# Lecture 7 - The Calvin Cycle and the Pentose Phosphate Pathway

Chem 454: Regulatory Mechanisms in Biochemistry

University of Wisconsin-Eau Claire

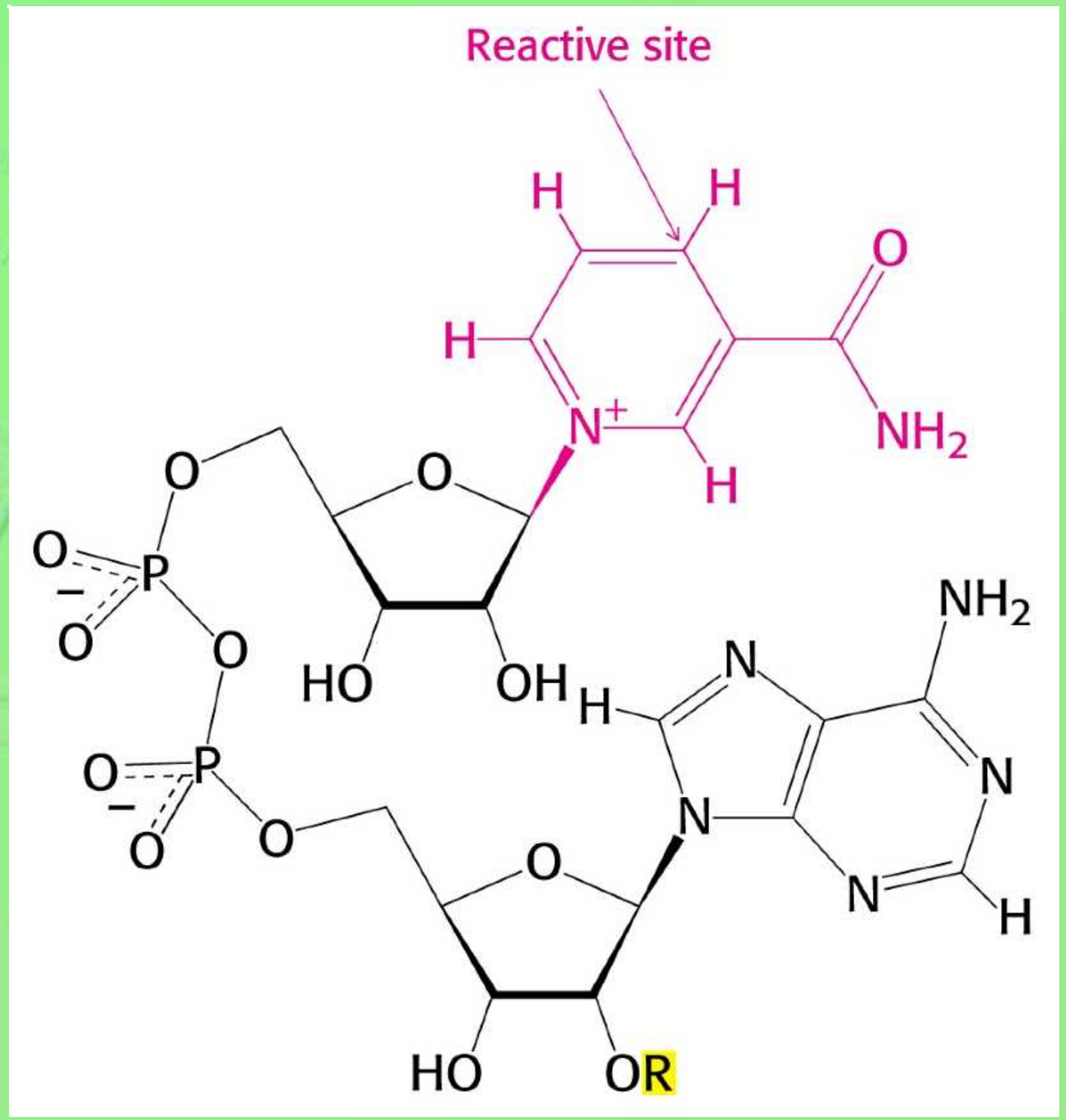
# Introduction

## The Calvin cycle

- The dark reactions of photosynthesis in green plants
- Reduces carbon from CO2 to hexose (C6H12O6)
- Requires ATP for free energy and NADPH as a reducing agent.

# Introduction

## NADH versus NADPH



# Introduction

## The Pentose Phosphate Pathway

- Used in all organisms
- Glucose is oxidized and decarboxylated to produce reduced NADPH
- Used for the synthesis and degradation of pentoses
- Shares reactions with the Calvin cycle

# 1. The Calvin Cycle

Source of carbon is CO2

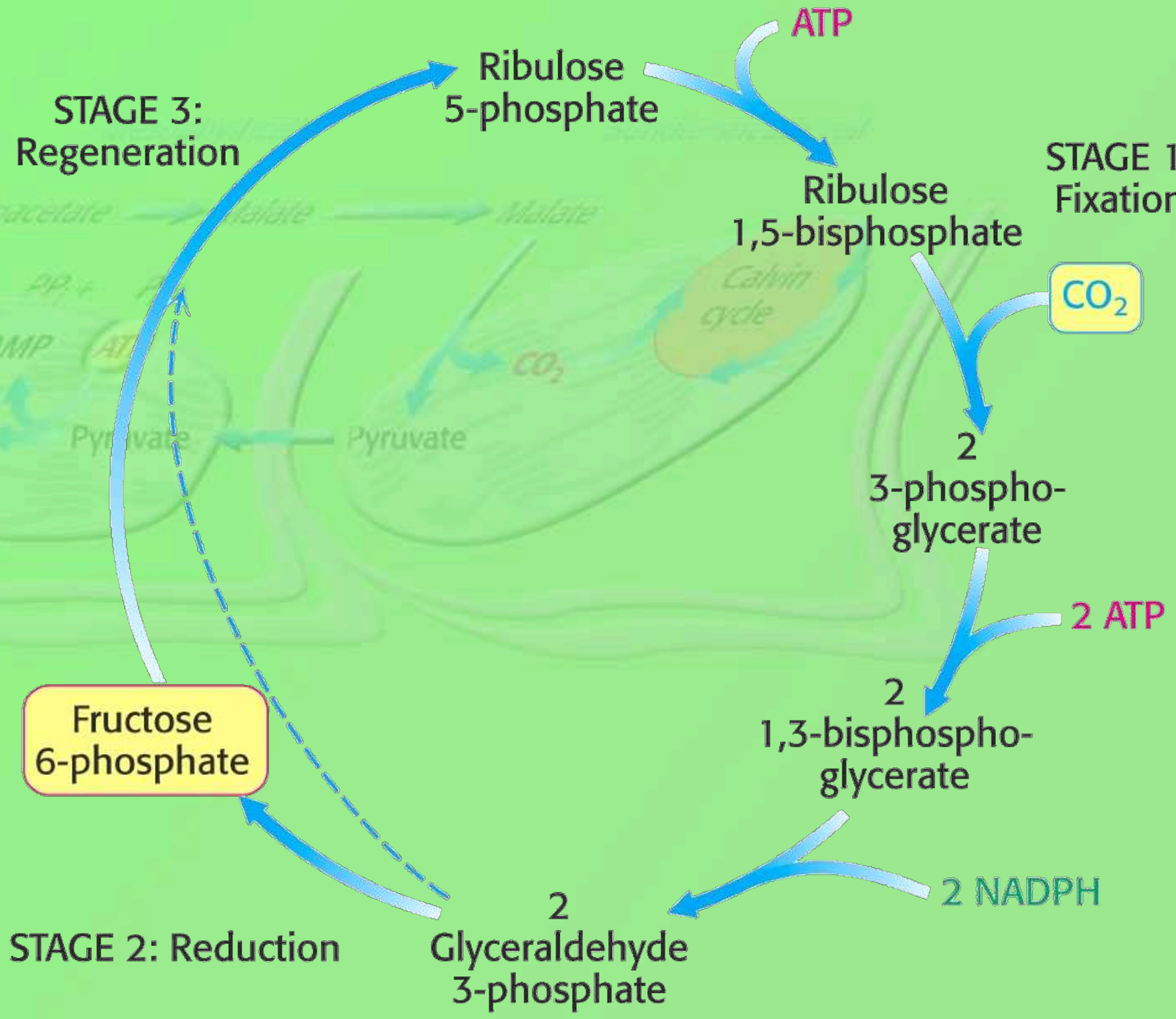
Takes place in the stroma of the chloroplasts

Comprises three stages

- Fixation of CO2 by ribulose 1,5-bisphosphate to form two 3-phosphoglycerate molecules
- Reduction of 3-phosphoglycerate to produce hexose sugars
- Regeneration of ribulose 1,5-bisphosphate

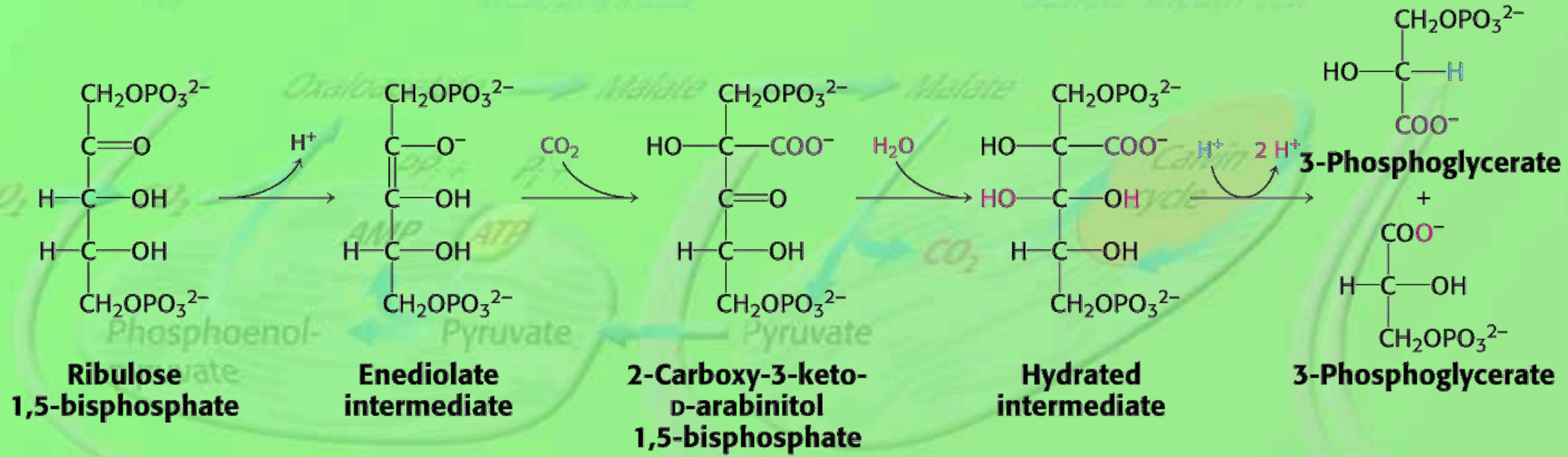
# 1. Calvin Cycle

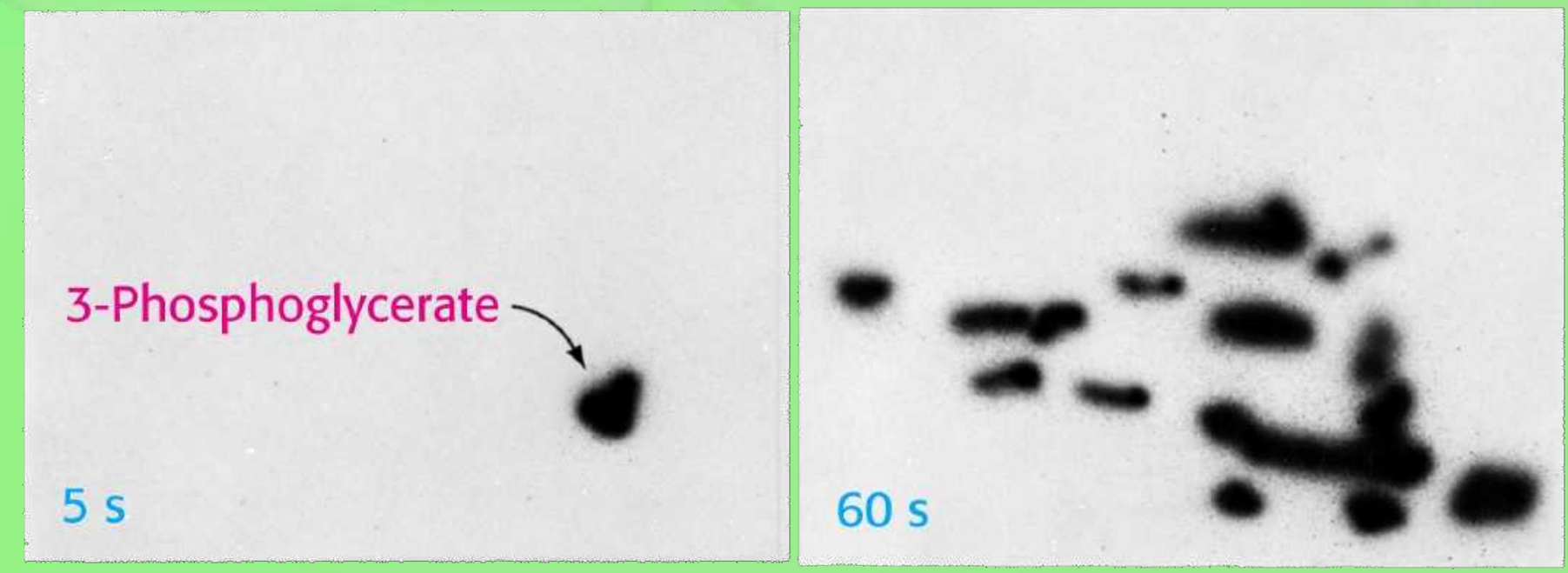
Three stages



# 1.1 Stage I: Fixation

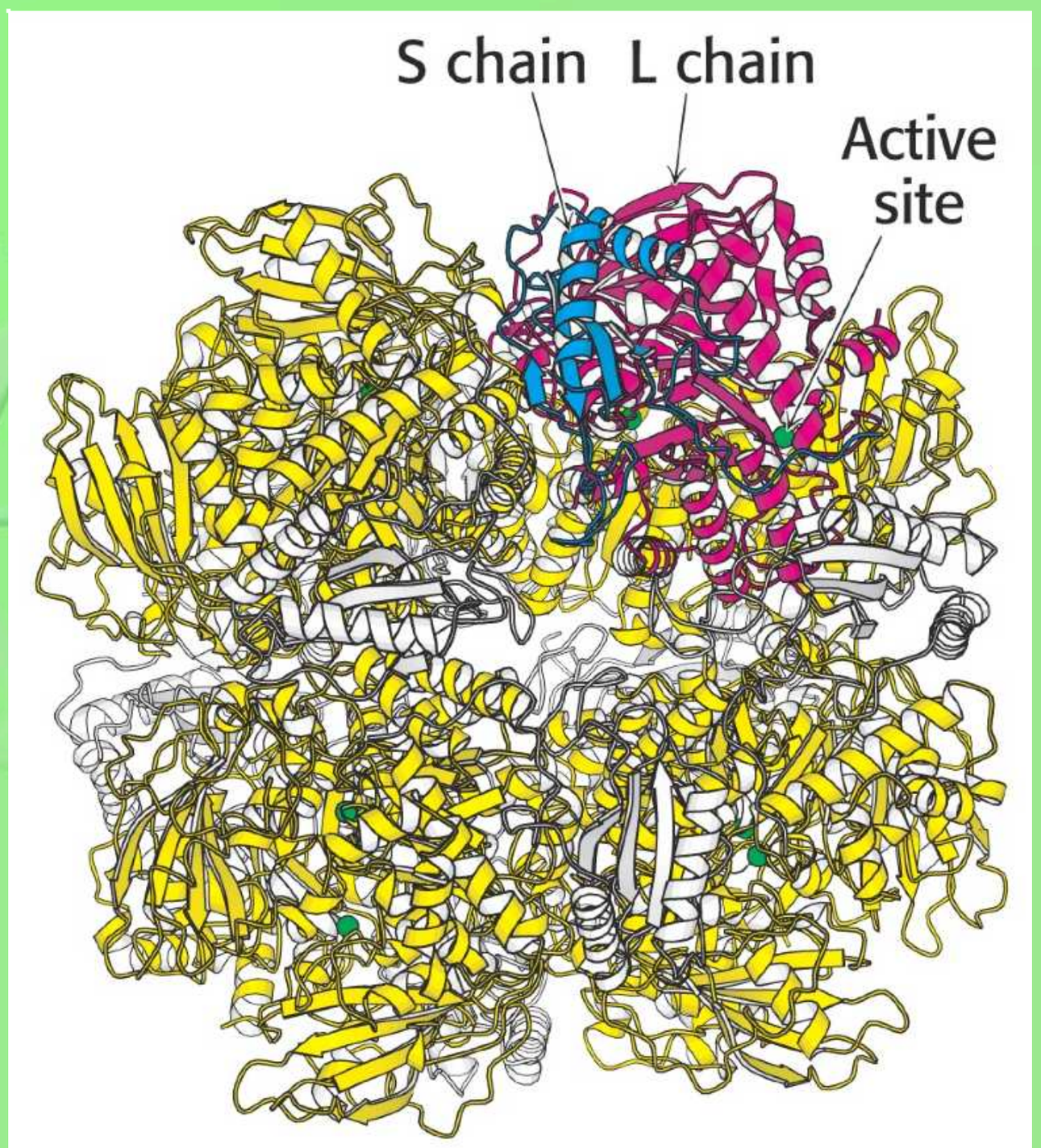
## Incorporation of CO2 into 3-phosphoglycerate



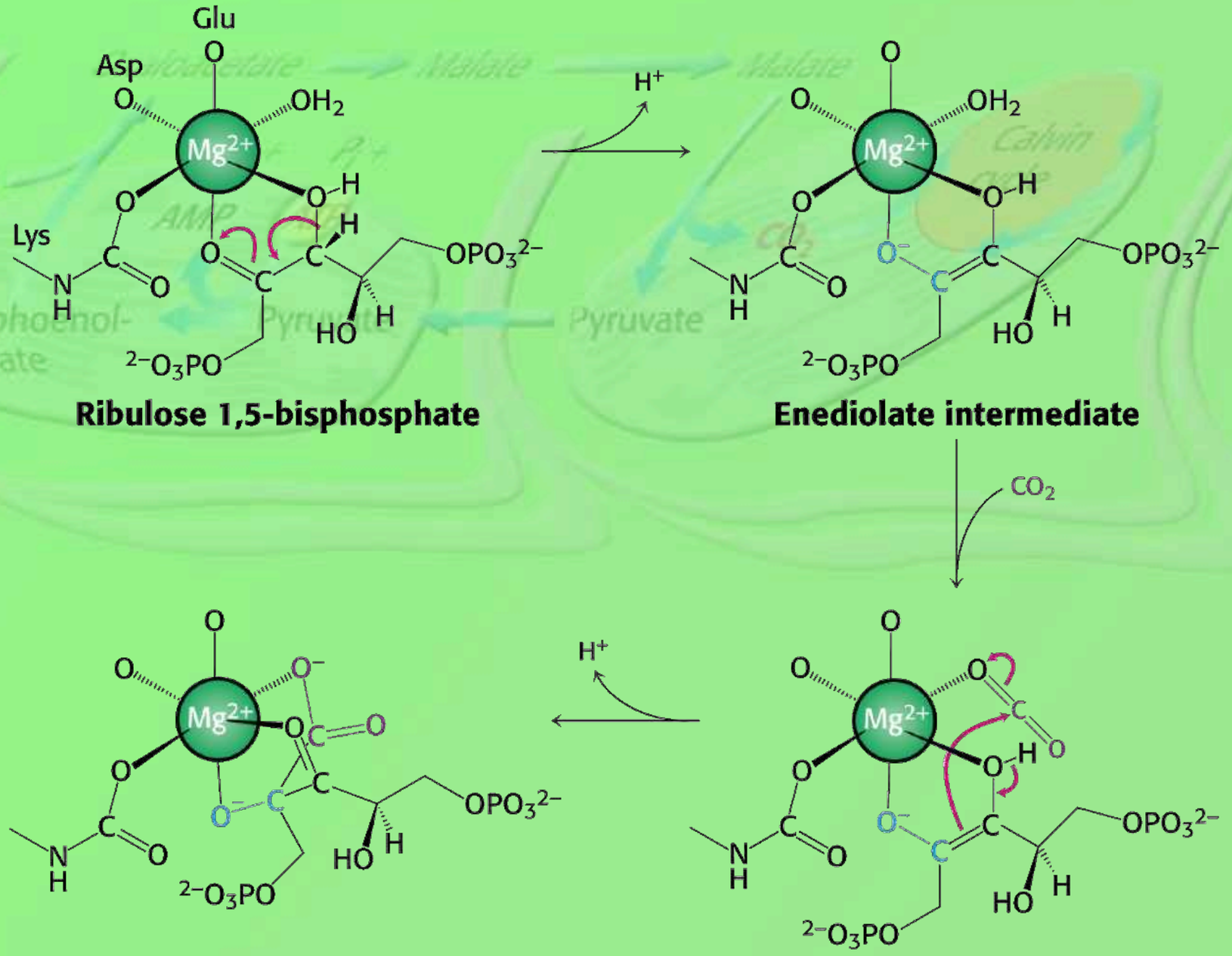
# 1.1 Stage I: Fixation

Rubisco: Ribulose 1,5-bisphosphate carboxylase/ oxygenase



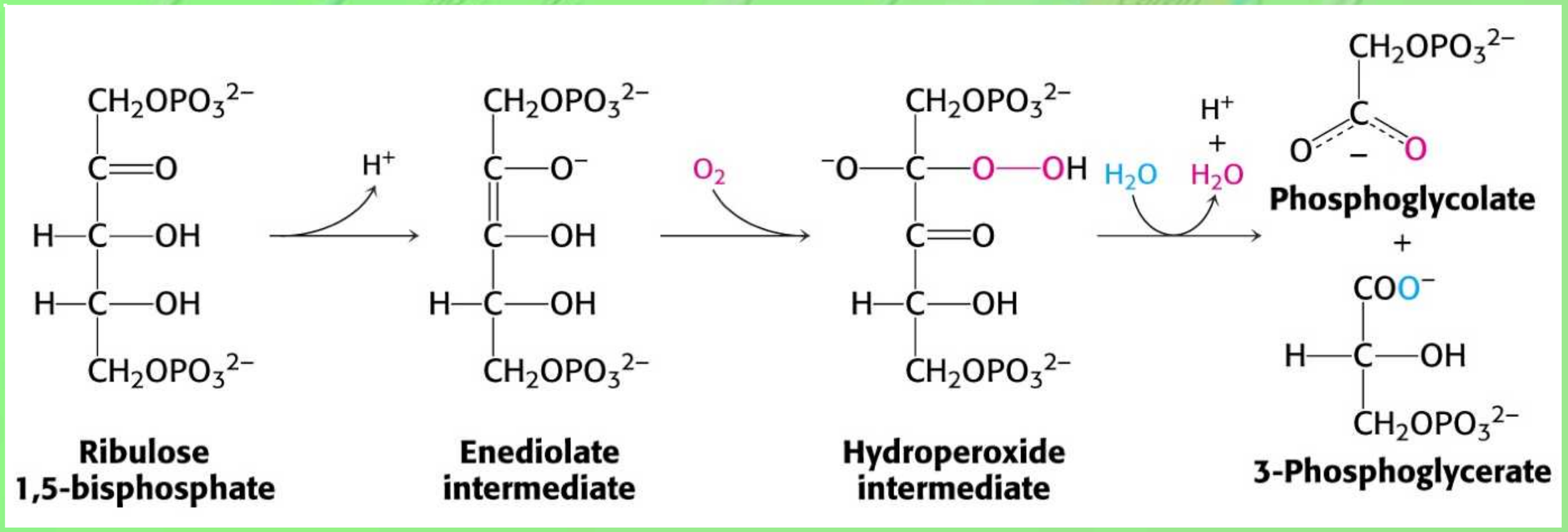
# 1.1 Stage I: Fixation

## Active site contains a divalent metal ion



# 1.2 Rubisco Oxygenase Activity

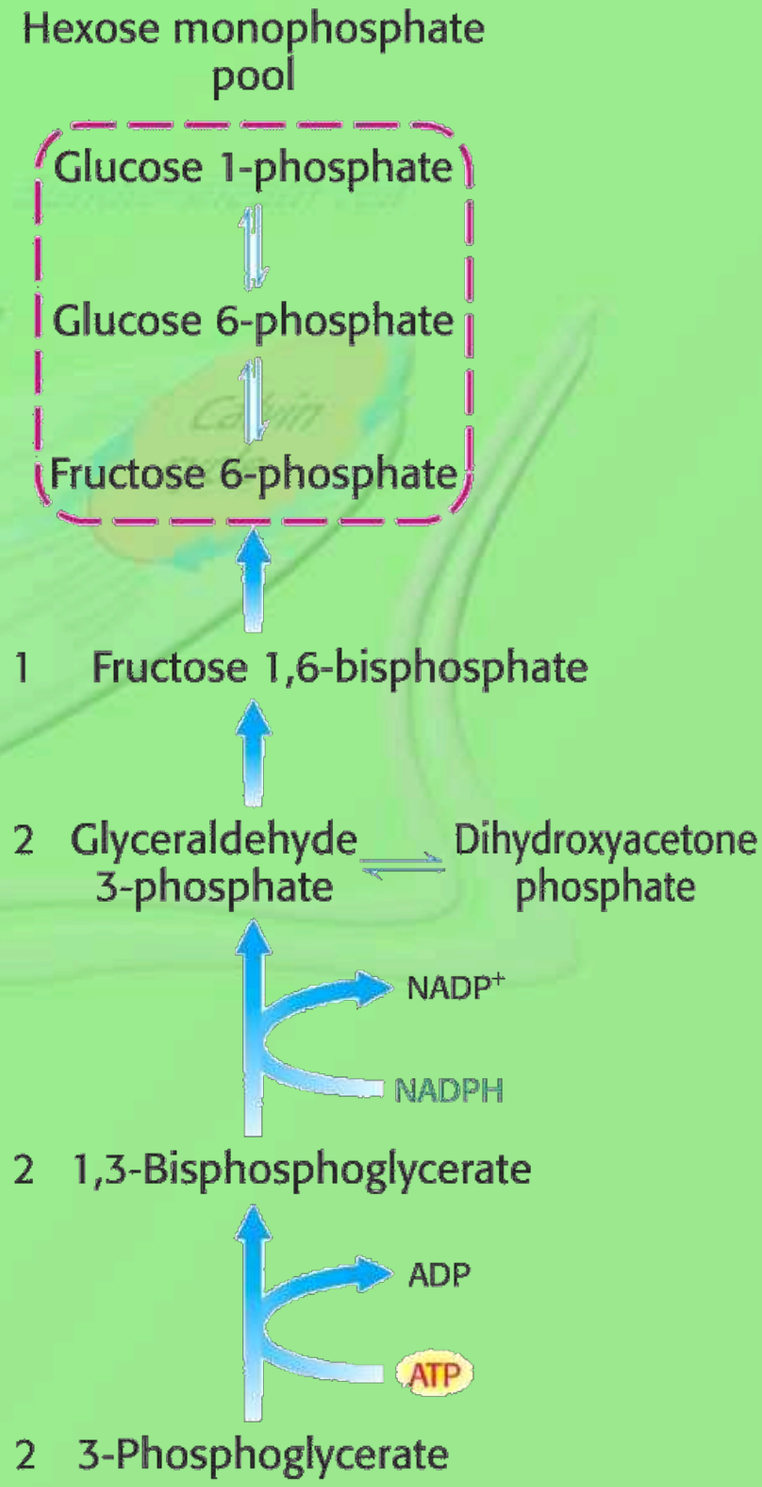
Rubisco also catalyzes a wasteful oxygenase reaction:



# 1.3 State II: Formation of Hexoses

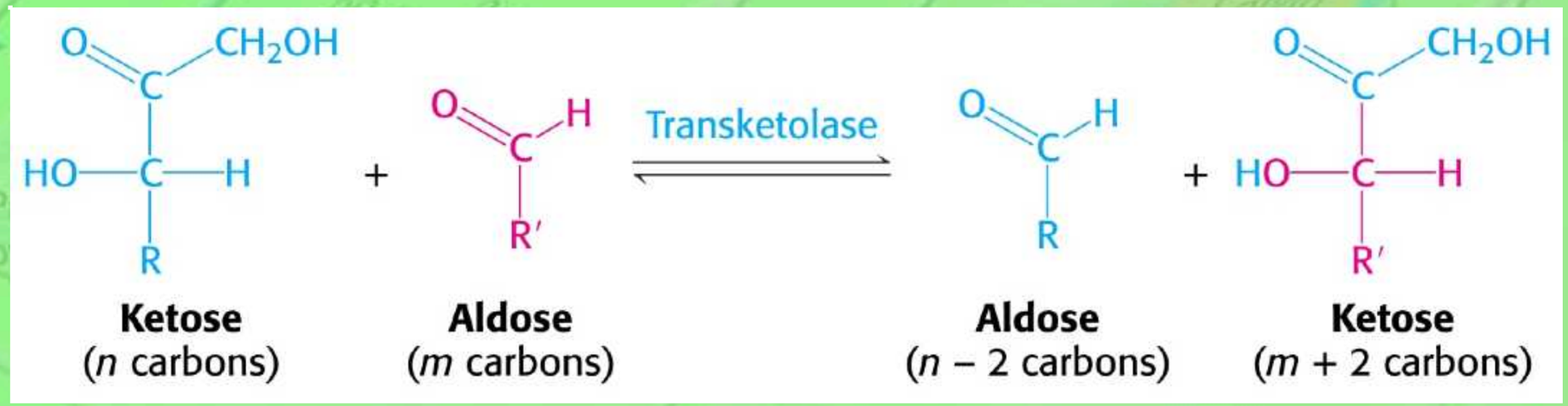
Reactions similar to those of gluconeogenesis

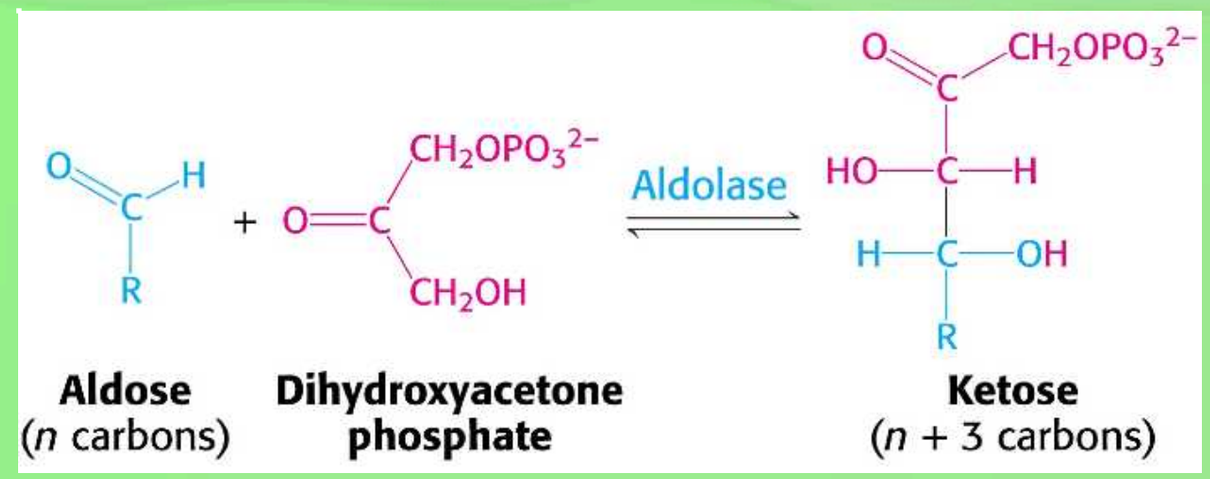
- But they take place in the chloroplasts
- And use NADPH instead of NADH



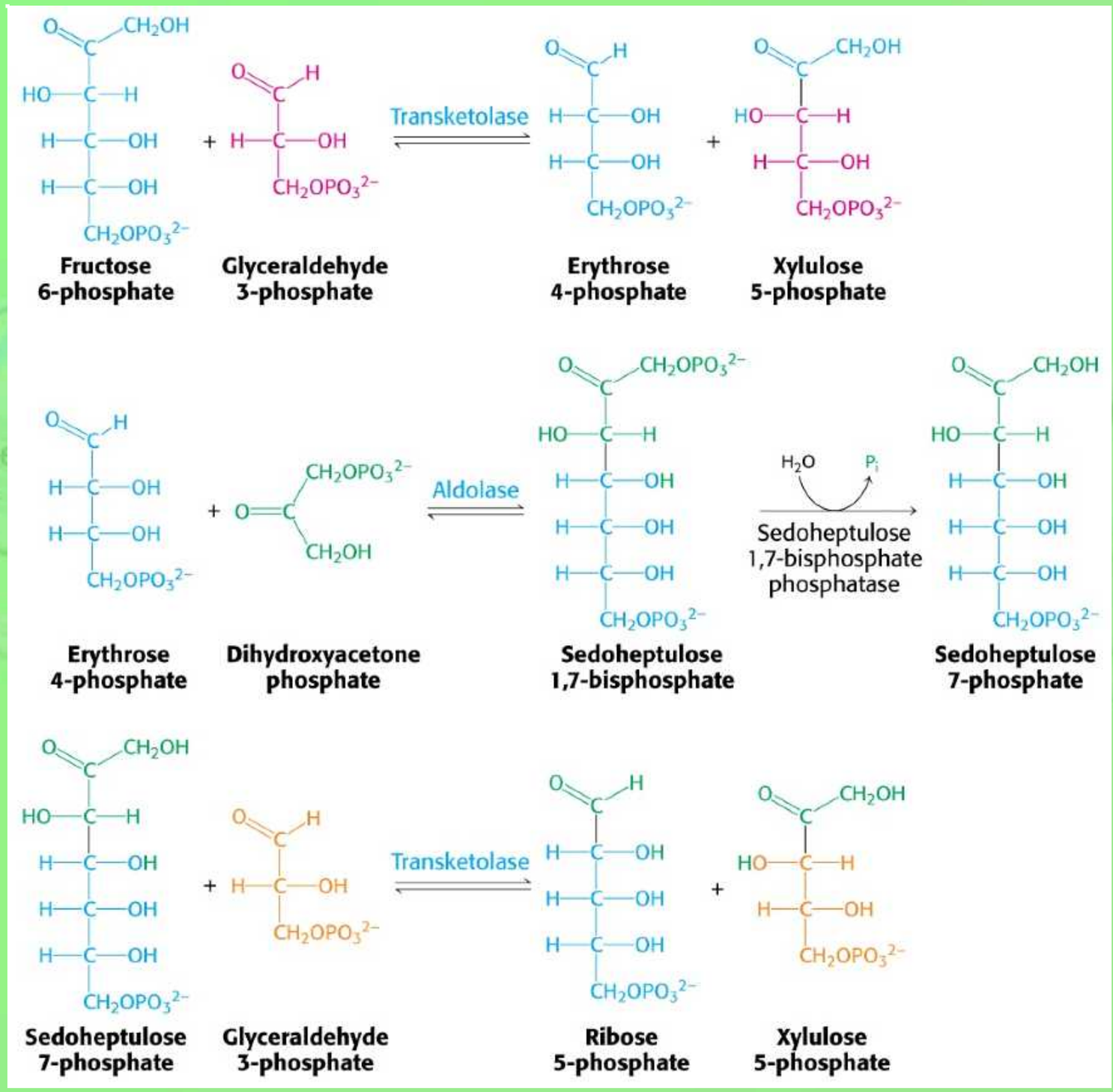
# 1.3 State III: Regeneration of Ribulose 1,5-Bisphosphate

Involves a sequence of transketolase and aldolase reactions.



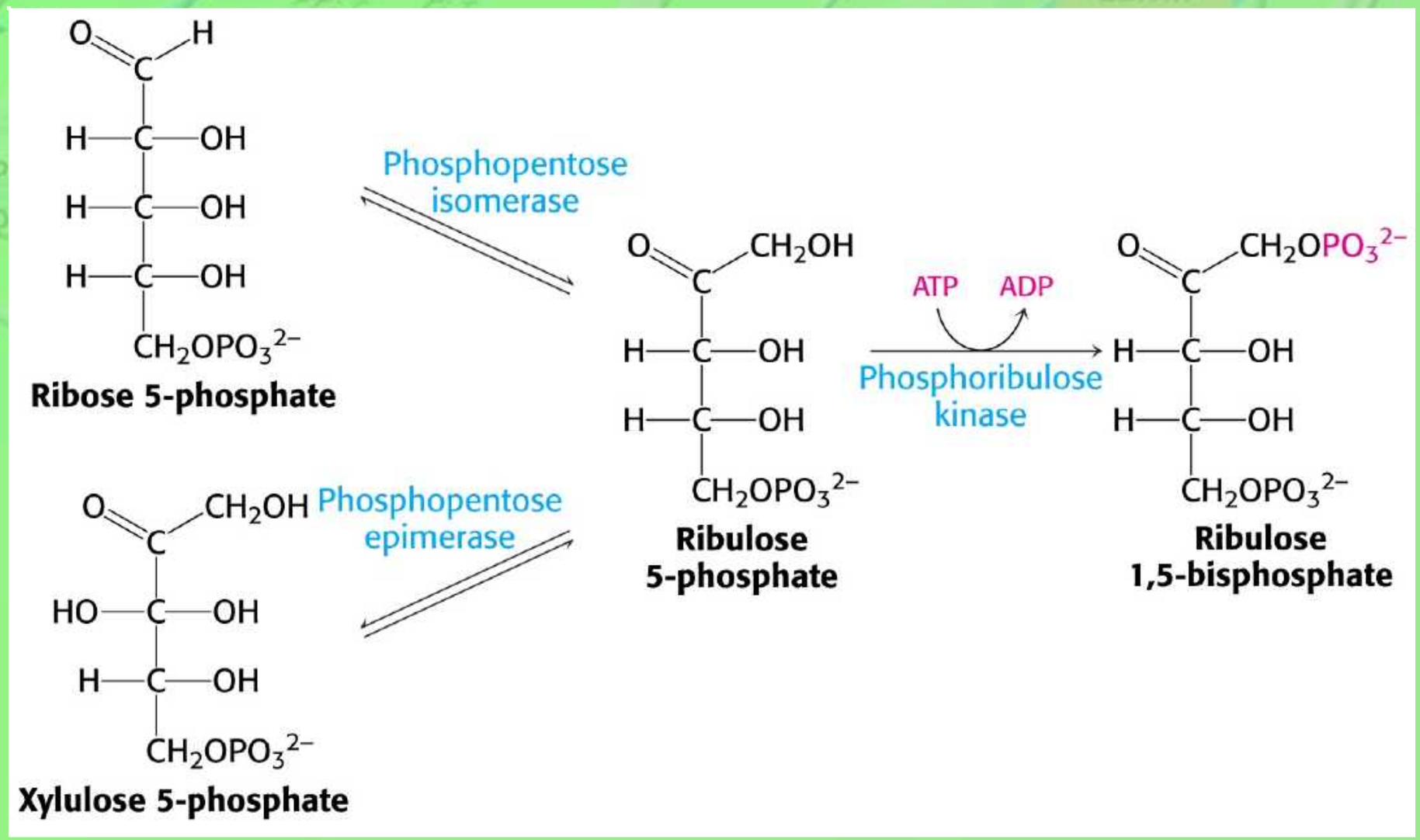



# 1.3 State III: Regeneration of Ribulose 1,5-Bisphosphate



# 1.3 State III: Regeneration of Ribulose 1,5-Bisphosphate

The resulting ribose 5-phosphate and xylulose 5-phosphate are converted to ribulose 5-phosphate by an *isomerase* and an *epimerase*



# 1.3 State III: Regeneration of Ribulose 1,5-Bisphosphate

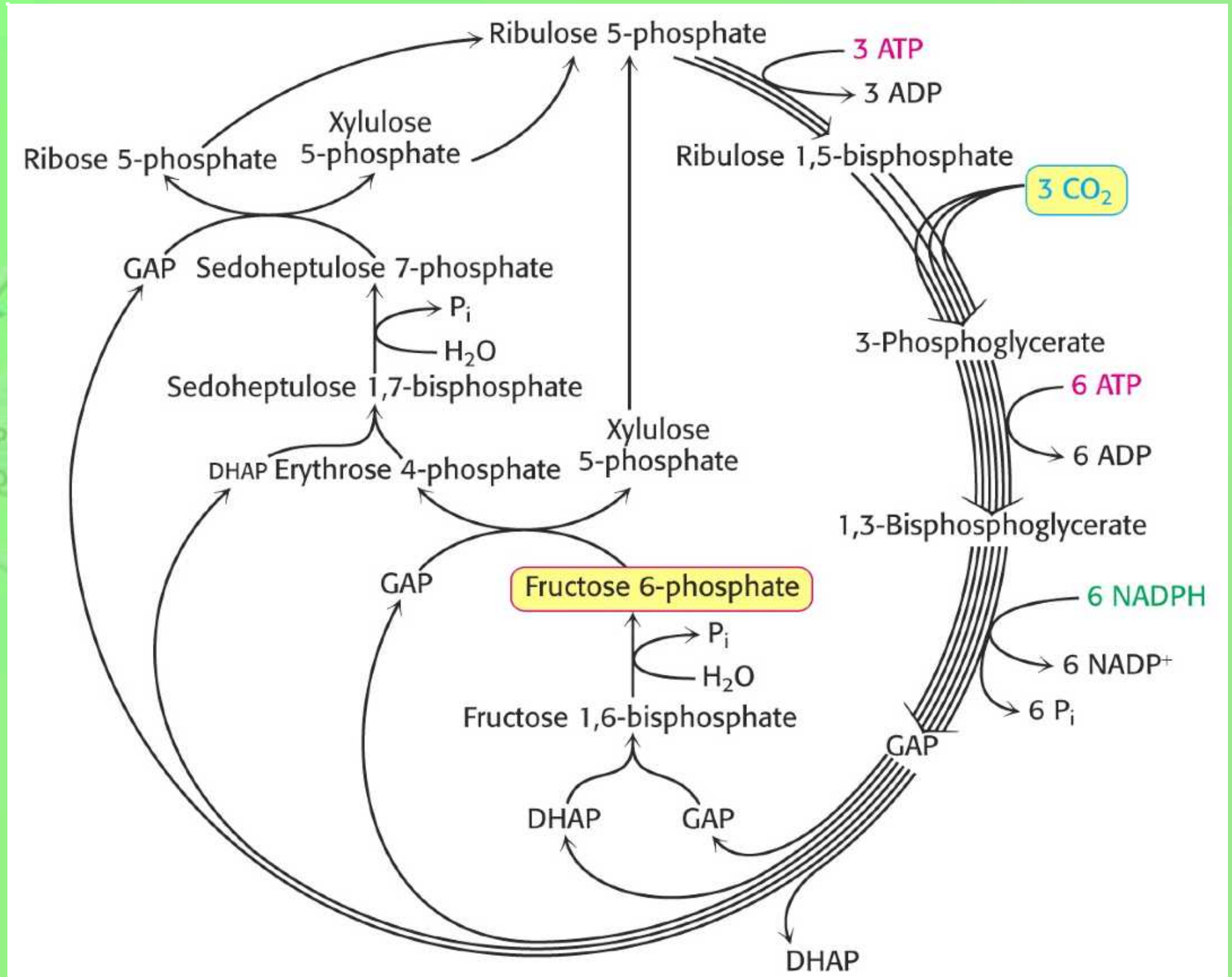
The net reaction for stage III

Fructose 6-phosphate + 2 glyceraldehyde 3-phosphate

+ dihydroxyacetone phosphate + 3ATP + $H_2O$ ⟶

3 ribulose 1,5-bisphosphate + 3 ADP + Pi

# 1.3 The Calvin Cycle



# 1.4 Balance Reaction for Calvin Cycle

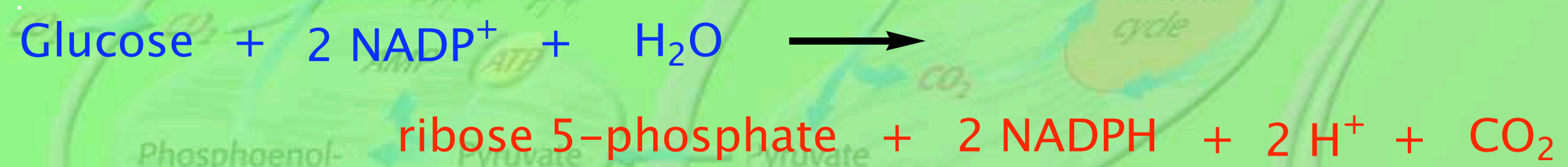
## Net Balanced Reaction

$$6\ CO_2 + 18\ ATP + 12\ NADPH + 12\ H_2O \longrightarrow$$

$$C_6H_{12}O_6 + 18\ ADP + 18\ Pi + 12\ NADP^+ + 6\ H^+$$

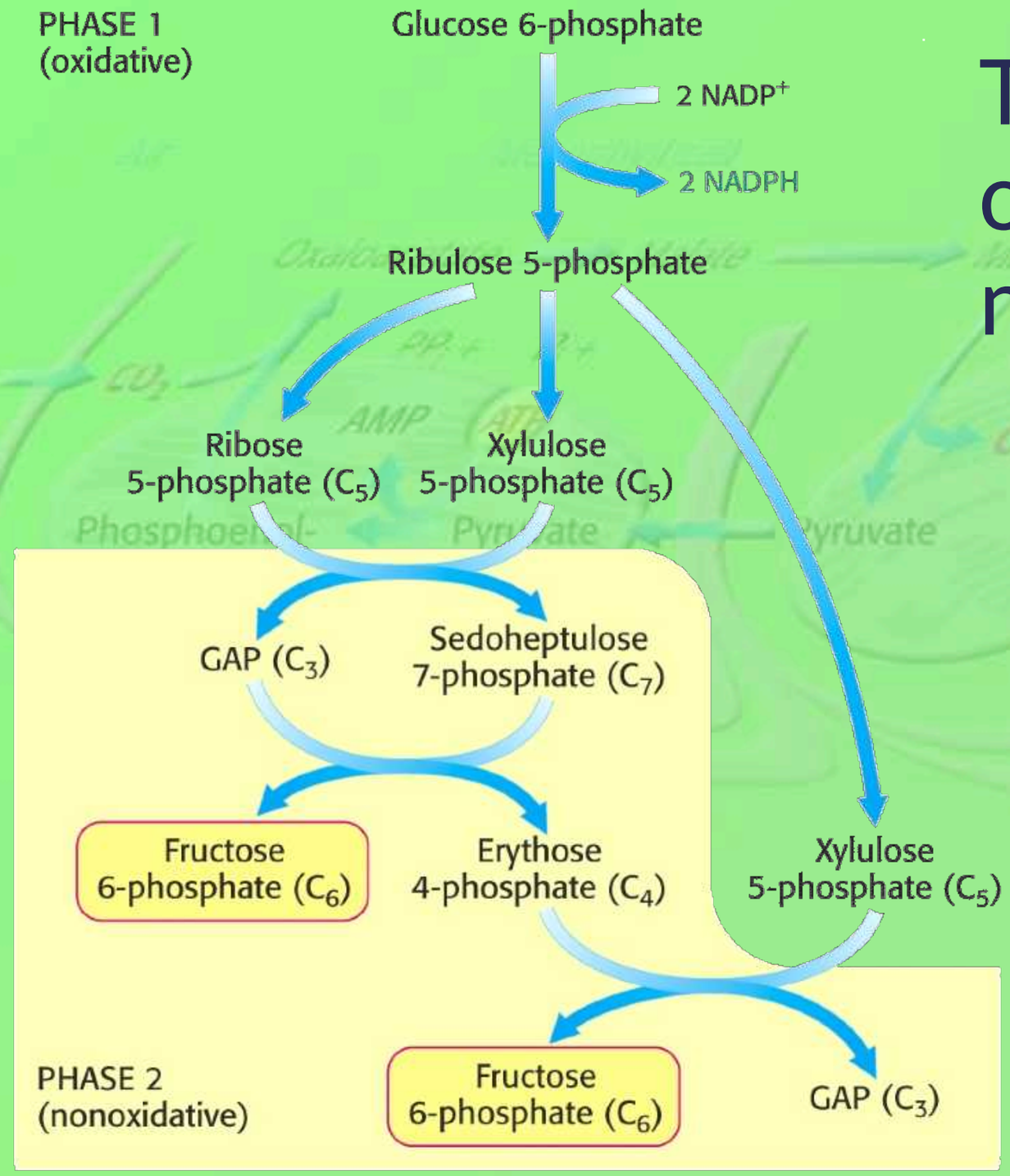
# 3. The Pentose Phosphate Pathway

Pathway is used to serve the NADPH needs of all organisms




It also provides a source of five carbon sugars

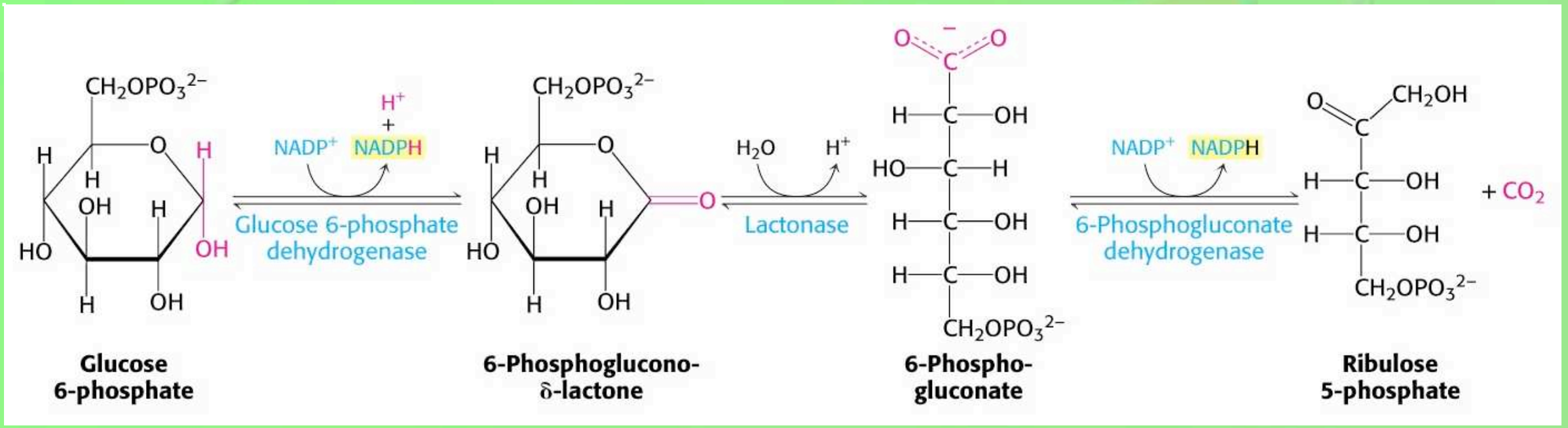
# 3. The Pentose Phosphate Pathway




There is an oxidative and nonoxidative phase.

# 3. Phase 1 of The Pentose Phosphate Pathway

There oxidative phase



# 3.2 Phase 2
# The Pentose Phosphate Pathway

The pentose phosphate pathway and glycolysis are linked by transketolase and transaldolase

- When the need for NADPH is greater than the need for ribose 5-phosphate, the ribose 5-phosphate is converted into the glycolytic intermediates glyceraldehyde 3-phosphate and fructose 6-phosphate

# 3.2 Phase 2
# The Pentose Phosphate Pathway

The pentose phosphate pathway and glycolysis are linked by transketolase and transaldolase

transketolase

$C_5 + C_5 \rightleftharpoons C_3 + C_7$

transaldolase

$C_3 + C_7 \rightleftharpoons C_6 + C_4$

transketolase

$C_4 + C_5 \rightleftharpoons C_6 + C_3$

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$C_5 + C_5 + C_5 \rightleftharpoons C_6 + C_6 + C_3$

# 3.2 Phase 2
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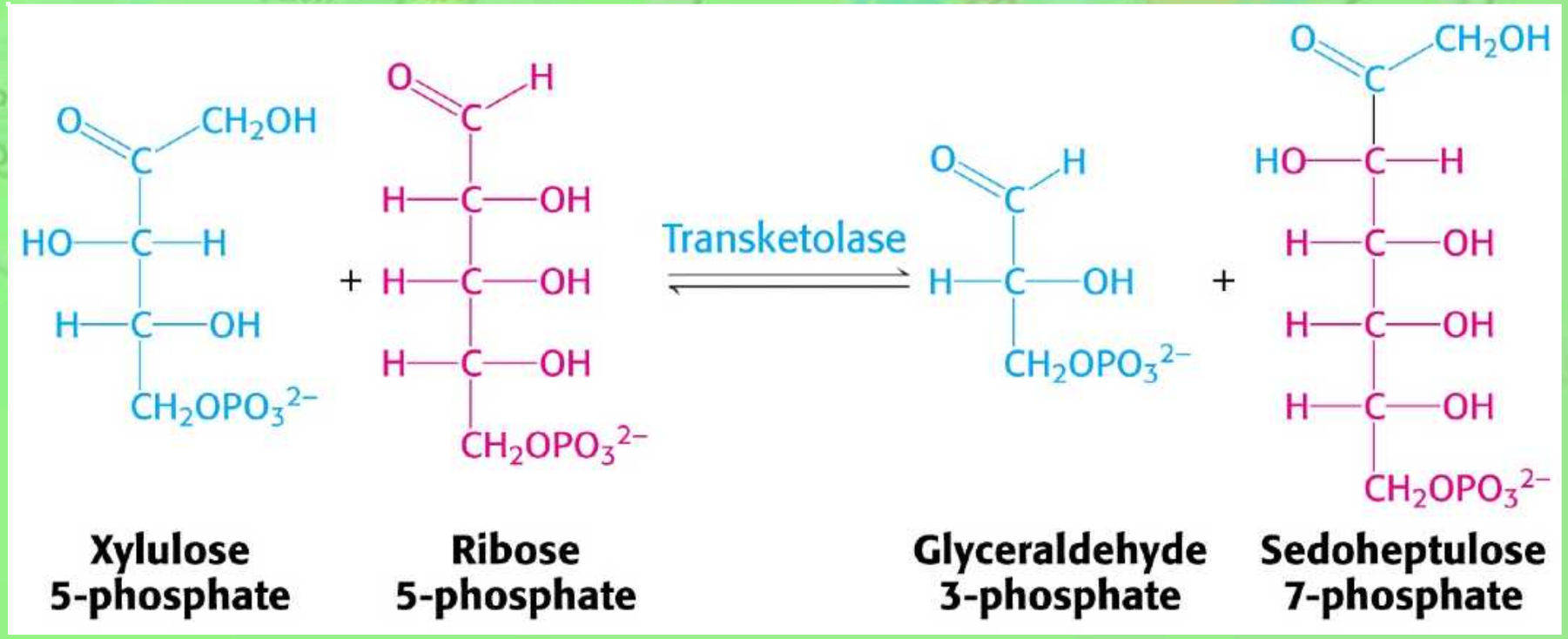

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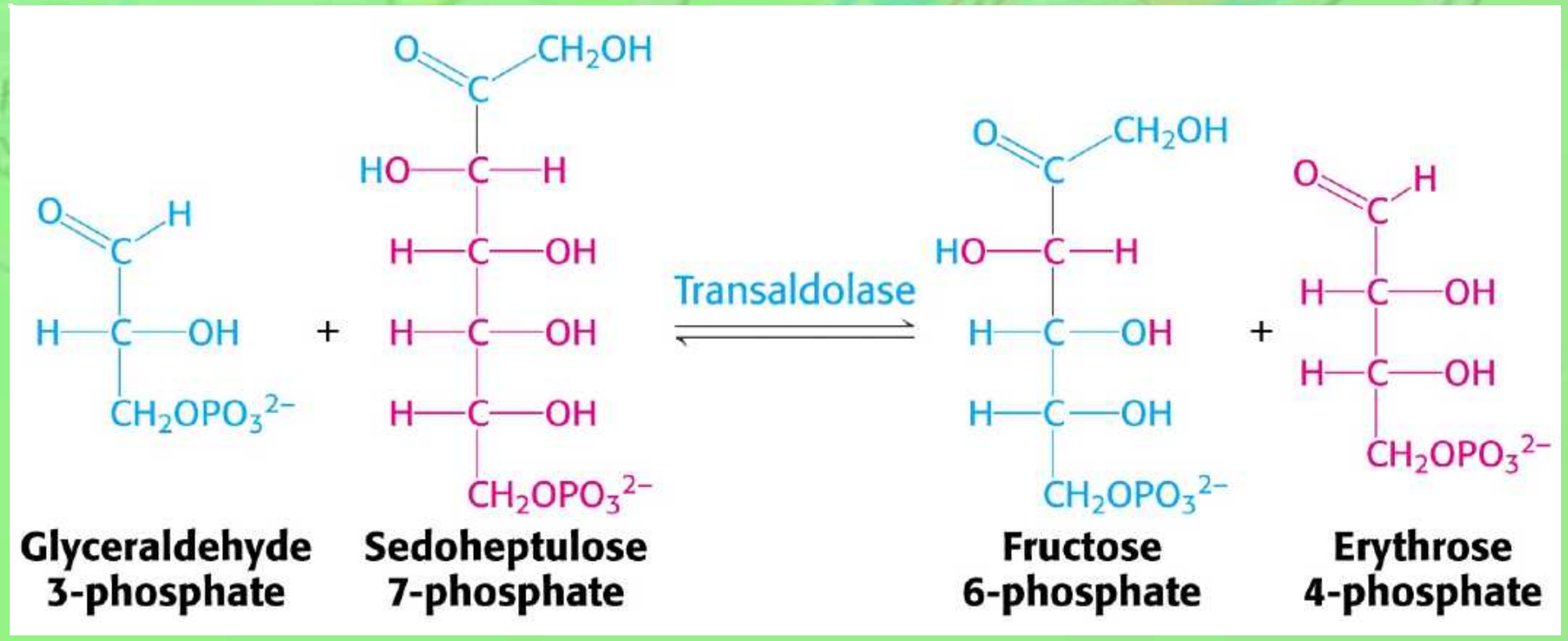

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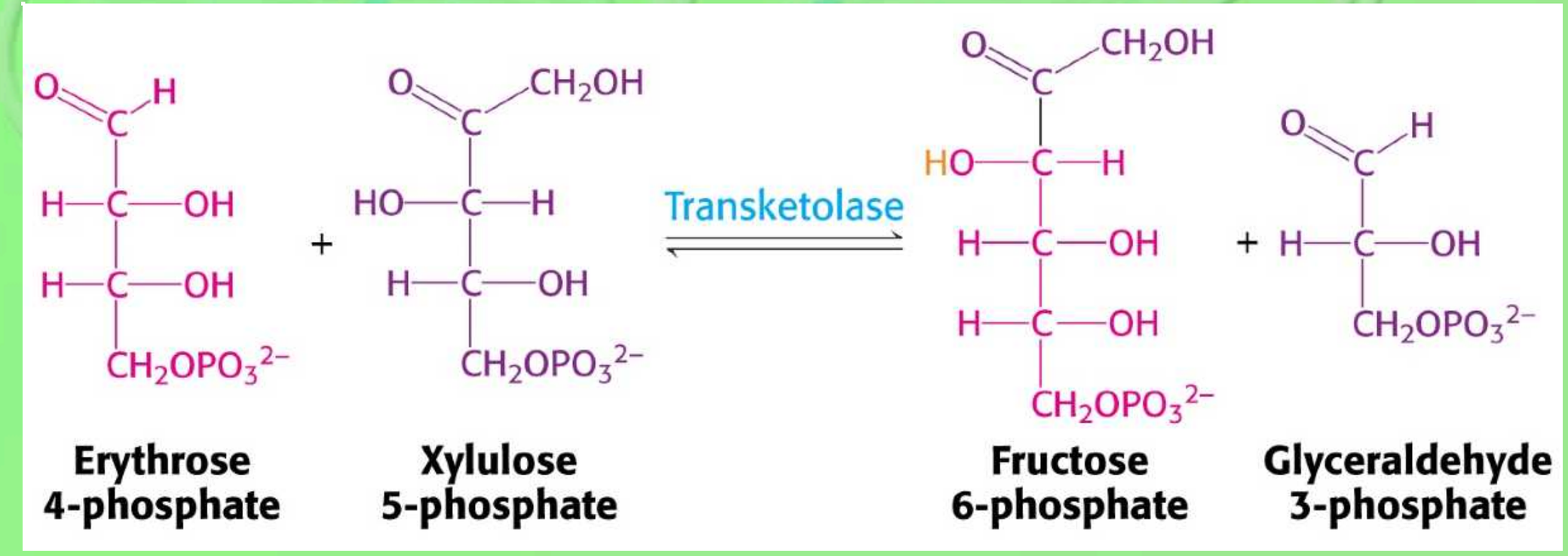
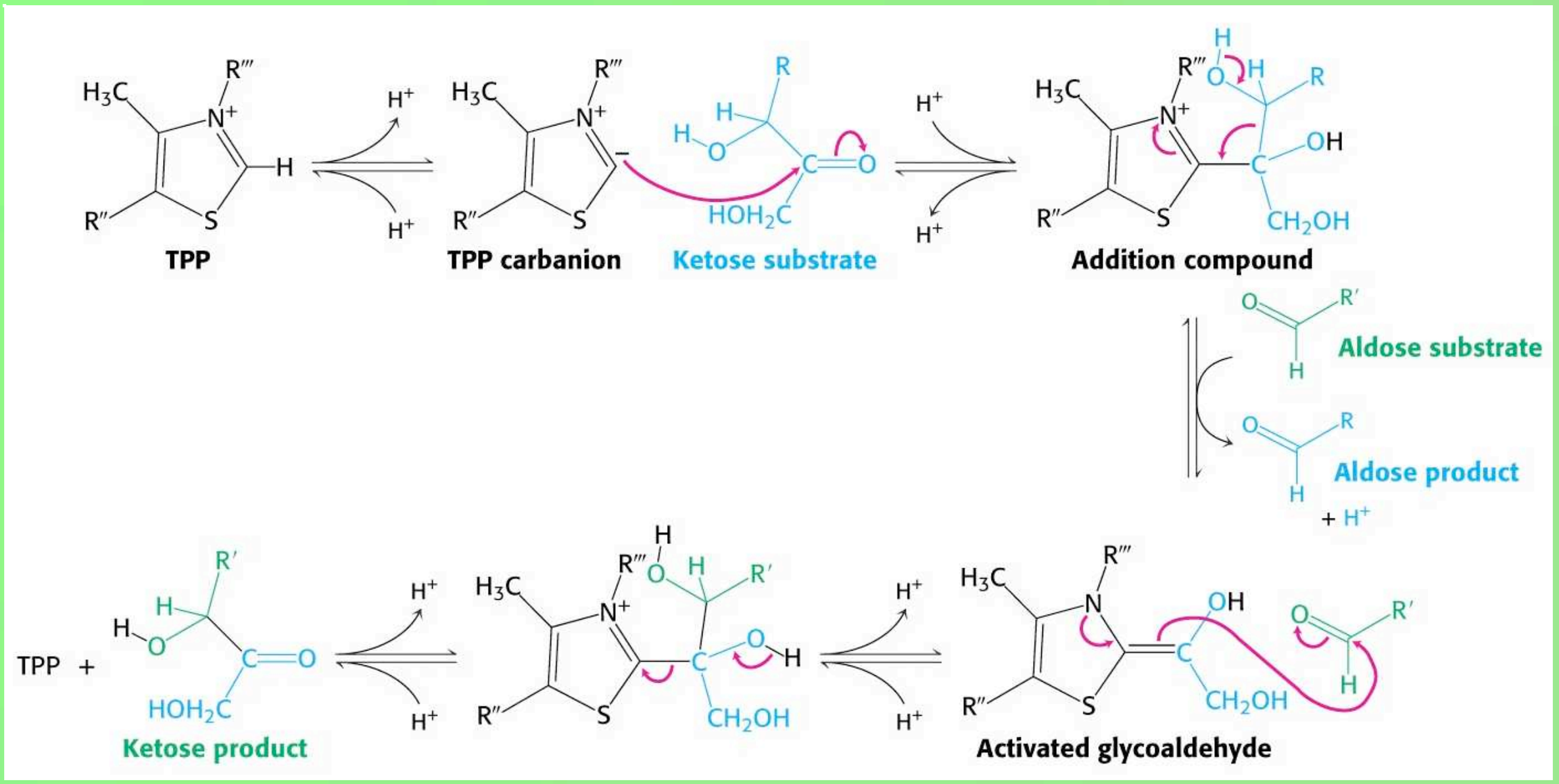


# 3.2 The Pentose Phosphate Pathway

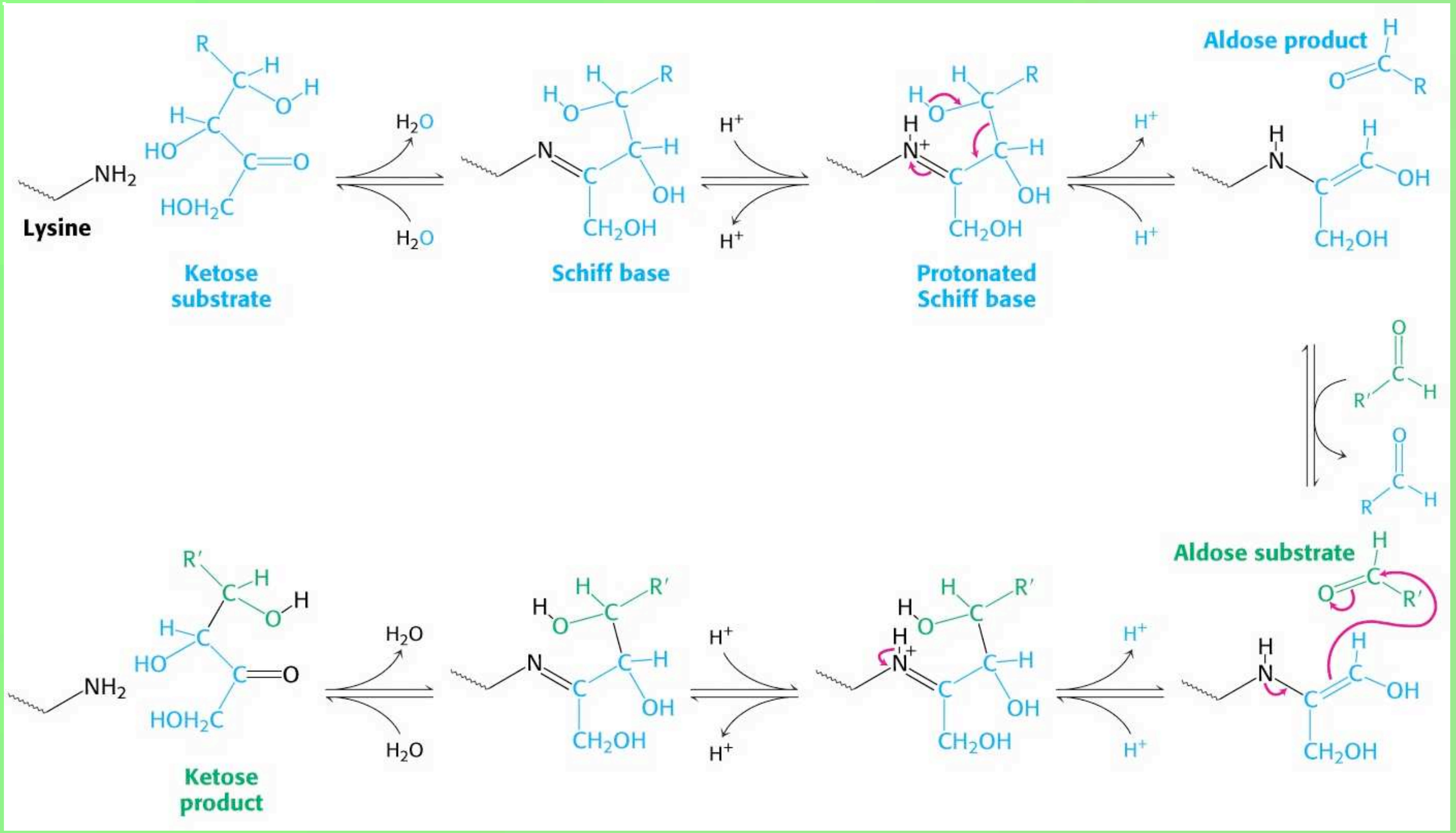
**TABLE 20.3 Pentose phosphate pathway**

| Reaction | Enzyme |
|---|---|
| **Oxidative phase** | |
| Glucose 6-phosphate + $NADP^+ \longrightarrow$ 6-phosphoglucono-δ-lactone + NADPH + $H^+$ | Glucose 6-phosphate dehydrogenase |
| 6-Phosphoglucono-δ-lactone + $H_2O \longrightarrow$ 6-phosphogluconate + $H^+$ | Lactonase |
| 6-Phosphogluconate + $NADP^+ \longrightarrow$ ribulose 5-phosphate + $CO_2$ + NADPH | 6-Phosphogluconate dehydrogenase |
| **Nonoxidative Phase** | |
| Ribulose 5-phosphate $\rightleftharpoons$ ribose 5-phosphate | Phosphopentose isomerase |
| Ribulose 5-phosphate $\rightleftharpoons$ xylulose 5-phosphate | Phosphopentose epimerase |
| Xylulose 5-phosphate + ribose 5-phosphate $\rightleftharpoons$ sedoheptulose 7-phosphate + glyceraldehyde 3-phosphate | Transketolase |
| Sedoheptulose 7-phosphate + glyceraldehyde 3-phosphate $\rightleftharpoons$ fructose 6-phosphate + erythrose 4-phosphate | Transaldolase |
| Xylulose 5-phosphate + erythrose 4-phosphate $\rightleftharpoons$ fructose 6-phosphate + glyceraldehyde 3-phosphate | Transketolase |

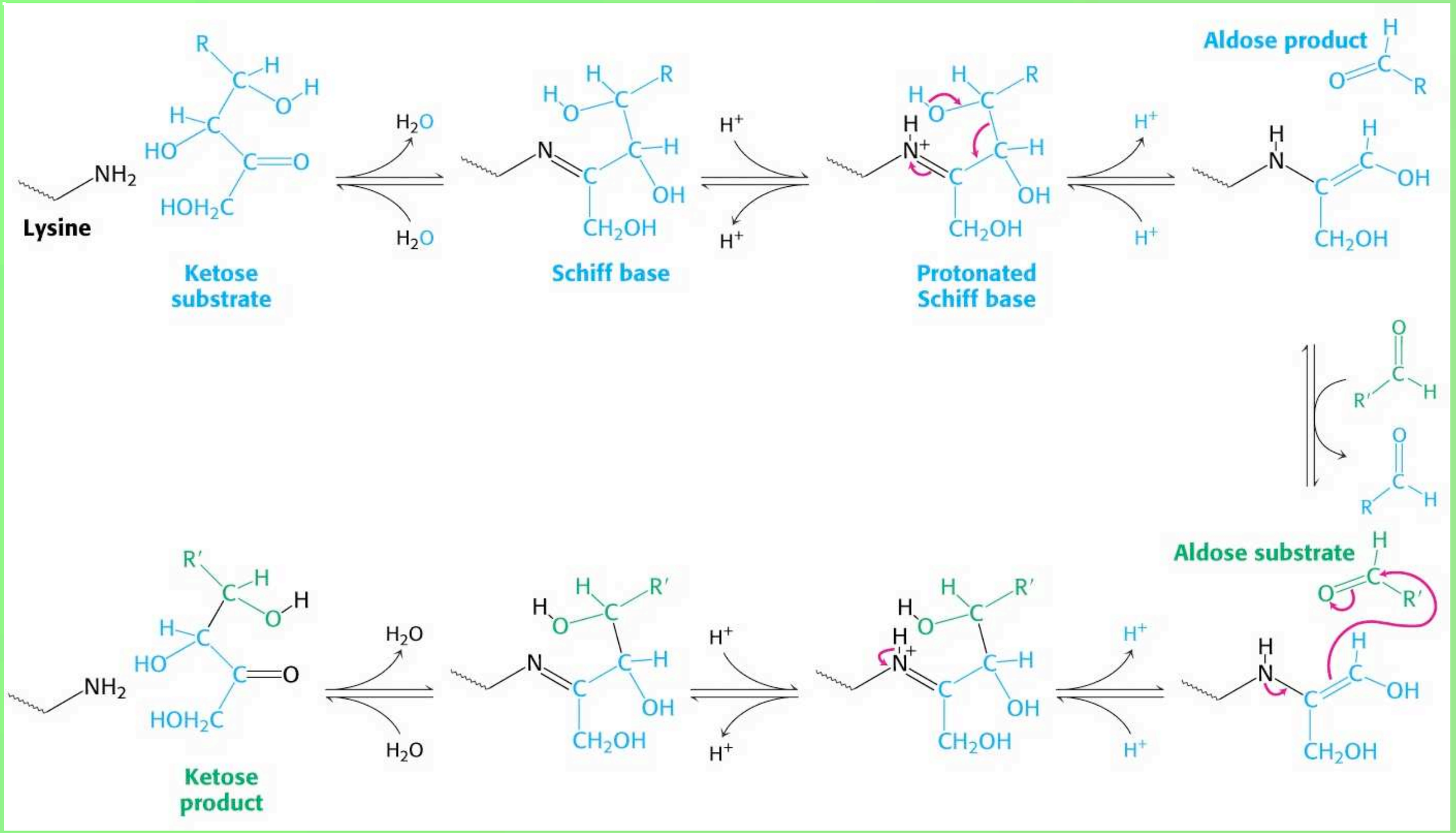
# 3.3 Transketolase Mechanism



# 3.3 Transaldolase Mechanism

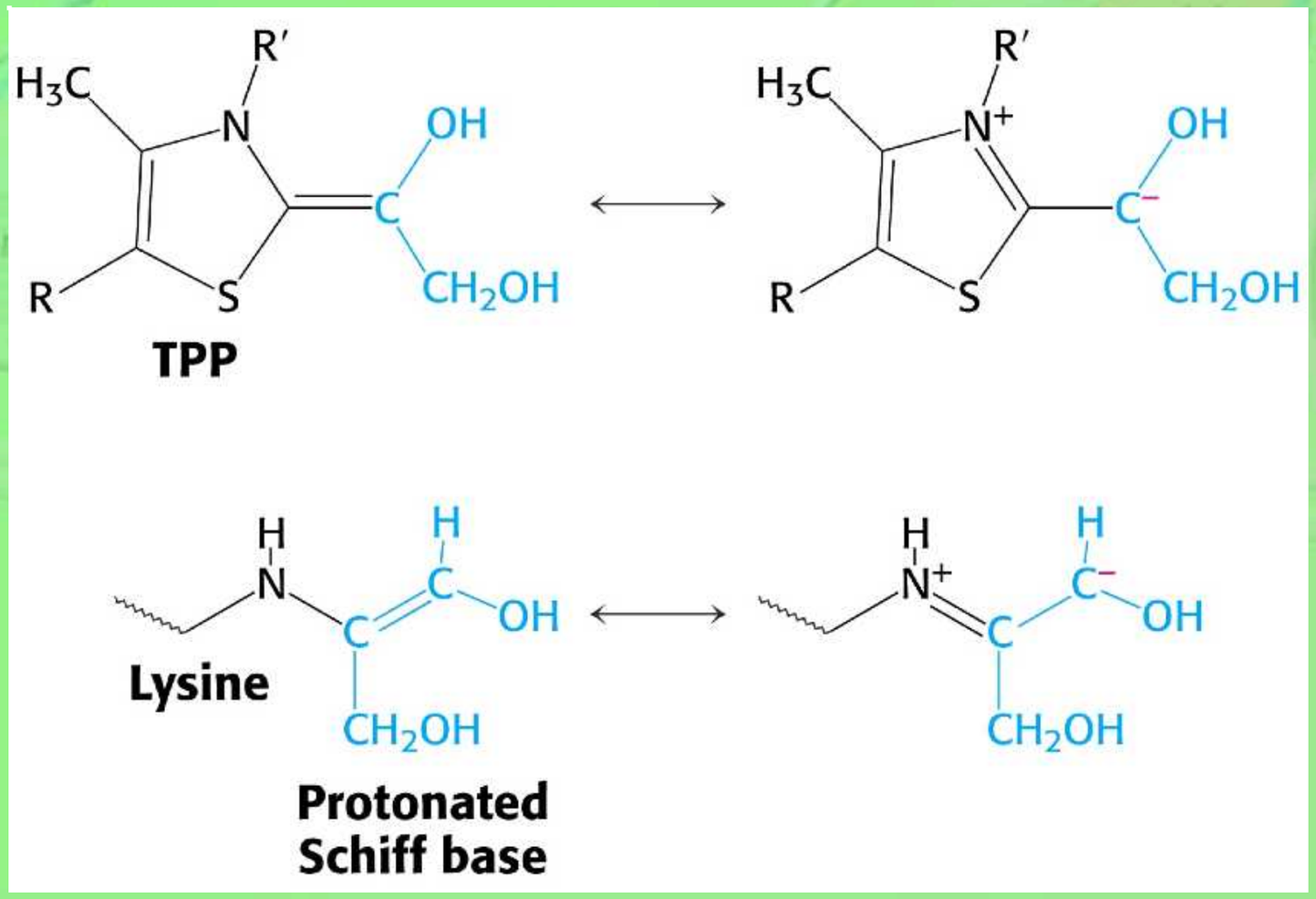


# 3.3 Transaldolase Mechanism



# 3.3 Transketoase and Transaldolase Mechanisms

Both mechanisms stabilize the carbanion intermediate



# 4. Coordination with Glycolysis