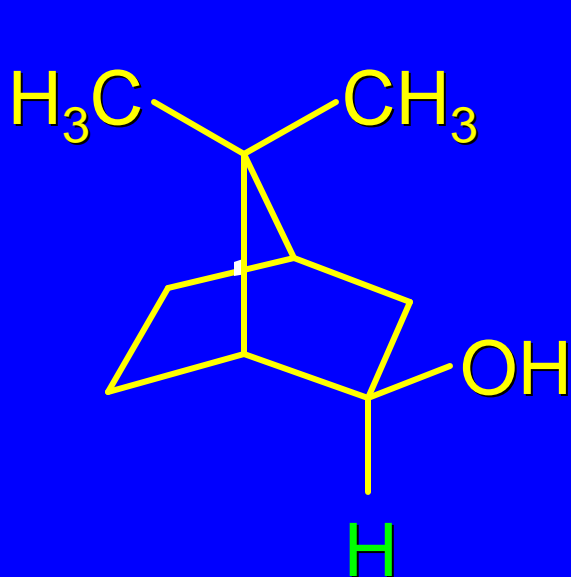
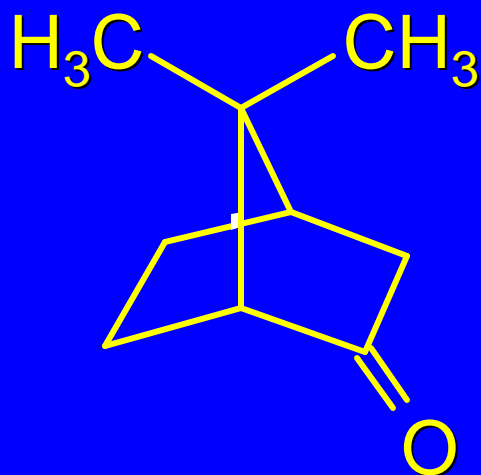


17.14

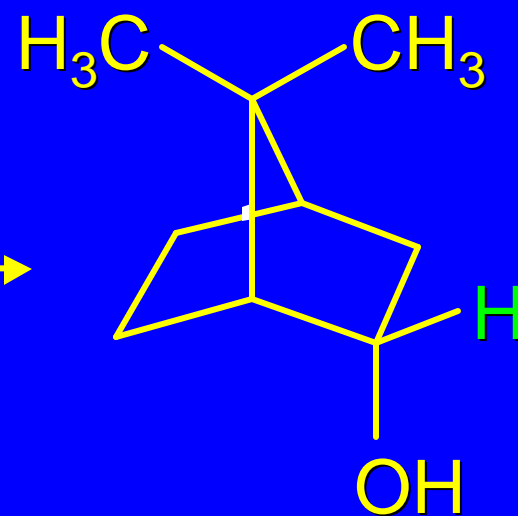
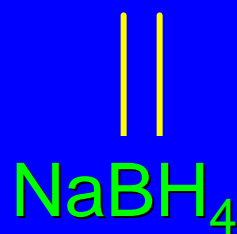
Stereoselective Addition to
Carbonyl Groups

Nucleophilic addition to carbonyl
groups sometimes leads to a mixture
of stereoisomeric products.

Example

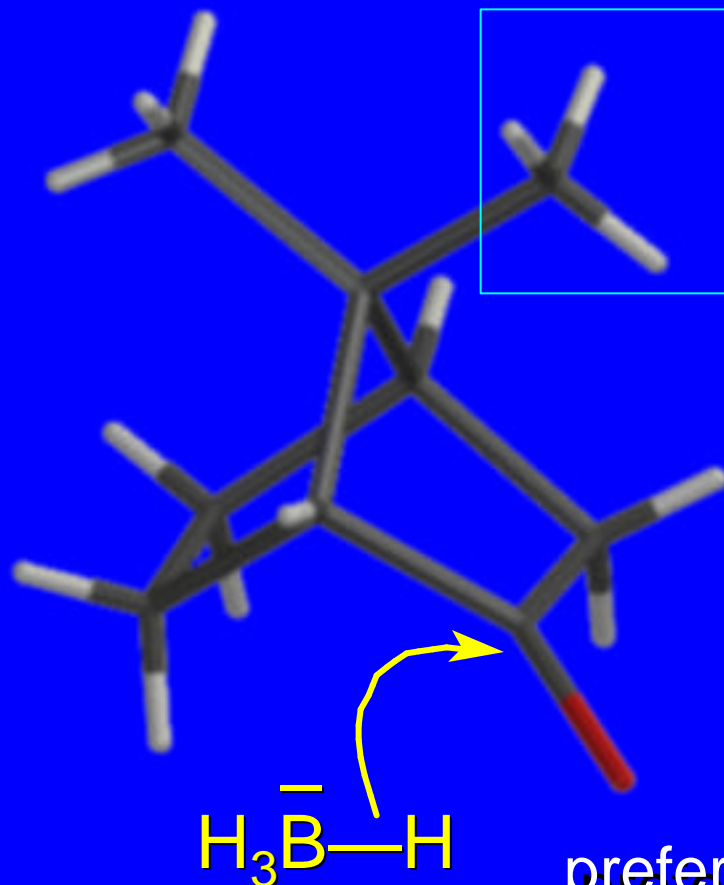


80%



20%

Steric Hindrance to Approach of Reagent

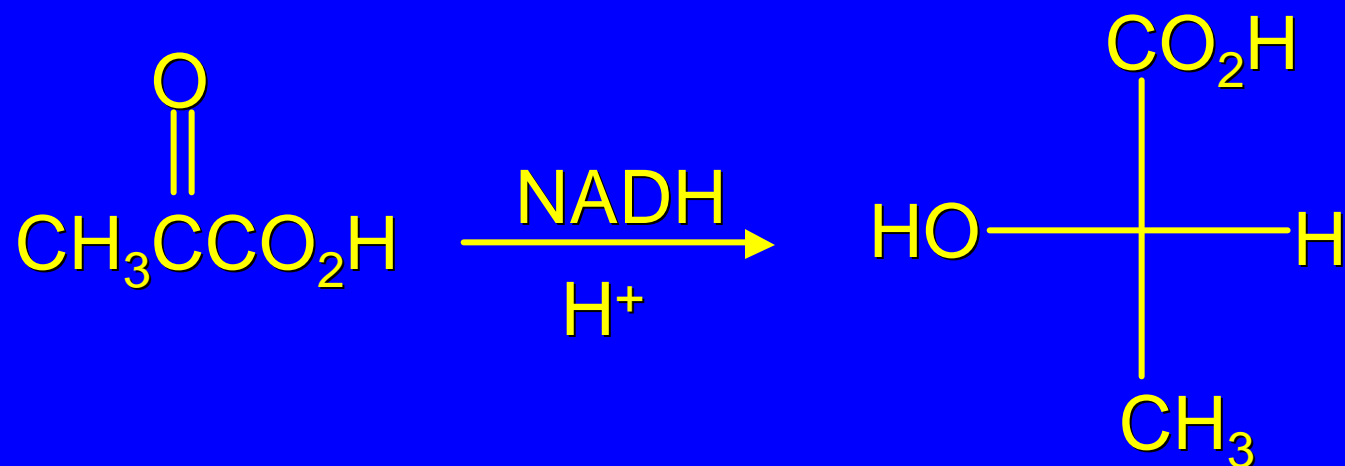


this methyl group hinders approach of nucleophile from top

preferred direction of approach is to less hindered (bottom) face of carbonyl group

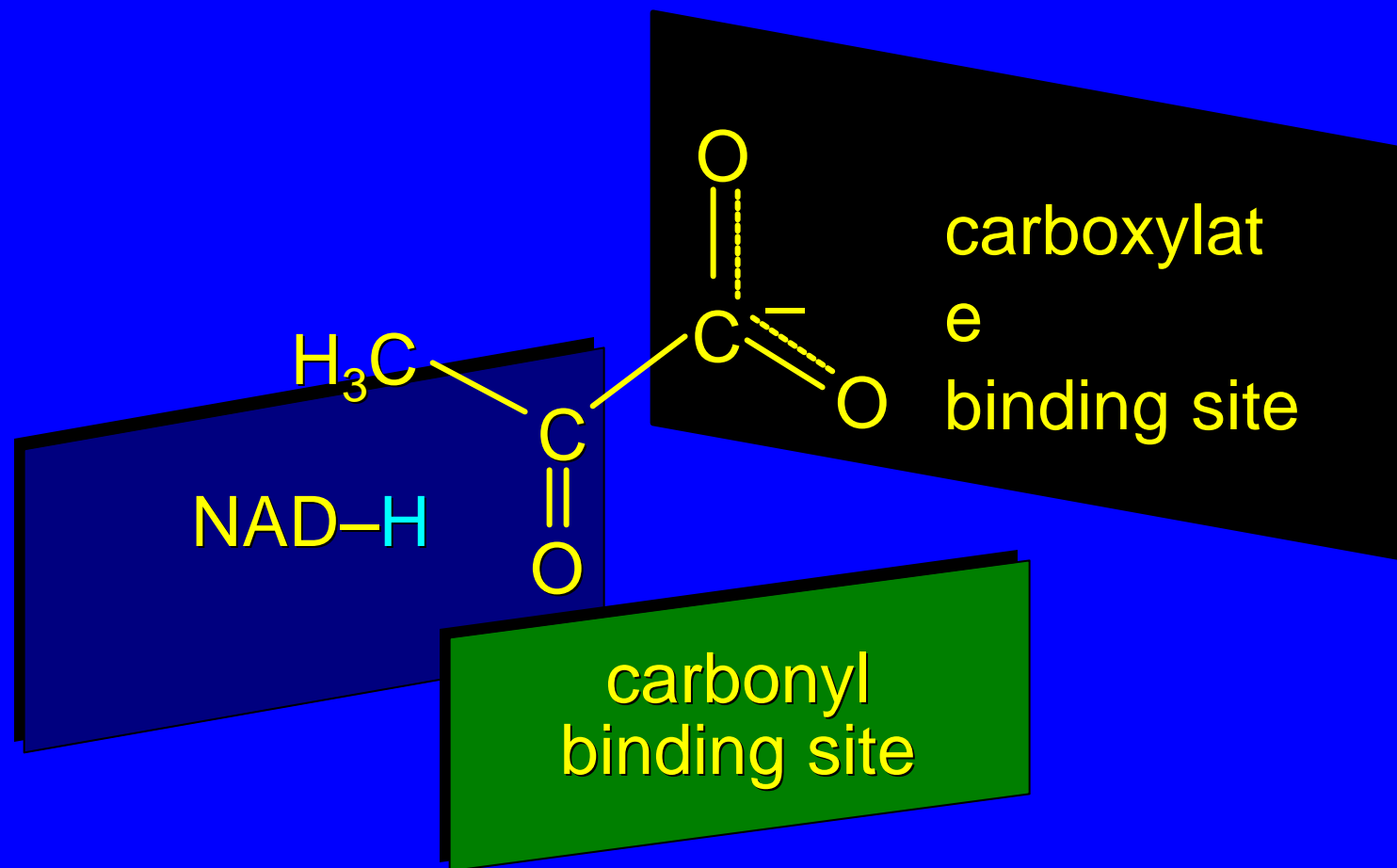
Biological reductions are highly stereoselective

pyruvic acid \rightarrow S-(+)-lactic acid



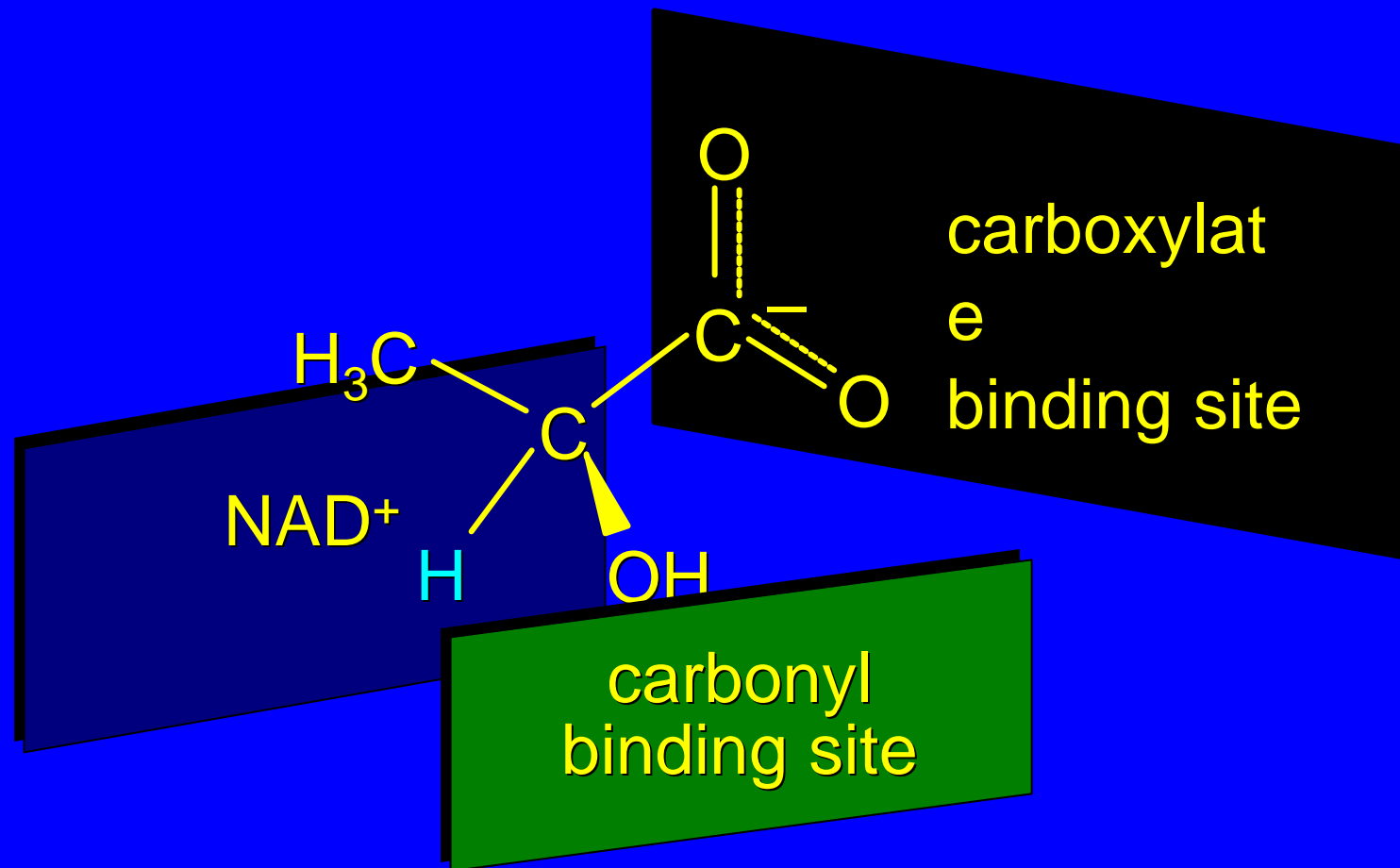
enzyme is *lactate dehydrogenase*

Figure 17.11



Pyruvate is bound at the active site of the enzyme

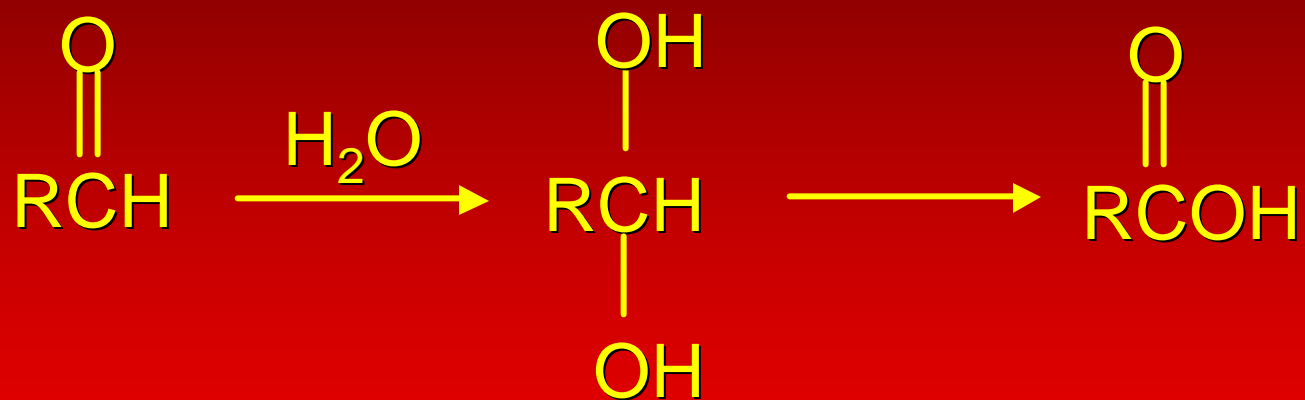
Figure 17.11



where it is reduced to (*S*)-(+)-lactate.

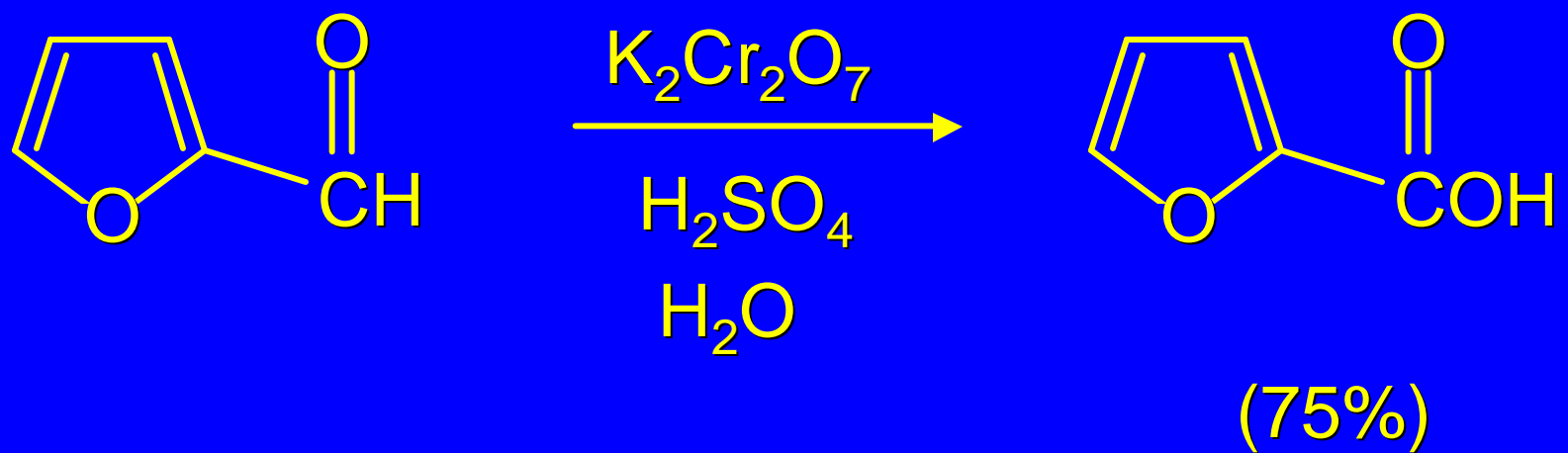
17.15

Oxidation of Aldehydes

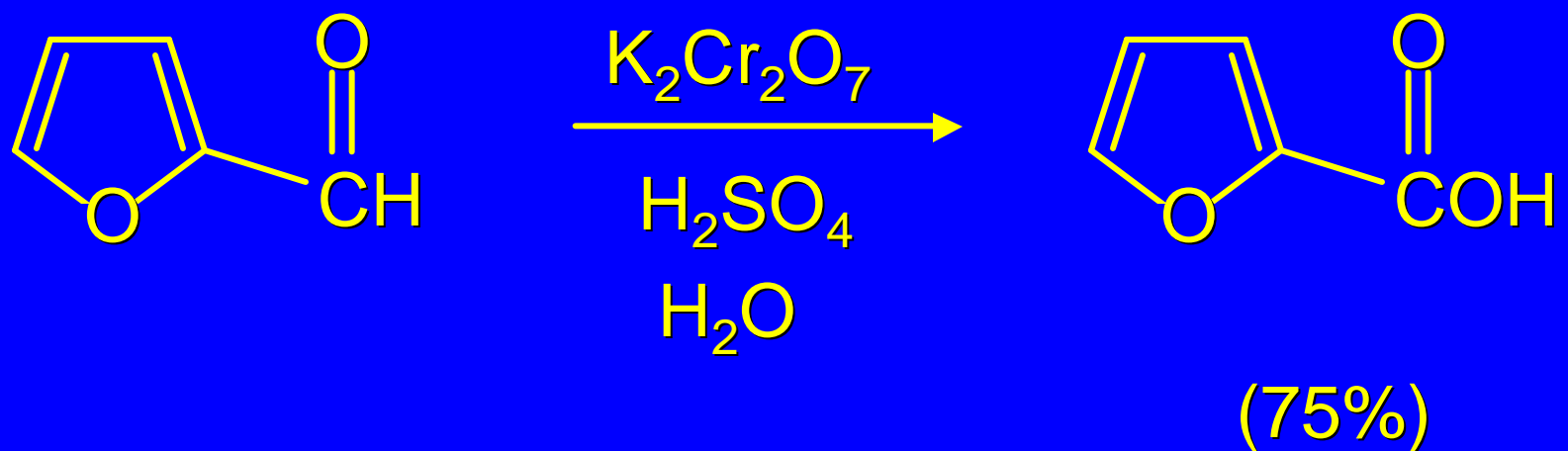


in aqueous solution

Example



Example



via



17.16

Baeyer-Villiger Oxidation
of Ketones

Oxidation of ketones with peroxy acids gives esters by a novel rearrangement.

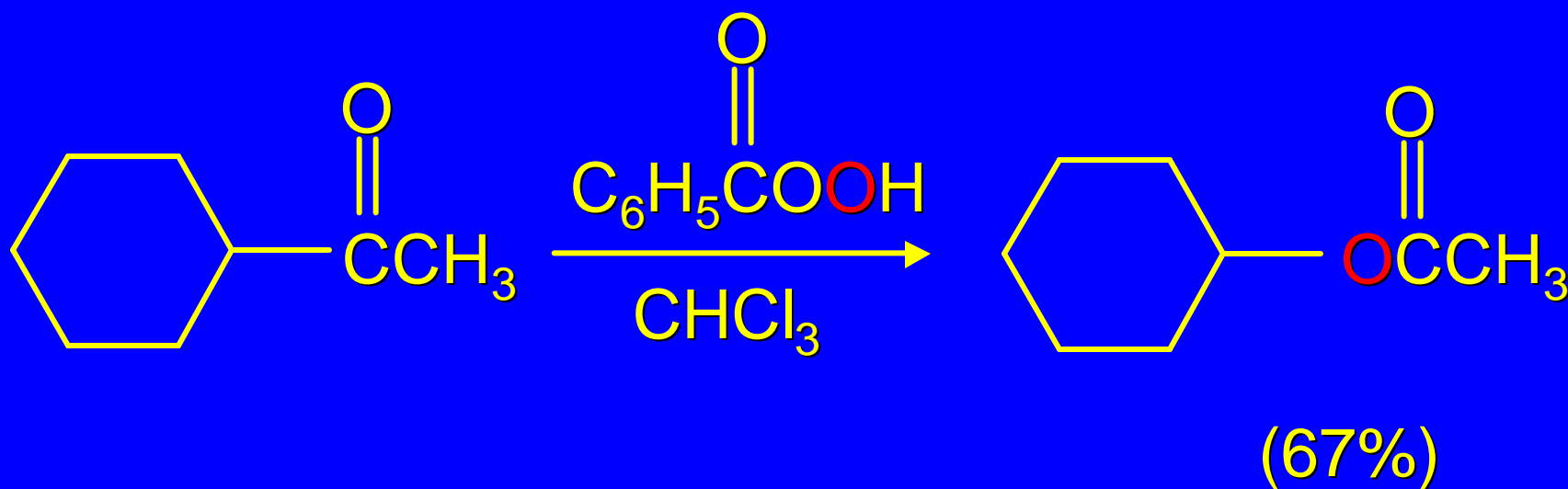
General



Ketone

Ester

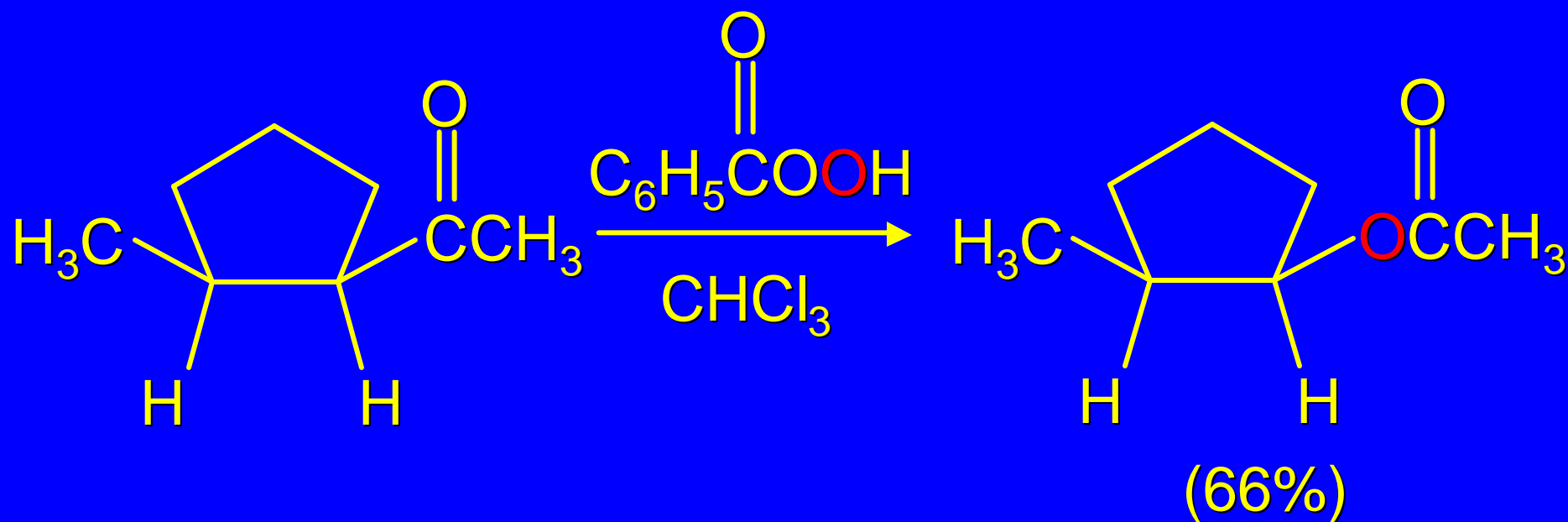
Example



Oxygen insertion occurs between carbonyl carbon and larger group.

Methyl ketones give acetate esters.

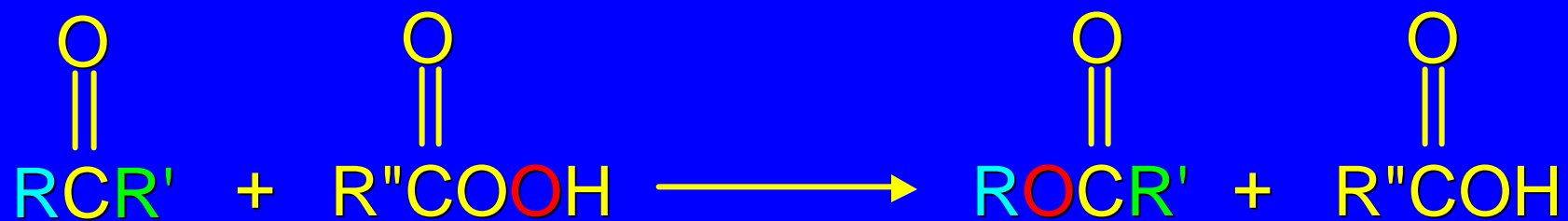
Stereochemistry



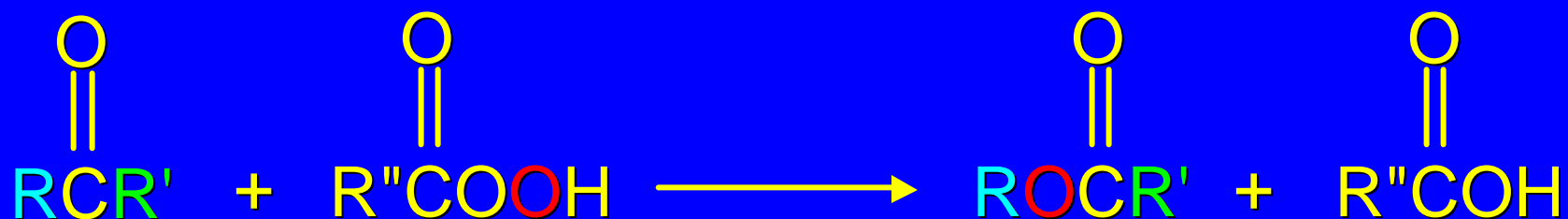
Reaction is stereospecific.

Oxygen insertion occurs with retention of configuration.

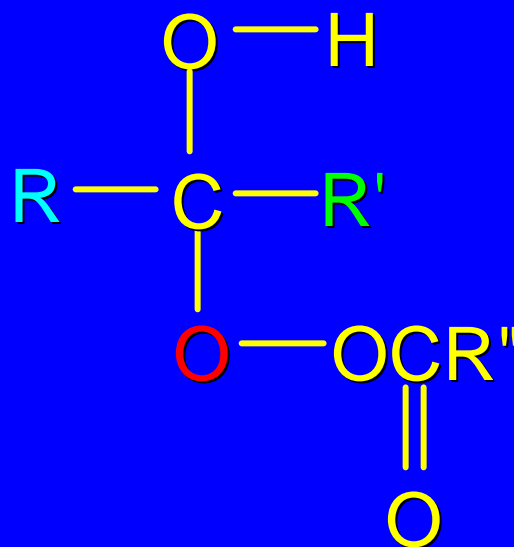
Mechanism



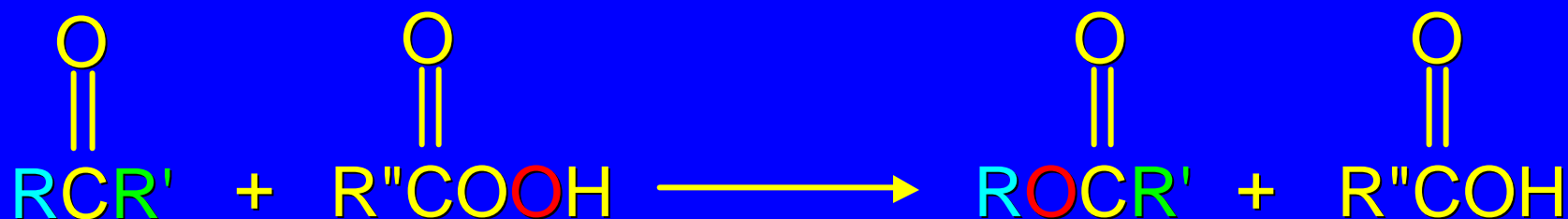
Mechanism



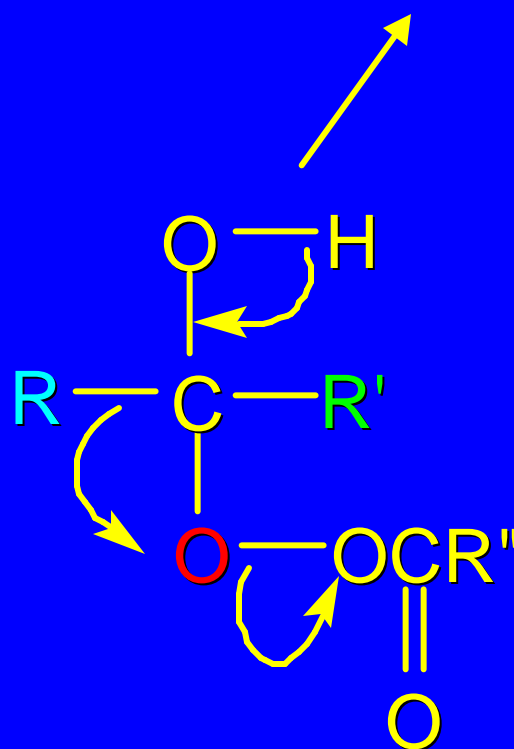
First step is nucleophilic addition of peroxy acid to the carbonyl group of the ketone.



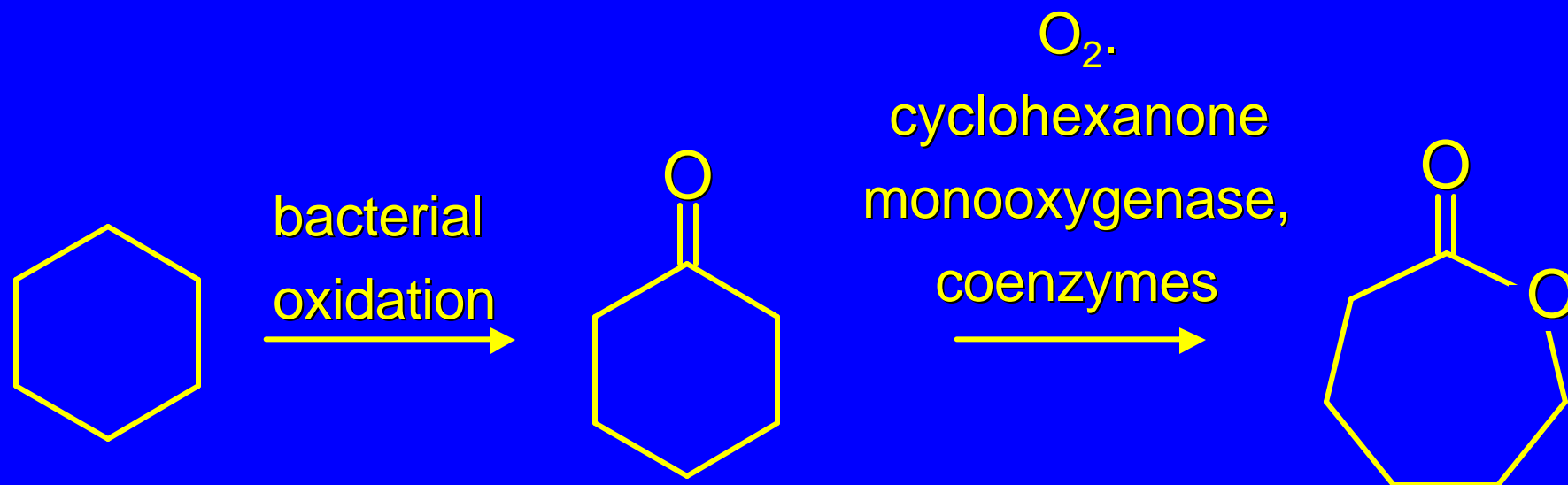
Mechanism



Second step is migration of group **R** from carbon to oxygen. The weak **O—O** bond breaks in this step.



Biological Baeyer-Villiger Oxidation



Certain bacteria use hydrocarbons as a source of carbon. Oxidation proceeds via ketones, which then undergo oxidation of the Baeyer-Villiger type.