19.13
Reactions of Carboxylic Acids: A Review and a Preview

Reactions of Carboxylic Acids

Reactions already discussed

Acidity (Sections 19.4-19.9)

Reduction with $LiAlH_4$ (Section 15.3)

Esterification (Section 15.8)

Reaction with Thionyl Chloride (Section 12.7)

Reactions of Carboxylic Acids

New reactions in this chapter

α–Halogenation

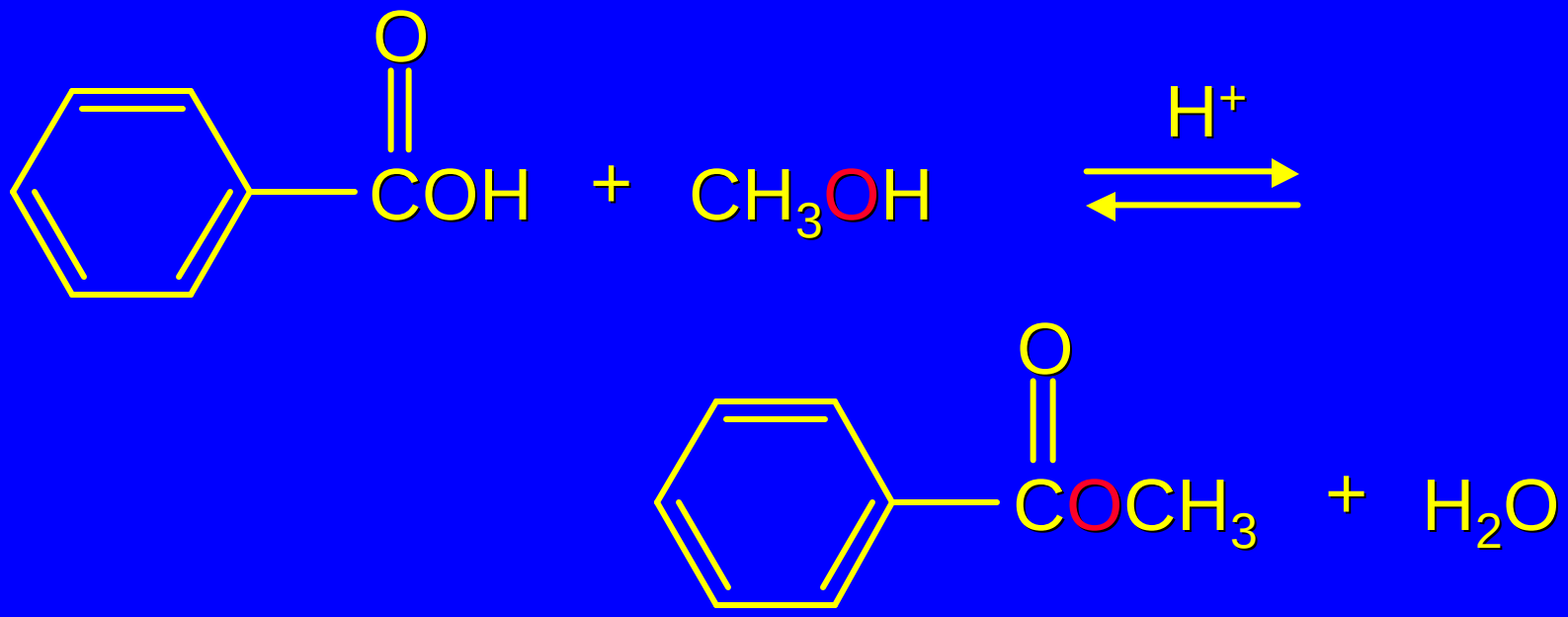
Decarboxylation

But first we revisit acid-catalyzed esterification to examine its mechanism.

19.14
Mechanism of Acid-Catalyzed Esterification

Acid-catalyzed Esterification

(also called Fischer esterification)



Important fact: the oxygen of the alcohol is incorporated into the ester as shown.

Mechanism of Fischer Esterification

The mechanism involves two stages:

1) formation of tetrahedral intermediate (3 steps)
2) dissociation of tetrahedral intermediate (3 steps)

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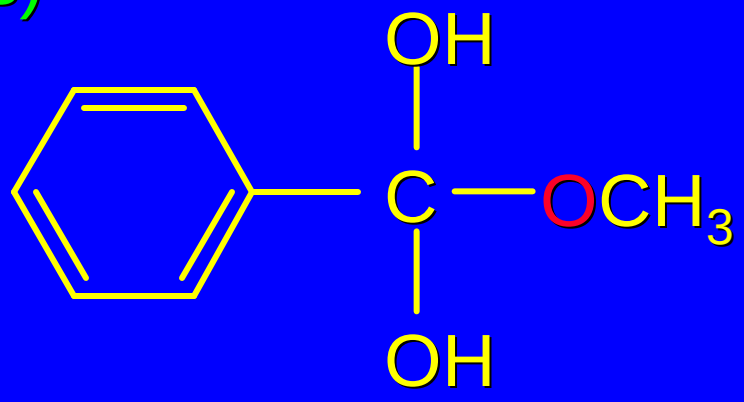
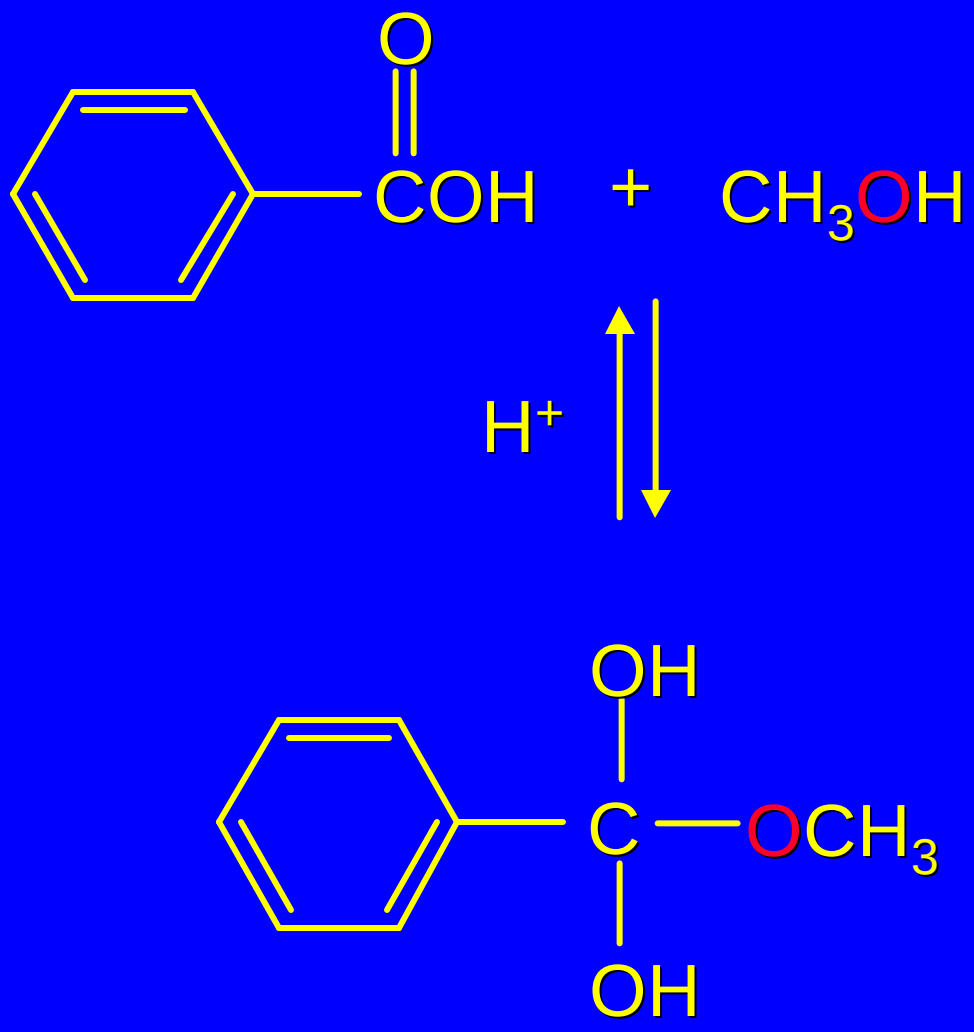


tetrahedral intermediate in esterification of benzoic acid with methanol

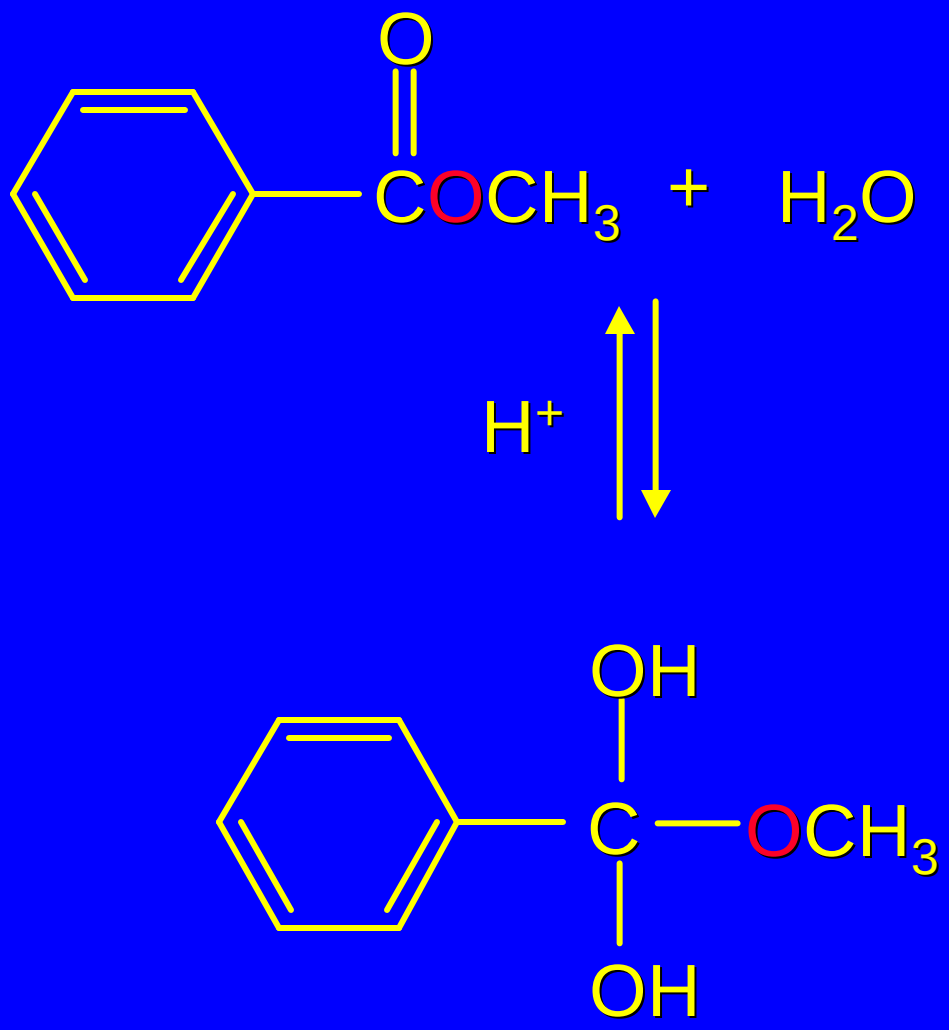
First stage: formation of tetrahedral intermediate



methanol adds to the carbonyl group of the carboxylic acid

the tetrahedral intermediate is analogous to a hemiacetal

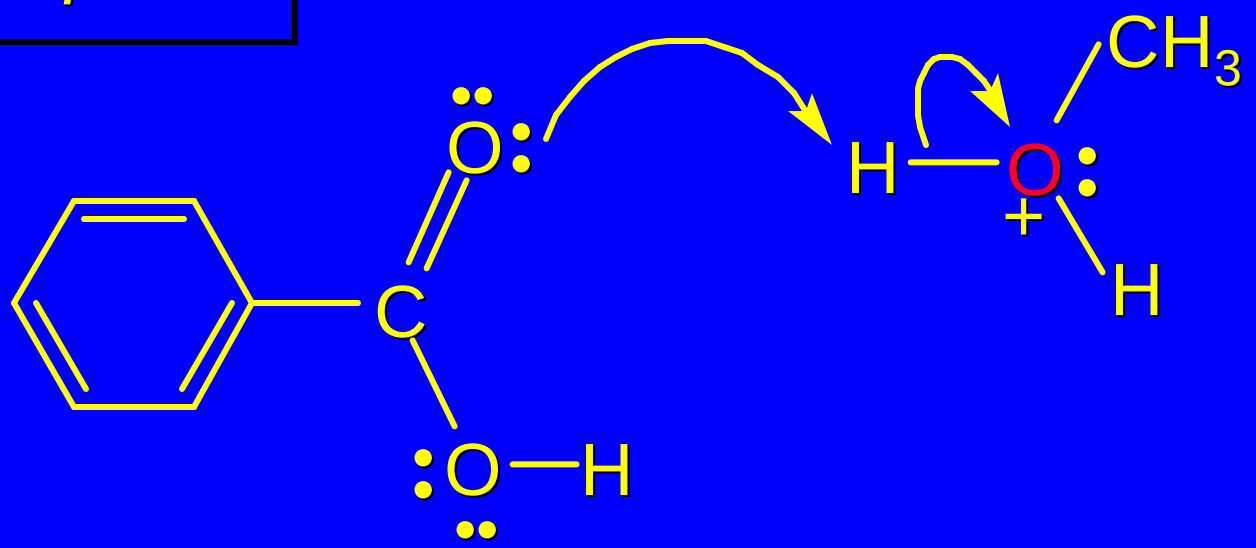
Second stage: conversion of tetrahedral intermediate to ester



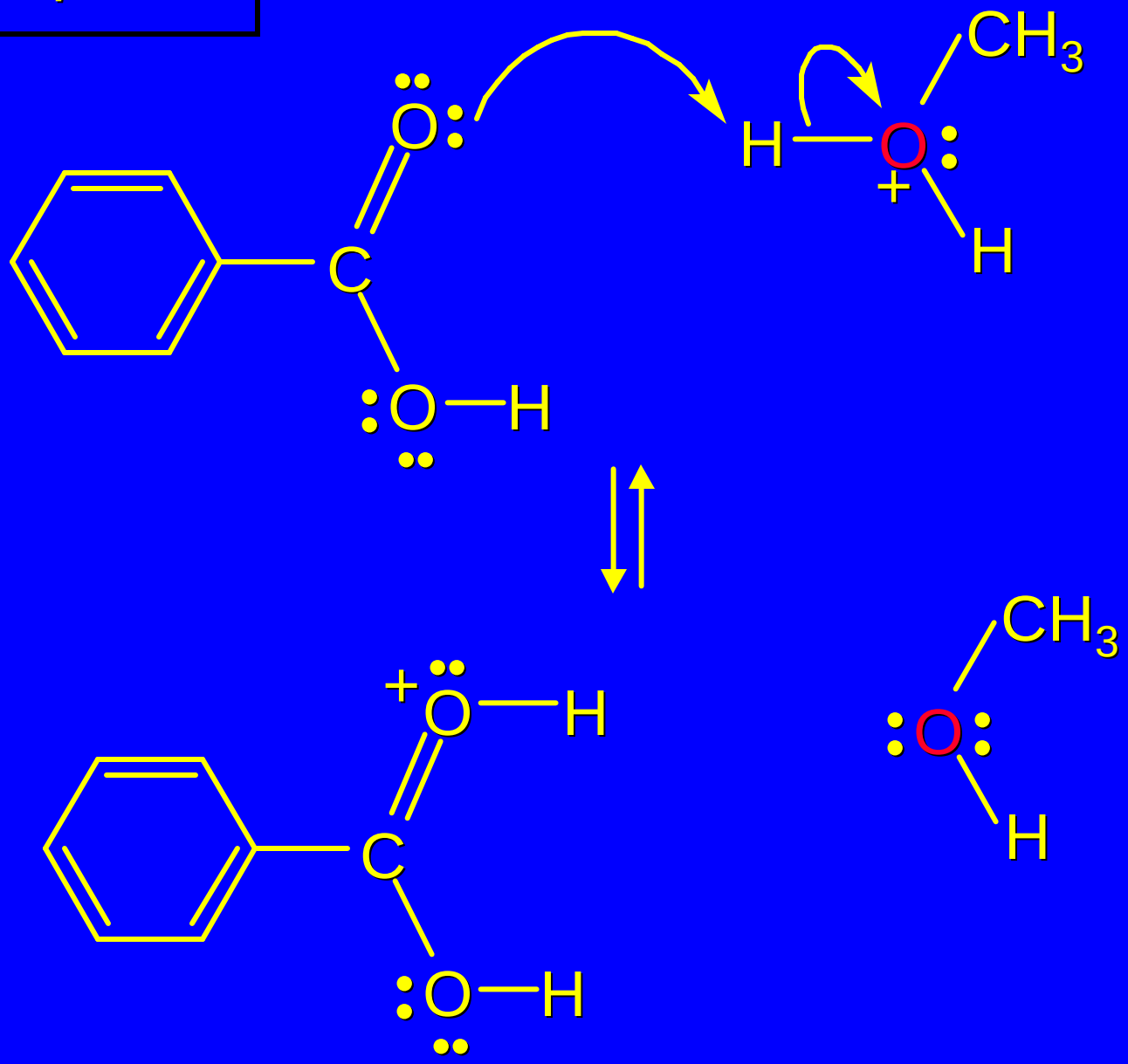
this stage corresponds to an acid-catalyzed dehydration

Mechanism of formation
of
tetrahedral intermediate

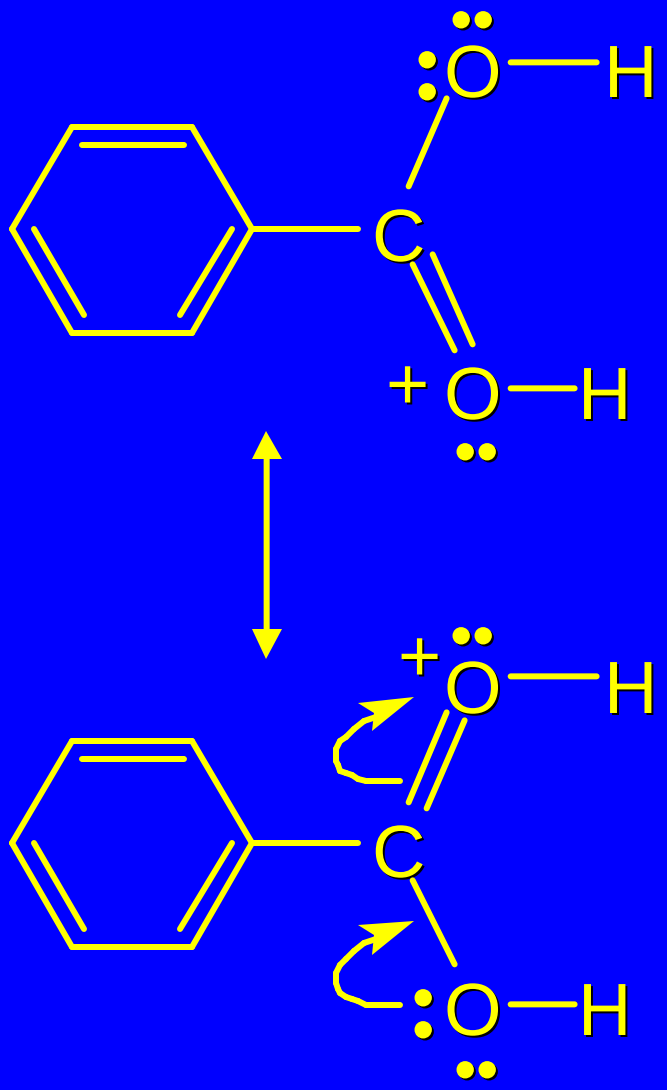
Step 1



Step 1

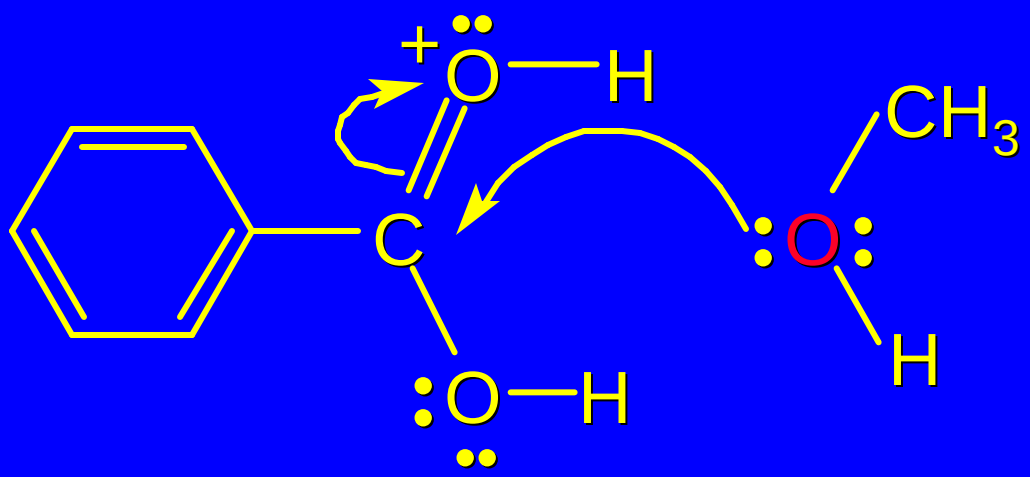


Step 1



carbonyl oxygen is protonated because cation produced is stabilized by electron delocalization (resonance)

Step 2



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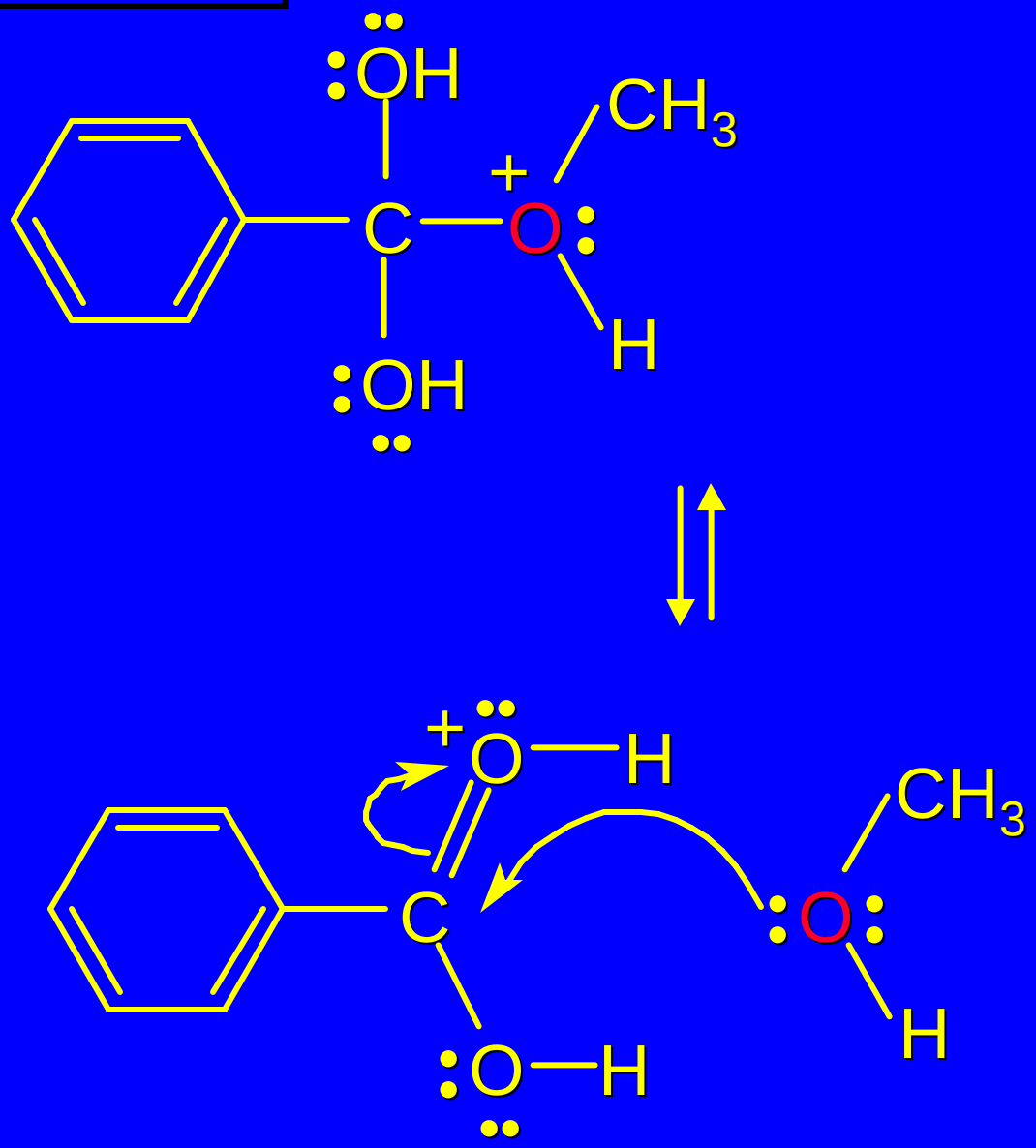
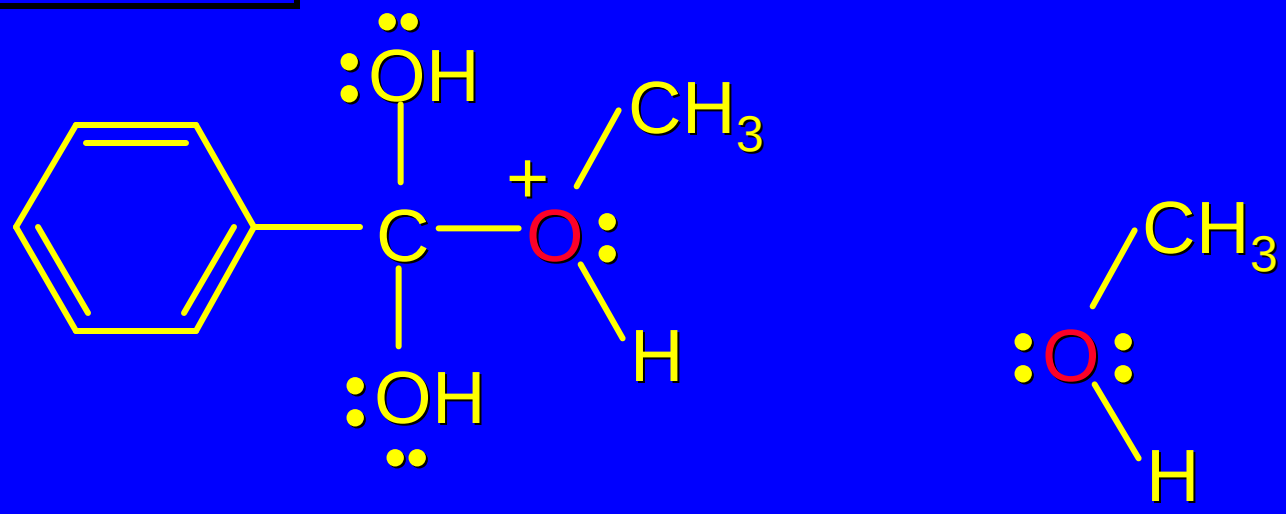


Step 3



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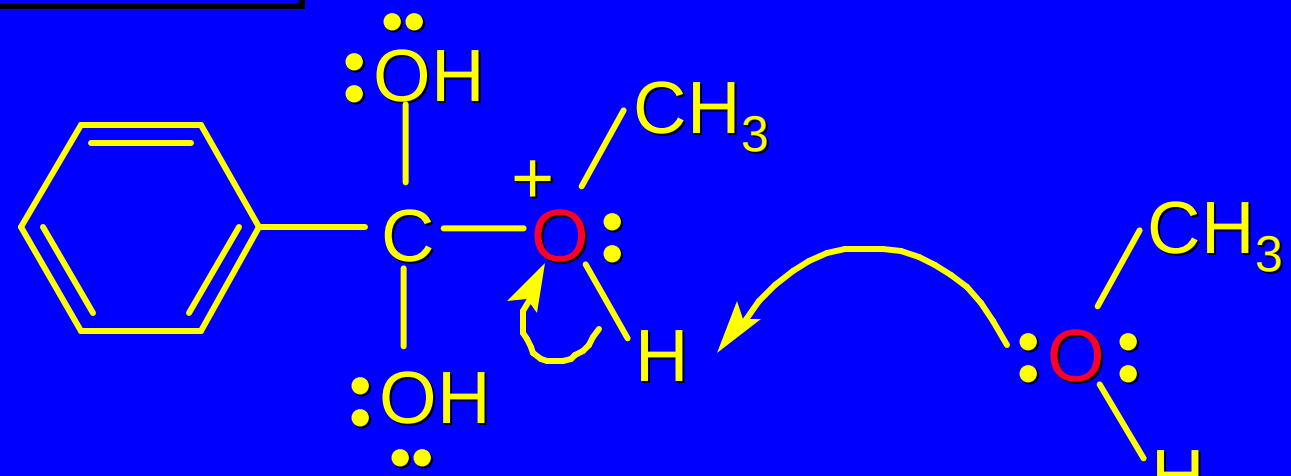
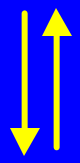
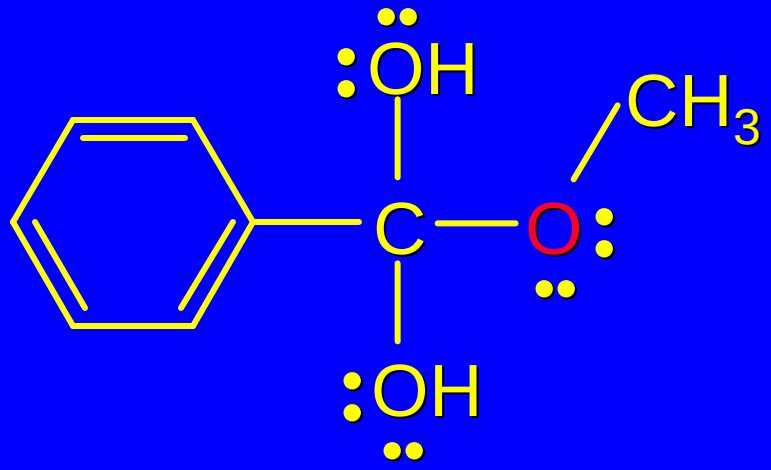
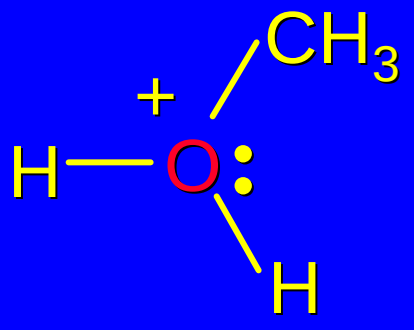


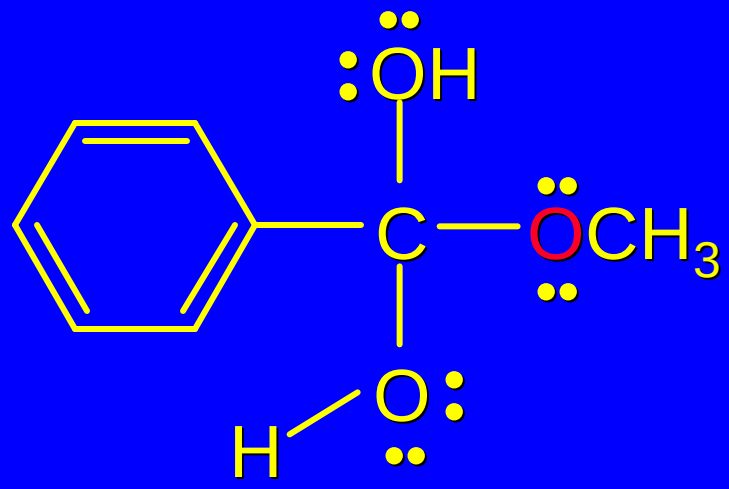




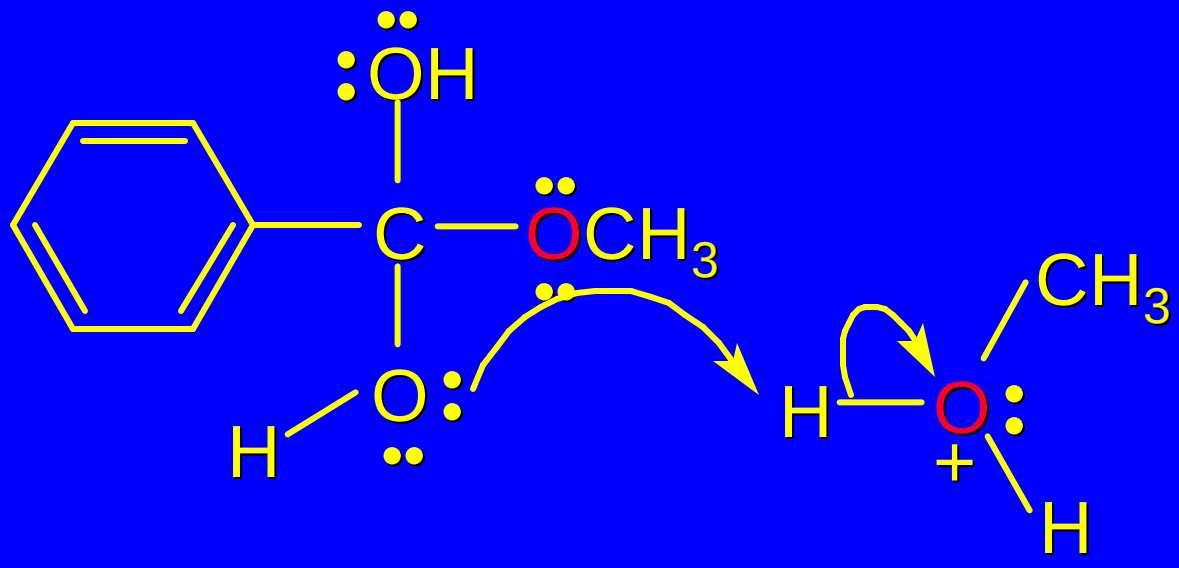


Tetrahedral intermediate
to
ester stage

Step 4



Step 4



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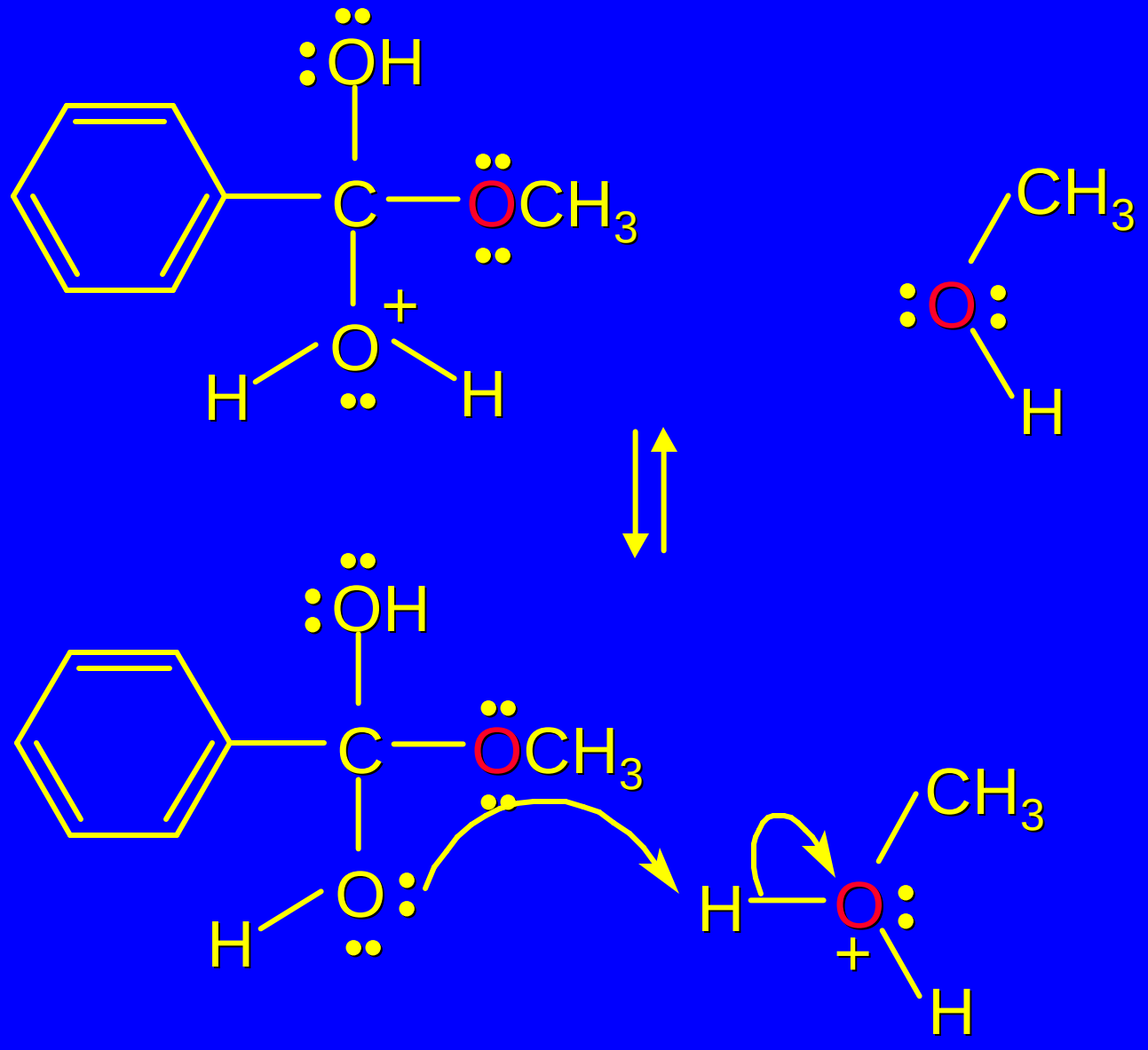
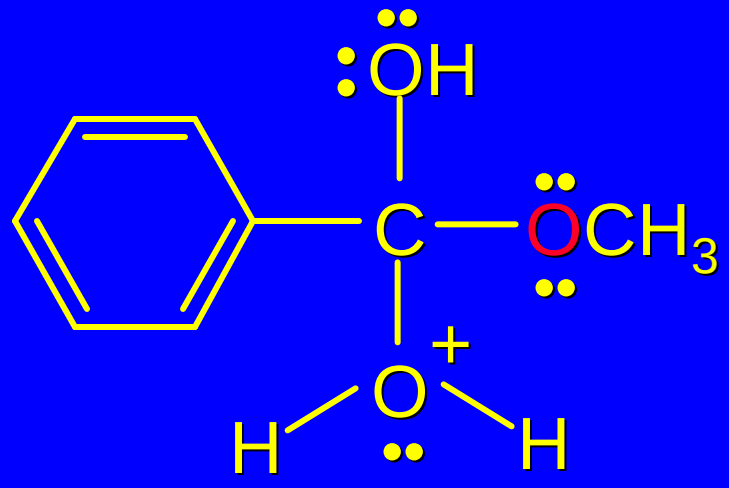


Step 5



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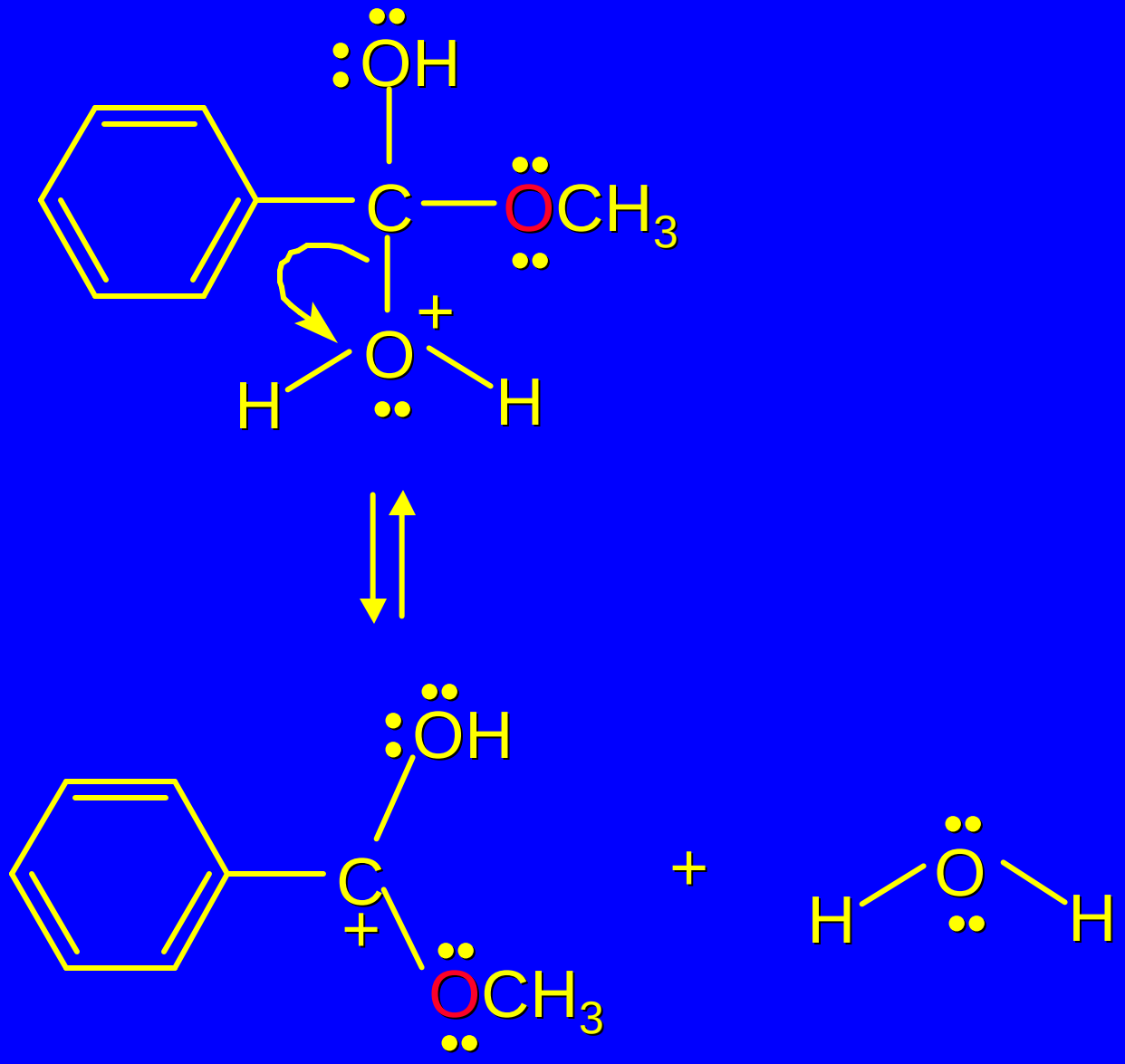

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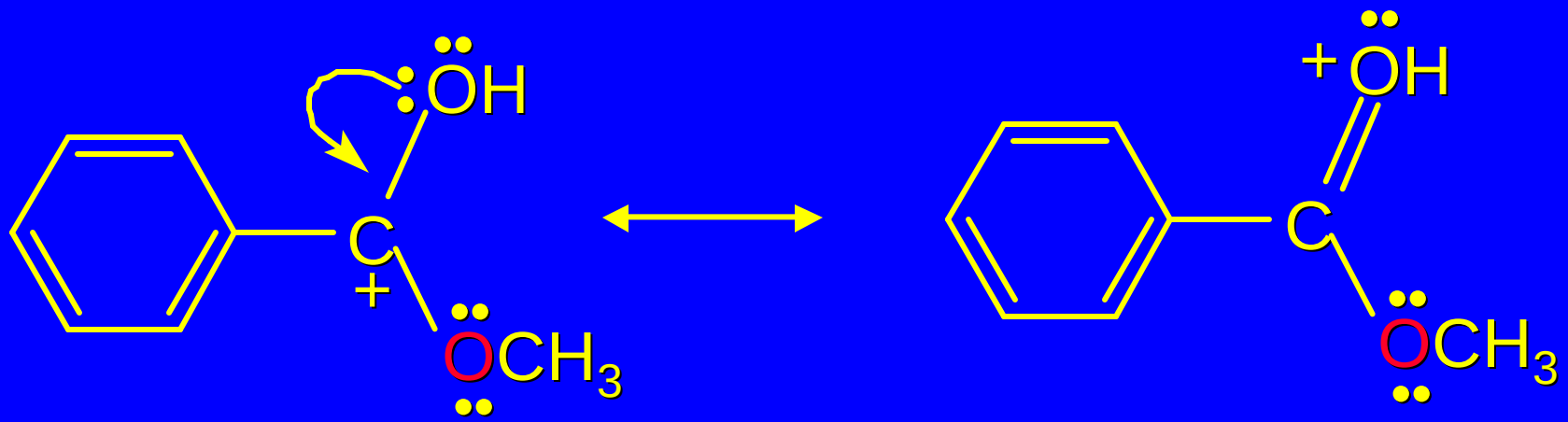

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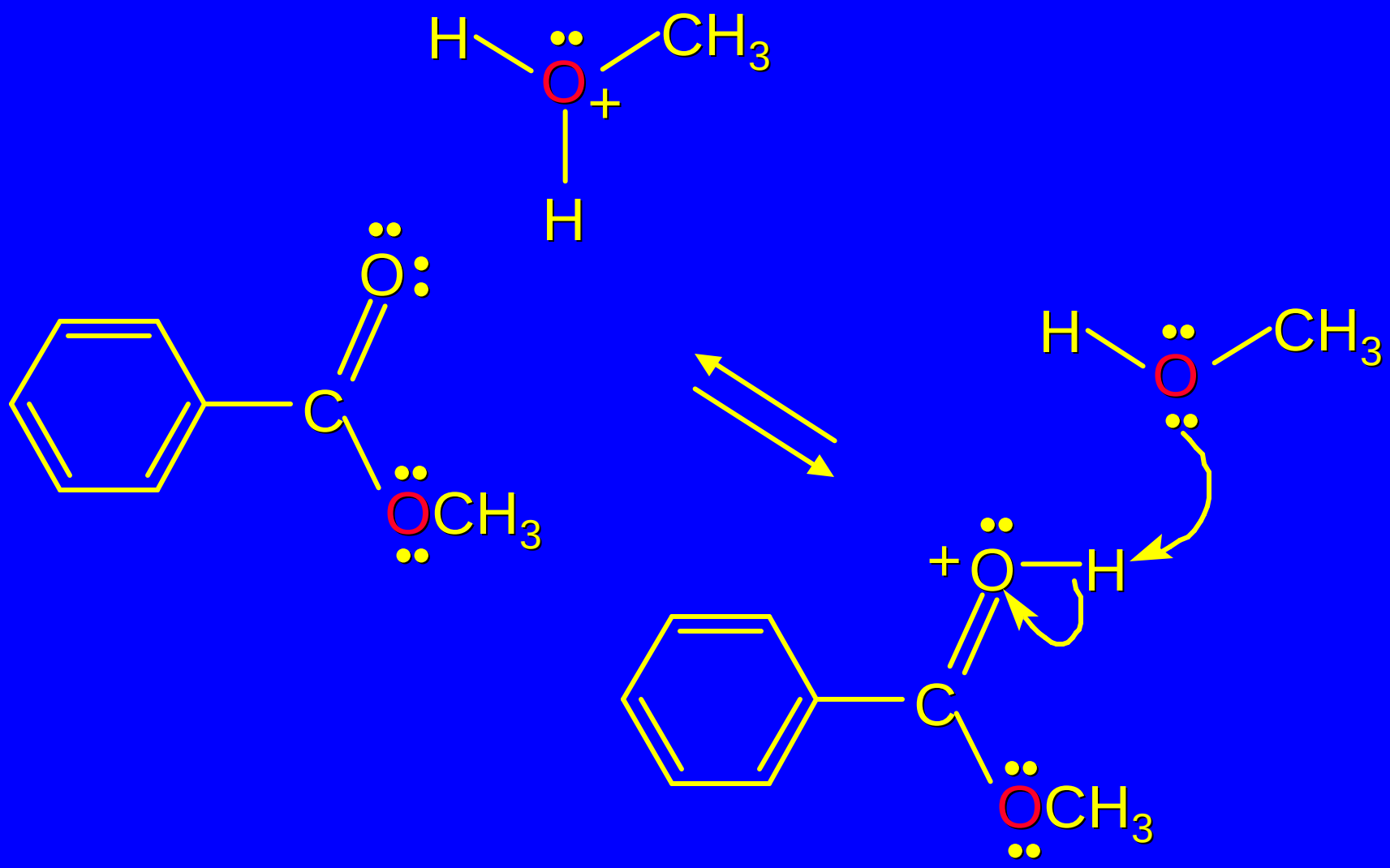


Key Features of Mechanism

Activation of carbonyl group by protonation of carbonyl oxygen

Nucleophilic addition of alcohol to carbonyl group forms tetrahedral intermediate

Elimination of water from tetrahedral intermediate restores carbonyl group

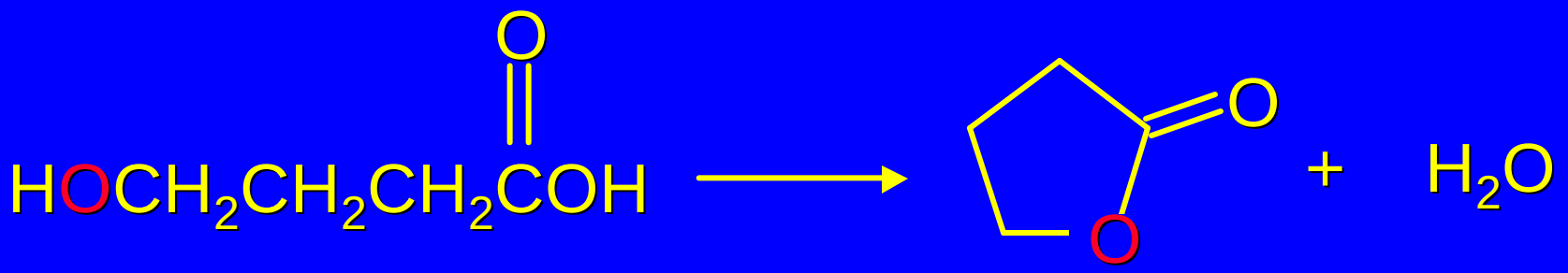
19.15
Intramolecular Ester Formation: Lactones

Lactones

Lactones are cyclic esters

Formed by intramolecular esterification in a compound that contains a hydroxyl group and a carboxylic acid function

Examples

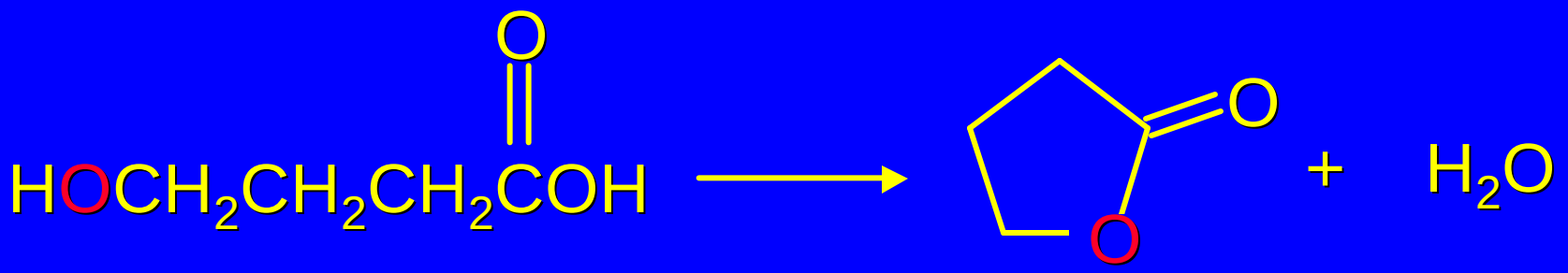


4-hydroxybutanoic acid 4-butanolide

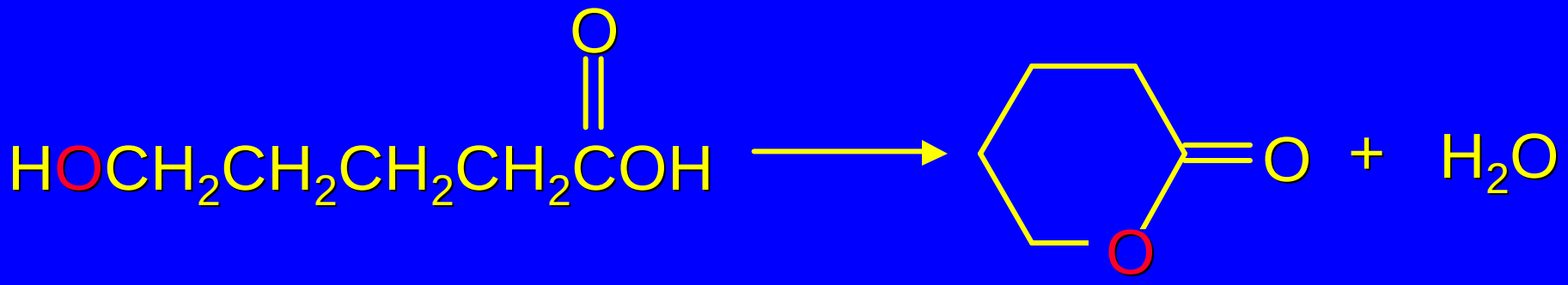
IUPAC nomenclature: replace the *-oic acid* ending of the carboxylic acid by *-olide*

identify the oxygenated carbon by number

Examples

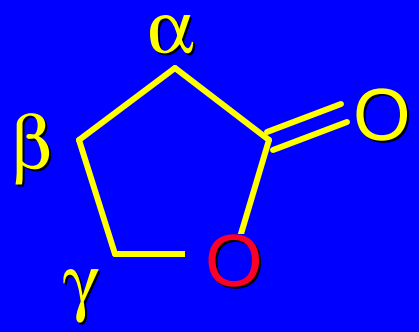


4-hydroxybutanoic acid 4-butanolide

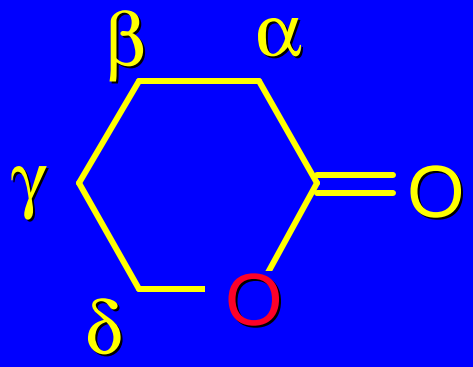


5-hydroxypentanoic acid 5-pentanolide

Common names



γ-butyrolactone



δ-valerolactone

Ring size is designated by Greek letter corresponding to oxygenated carbon

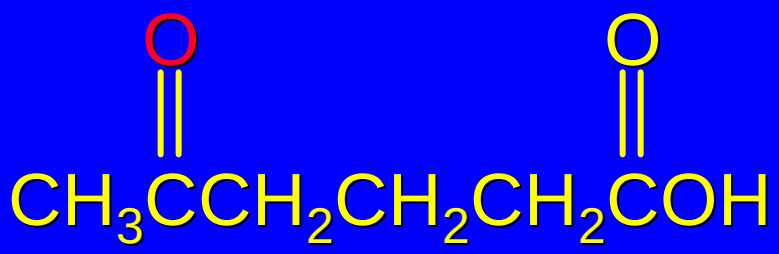
A γ lactone has a five-membered ring

A δ lactone has a six-membered ring

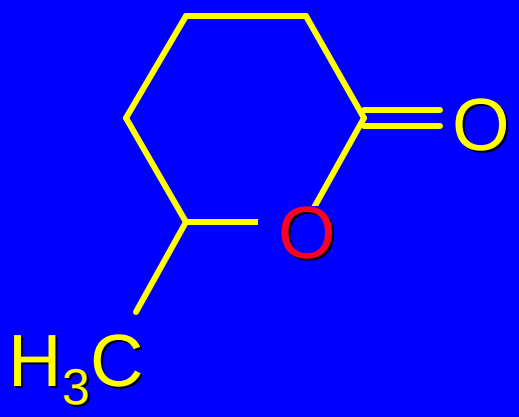
Lactones

Reactions designed to give hydroxy acids often yield the corresponding lactone, especially if the resulting ring is 5- or 6-membered.

Example

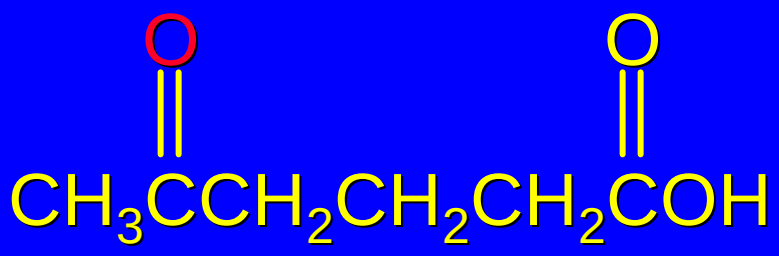


1. $NaBH_4$
2. H_2O, H^+



5-hexanolide (78%)

Example



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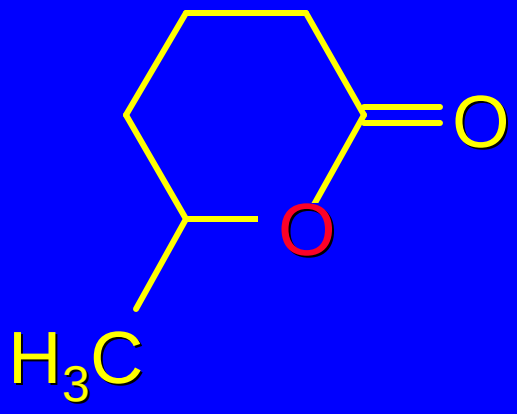

5-hexanolide (78%)

via: