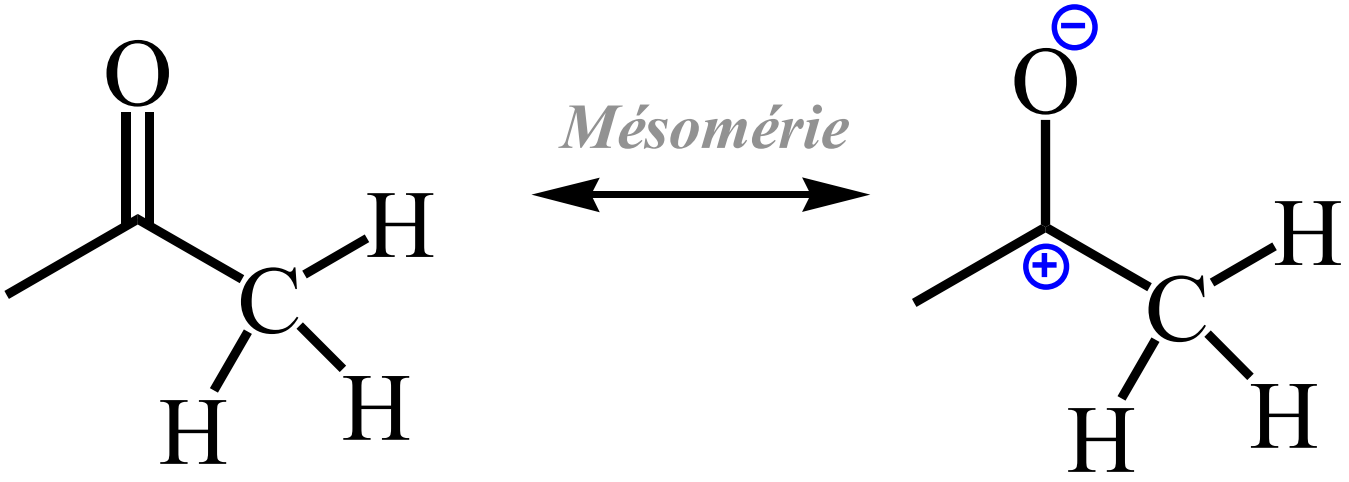


D-(+)-glucose

D-(-)-fructose

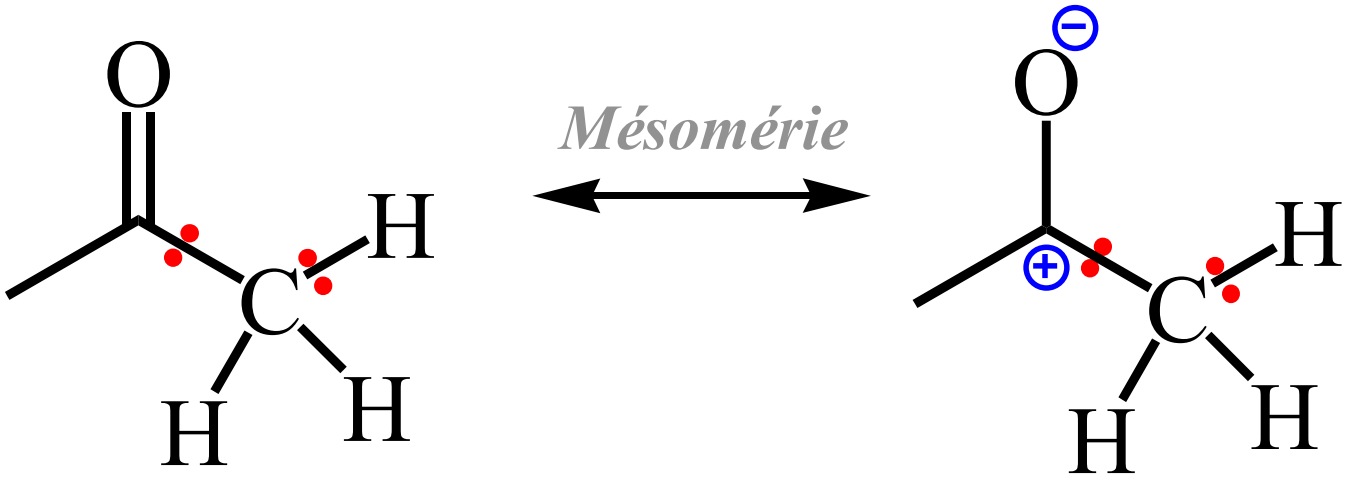
Acidité des composés carbonylés

Notion de tautomérie



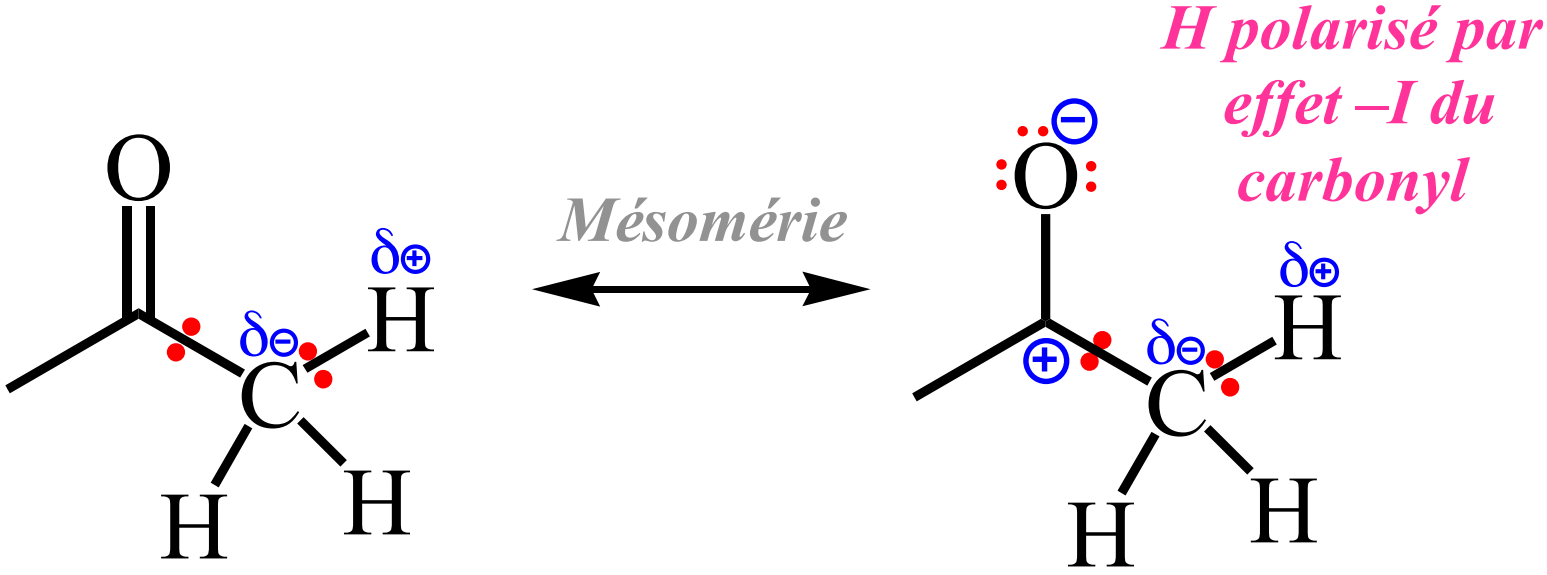
Acidité des composés carbonylés

Notion de tautomérie

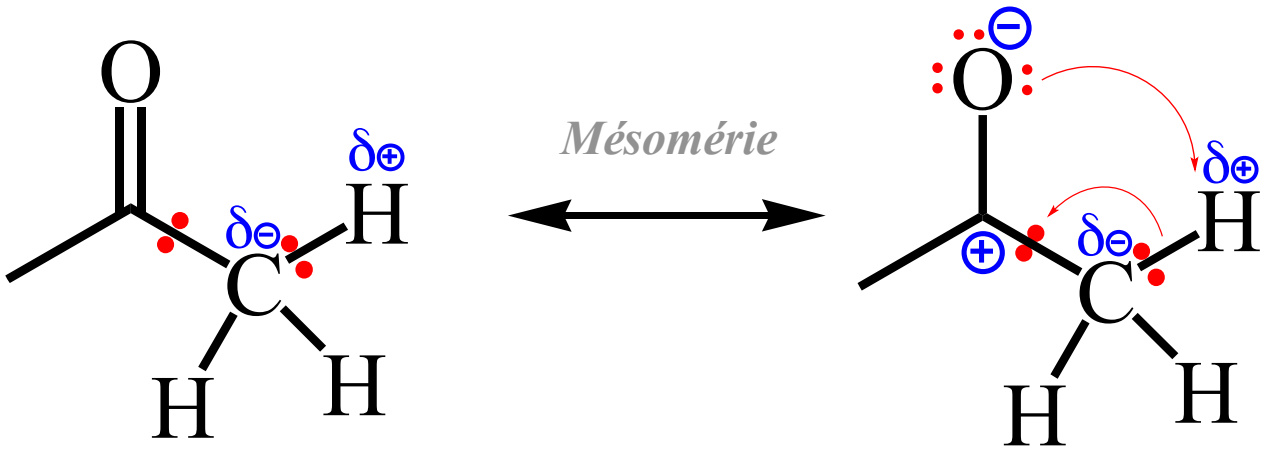


Acidité des composés carbonylés

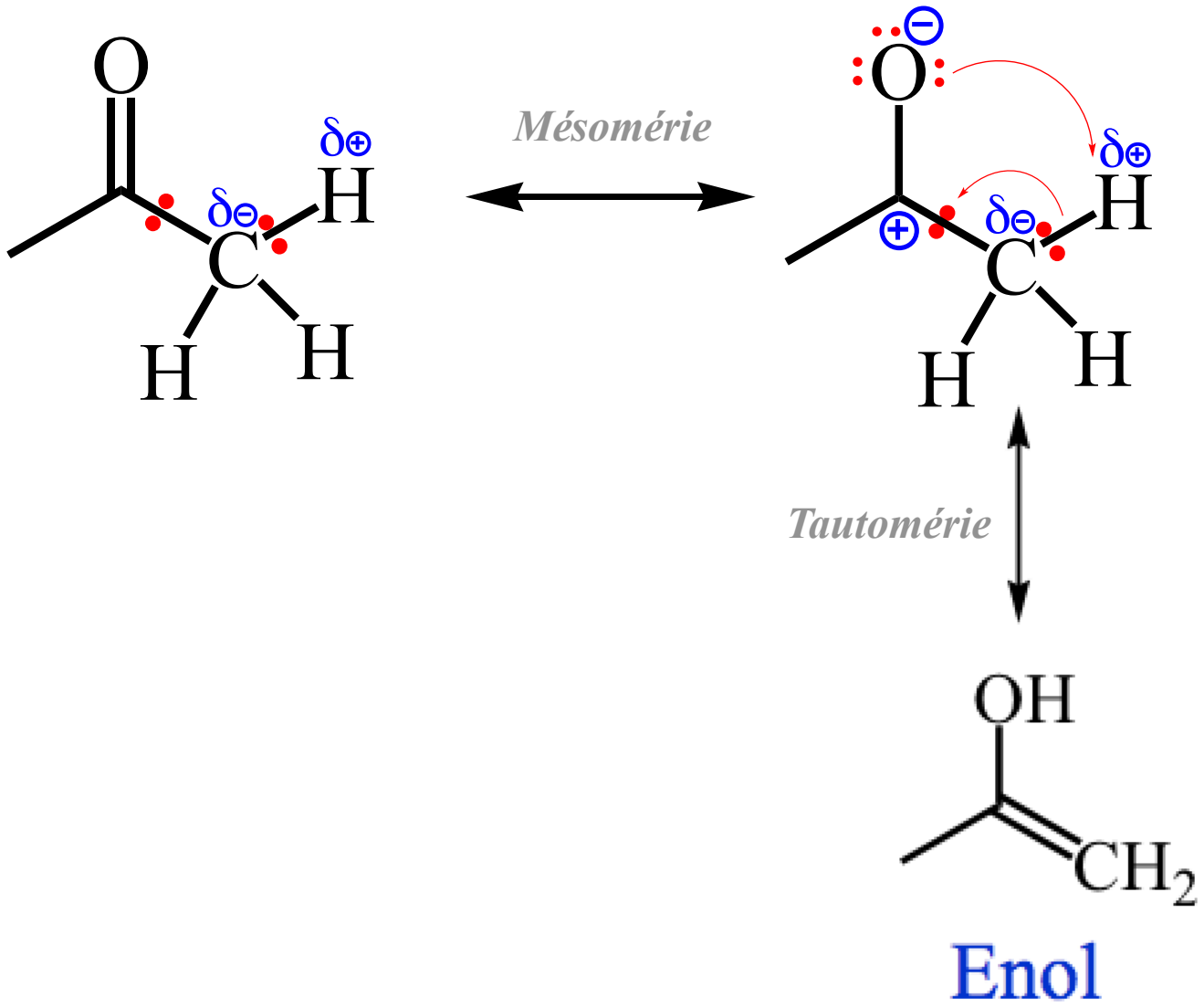
Notion de tautomérie



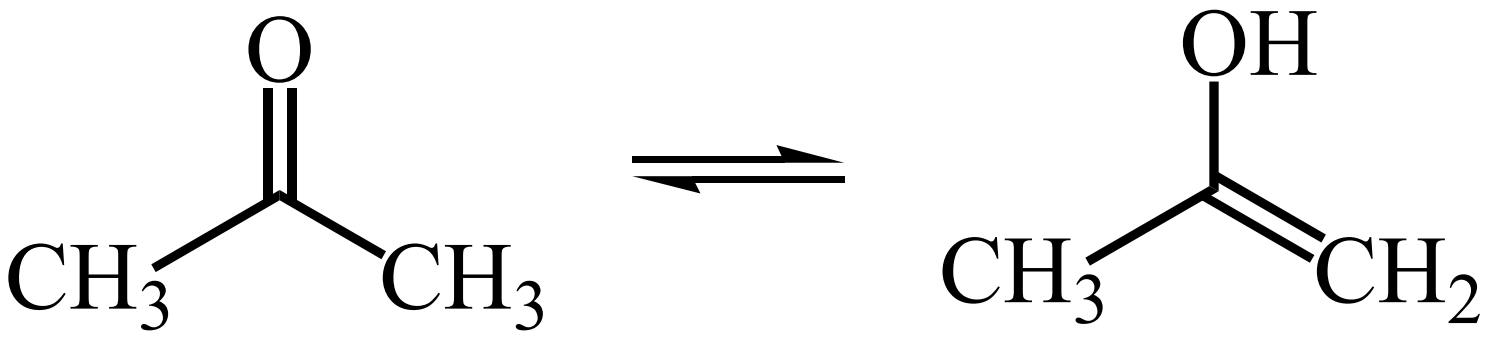
Tautomérie



Tautomérie



La tautomérie céto-énolique

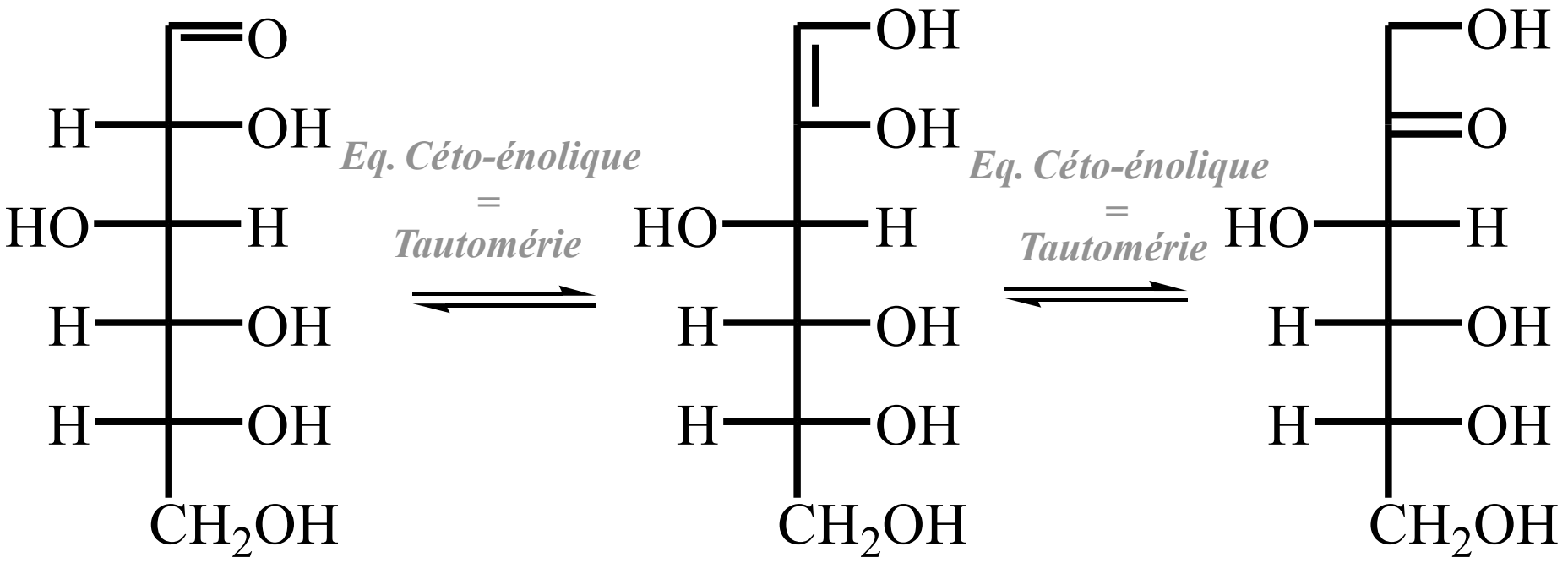


Forme cétone

Forme énol
(0,0000006%)

La Tautomérisation

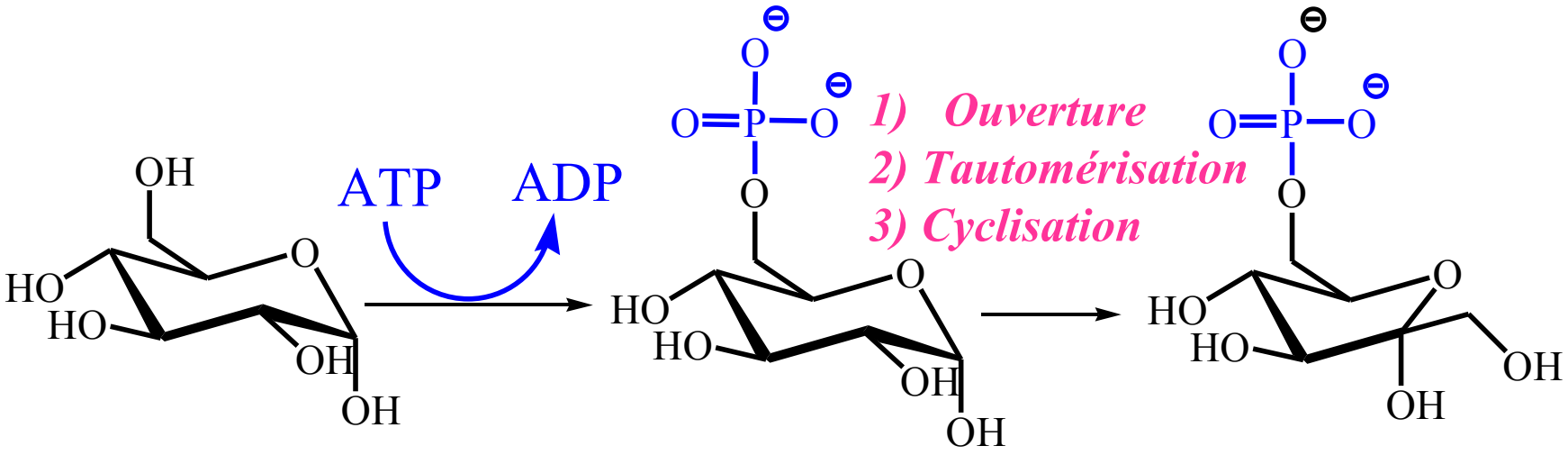
Glucose → Fructose



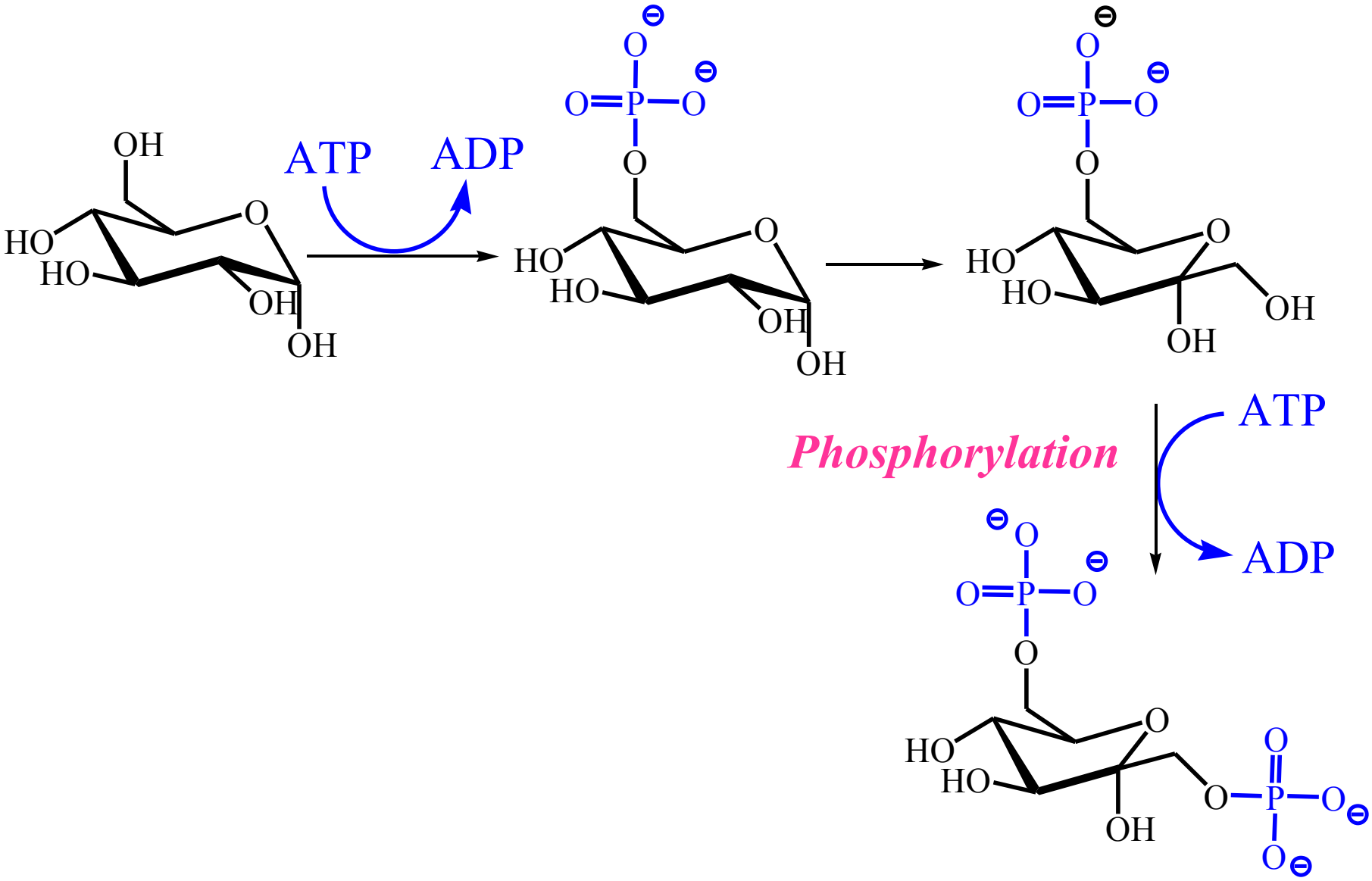
D-(+)-glucose

D-(-)-fructose

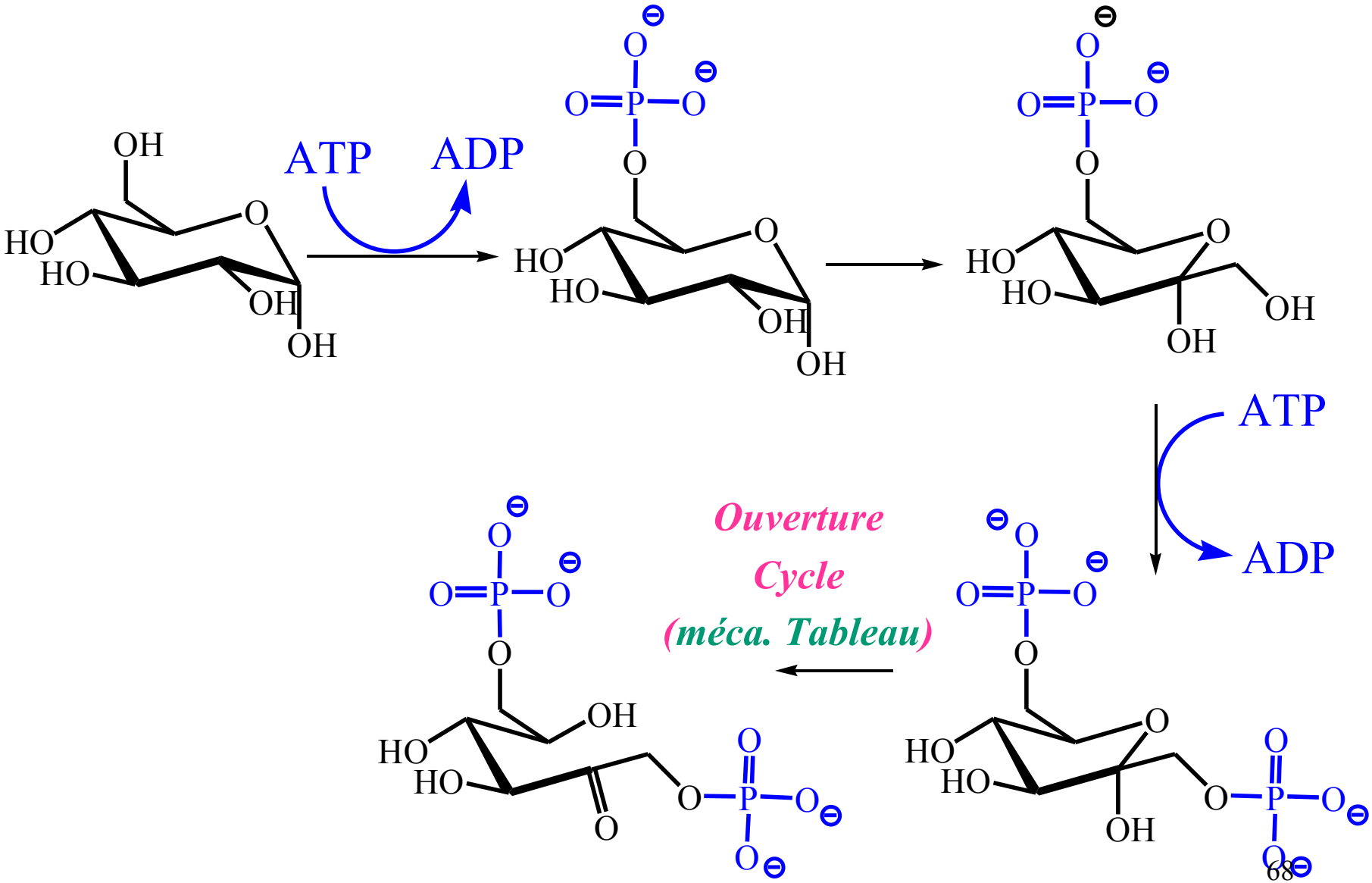
La glycolyse



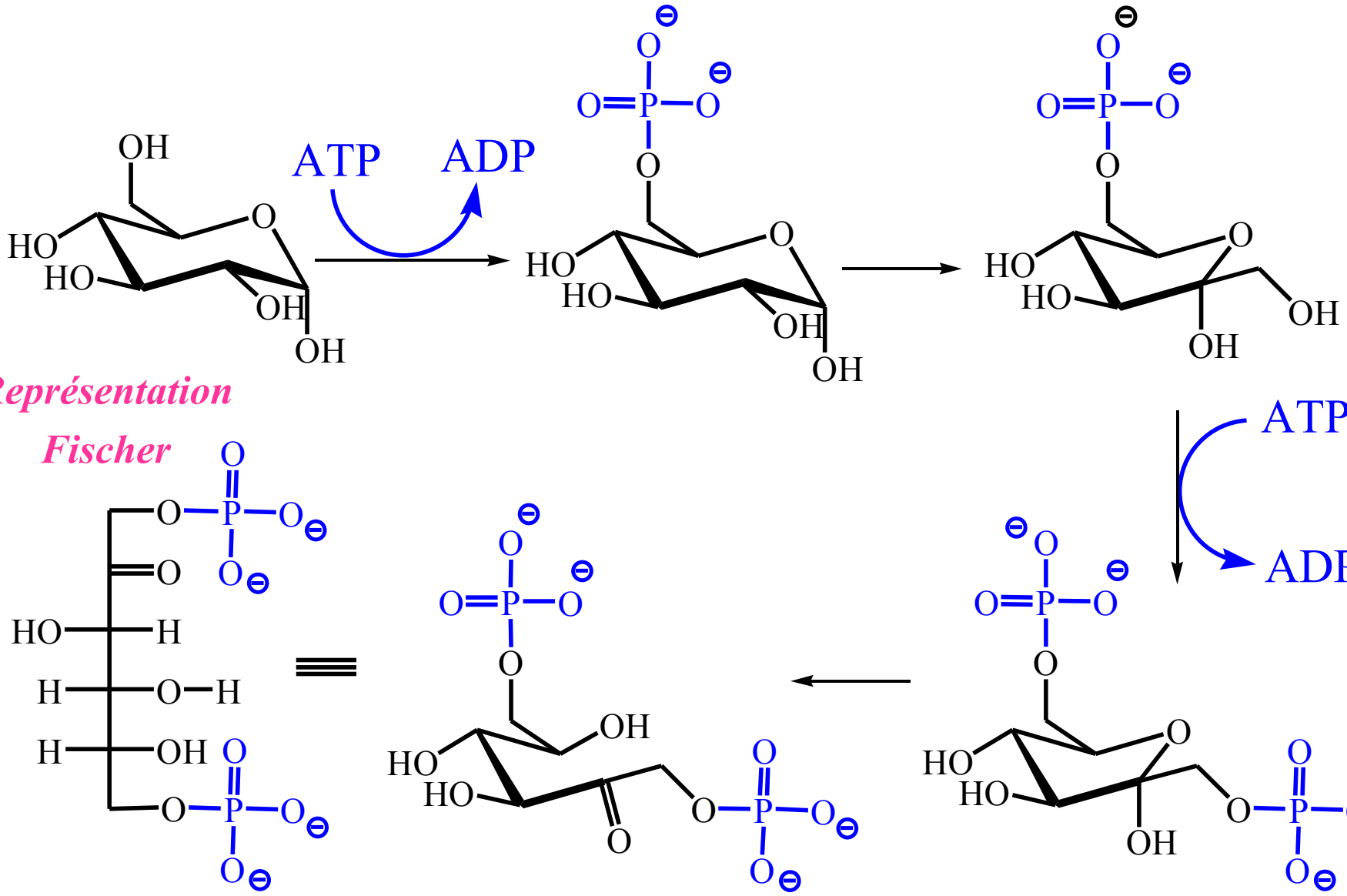
La glycolyse



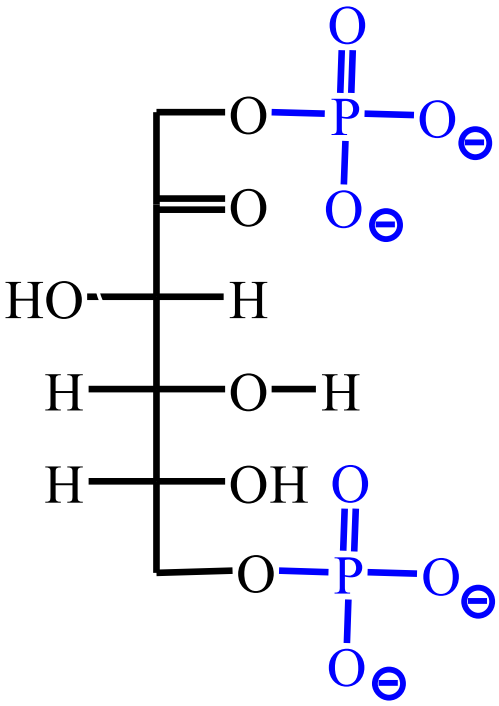
La glycolyse



La glycolyse



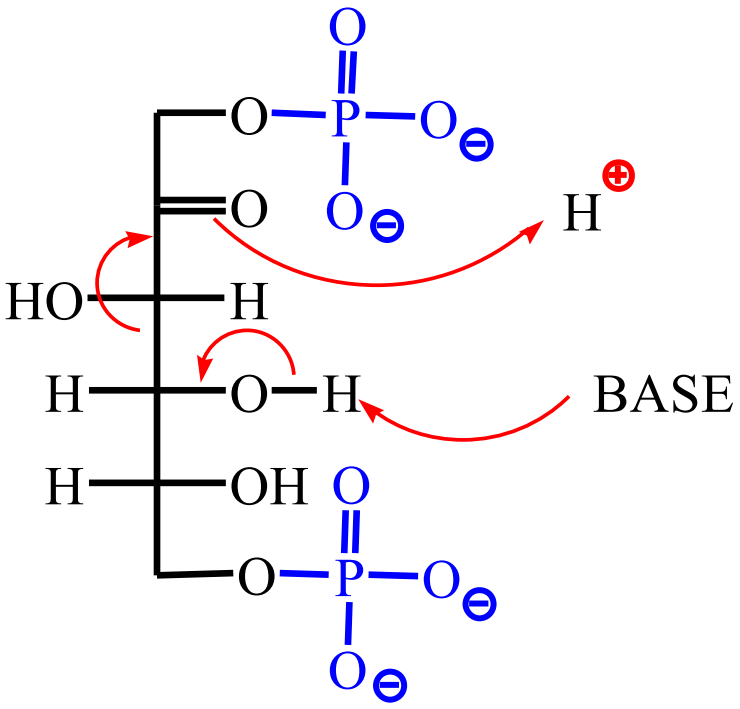
Obtention du GAP



Rétro-aldolisation

(= *inverse de l'aldolisation*)

Obtention du GAP

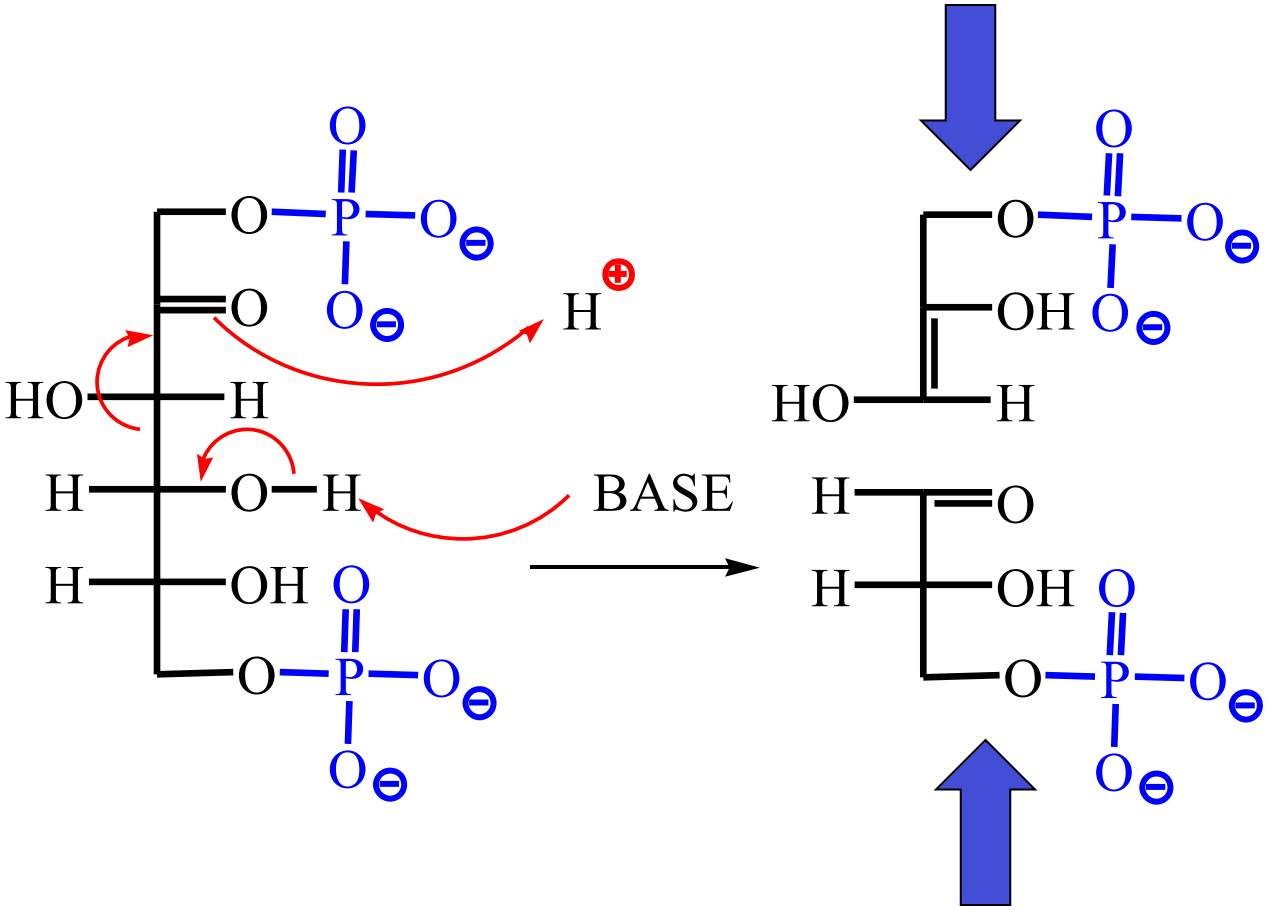


Rétro-aldolisation

(=> *clivage liaison C-C*)

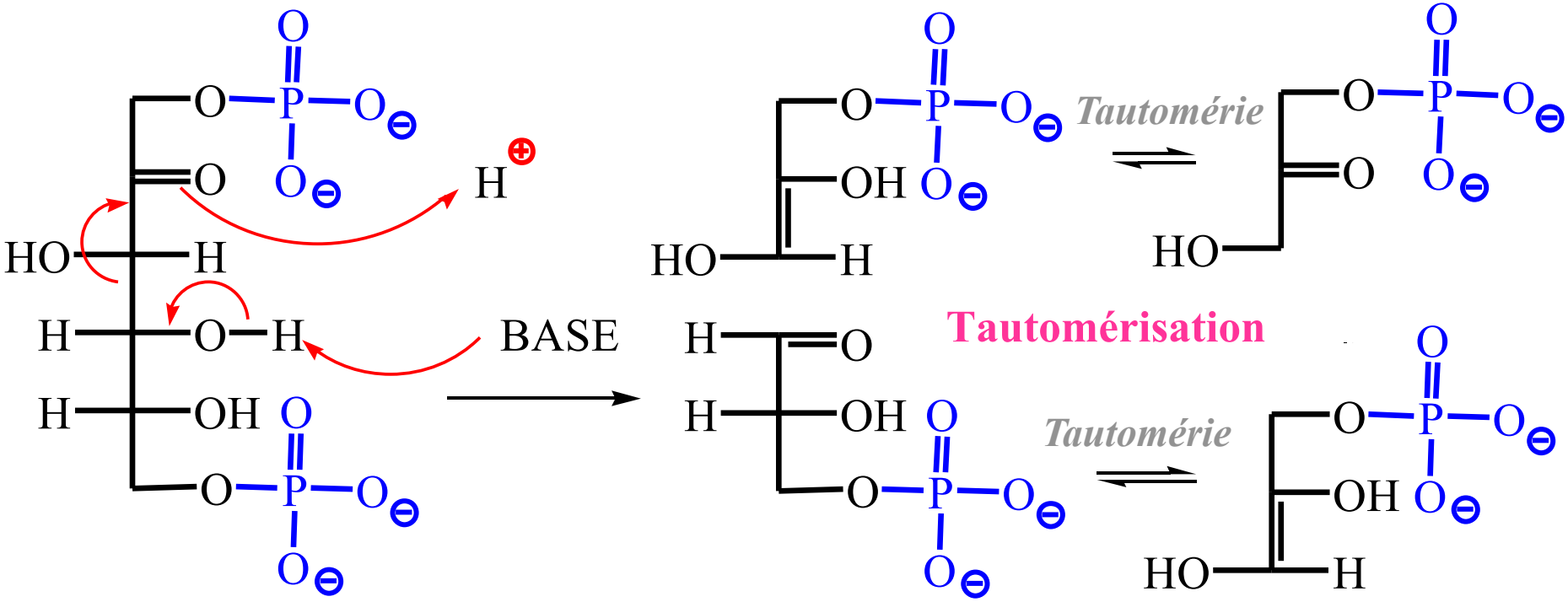
Obtention du GAP

Dihydroxyacétone phosphate (DHAP)

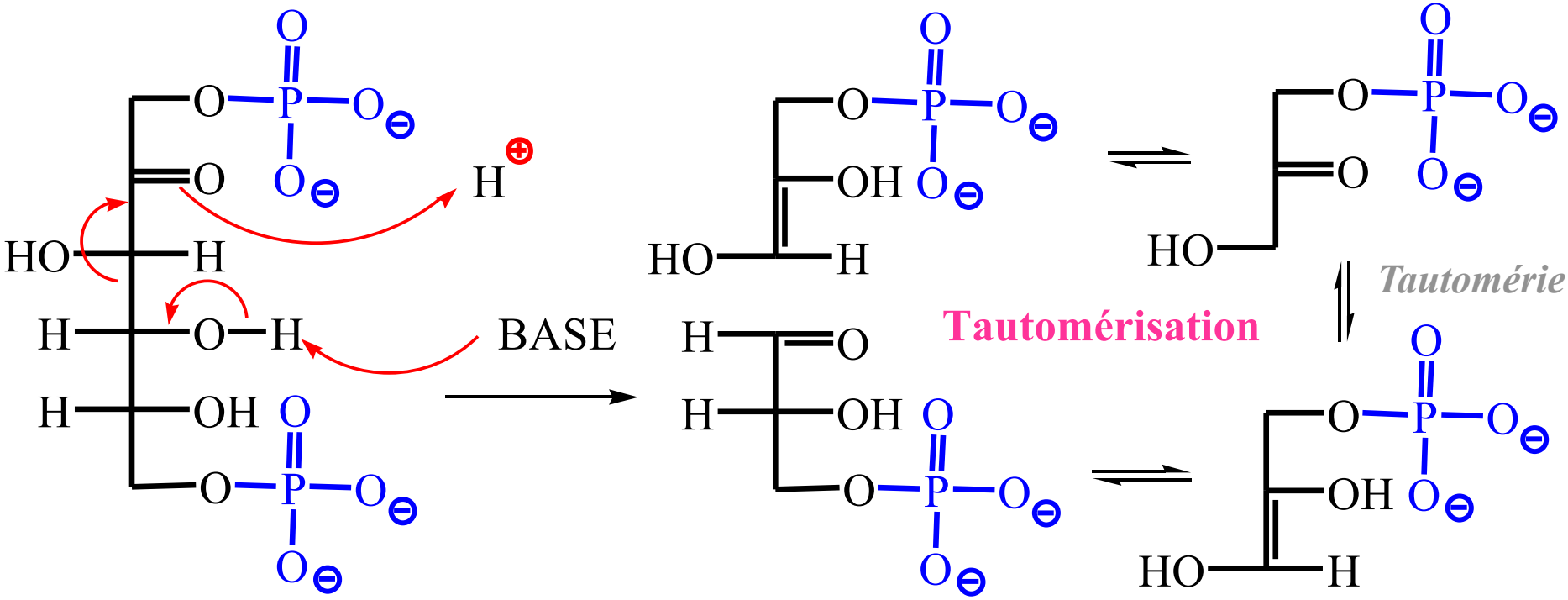


Glycéraldéhyde-3-phosphate (GAP)

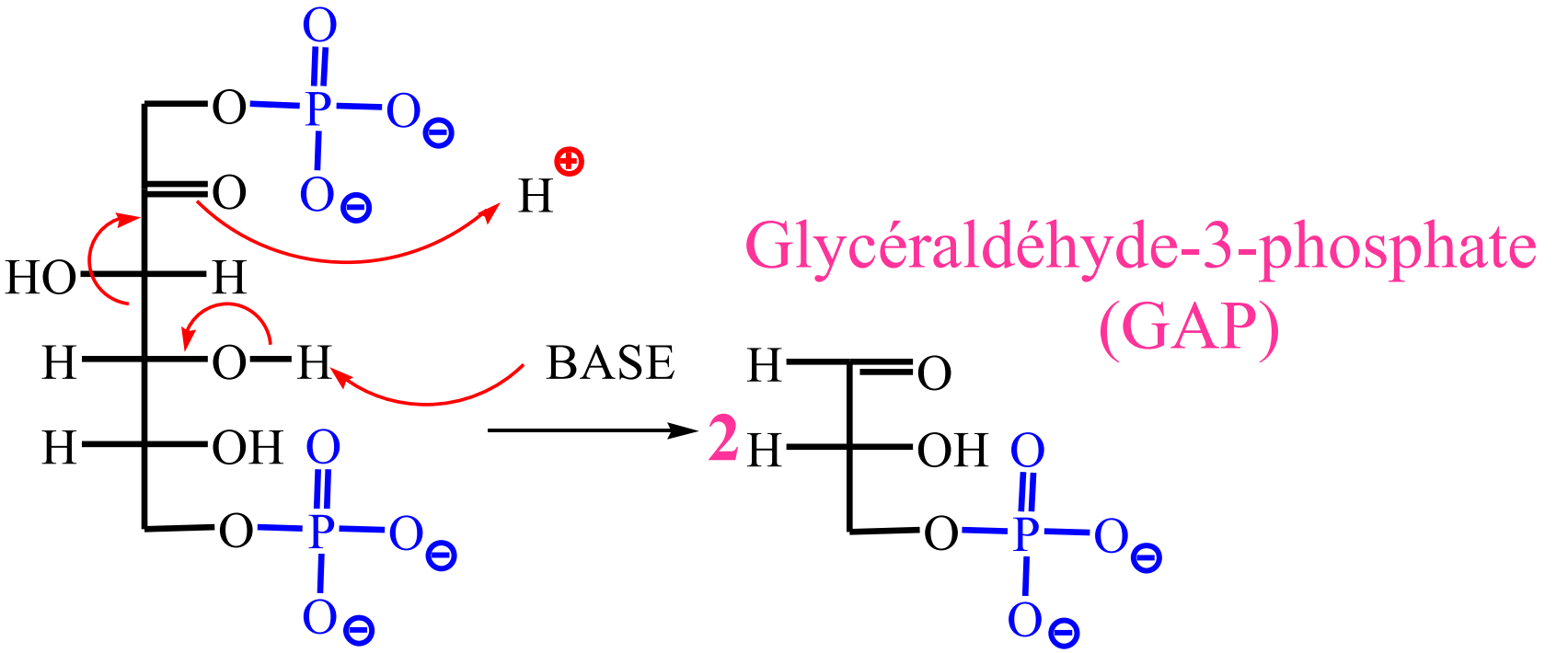
Obtention du GAP



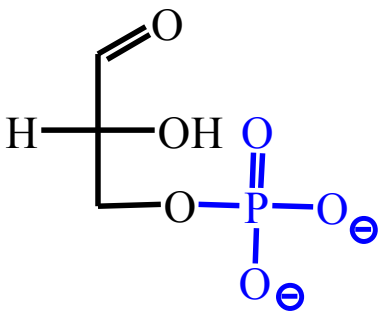
Obtention du GAP



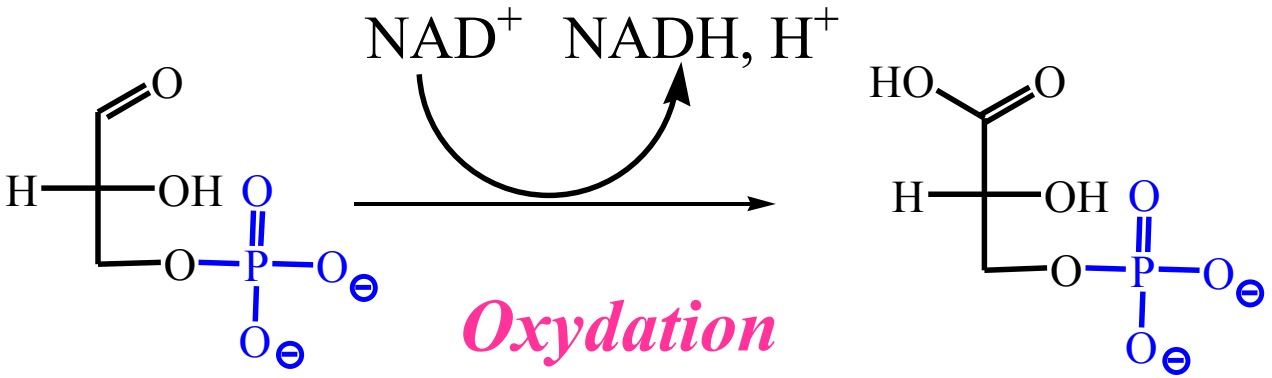
Obtention du GAP



Obtention du Pyruvate



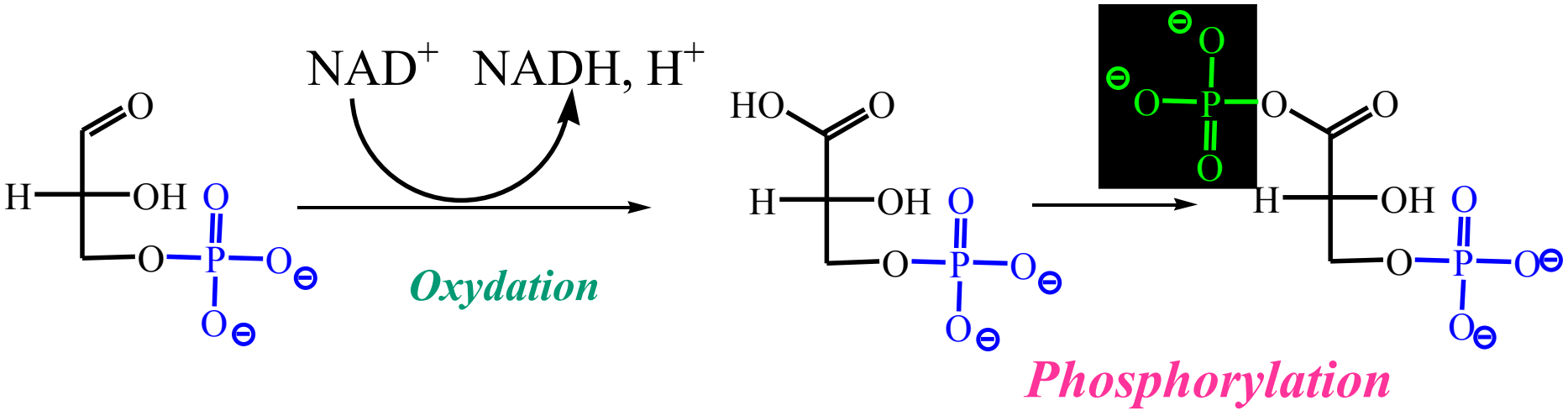
Obtention du Pyruvate



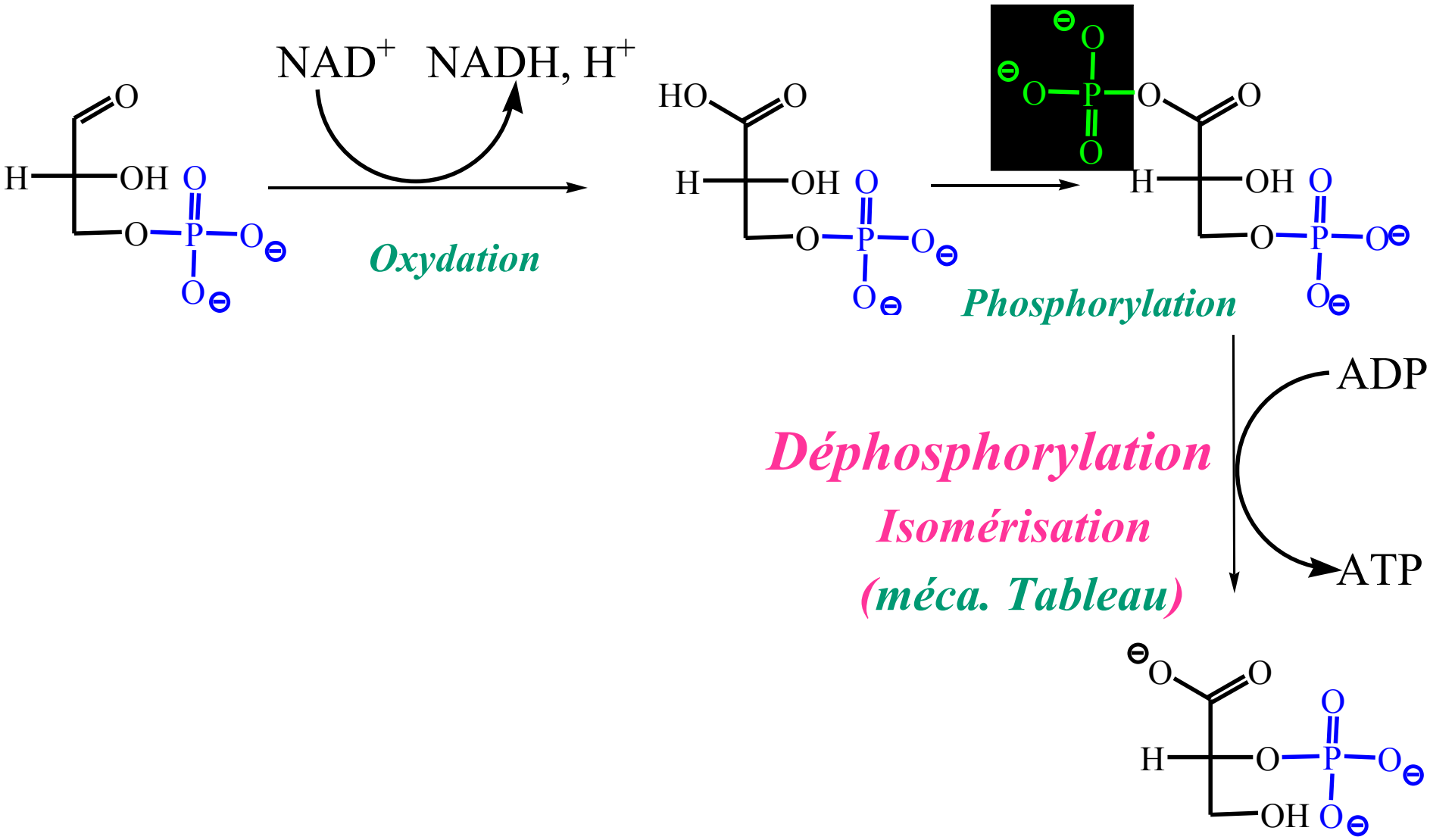
Oxydation

(aldehyde→ acide carbo.)

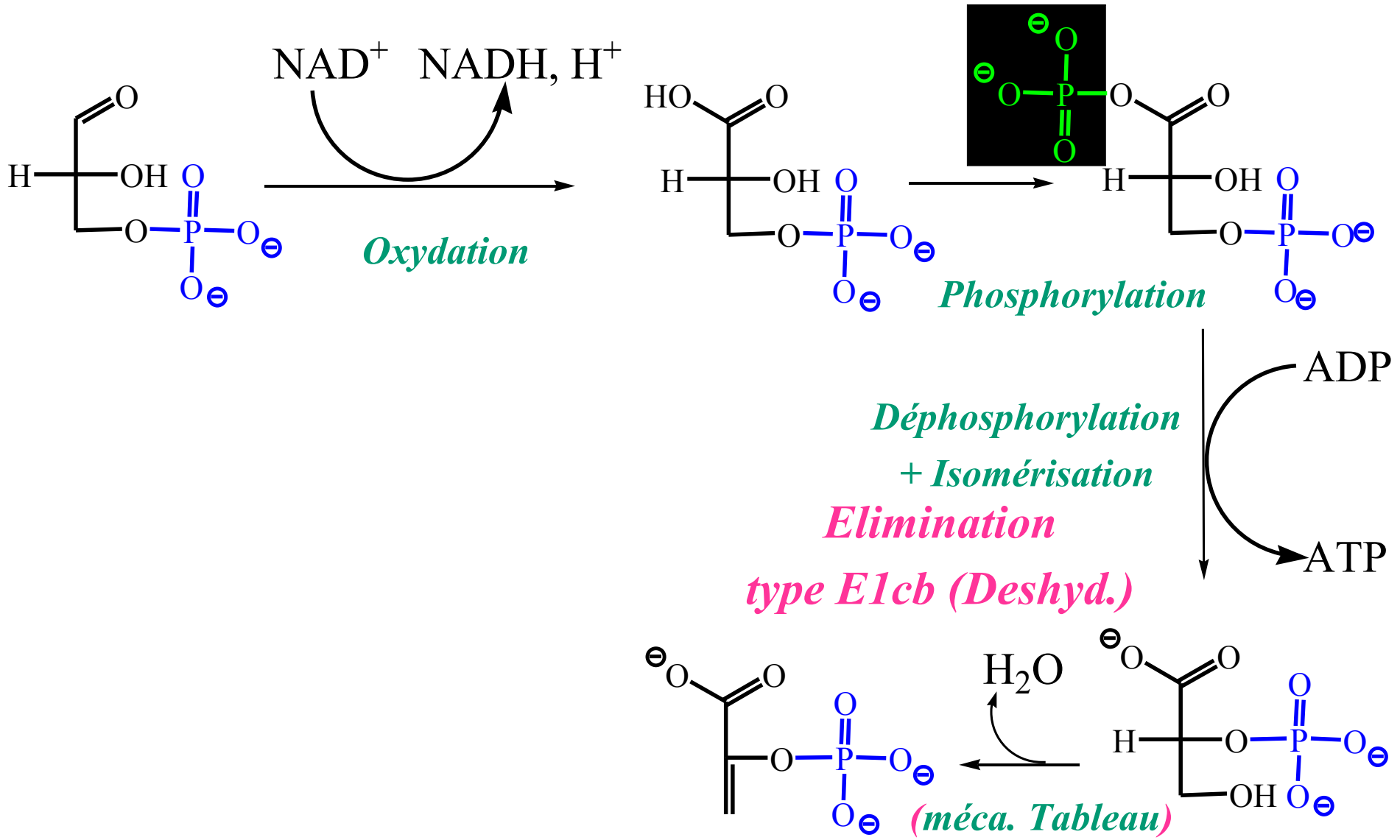
Obtention du Pyruvate



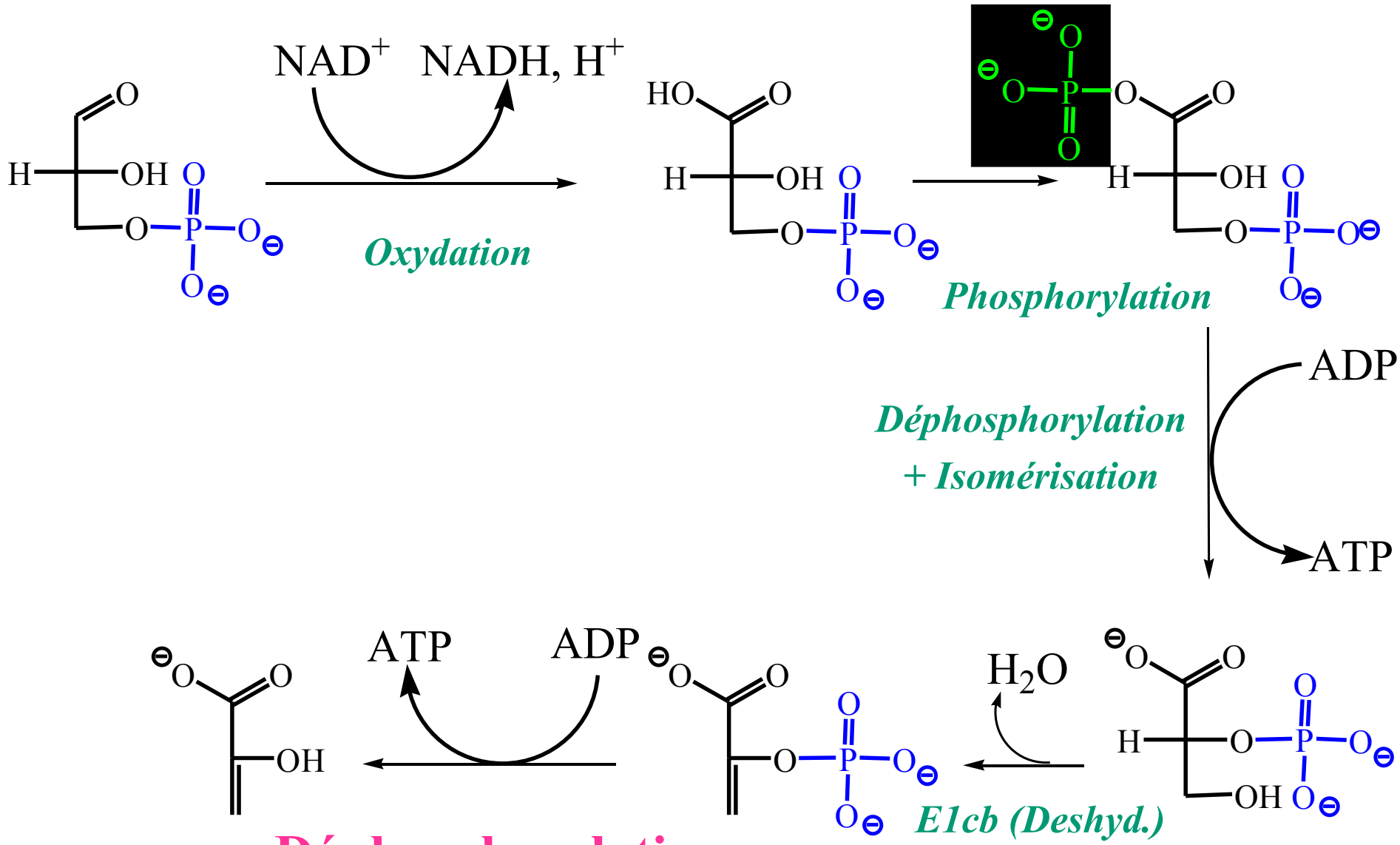
Obtention du Pyruvate



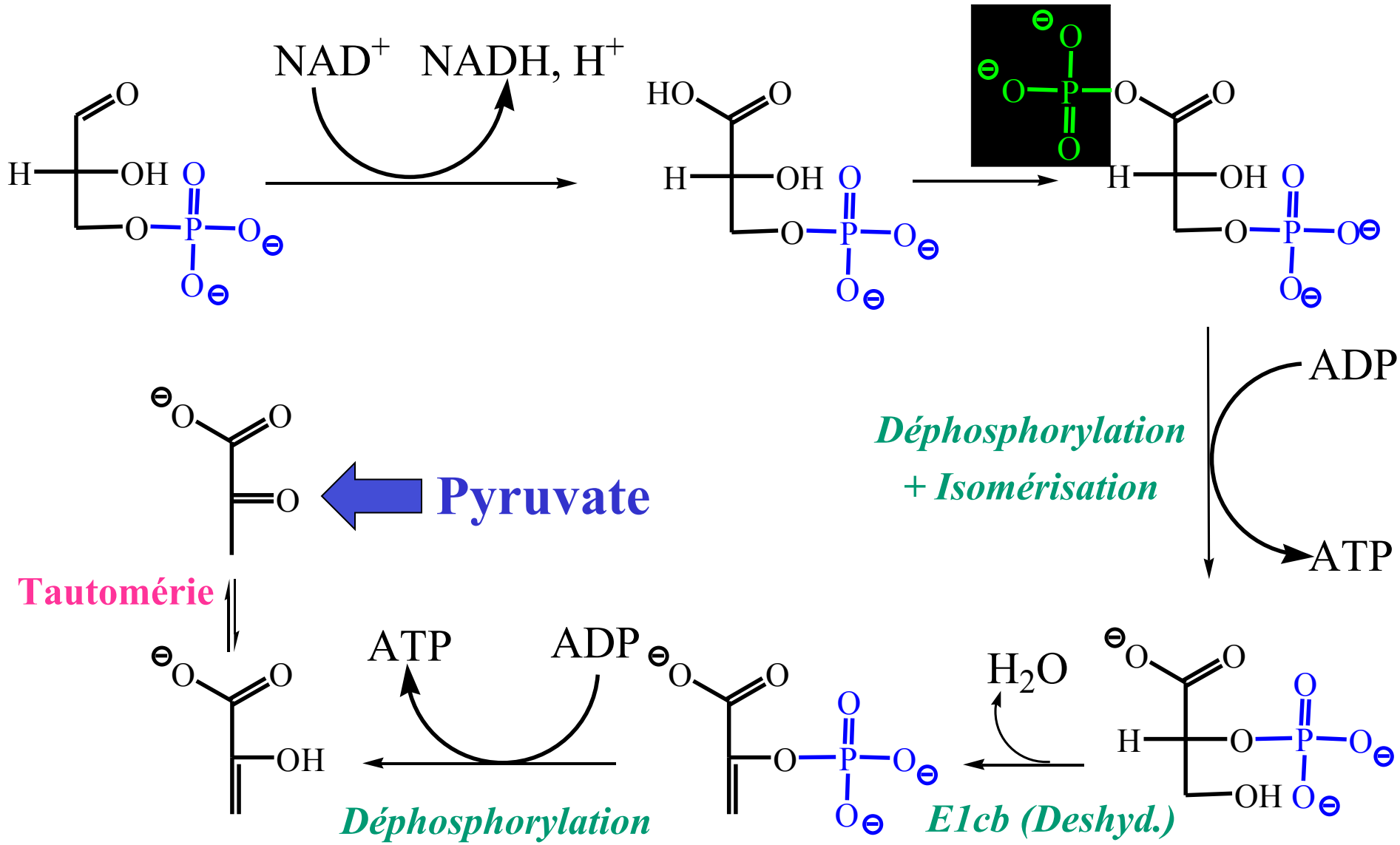
Obtention du Pyruvate

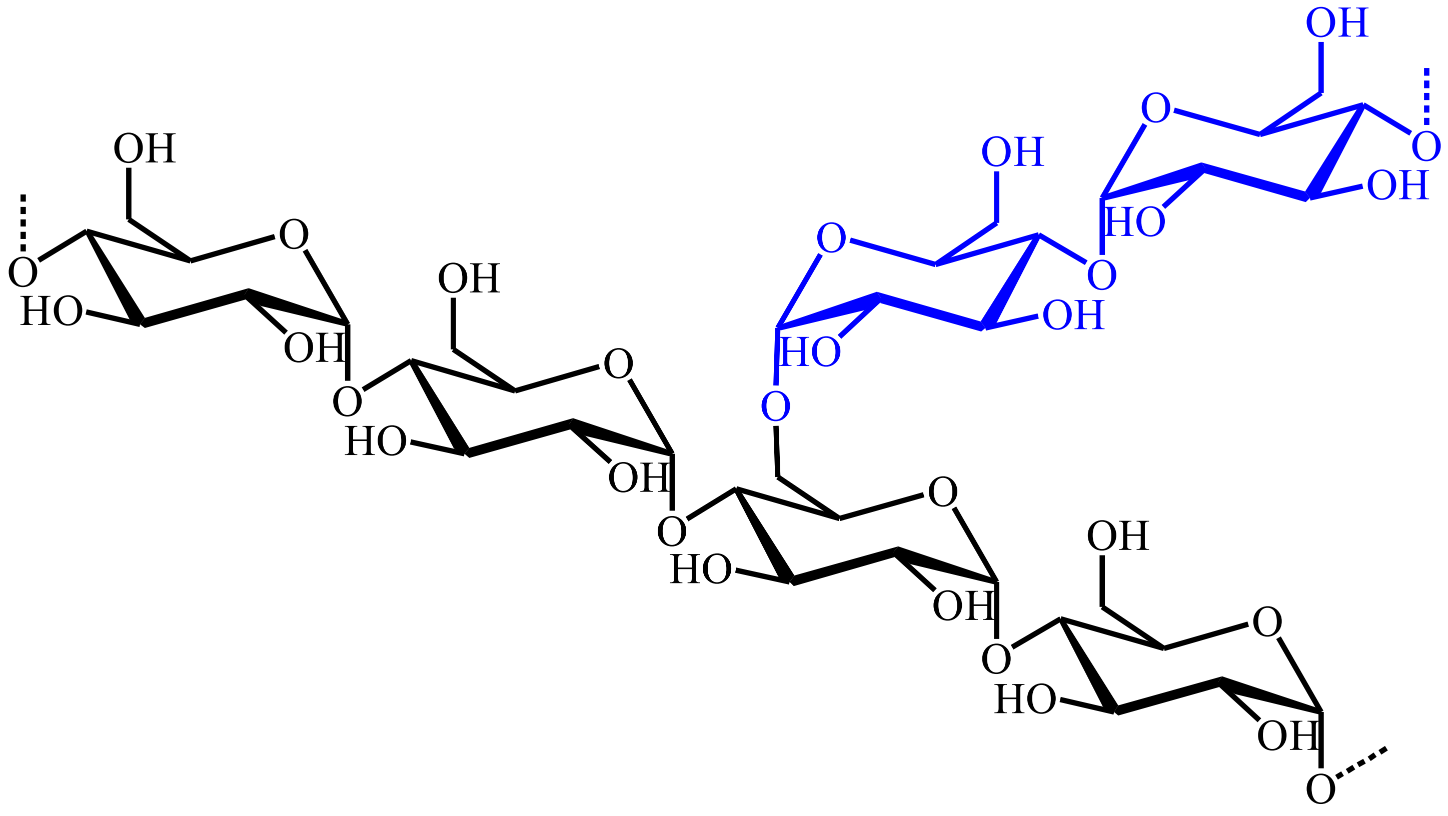


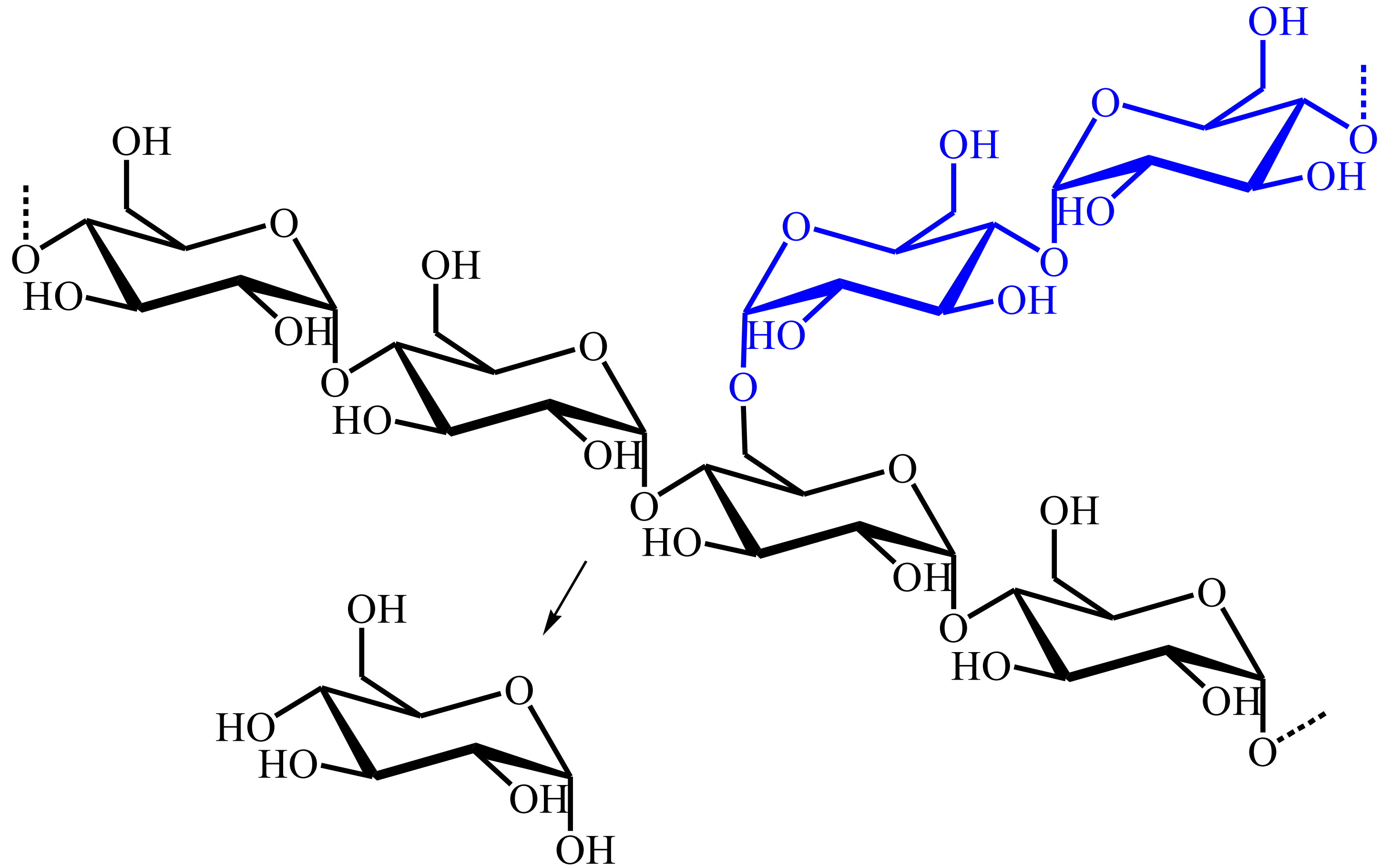
Obtention du Pyruvate



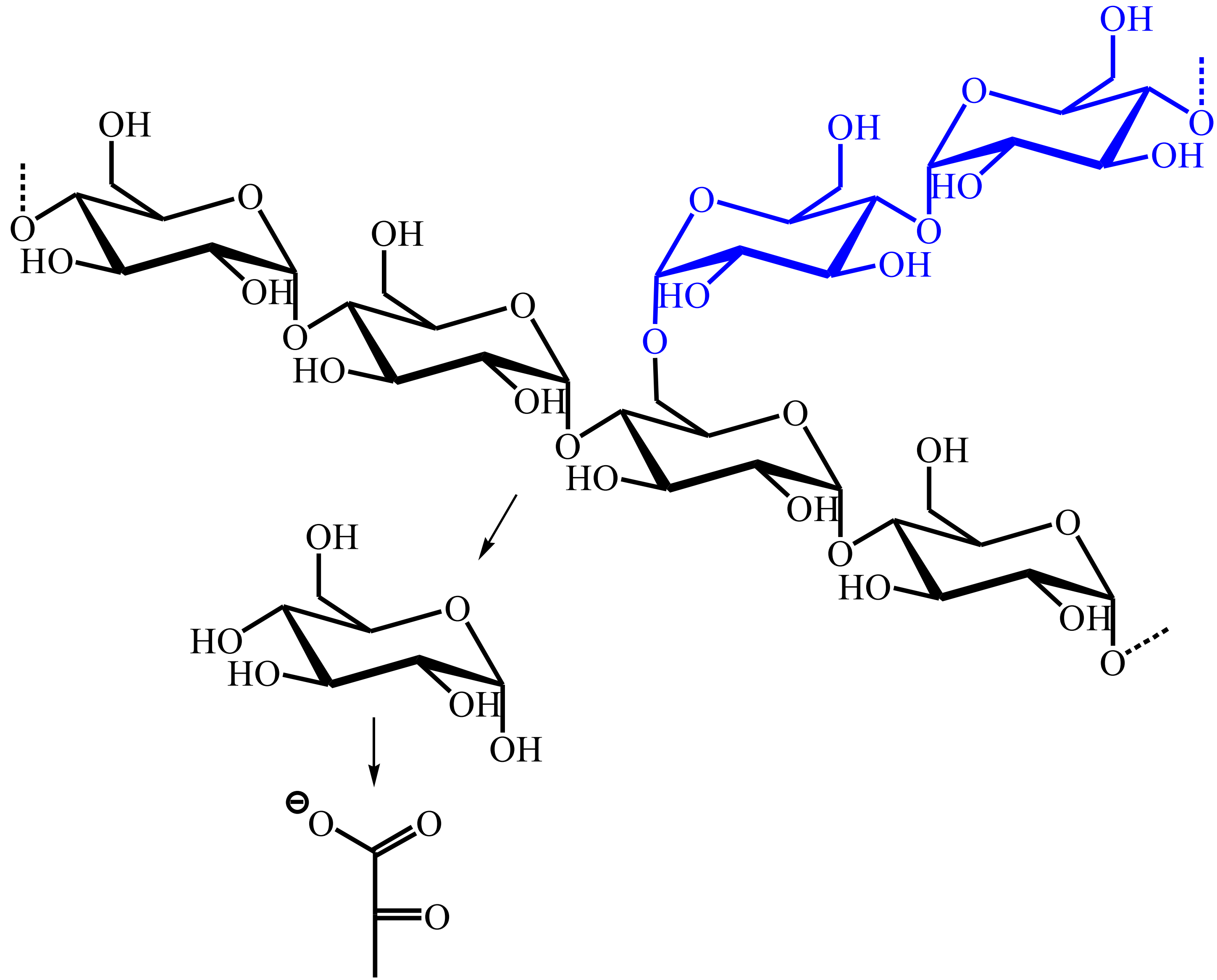
Obtention du Pyruvate



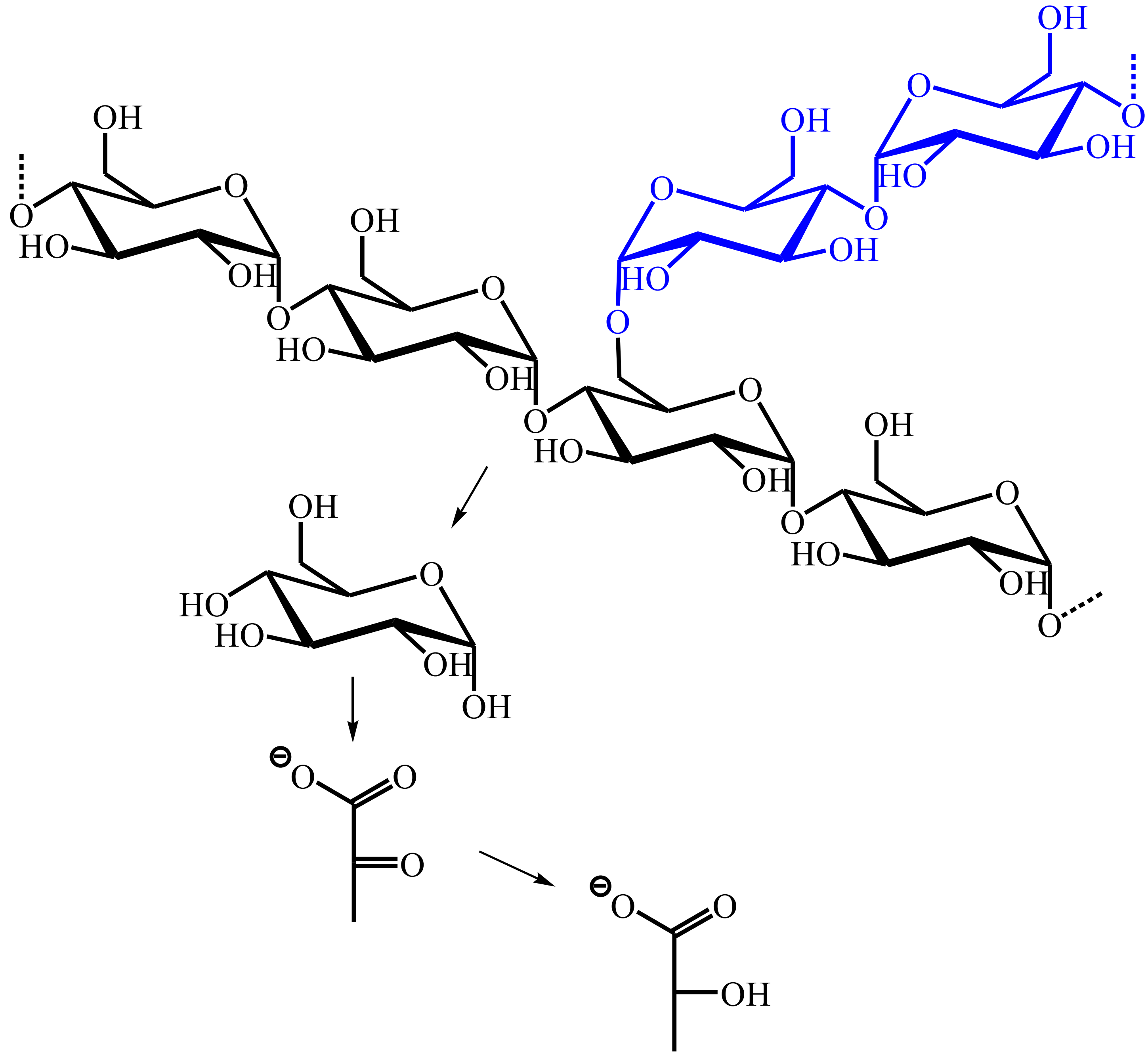

OH
O
OH
O
OH
O
HO
OH
O
OH
O
O
HO
OH
O
HO
OH
O
OH
O
HO
OH
O
HO
OH
O
OH
O
HO
OH
O
HO
OH
O



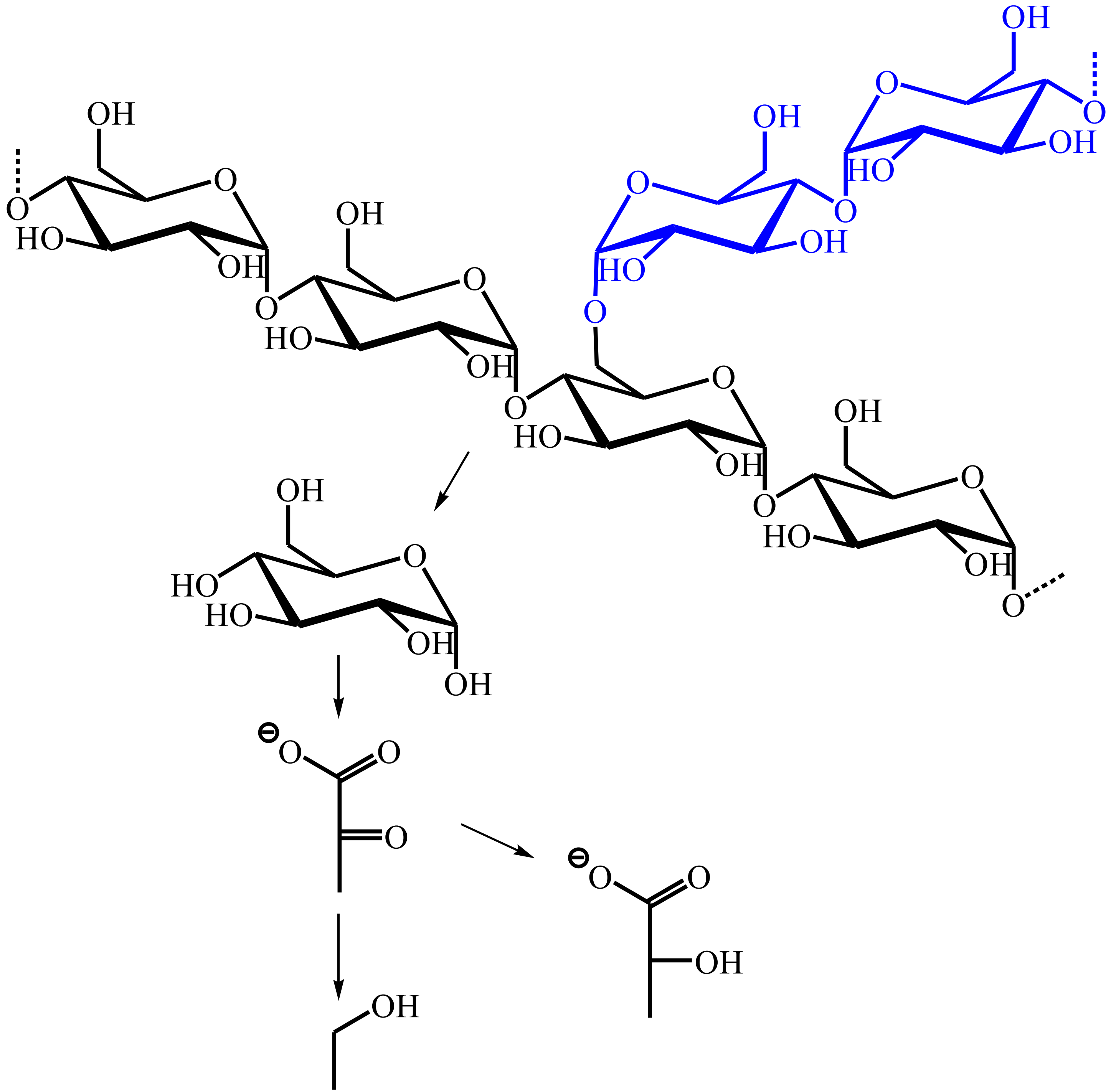
OH
O
HO
OH



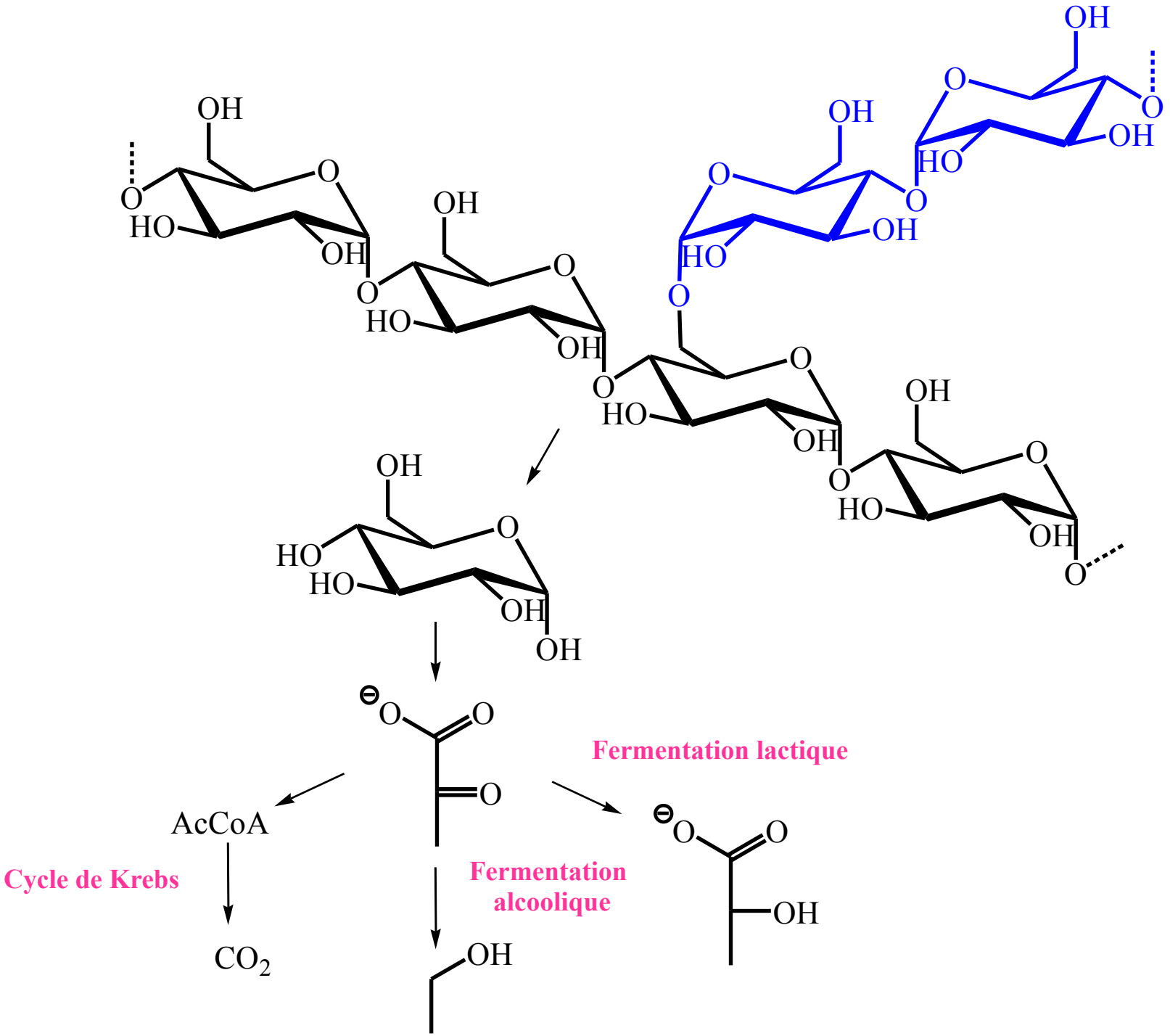
OH
O
HO
OH
O



OH
O
HO
OH
O
OH
O
HO
OH
OH
O
HO
OH
O
OH
O
HO
OH
O
OH
O
HO
OH
O
O
OH
O
HO
OH
O
OH
O
HO
OH
O
OH
O
HO
HO
OH
OH
O
O
O
O
O
OH



OH
O
HO
OH
O
O
OH
O
HO
OH
O
OH
HO
OH
O
O
O
OH
OH
HO
O
OH
O
HO
OH
O
OH
O
HO
OH
O
OH
O
HO
HO
OH
OH
O
O
O
O
O
O
OH
OH


AcCoA
Cycle de Krebs
CO_2
Fermentation alcoolique
Fermentation lactique