15.6
Reactions of Alcohols:
A Review and a Preview

Table 15.2 Review of Reactions of Alcohols

reaction with hydrogen halides

reaction with thionyl chloride

reaction with phosphorous tribromide

acid-catalyzed dehydration

conversion to *p*-toluenesulfonate esters

New Reactions of Alcohols in This Chapter

conversion to ethers

esterification

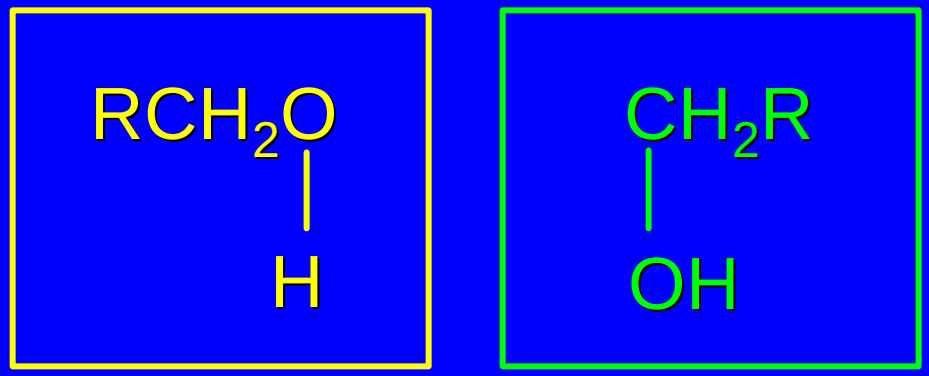
esters of inorganic acids

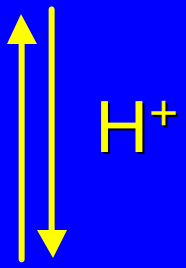
oxidation

cleavage of vicinal diols

15.7
Conversion of Alcohols to Ethers

Conversion of Alcohols to Ethers





$RCH_2O—CH_2R + H—OH$

acid-catalyzed

referred to as a "condensation"

equilibrium; most favorable for primary alcohols

Example

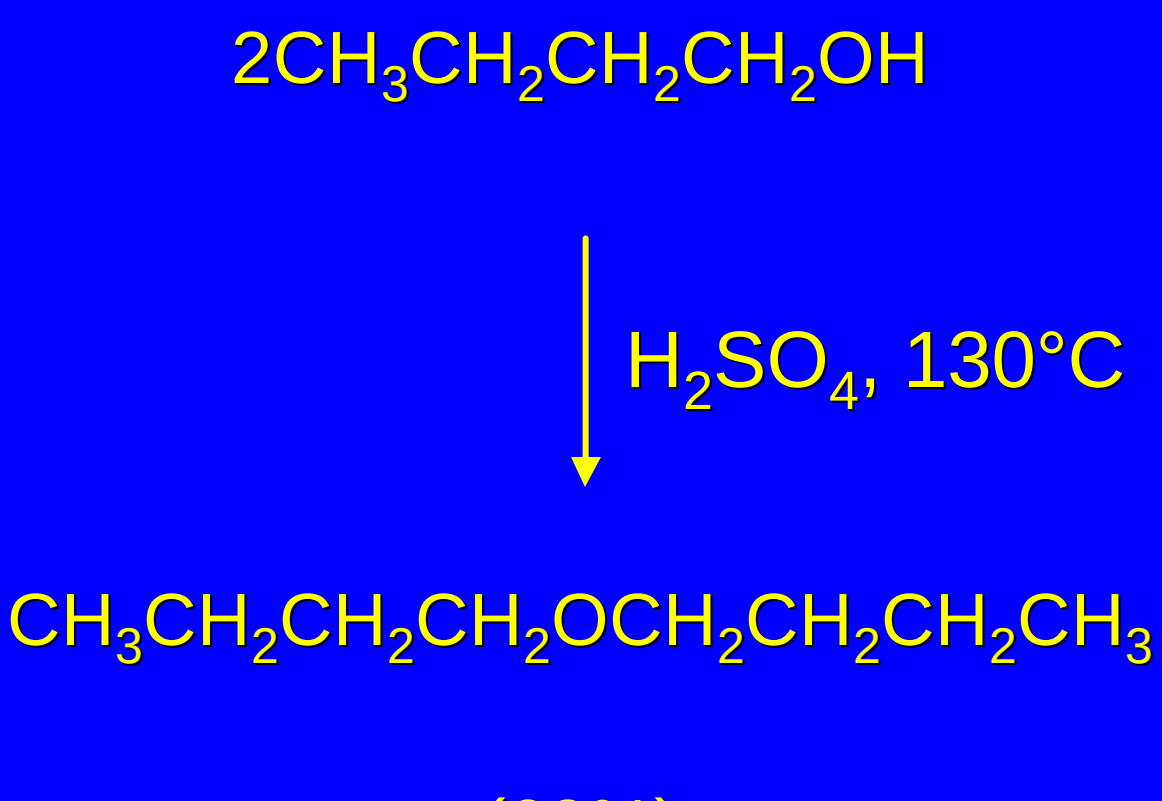

2CH3CH2CH2CH2OH
H2SO4, 130°C
CH3CH2CH2CH2OCH2CH2CH2CH3
(60%)

Figure 15.2 Mechanism of Formation of Diethyl Ether

Step 1:

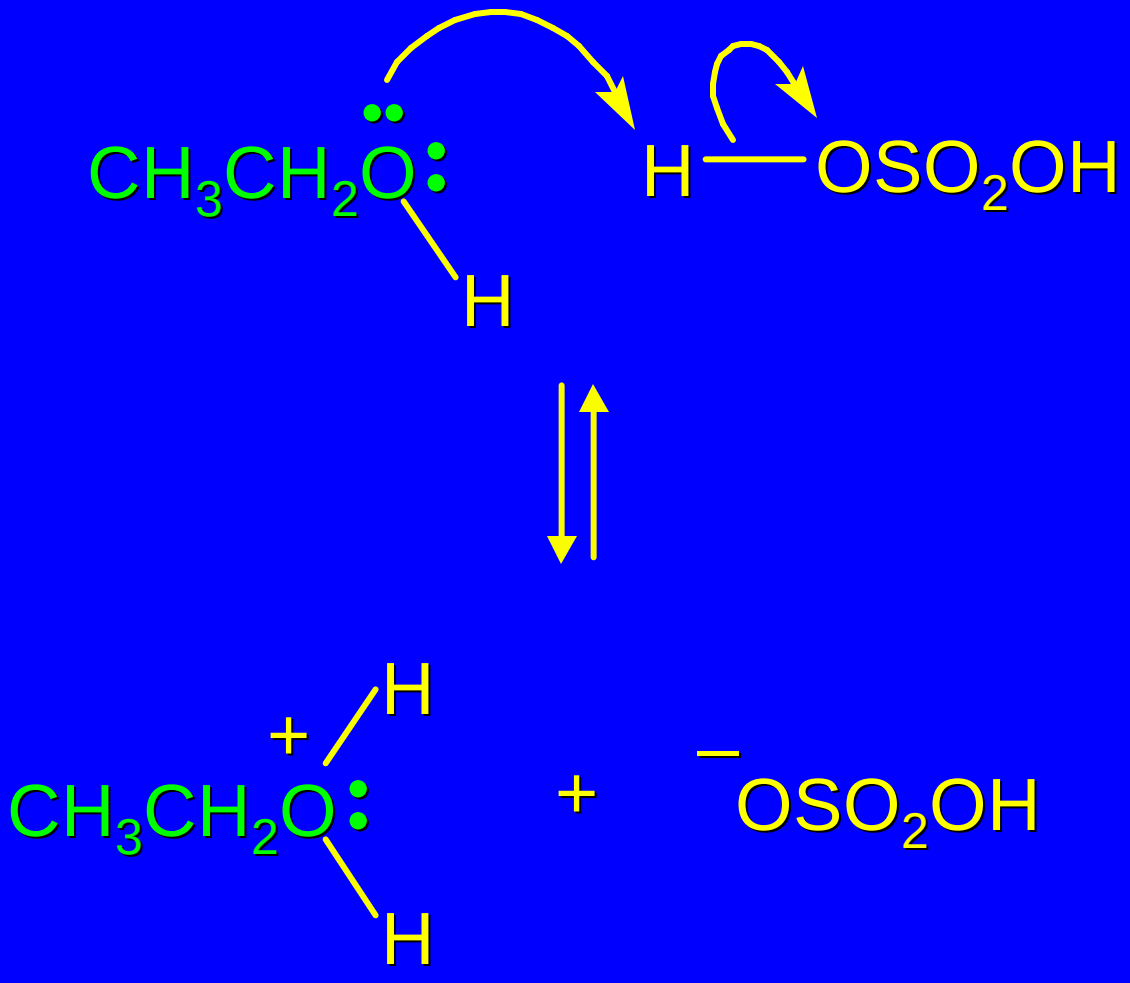


Figure 15.2 Mechanism of Formation of Diethyl Ether

Step 2:

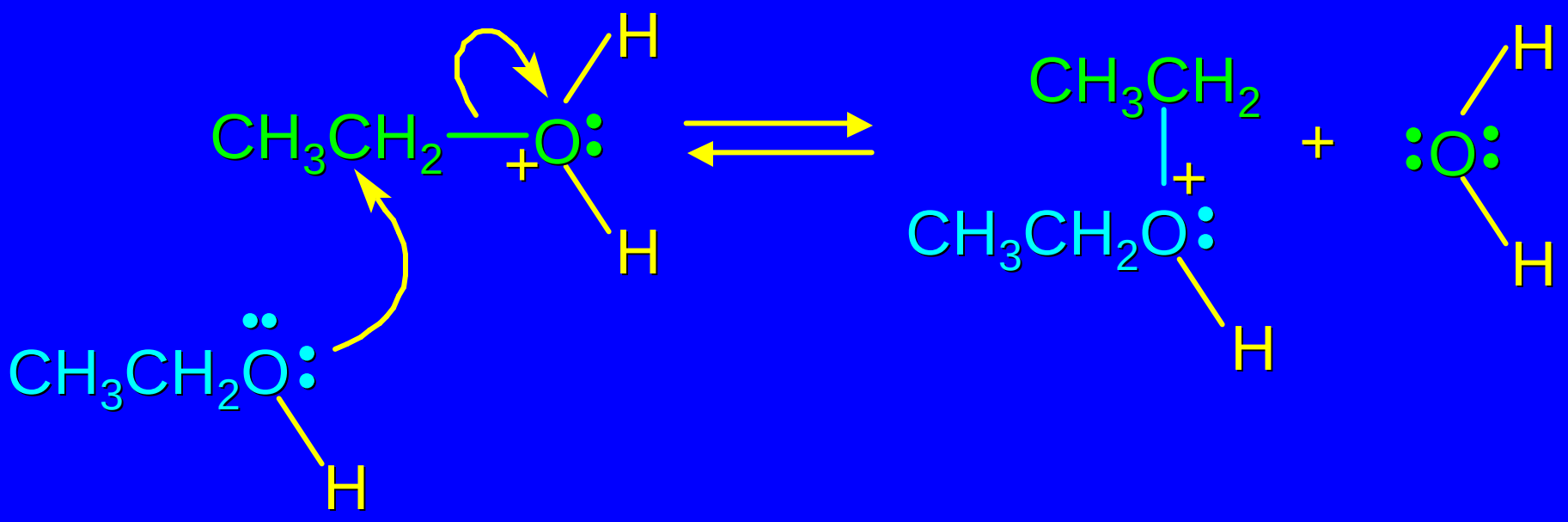
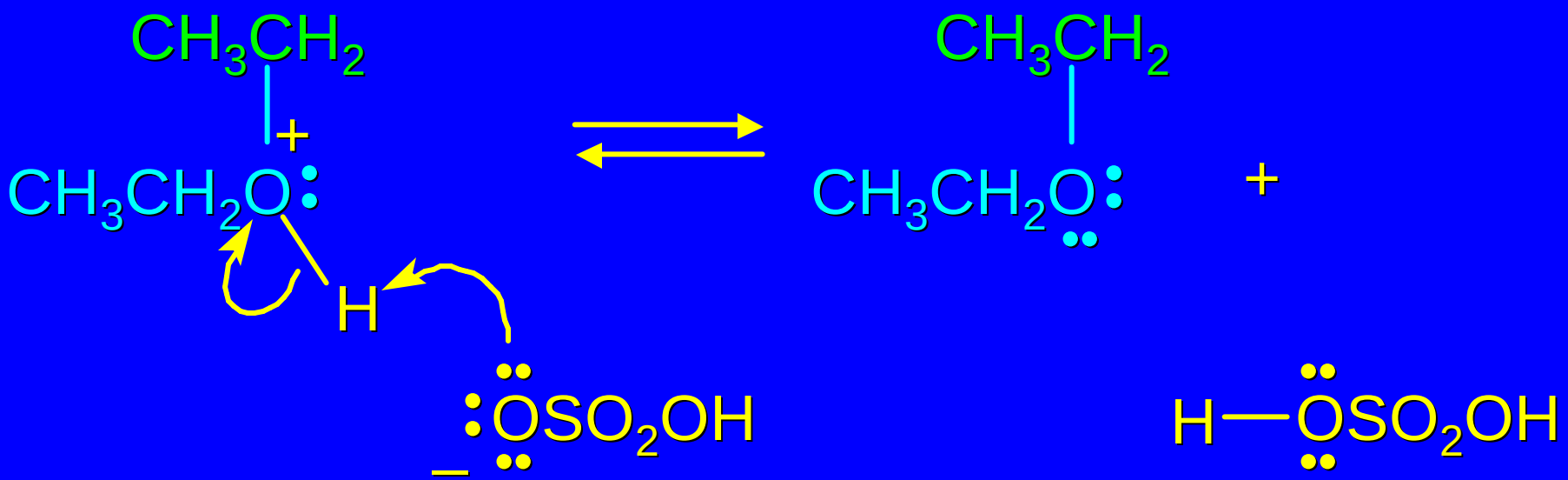


Figure 15.2 Mechanism of Formation of Diethyl Ether

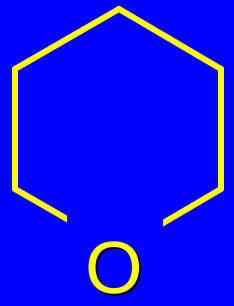
Step 3:



Intramolecular Analog

$HOCH_2CH_2CH_2CH_2CH_2OH$

H_2SO_4, 130°



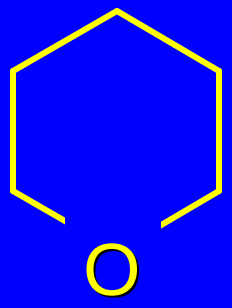
(76%)

reaction normally works well only for 5- and 6-membered rings

Intramolecular Analog

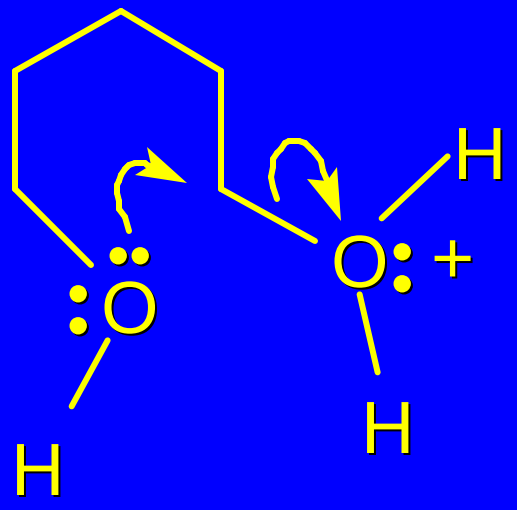
$HOCH_2CH_2CH_2CH_2CH_2OH$

H_2SO_4, 130°



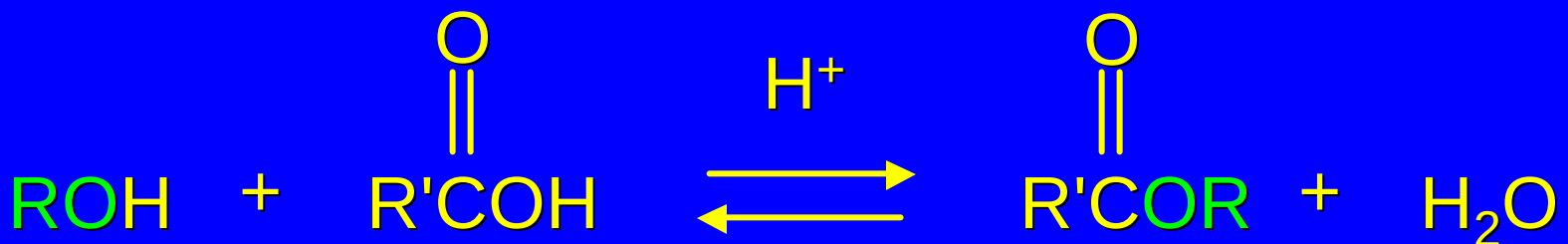
(76%)

via:



15.8
Esterification

Esterification



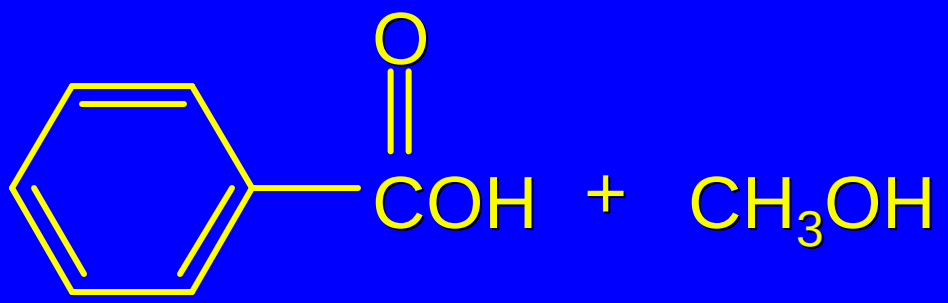
condensation

Fischer esterification

acid catalyzed

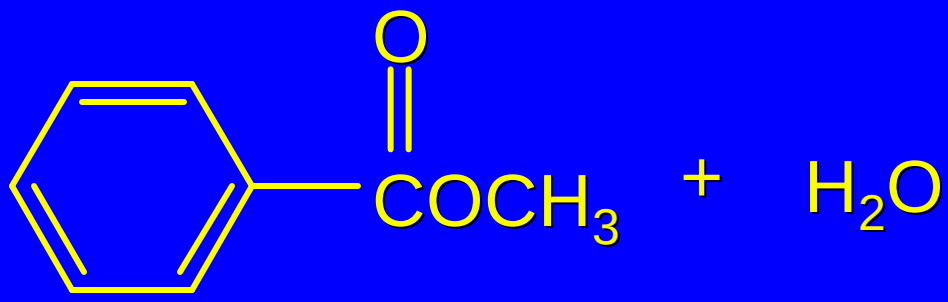
reversible

Example of Fischer Esterification



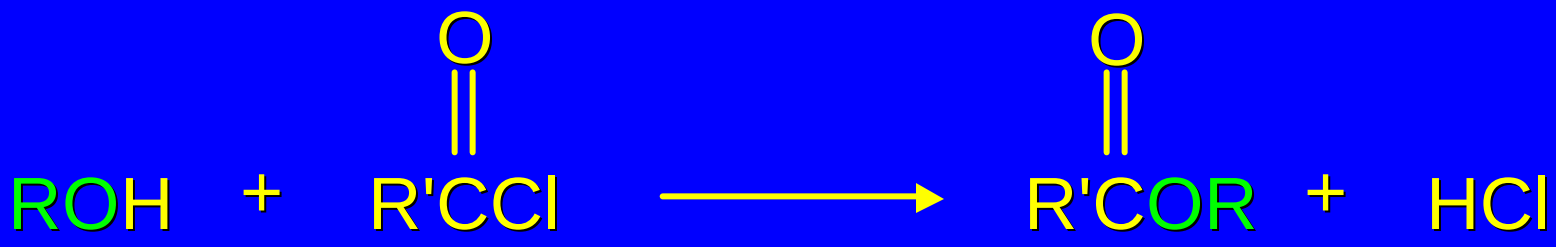
0.1 mol 0.6 mol

H_2SO_4



70% yield based on benzoic acid

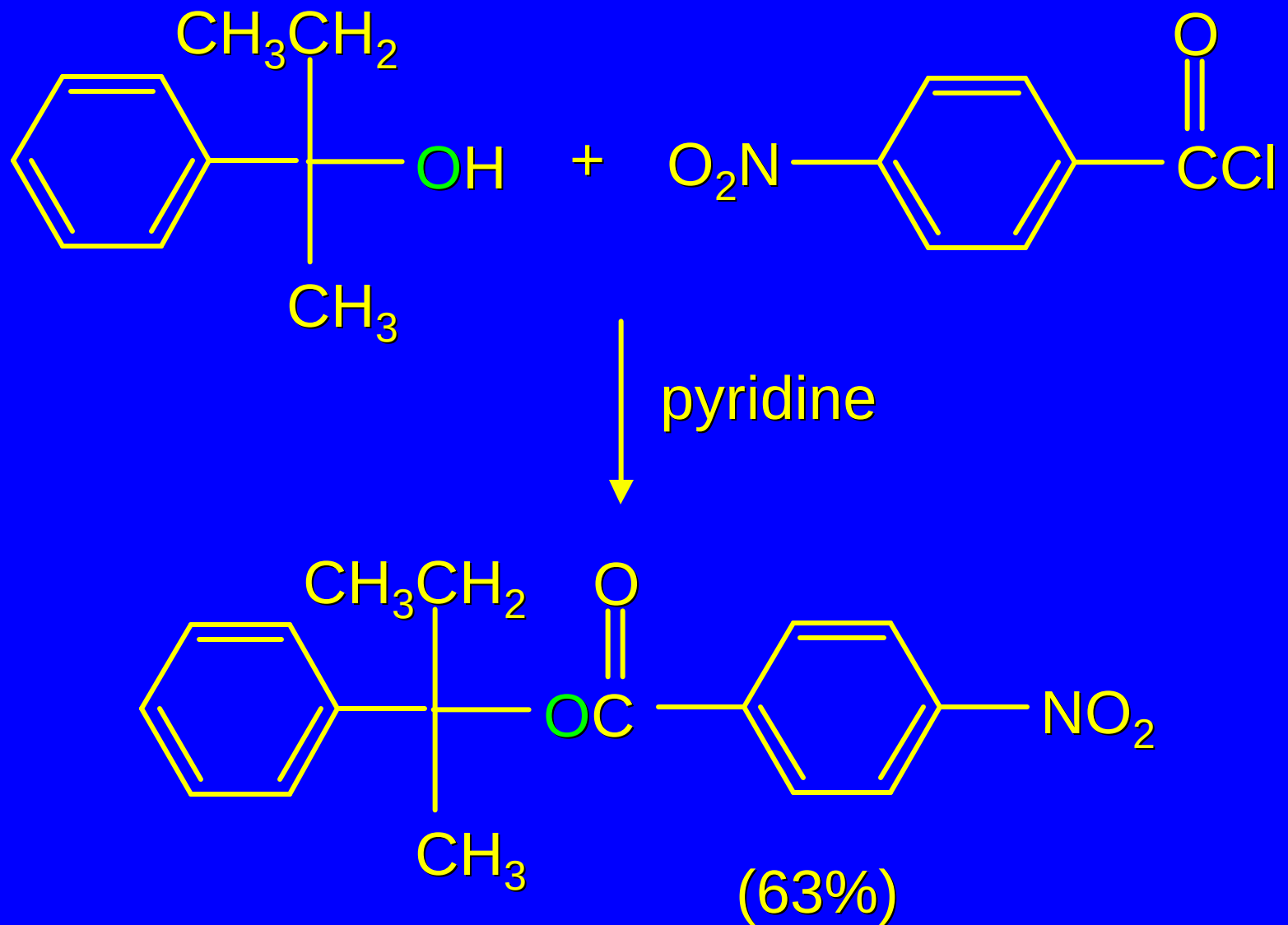
Reaction of Alcohols with Acyl Chlorides



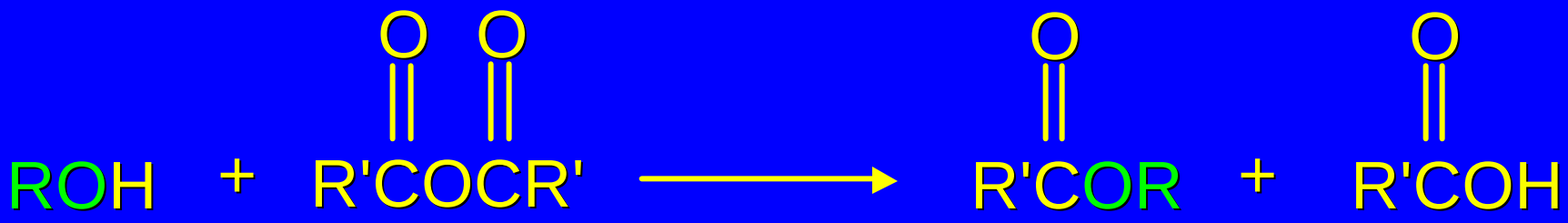
high yields

not reversible when carried out
in presence of pyridine

Example

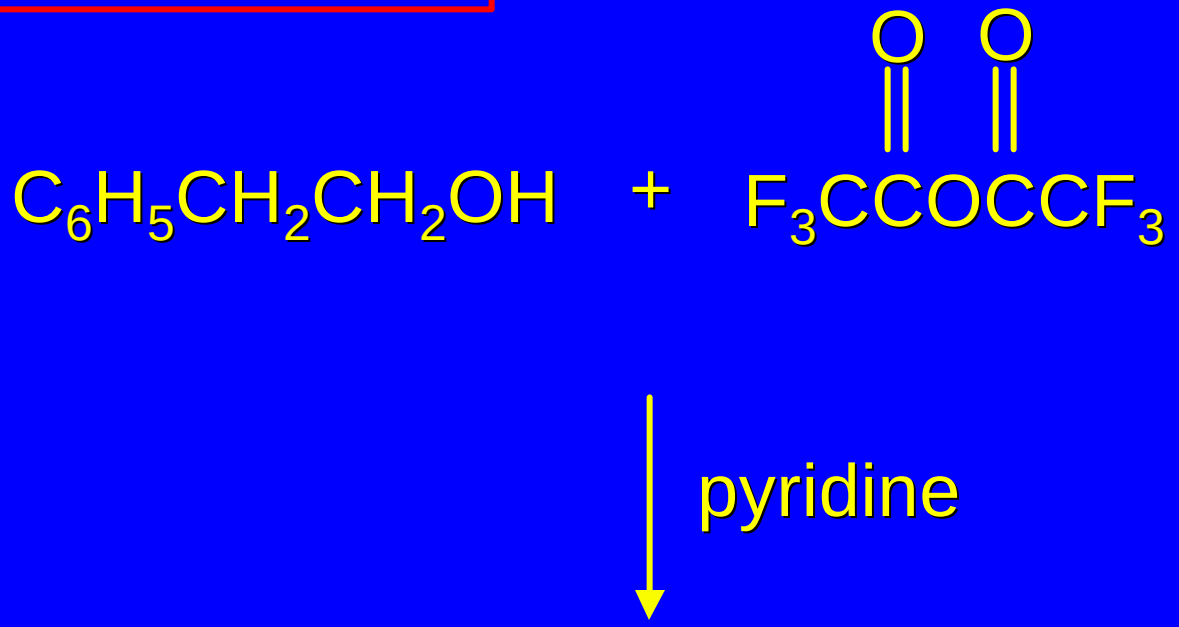


Reaction of Alcohols with Acid Anhydrides



analogous to reaction with acyl chlorides

Example

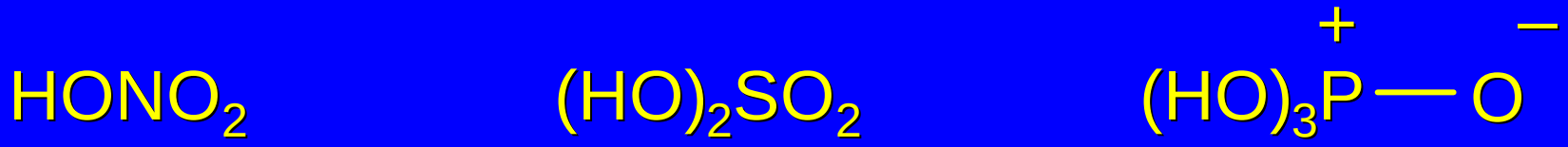


(83%)

15.9
Esters of Inorganic Acids

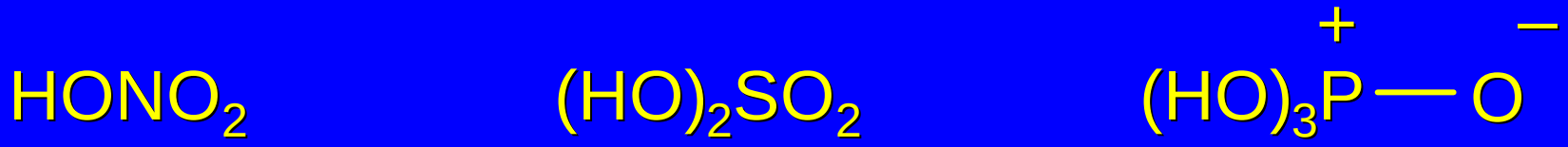
Esters of Inorganic Acids

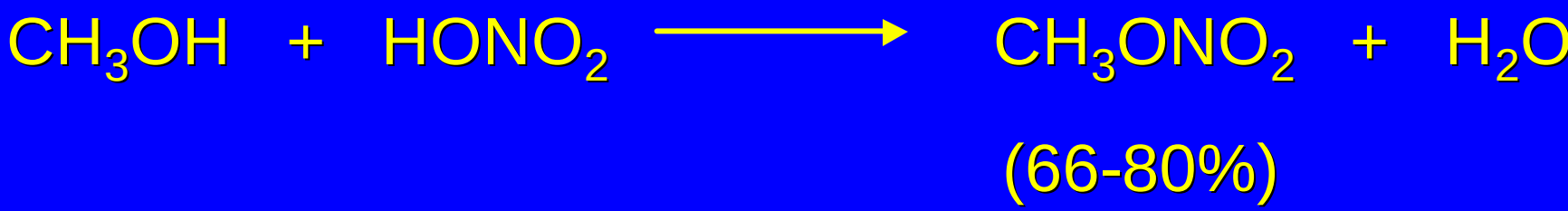
EWG is an electron-withdrawing group



Esters of Inorganic Acids

EWG is an electron-withdrawing group

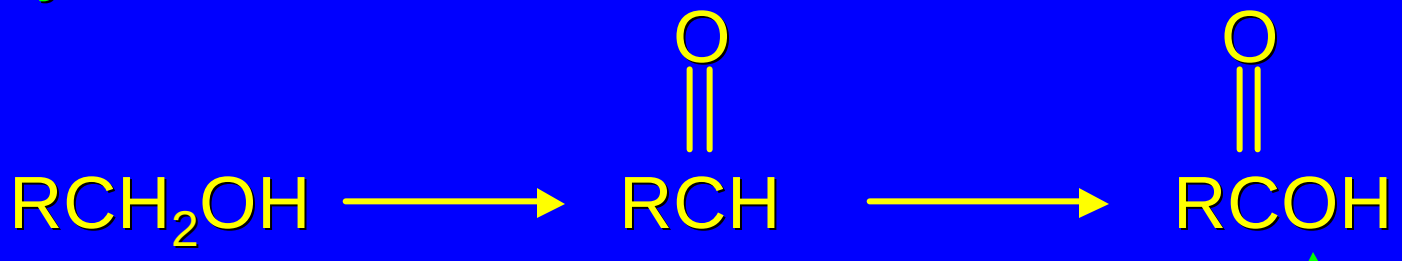




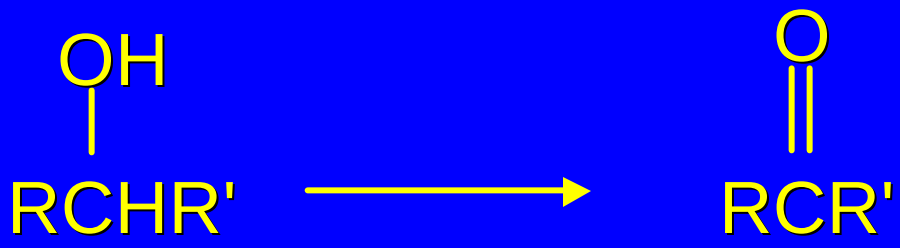
15.10
Oxidation of Alcohols

Oxidation of Alcohols

Primary alcohols



Secondary alcohols



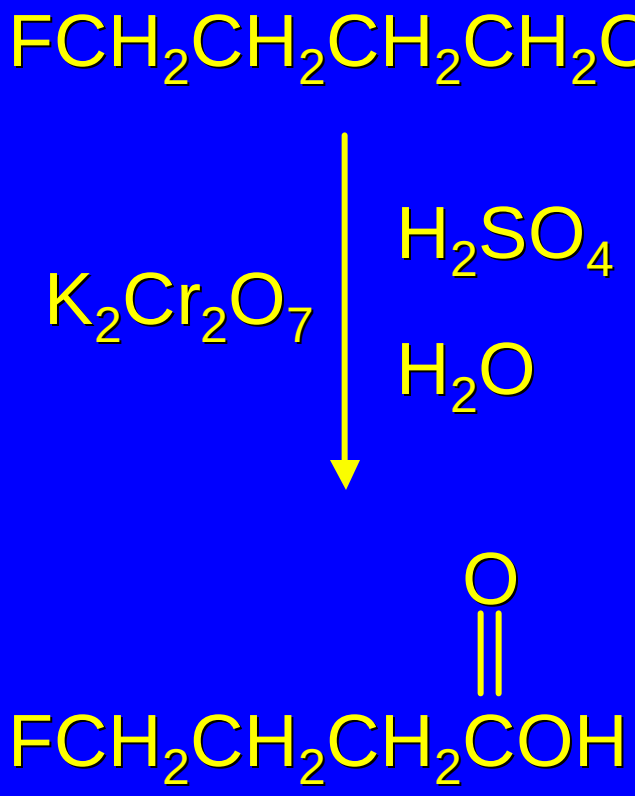
from H_2O

Typical Oxidizing Agents

Aqueous solution

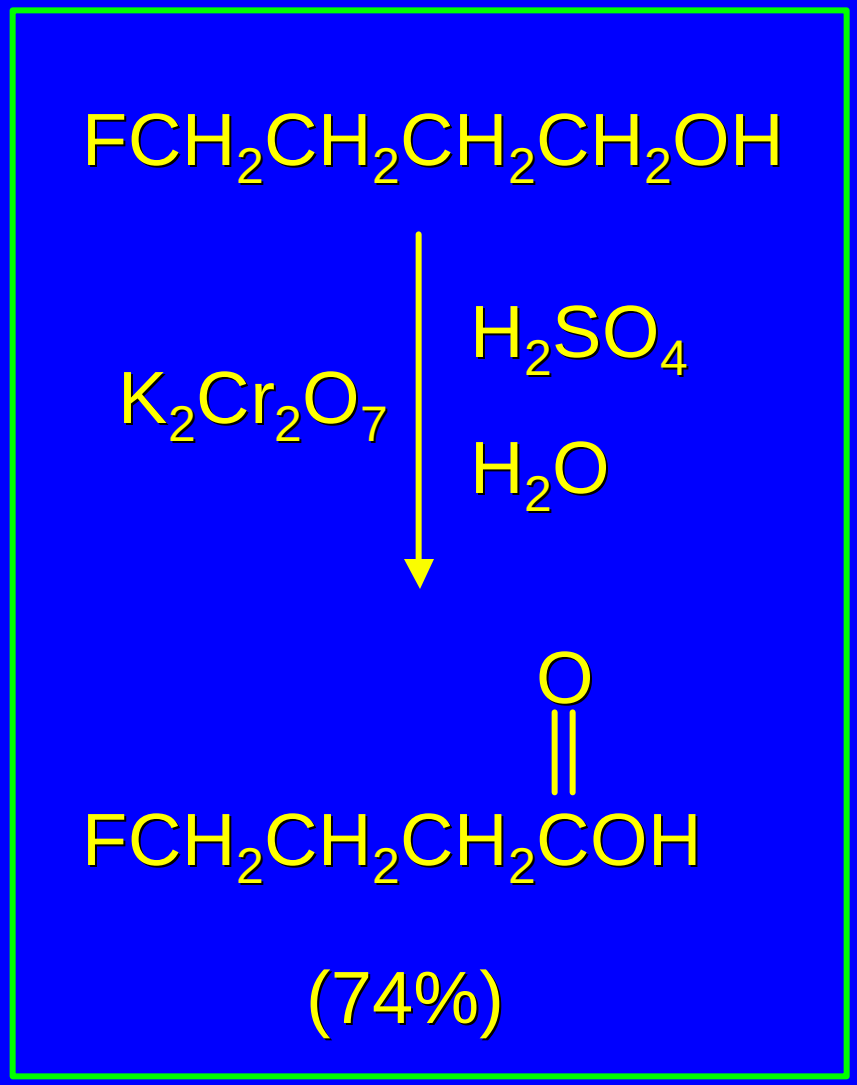
Mn(VII)	Cr(VI)
$KMnO_4$	H_2CrO_4
	$H_2Cr_2O_7$

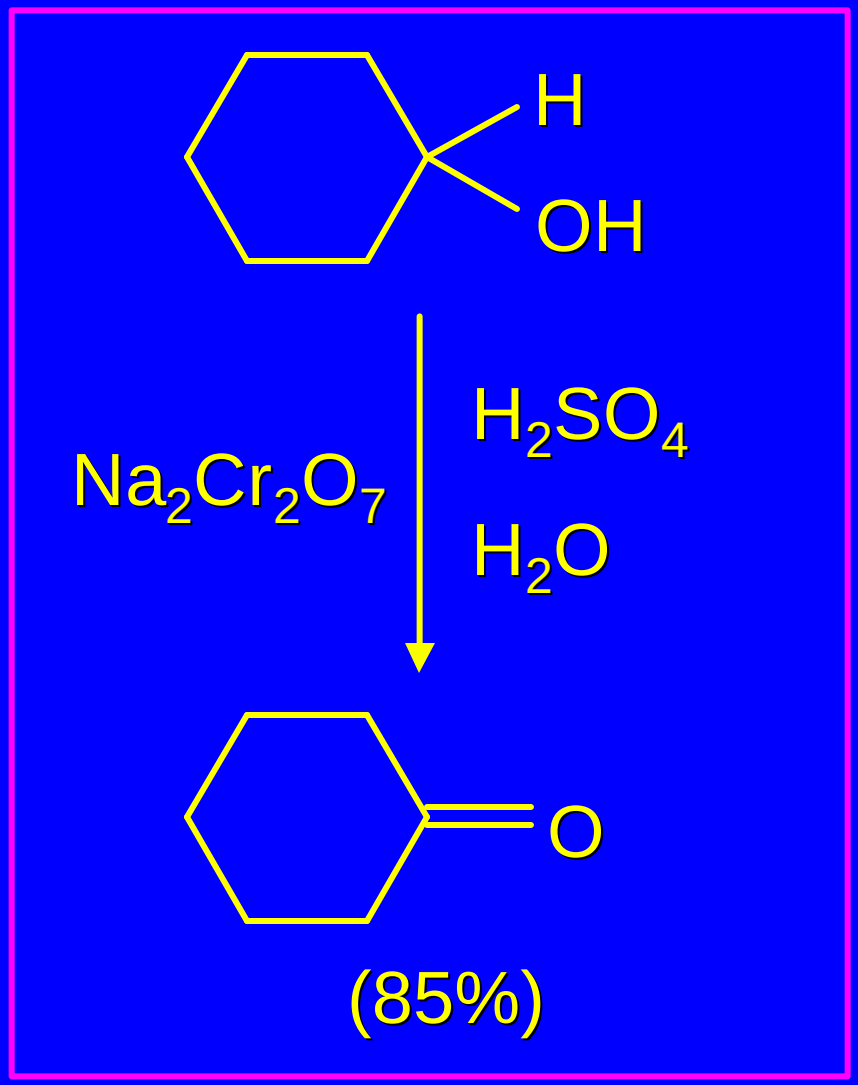
Aqueous Cr(VI)



(74%)

Aqueous Cr(VI)





Nonaqueous Sources of Cr(VI)

All are used in CH_2Cl_2

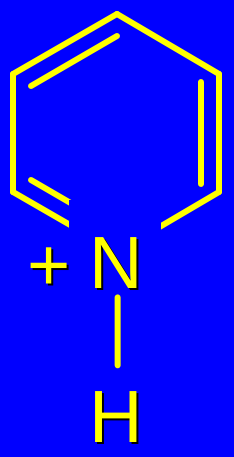
Pyridinium dichromate (PDC)

$(C_5H_5NH^+)_2\ \ Cr_2O_7^{2-}$

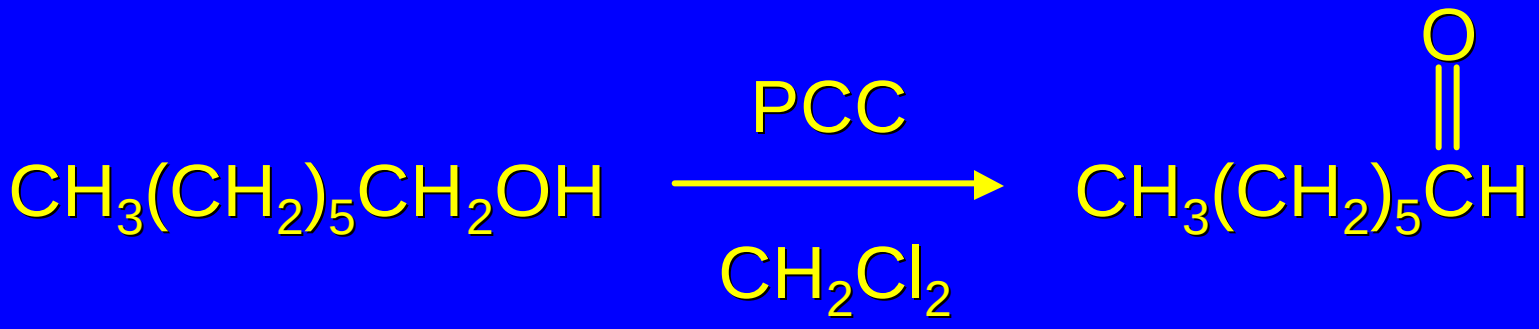
Pyridinium chlorochromate (PCC)

$C_5H_5NH^+\ \ ClCrO_3^-$

Example: Oxidation of a primary alcohol with PCC



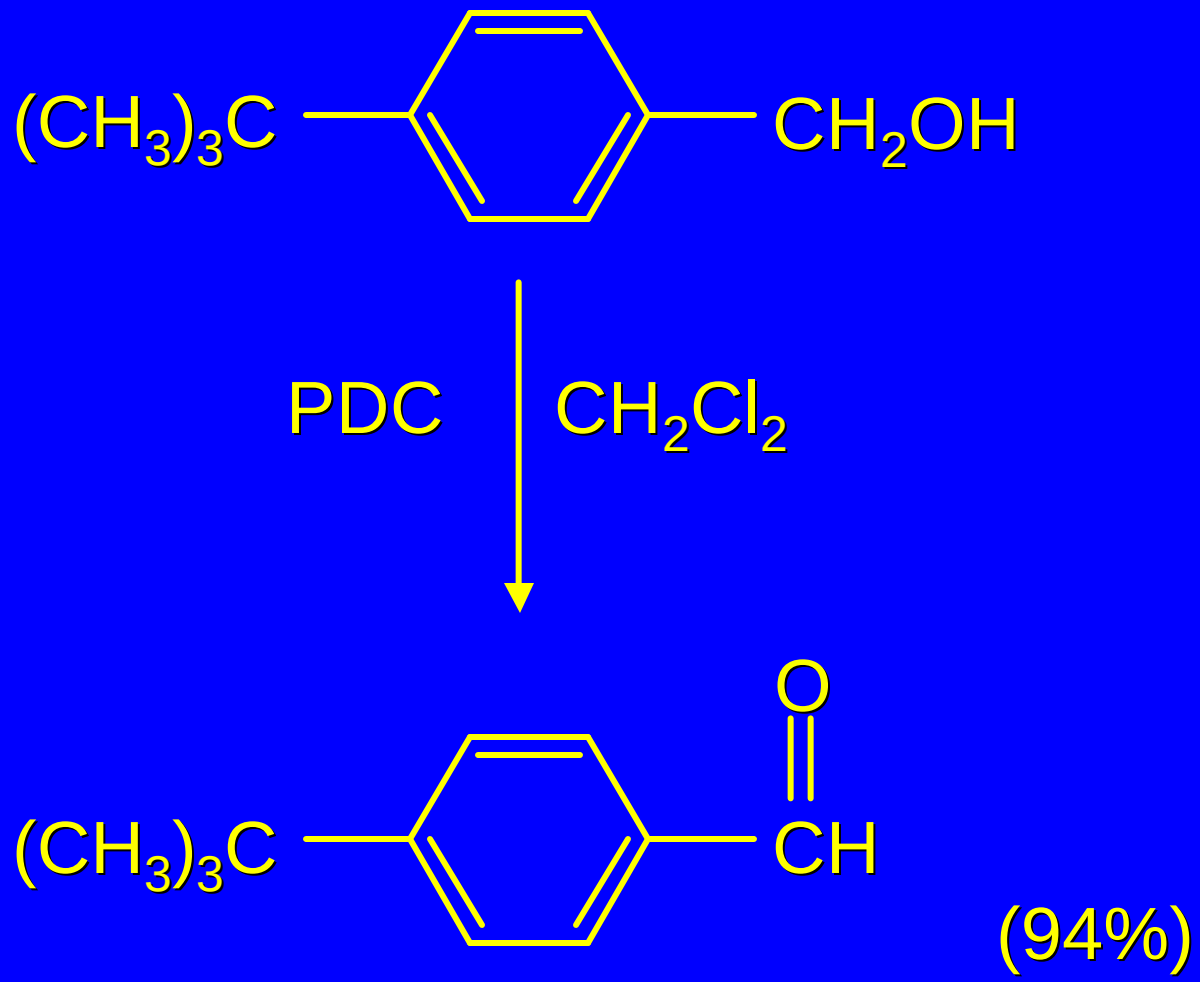
$ClCrO_3^-$



$CH_3(CH_2)_5CH_2OH$ → $CH_3(CH_2)_5CH$

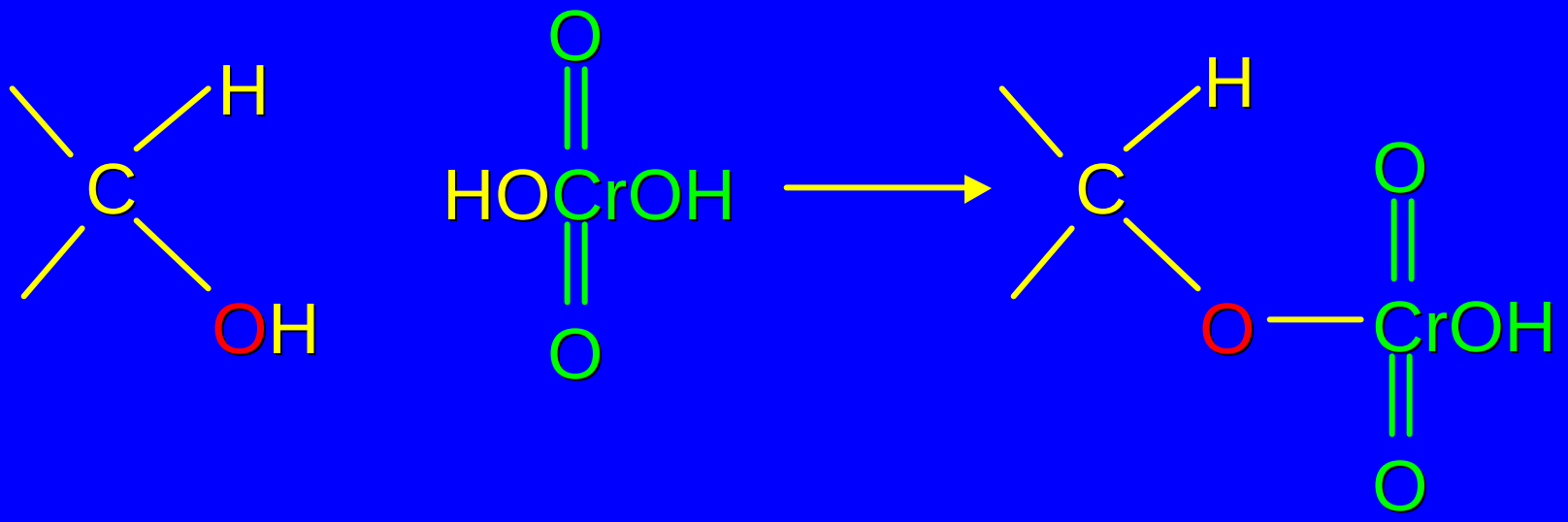
(78%)

Example: Oxidation of a primary alcohol with PDC



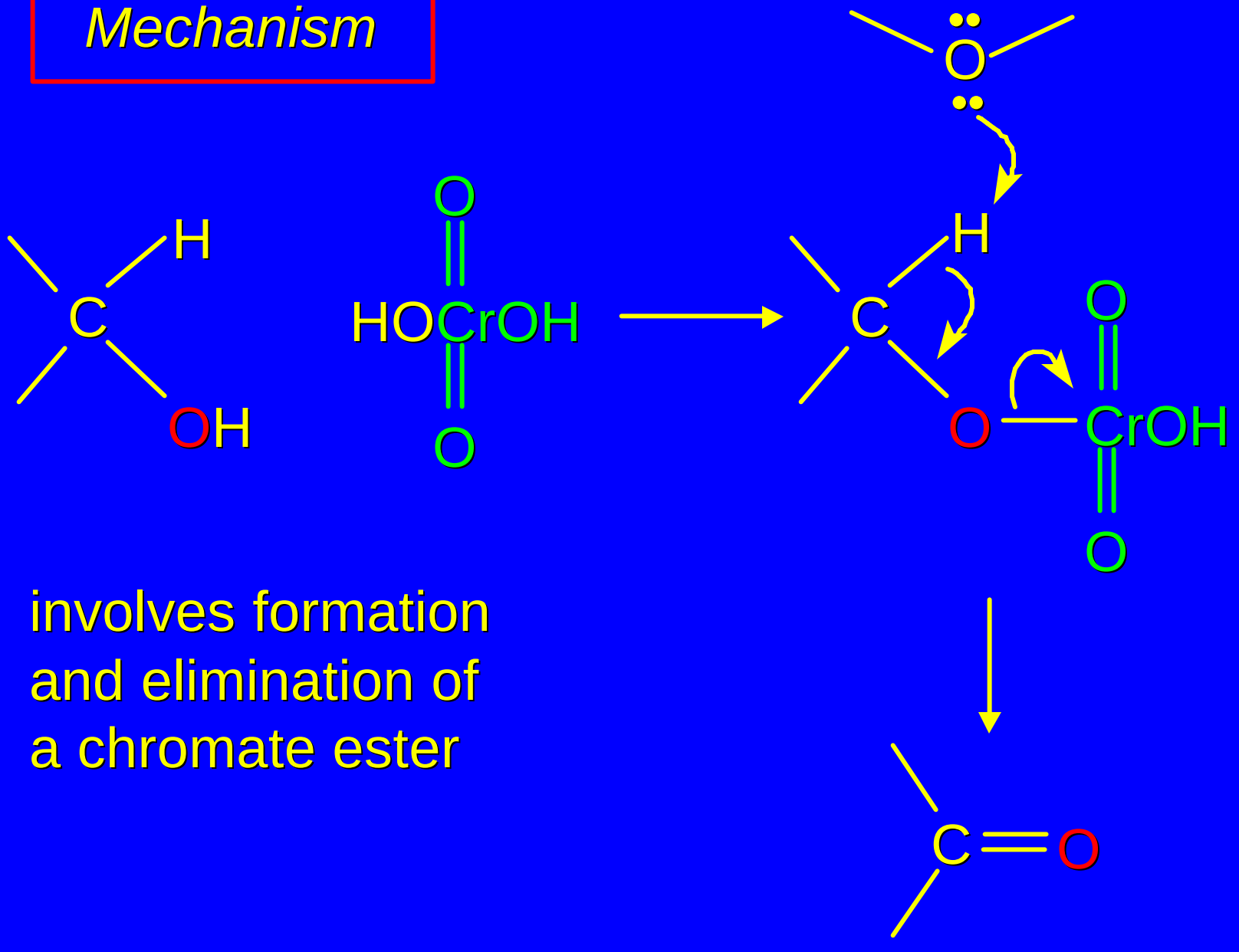
(94%)

Mechanism



involves formation
and elimination of
a chromate ester

Mechanism



involves formation
and elimination of
a chromate ester

15.11
Biological Oxidation of Alcohols

Enzyme-catalyzed

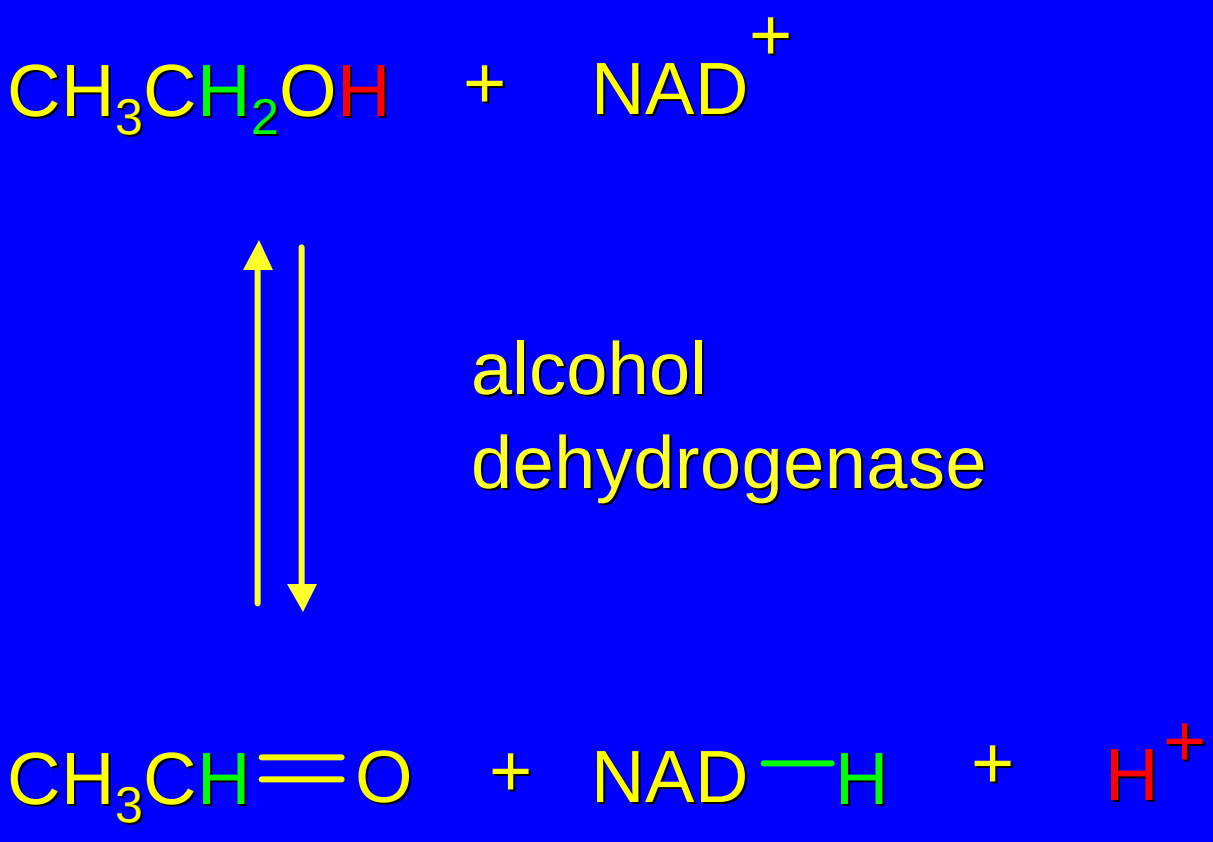
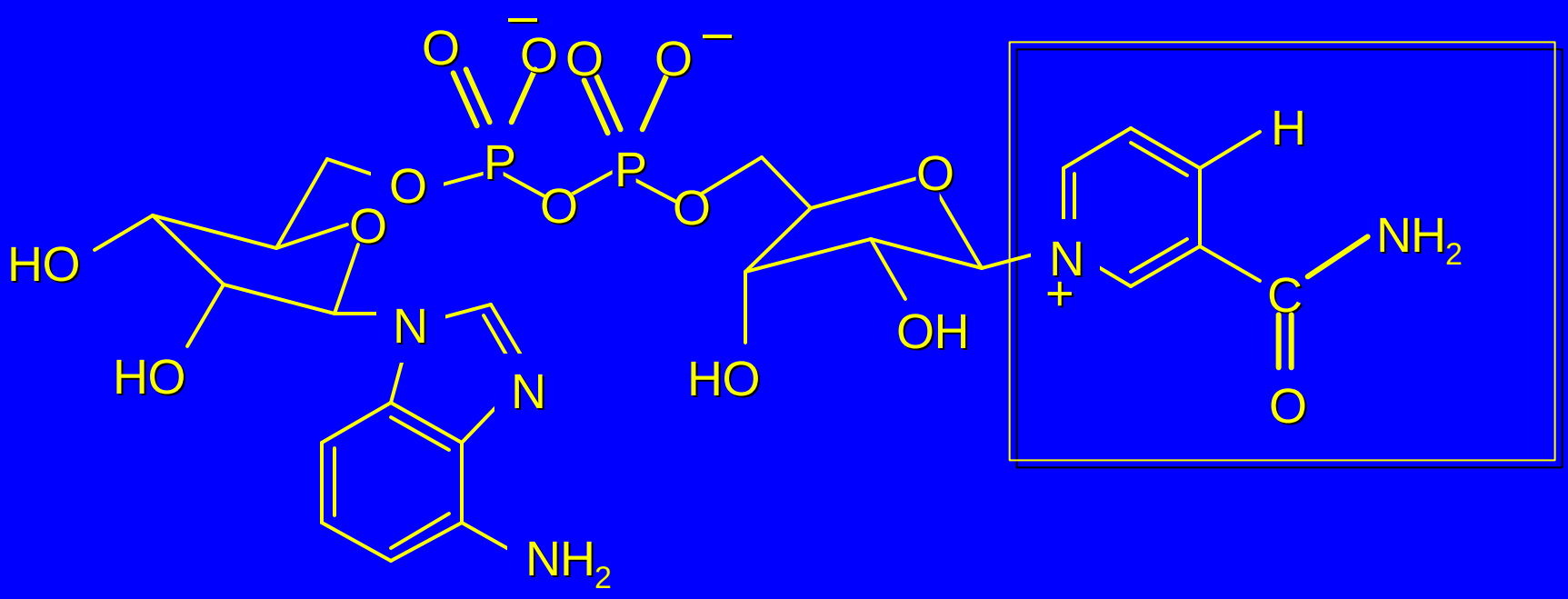
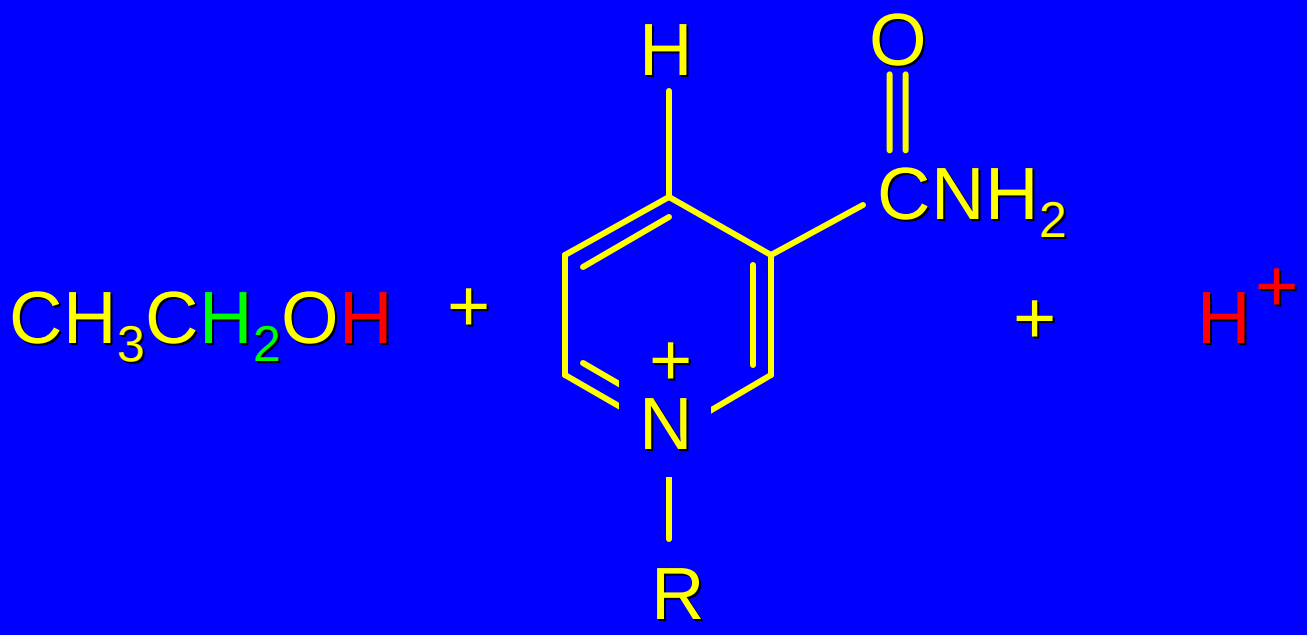


Figure 15.3 Structure of NAD^+

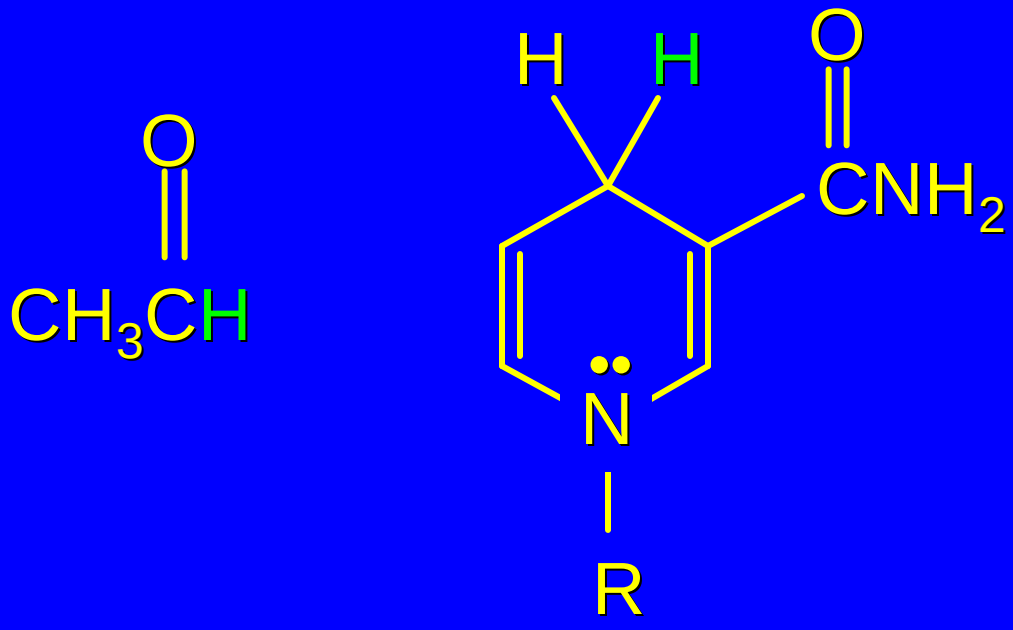


nicotinamide adenine dinucleotide (oxidized form)

Enzyme-catalyzed

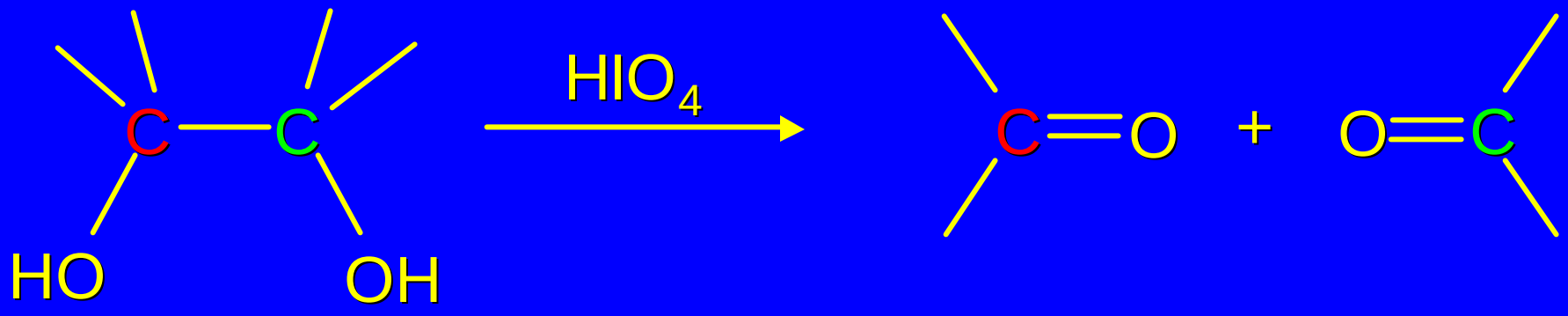


Enzyme-catalyzed

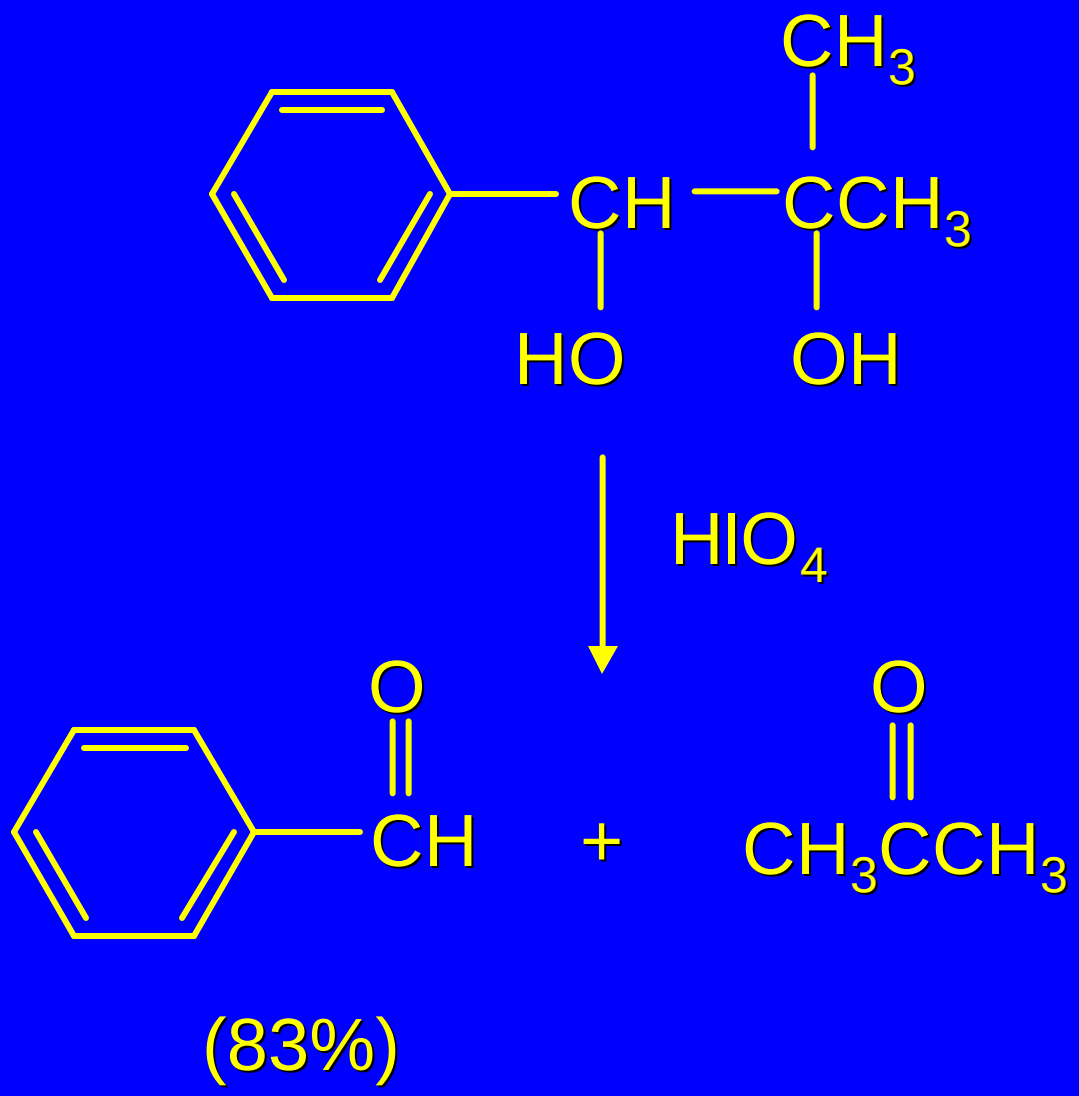


15.12
Oxidative Cleavage of Vicinal Diols

Cleavage of Vicinal Diols by Periodic Acid



Cleavage of Vicinal Diols by Periodic Acid



Cyclic Diols are Cleaved