Chem 109 C

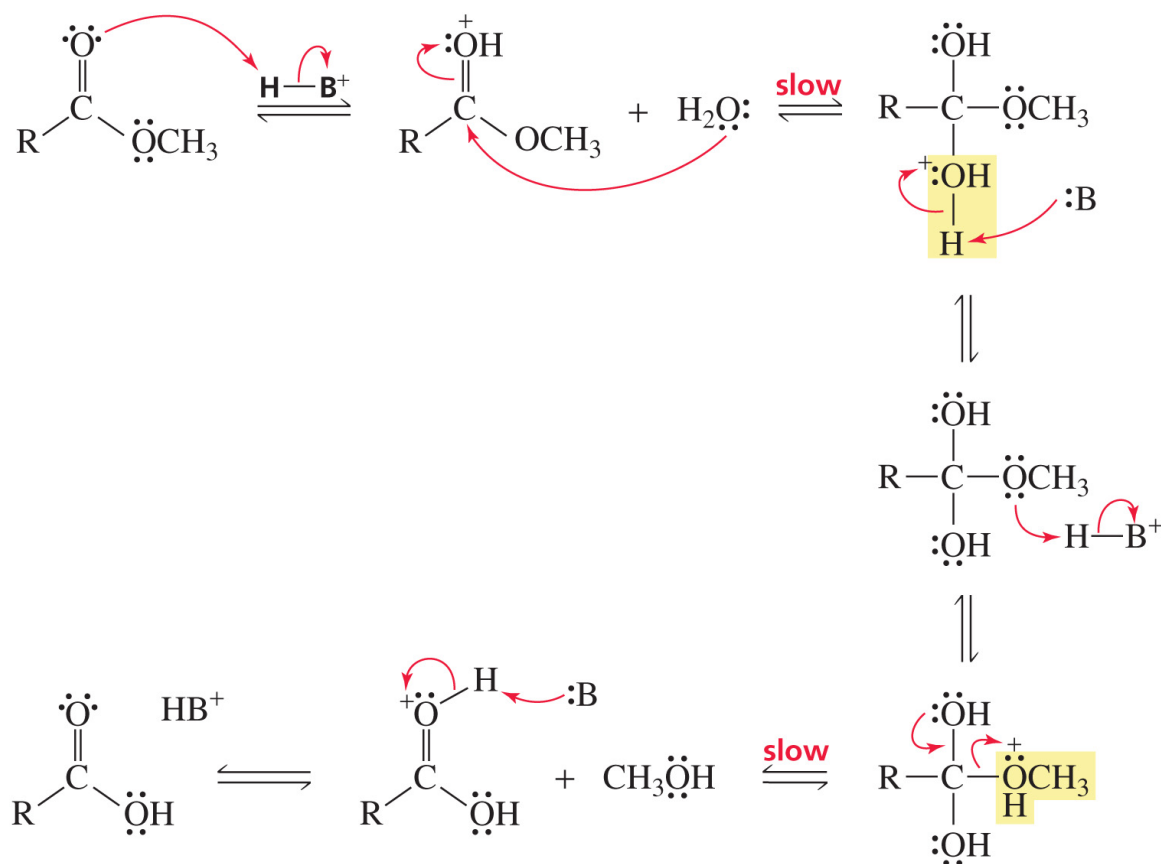## Fall 2014

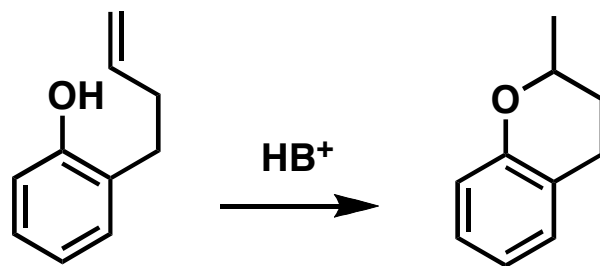**Armen Zakarian**
Office: Chemistry Bldn 2217

PROBLEM 3

Are the slow steps here general-acid catalyzed or specific-acid catalyzed?
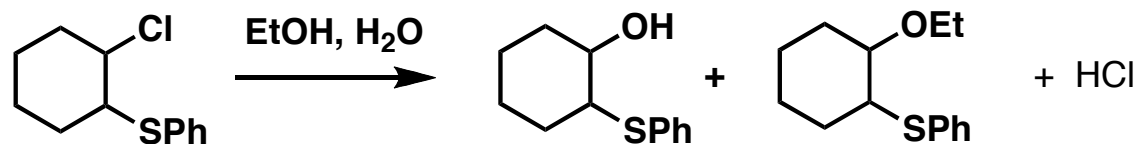
PROBLEM 4

The following reaction occurs by a general-acid catalyzed mechanism:

Propose a mechanism for this reaction

*in more detail...*

cis   vs.   *trans*

- **conformational analysis**
- **stereochemistry of products**
- **other examples of neighboring group participation**

"intramolecular catalysis", "neighboring group participation", "anchimeric assistance" are interchangeable terms
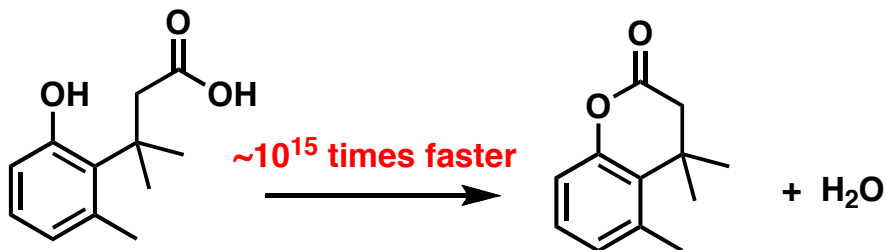
4

intramolecular and intermolecular reactions
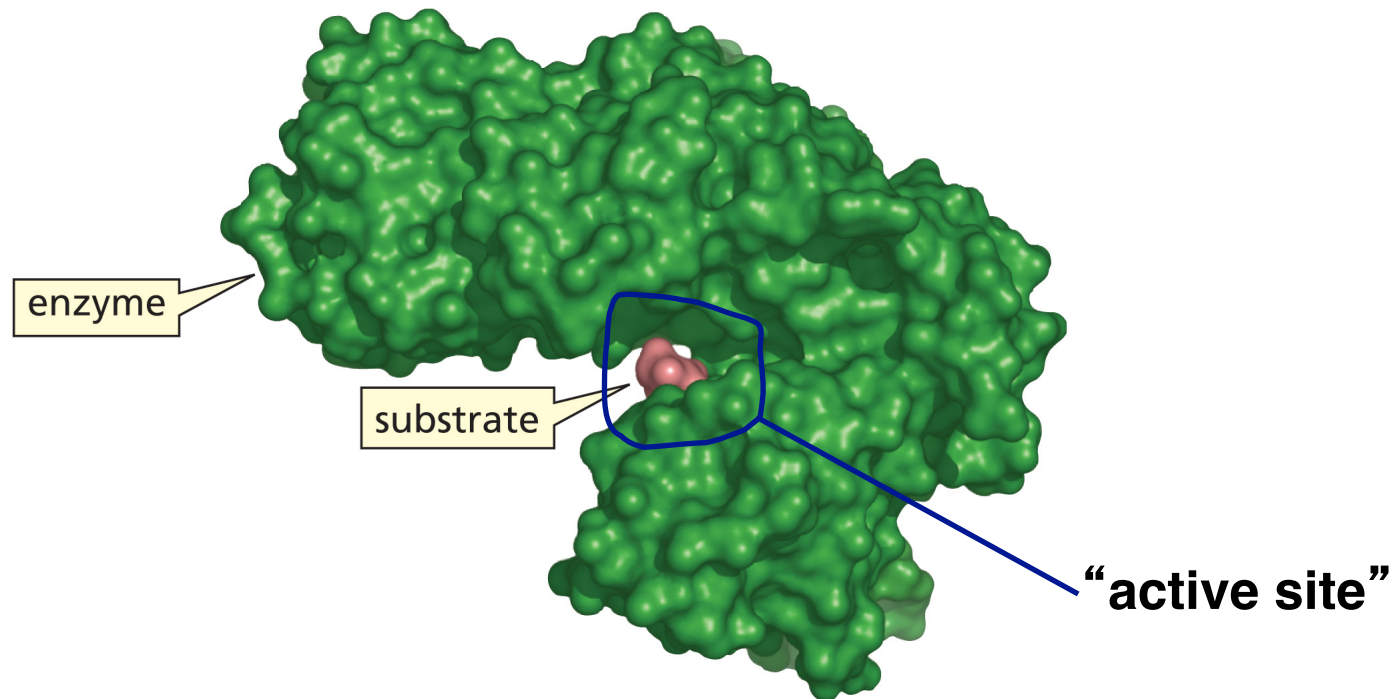why are intramolecular reactions faster?

intermolecular reaction:
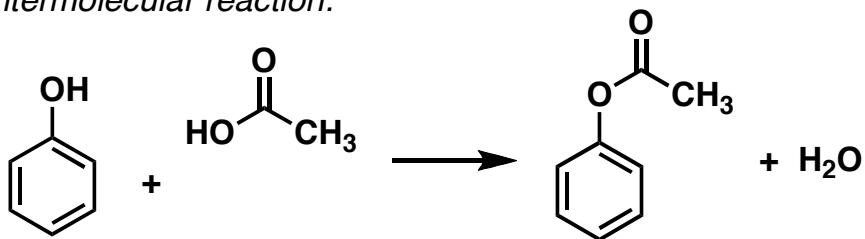
+ H_2O

intramolecular reaction:

~10^{15} times faster

+ H_2O

"intramolecular catalysis", "neighboring group participation", "anchimeric assistance" are interchangeable terms

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catalysis in biological reactions

enzyme
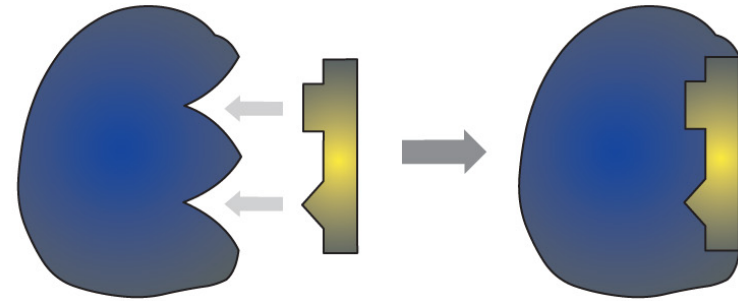
substrate $\longrightarrow$ **product**

enzyme

substrate

"active site"

enzymes show high substrate specificity
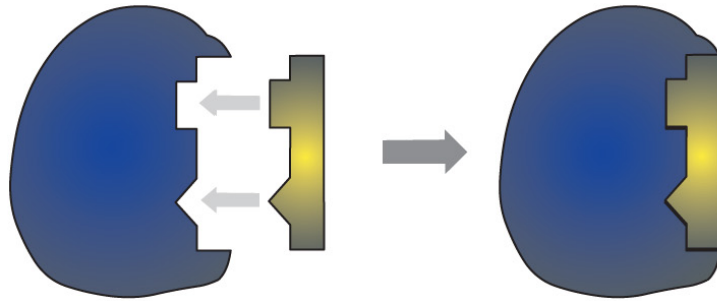
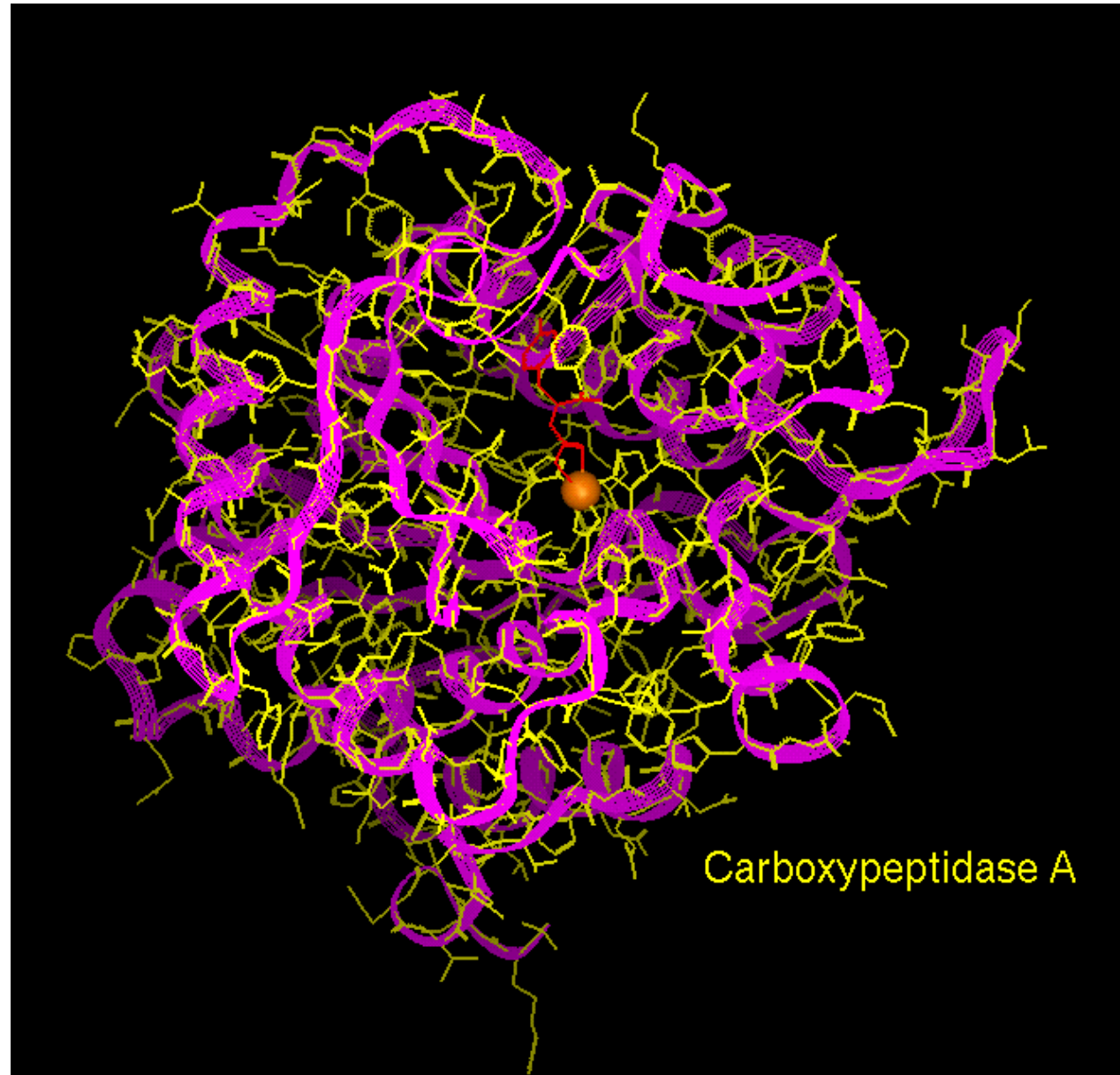
lock-and-key model   induced-fit model

names: [activity]-ase

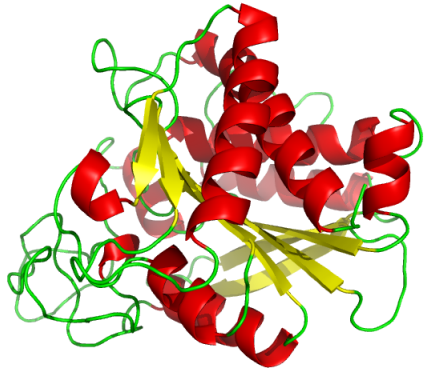*kinase, protease, lipase*, dehydrogenase, etc.

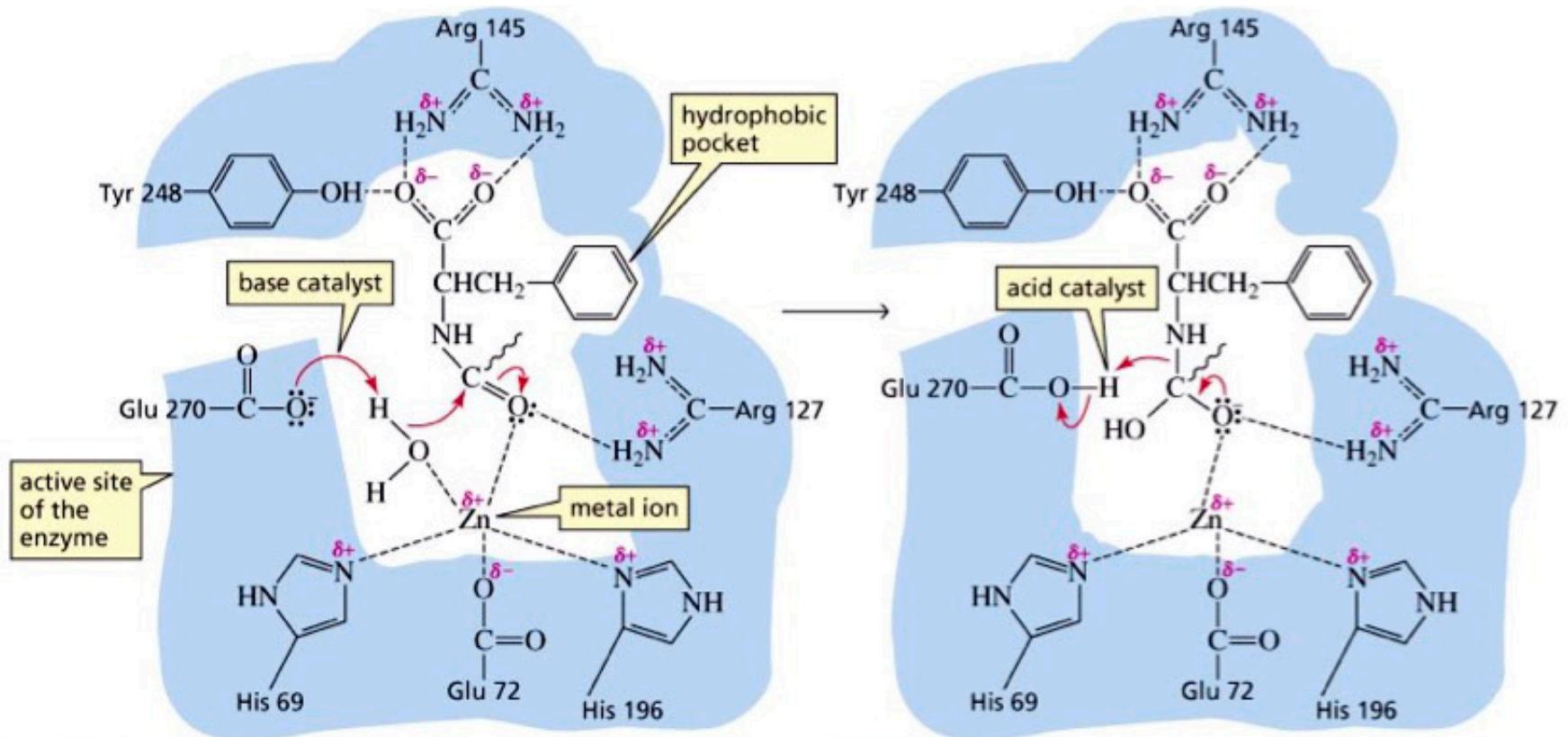*factors contributing to high catalytic activity of enzymes:*

- reacting groups are properly oriented in active site

- acid/base or metal ions are at active site

- stabilization of transition states and intermediates

Carboxypeptidase A
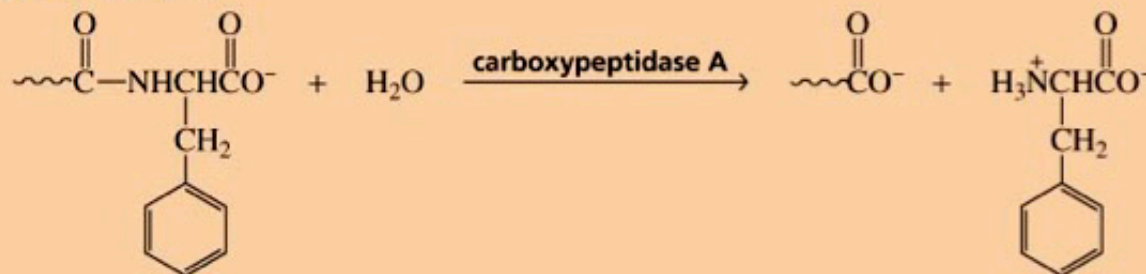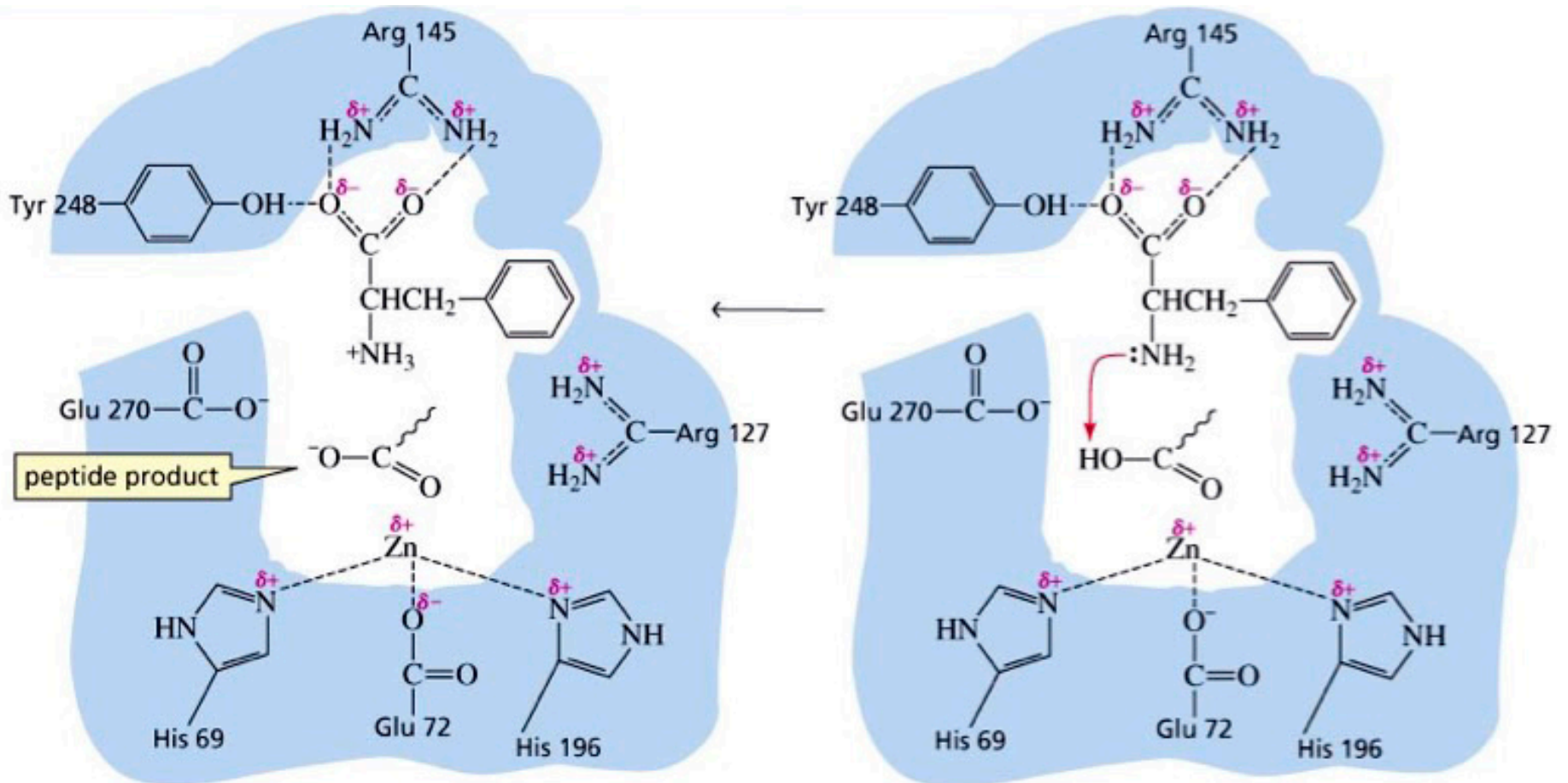
examples: carboxypeptidase A

examples: carboxypeptidase A
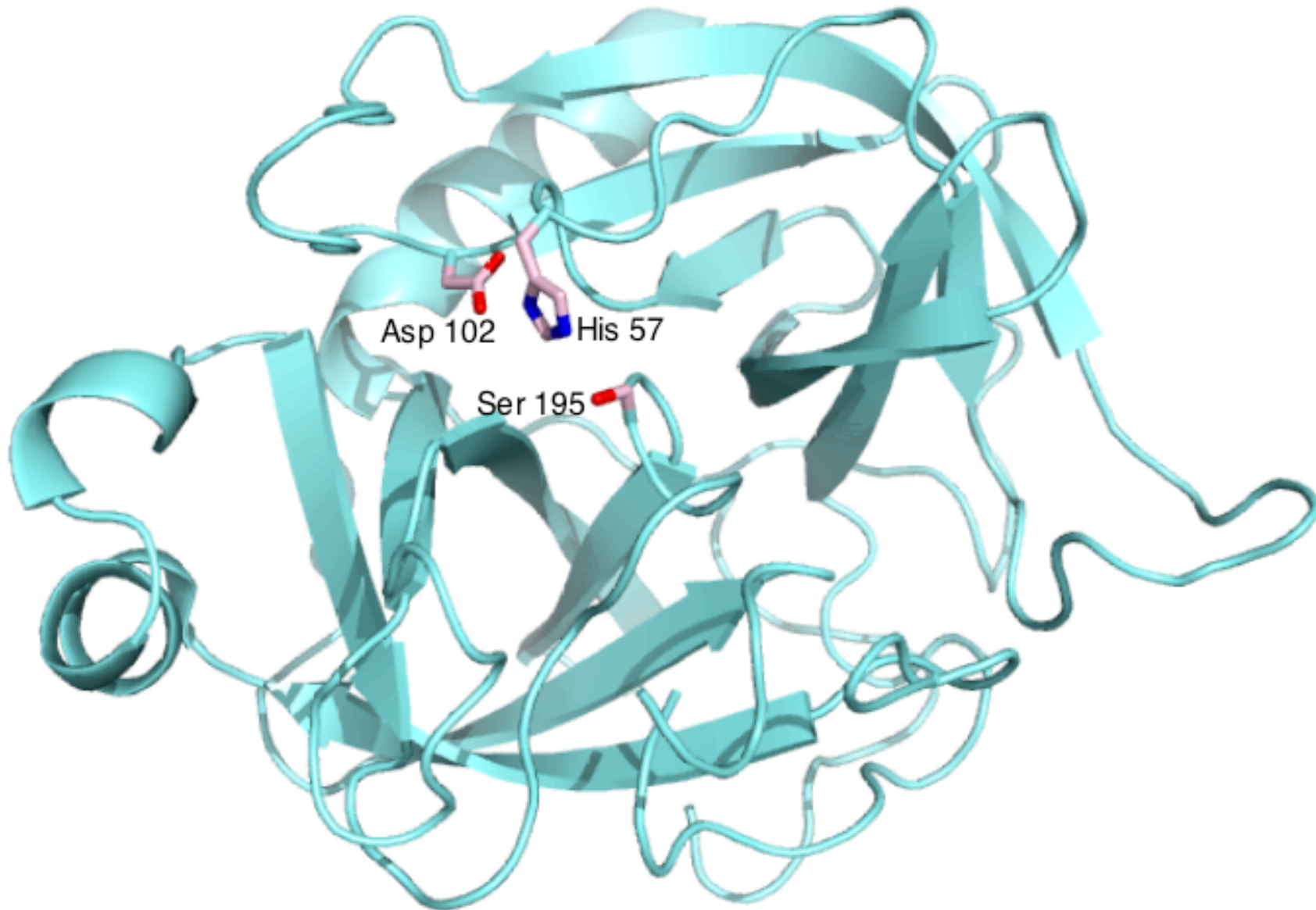
examples: serine proteases - chymotrypsin
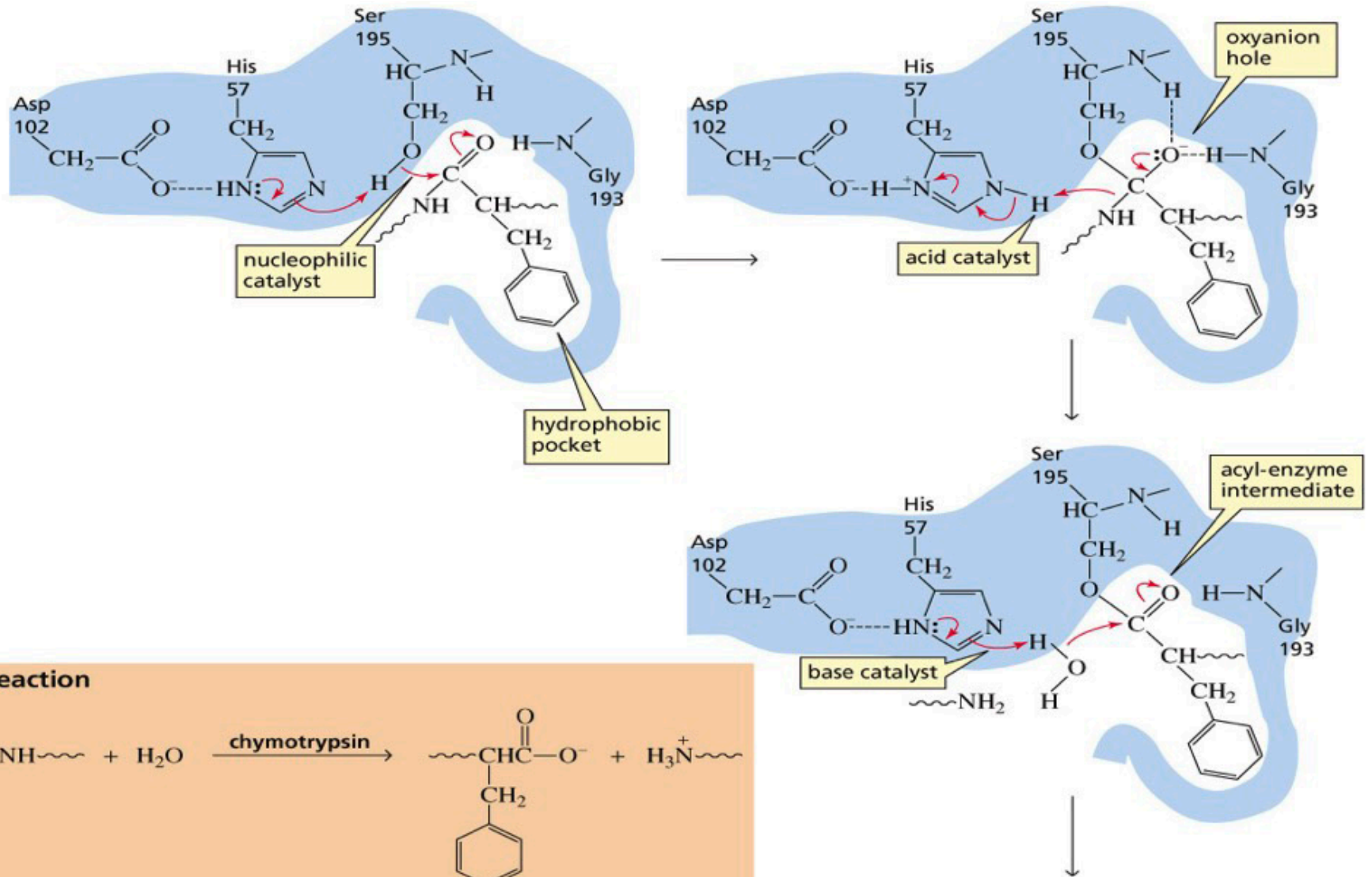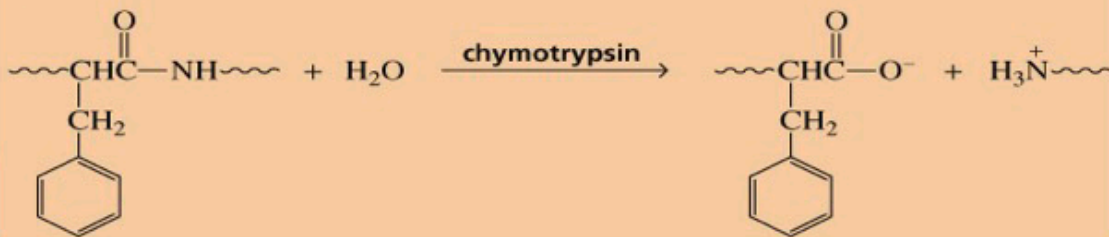
examples: serine proteases - chymotrypsin

Overall Reaction

examples: serine proteases - chymotrypsin

Overall Reaction
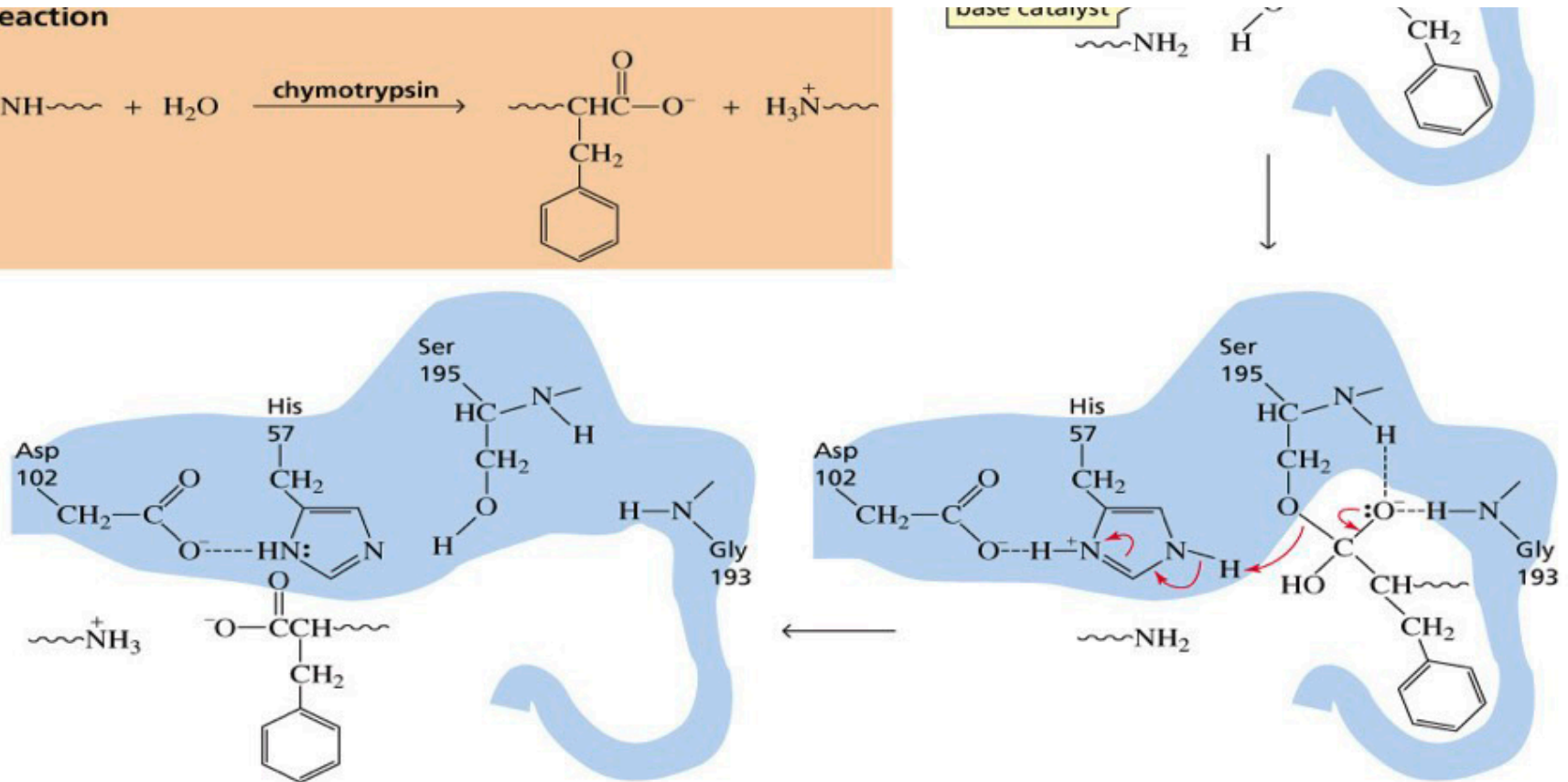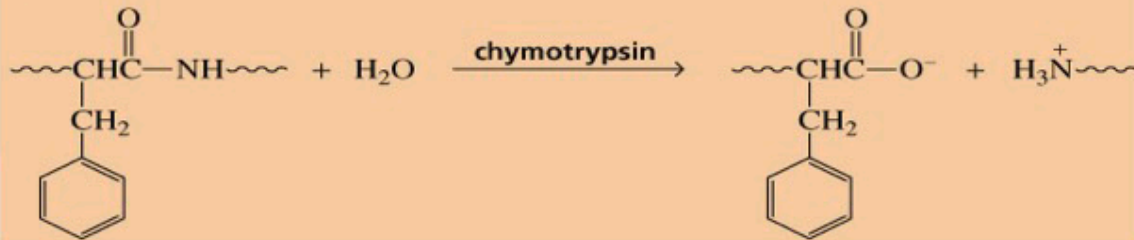
examples: glucose-6-phosphate isomerase

Overall Reaction

glucose-6-phosphate isomerase

glucose-6-phosphate

fructose-6-phosphate

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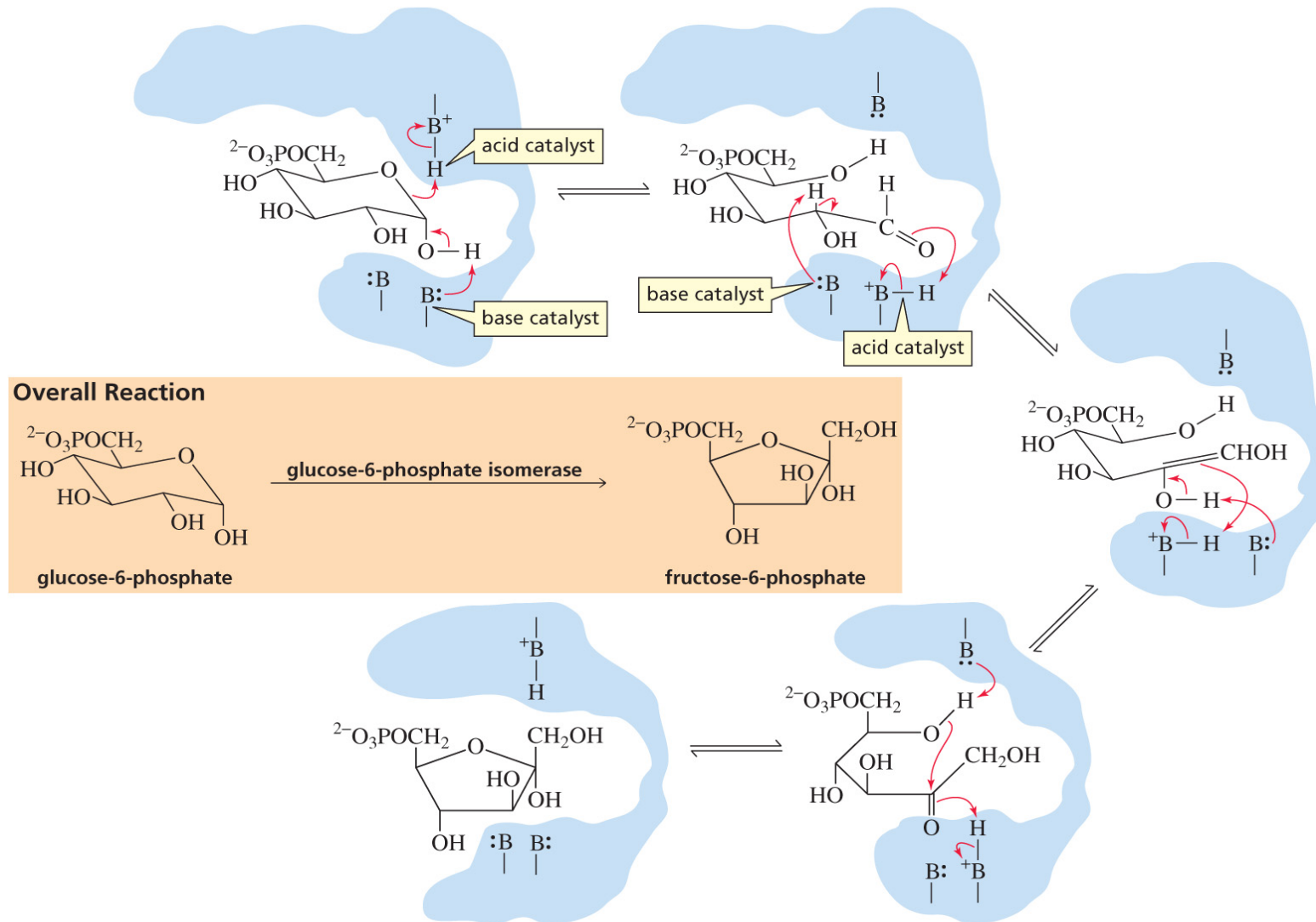
- **specific-acid/specific-base catalysis**
- **general-acid/general-base catalysis**
- **nucleophilic catalysis**
- **metal-ion catalysis: three types of activation**

- **intramolecular reactions**
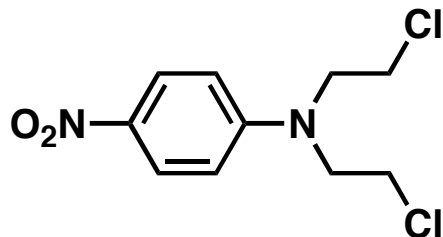- **intramolecular catalysis/anchimeric assistance**

- **enzymes: substrate specificity**
  - *active site*

Propose a mechanism for the following reaction
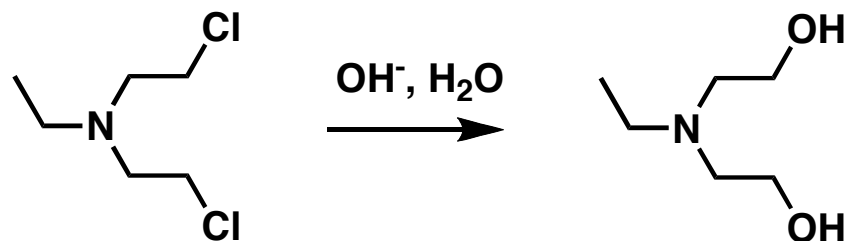
Why is this reaction slower with the following compound

summary of previous sections

Catalysis (ch 23)

definition of catalyst, energy diagrams illustrating catalytic action

types of catalysis:

acid: specific and general

base: specific and general

nucleophilic: stronger Nu are better catalysts

metal-ion: types of activation

intramolecular reactions

why are they faster? effective molarity etc...

intramolecular catalysis: examples of each class (acid, base, Nu, metal)

overview of enzyme catalyzed reactions:

names of enzyme ("substrate" …..ase)

lock-and-key model

induced-fit model