Chapter 15
Alcohols, Diols, and Thiols

15.1

Sources of Alcohols

Methanol

Methanol is an industrial chemical

end uses: solvent, antifreeze, fuel

principal use: preparation of formaldehyde

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end uses: solvent, antifreeze, fuel

principal use: preparation of formaldehyde

prepared by hydrogenation of carbon monoxide

$$CO + 2H_2 \varnothing CH_3OH$$

Ethanol

Ethanol is an industrial chemical

Most ethanol comes from fermentation

Synthetic ethanol is produced by hydration of ethylene

Synthetic ethanol is denatured (made unfit for drinking) by adding methanol, benzene, pyridine, castor oil, gasoline, etc.

Other alcohols

Isopropyl alcohol is prepared by hydration of propene.

All alcohols with four carbons or fewer are readily available.

Most alcohols with five or six carbons are readily available.

Sources of alcohols

Reactions discussed in earlier chapters (Table 15.1)

- Hydration of alkenes
- Hydroboration-oxidation of alkenes
- Hydrolysis of alkyl halides
- Syntheses using
  - Grignard reagents
  - organolithium reagents

Sources of alcohols

New methods in Chapter 15

Reduction of aldehydes and ketones

Reduction of carboxylic acids

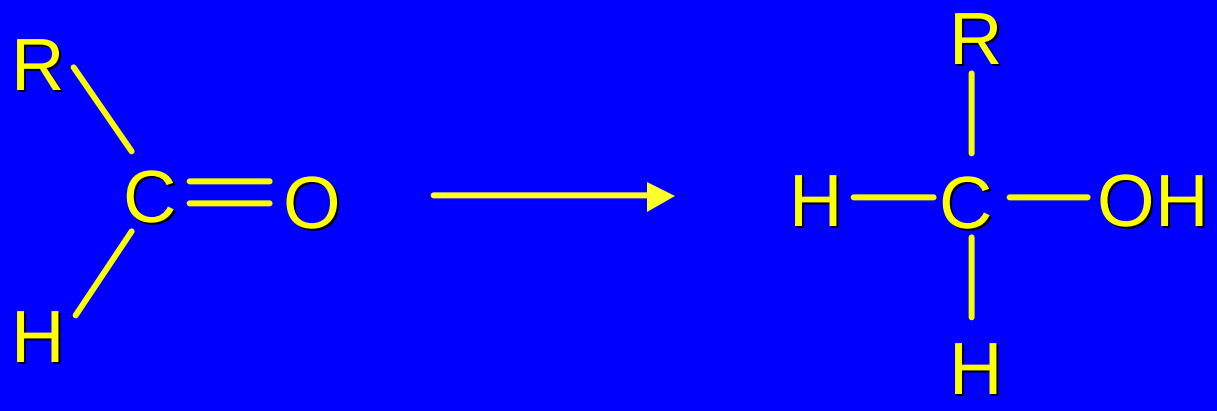
Reduction of esters

Reaction of Grignard reagents with epoxides

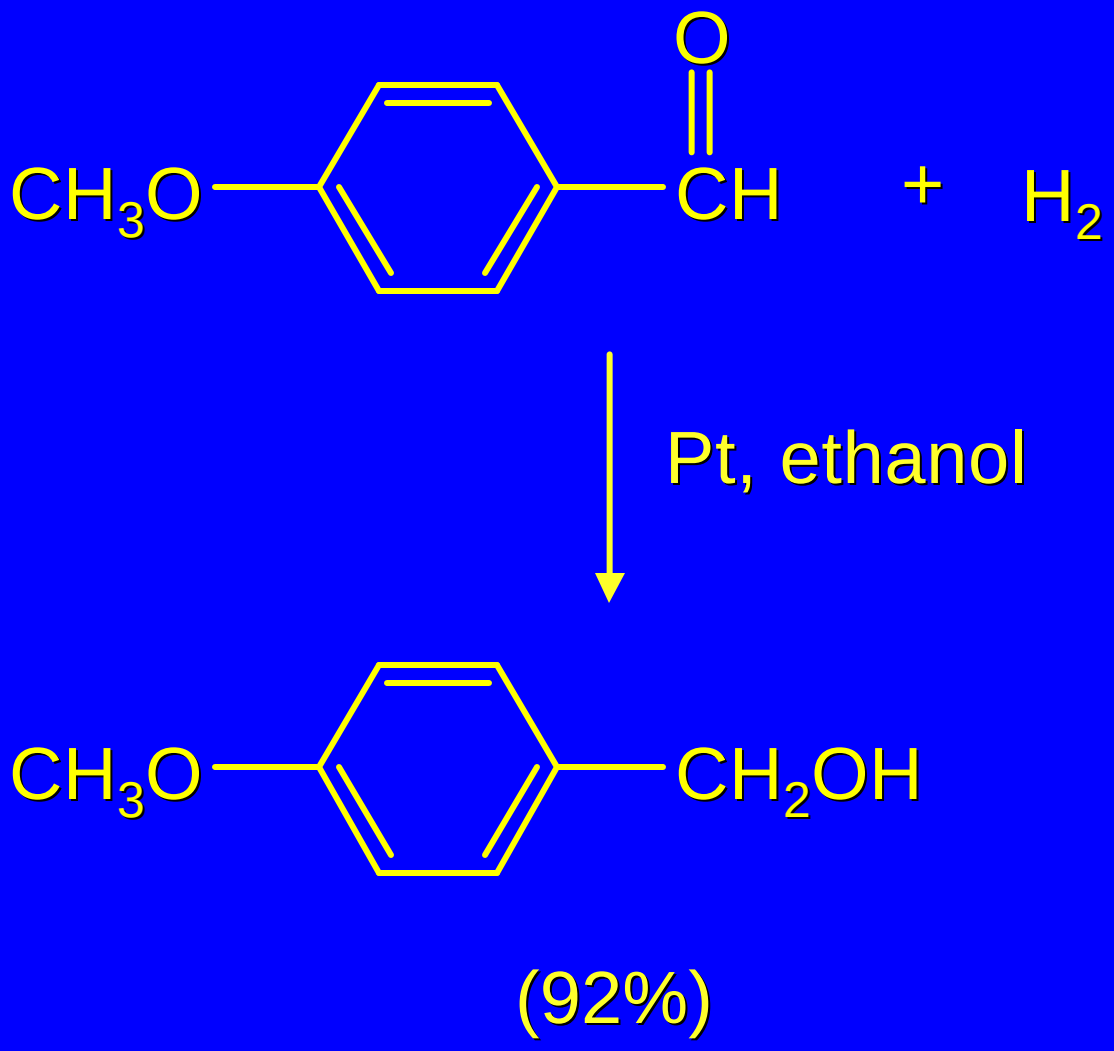
Diols by hydroxylation of alkenes

15.2
Preparation of Alcohols
by
Reduction of Aldehydes and Ketones

Reduction of Aldehydes Gives Primary Alcohols

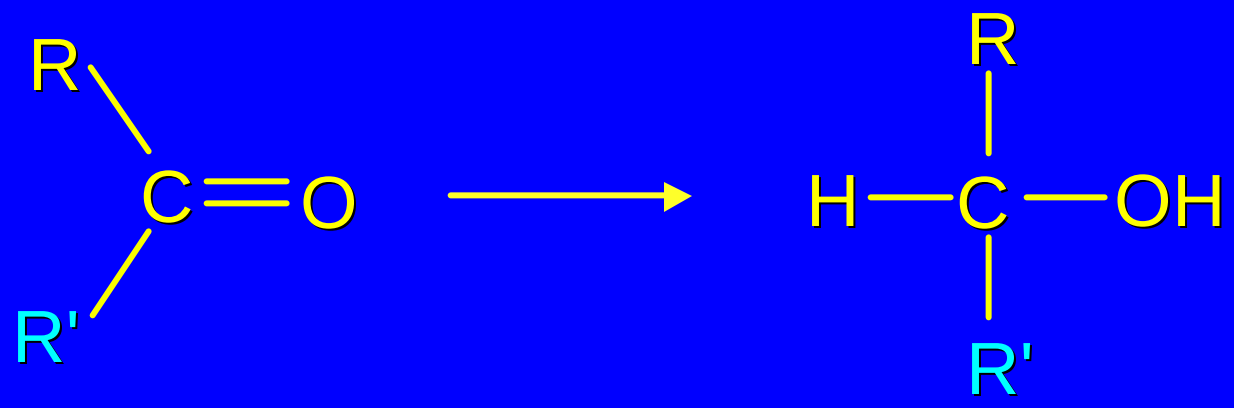


Example: Catalytic Hydrogenation

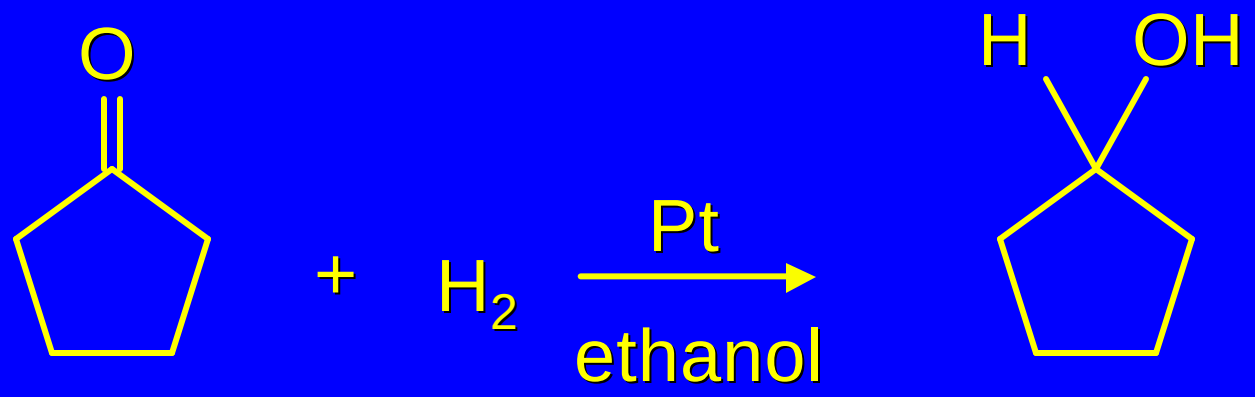


(92%)

Reduction of Ketones Gives Secondary Alcohols

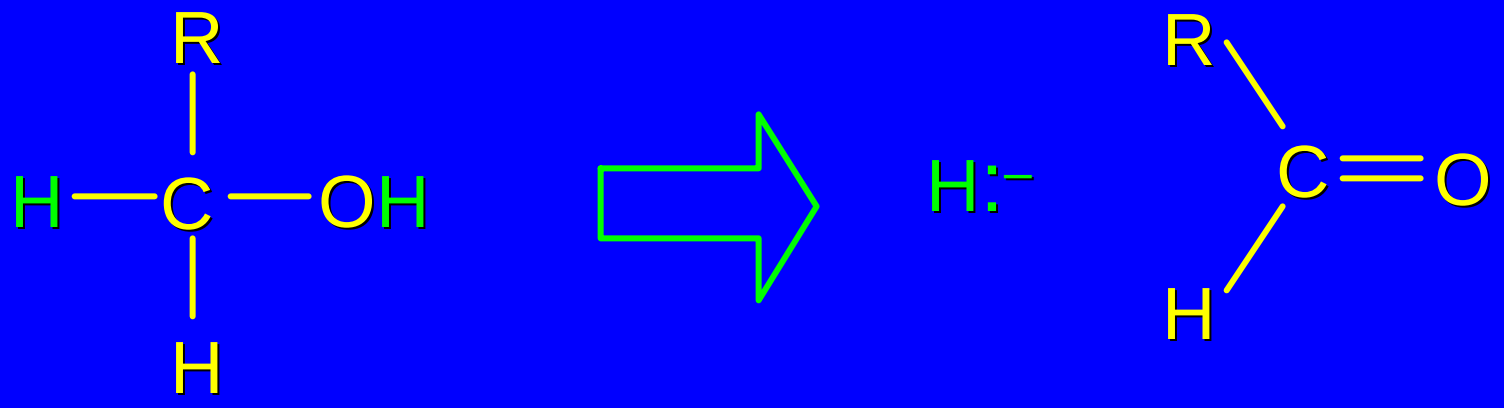


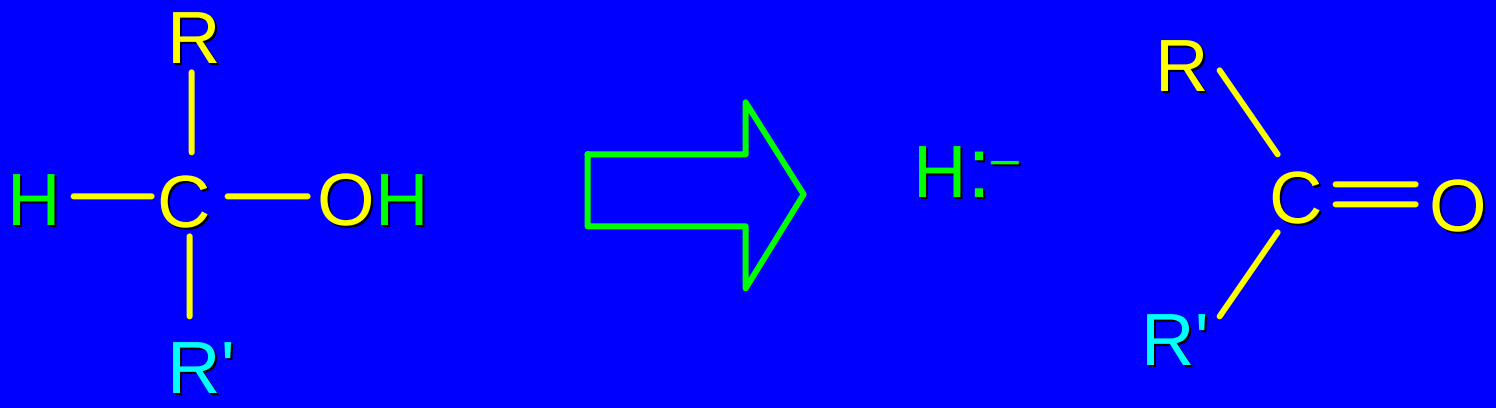
Example: Catalytic Hydrogenation



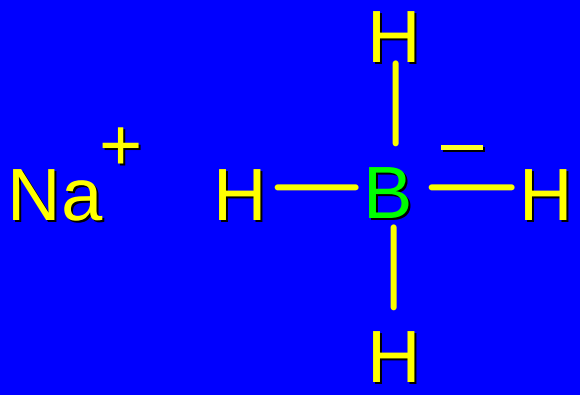
(93-95%)

Retrosynthetic Analysis

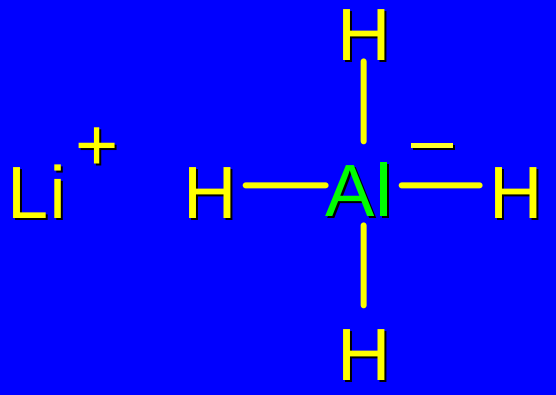




Metal Hydride Reducing Agents



Sodium
borohydride

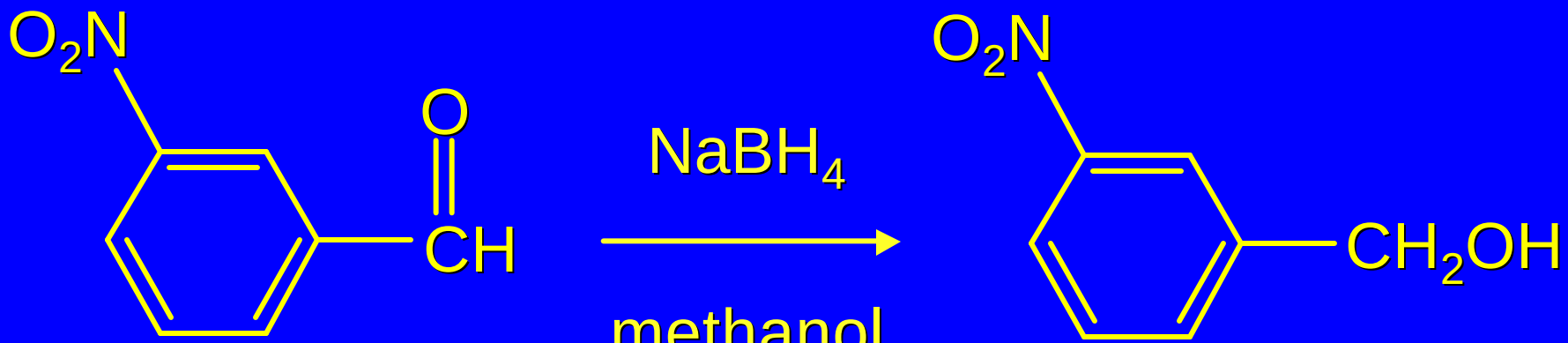


Lithium
aluminum hydride

act as hydride donors

Examples: Sodium Borohydride

Aldehyde



(82%)

Ketone

(84%)

Lithium aluminum hydride

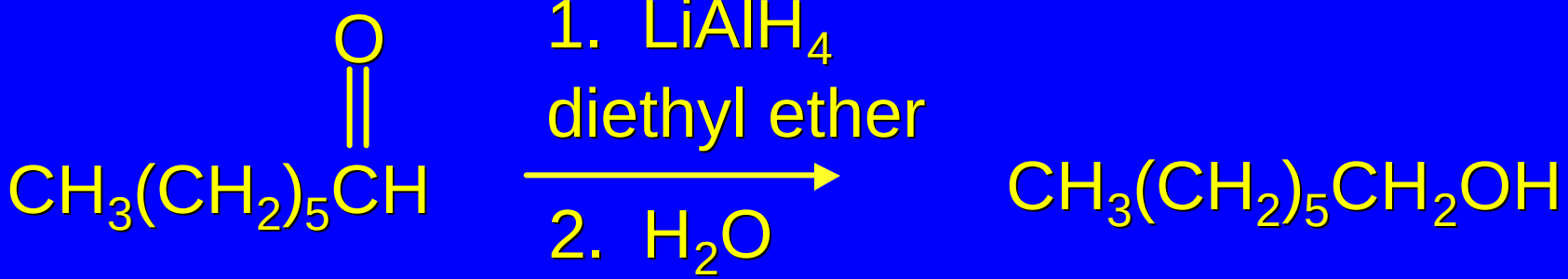
more reactive than sodium borohydride

cannot use water, ethanol, methanol etc. as solvents

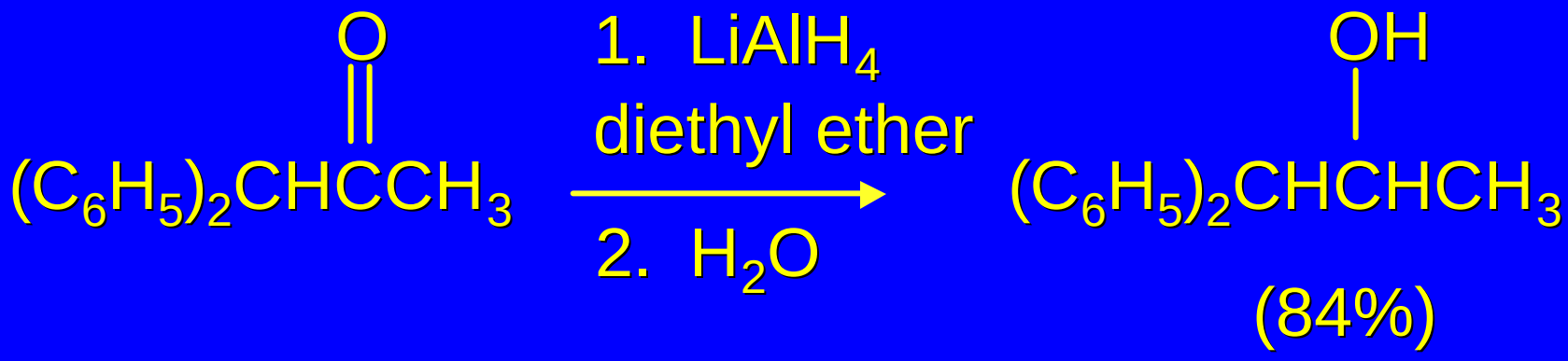
diethyl ether is most commonly used solvent

Examples: Lithium Aluminum Hydride

Aldehyde

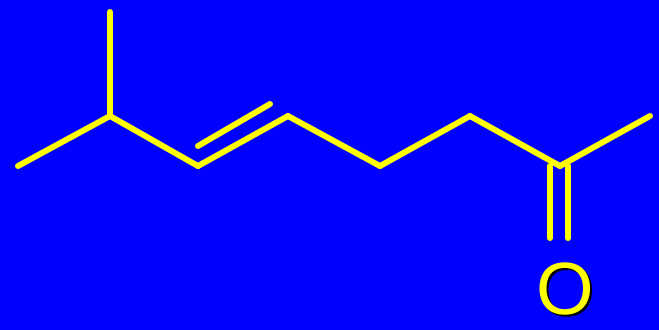


Ketone



Selectivity

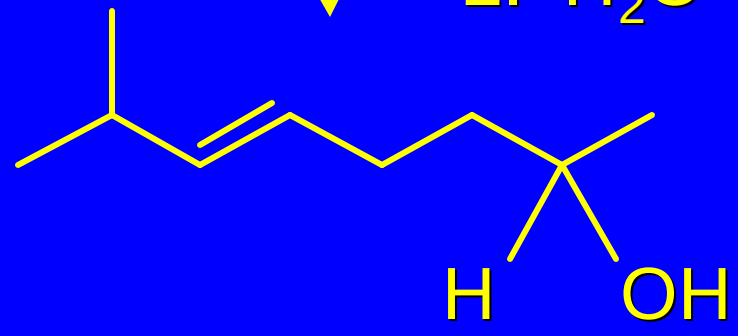
neither $NaBH_4$ or $LiAlH_4$ reduces isolated double bonds



1. $LiAlH_4$
diethyl ether

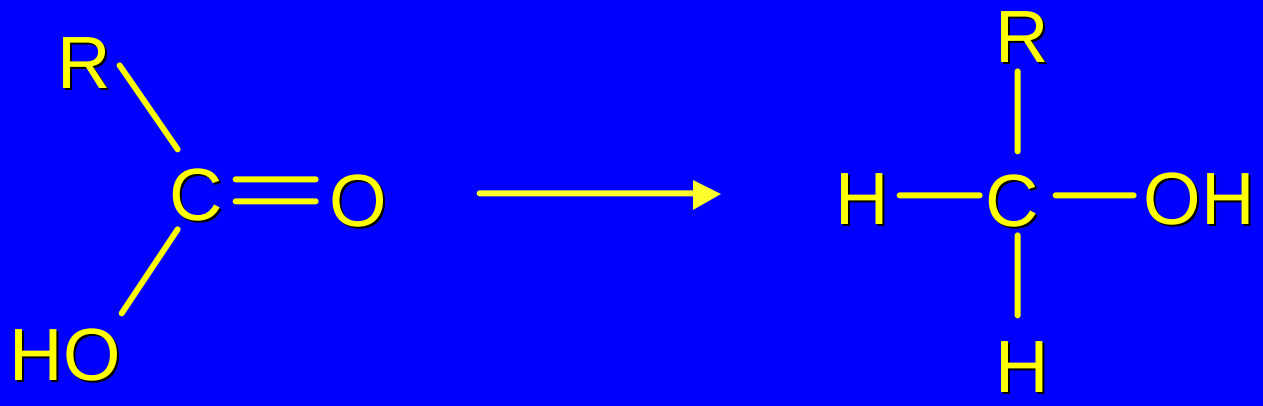
2. H_2O

(90%)



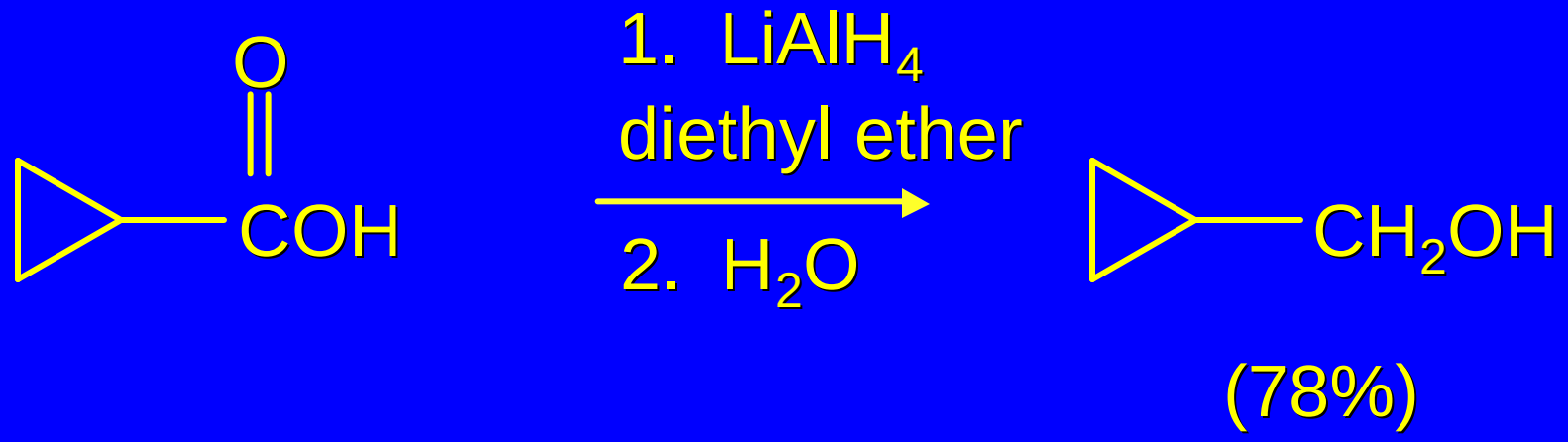
15.3
Preparation of Alcohols By Reduction of Carboxylic Acids and Esters

Reduction of Carboxylic Acids
Gives Primary Alcohols



lithium aluminum hydride is only
effective reducing agent

Example: Reduction of a Carboxylic Acid



(78%)

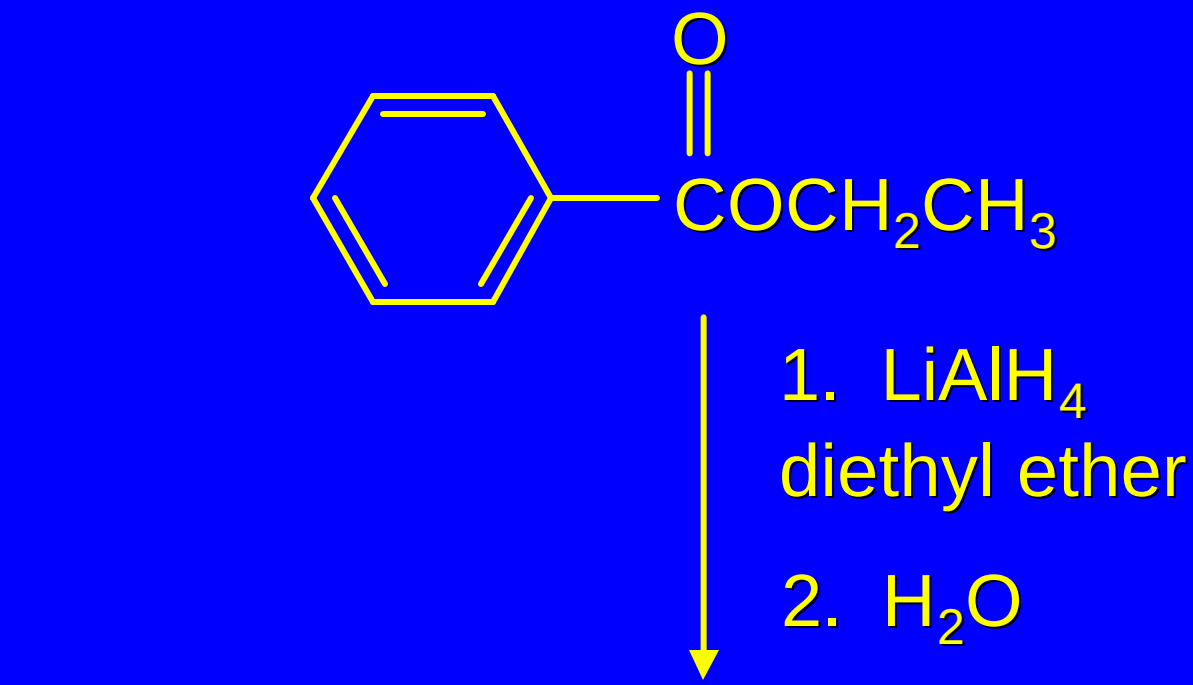
Reduction of Esters Gives Primary Alcohols

Lithium aluminum hydride preferred for laboratory reductions

Sodium borohydride reduction is too slow to be useful

Catalytic hydrogenolysis used in industry but conditions difficult or dangerous to duplicate in the laboratory (special catalyst, high temperature, high pressure

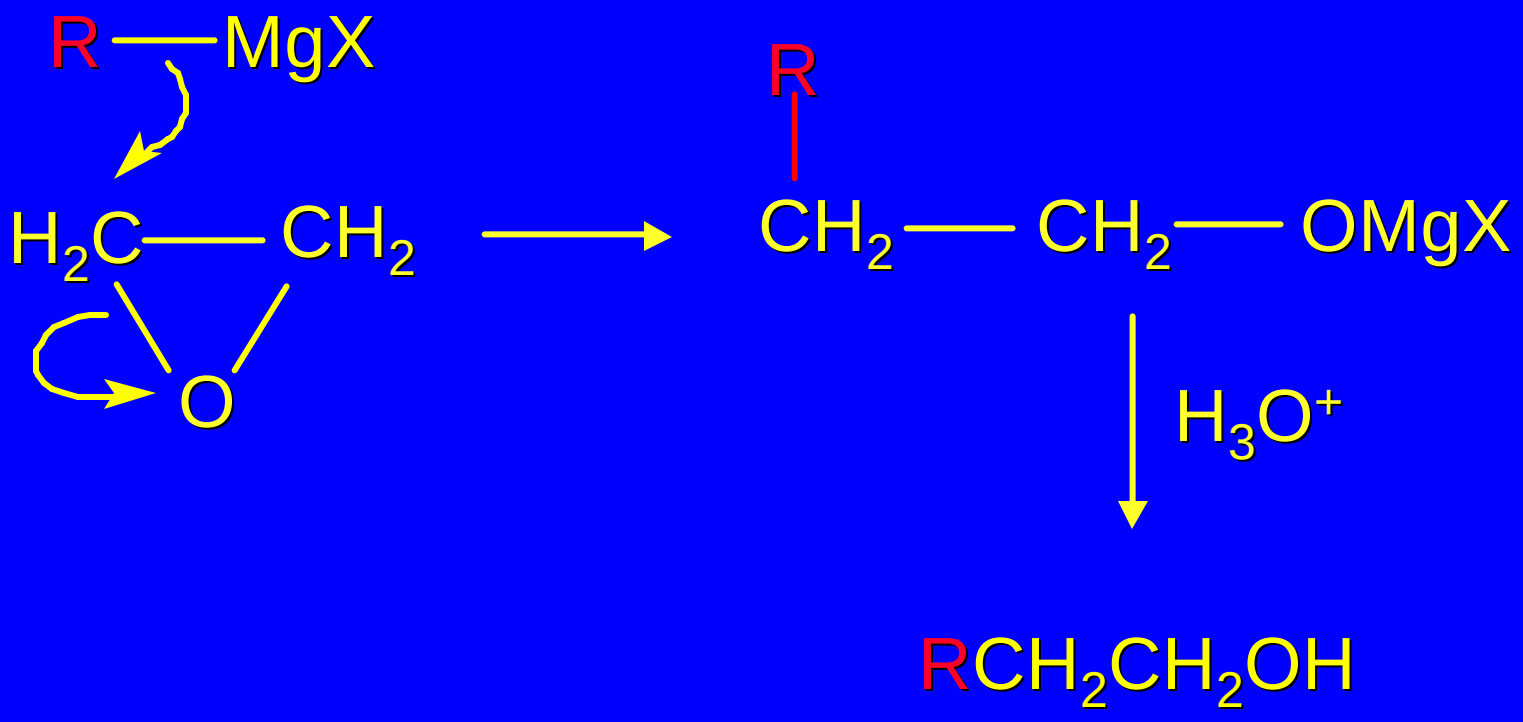
Example: Reduction of a Carboxylic Acid



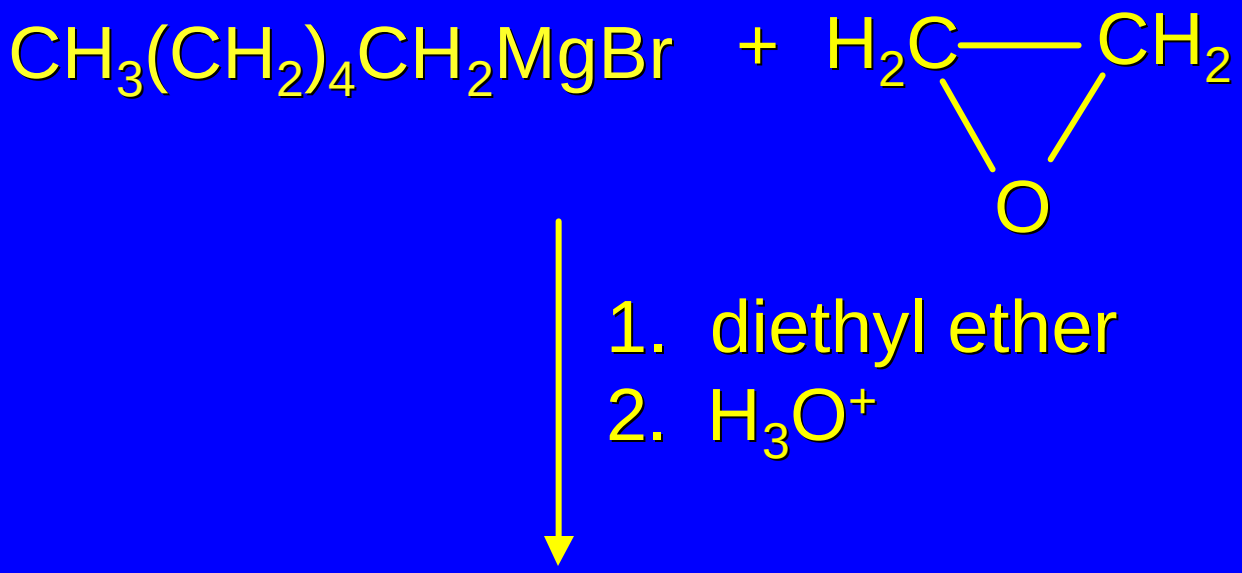
(90%)

15.4
Preparation of Alcohols From Epoxides

Reaction of Grignard Reagents with Epoxides



Example


CH3(CH2)4CH2MgBr + H2C CH2
O
1. diethyl ether
2. H3O+
CH3(CH2)4CH2CH2CH2OH
(71%)

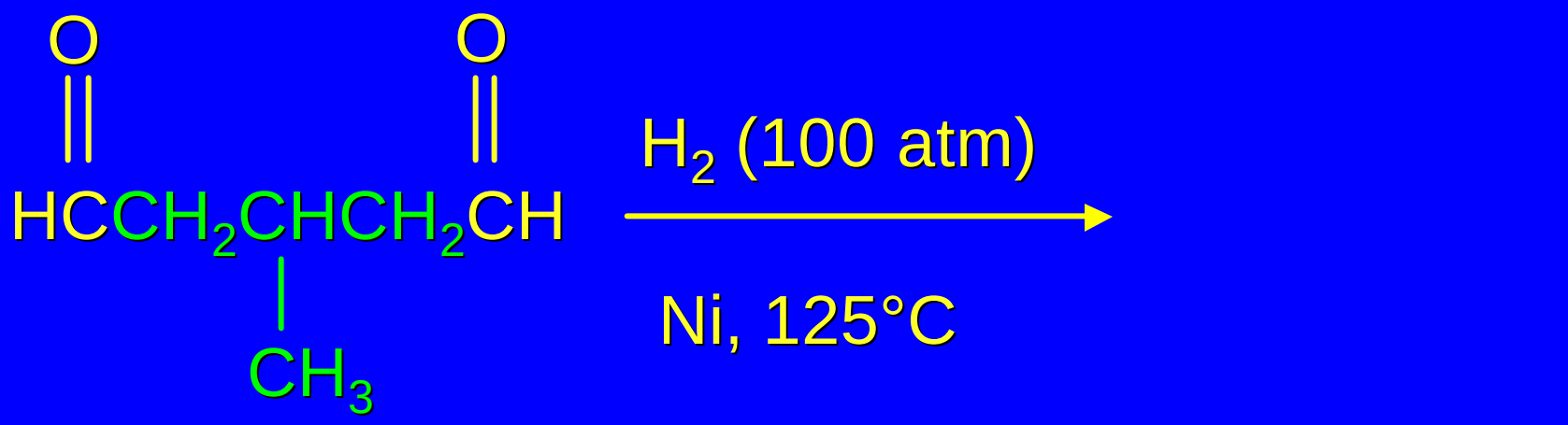
15.5
Preparation of Diols

Diols are prepared by...

reactions used to prepare alcohols

hydroxylation of alkenes

Example: reduction of a dialdehyde



$HOCH_2CH_2CHCH_2CH_2OH$

CH_3

3-Methyl-1,5-pentanediol

(81-83%)

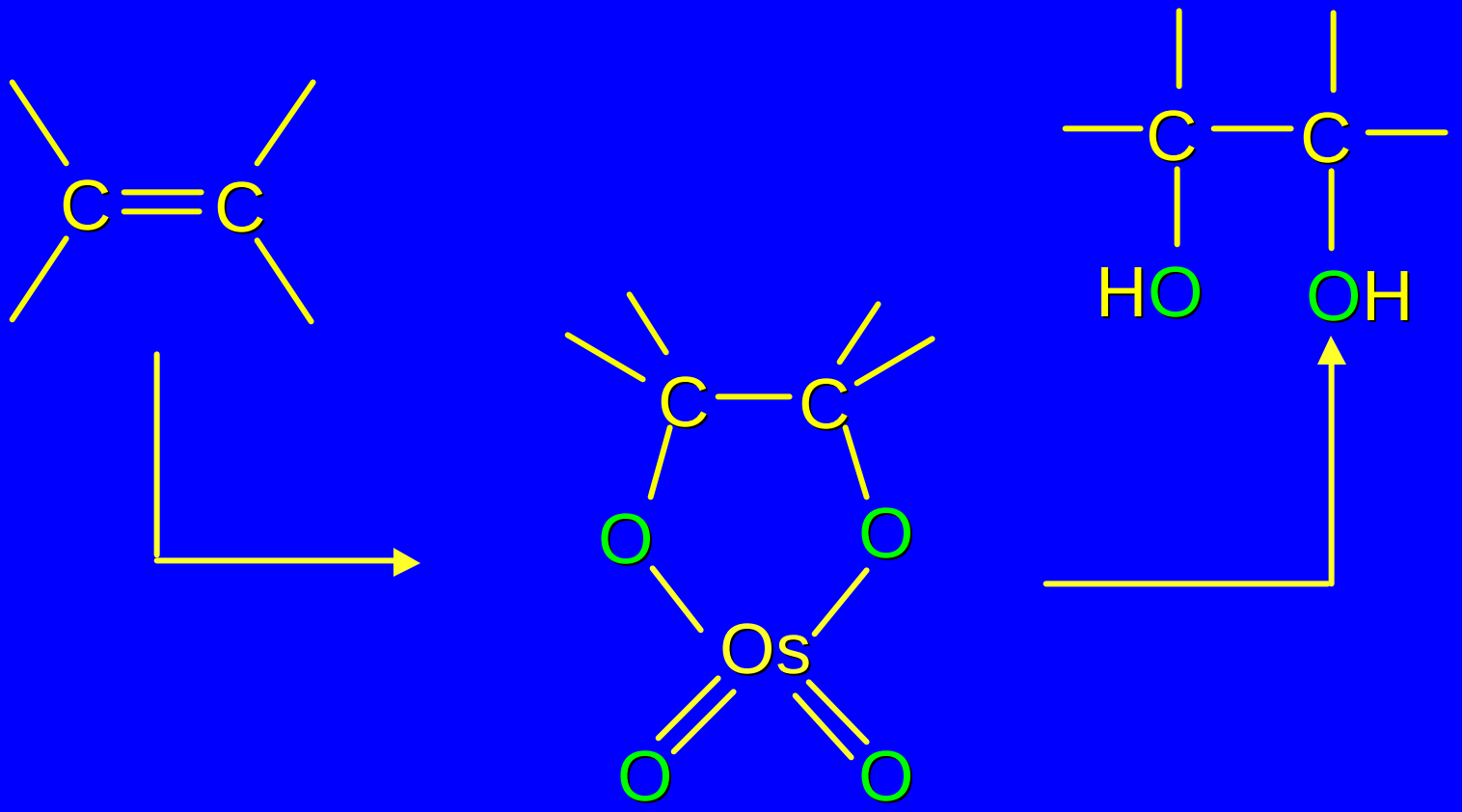
Hydroxylation of Alkenes Gives Vicinal Diols

vicinal diols have hydroxyl groups on adjacent carbons

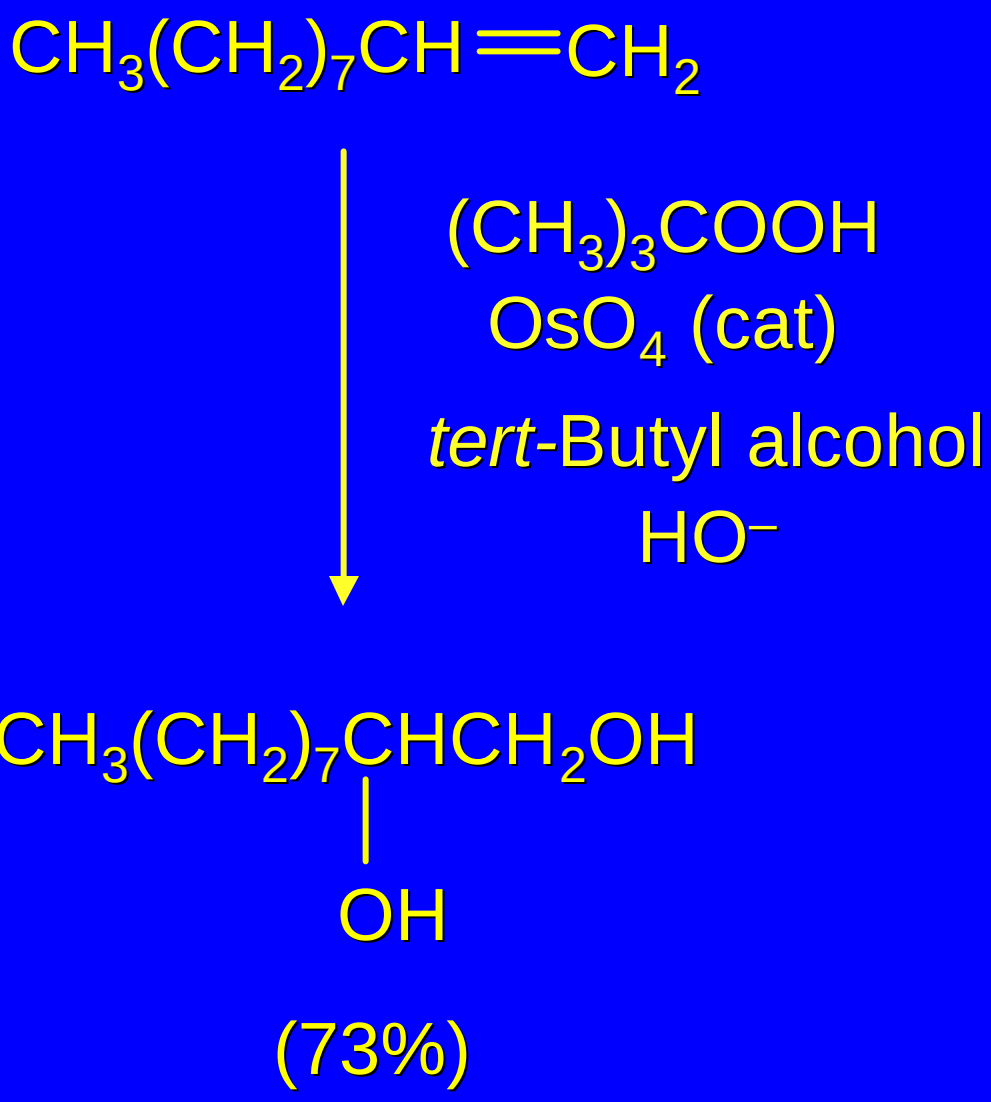
ethylene glycol ($HOCH_2CH_2OH$) is most familiar example

Osmium Tetraoxide is Key Reagent

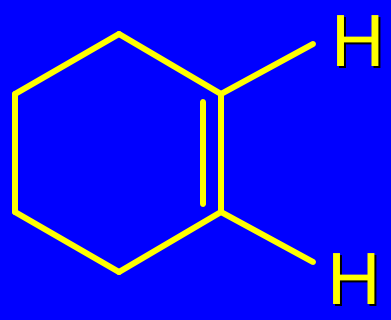
syn addition of —OH groups to each carbon of double bond



Example


CH3(CH2)7CH=CH2
(CH3)3COOH
OsO4 (cat)
tert-Butyl alcohol
HO−
CH3(CH2)7CHCH2OH
OH
(73%)

Example

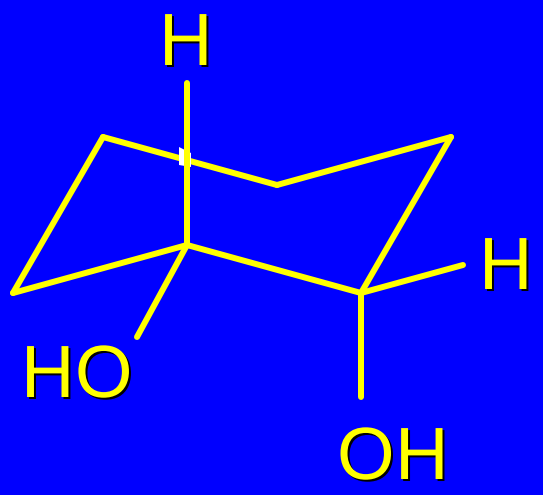


$(CH_3)_3COOH$

OsO_4 (cat)

tert-Butyl alcohol

HO^-



(62%)