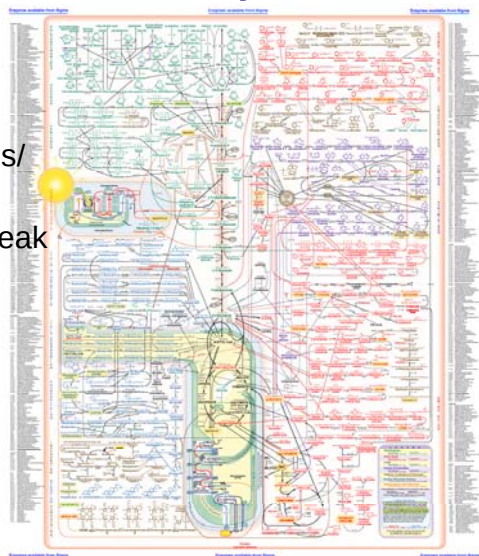


Four categories of enzymes

1. Group transfer reactions
2. Oxidations/reductions
3. Eliminations/isomerizations/rearrangements
4. Reactions that make or break C-C bonds



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Group transfer reactions

Transfer of an electrophilic group from one nucleophile to another

- Acyl group transfer
- Phosphoryl group transfer
 - Phosphatase
 - Mutase
 - Kinase
 - Phosphodiesterase
 - Nucleotidyl transferase
- Glycosyl group transfer

Note similarities in reactions

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Glycosyl group transfer

Eliminations/isomerizations/rearrangements

- reversible reactions:
 - elimination is reverse of addition
 - aldo to keto isomerization is reverse of keto to aldo isomerization
 - keep reversibility in mind

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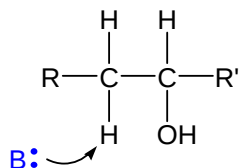
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Elimination

- “dehydratase” if water is eliminated



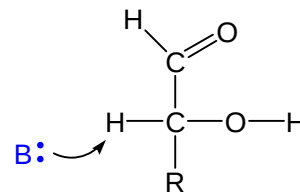
- draw it backwards and you have a “hydratase”

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Isomerization (isomerase)

- aldo to keto sugar is an important example
- reverse would be keto to aldo sugar



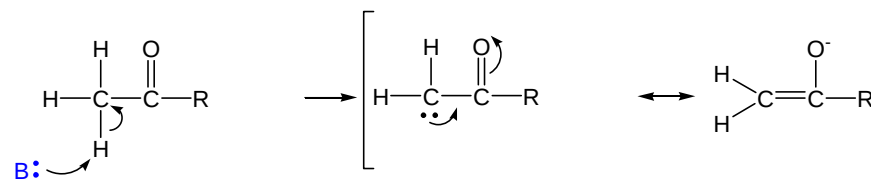
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Rearrangement

Aldol condensation/cleavage

- aldehyde + ketone, or ketone + ketone
- First step: generate resonance-stabilized carbanion



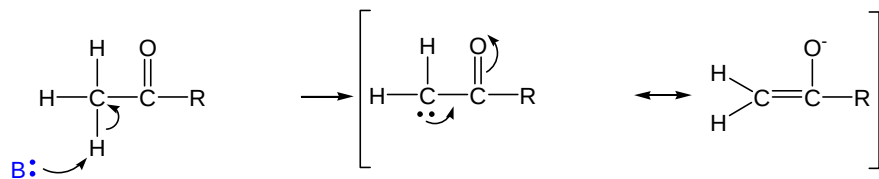
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Aldol condensation/cleavage



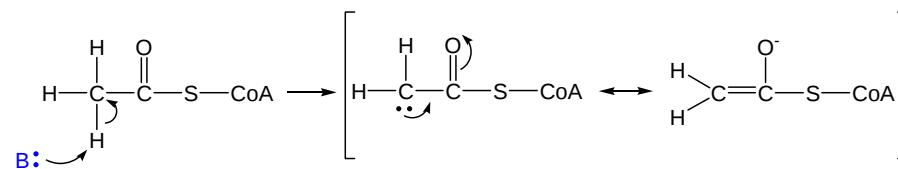
Lower the activation energy barrier by forming a Schiff base!

What else might stabilize the enolate?

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Claisen condensation/cleavage



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Eliminations/isomerizations/rearrangements

- Dehydration
- Aldo-keto isomerization
- Rearrange C skeletons

C-C bond formation and breakage

- Aldol condensation
 - Claisen condensation
 - Carboxylation and decarboxylation
 - Prenyl (isoprenoid) transfers
- Reversible (condensation/cleavage)