# ORGANIC CHEMISTRY



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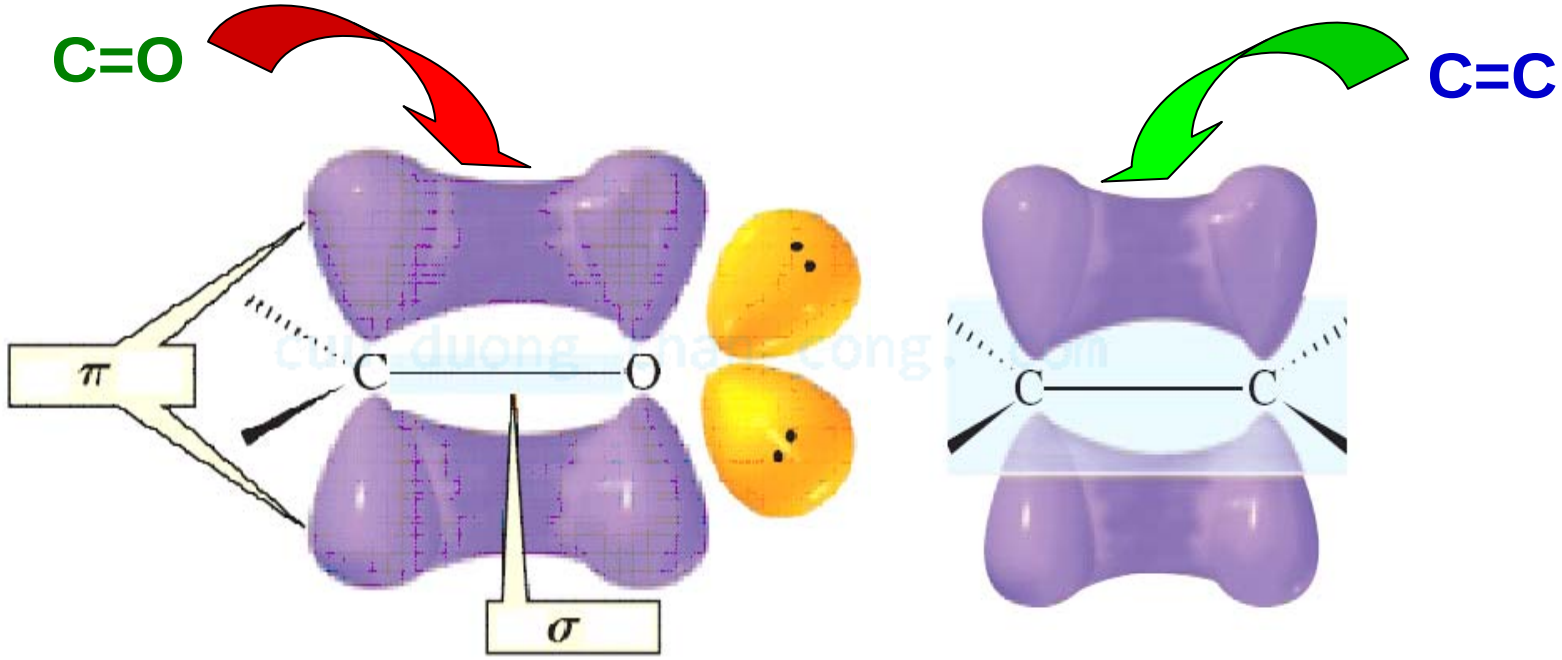
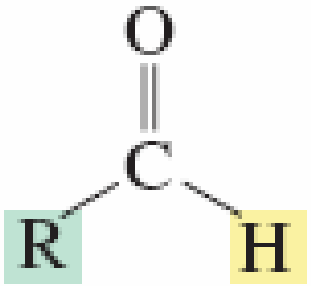
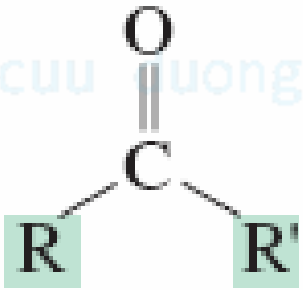
# *Chapter 11*: ALDEHYDES-KETONES

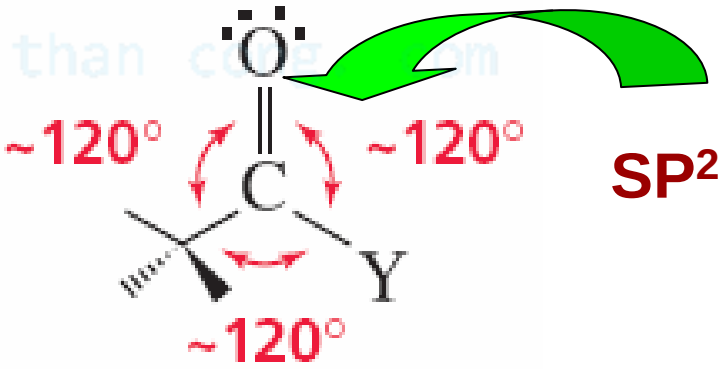



an aldehyde



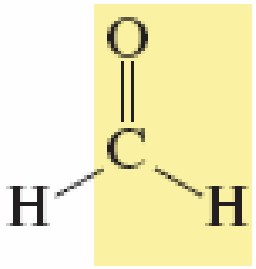

a ketone



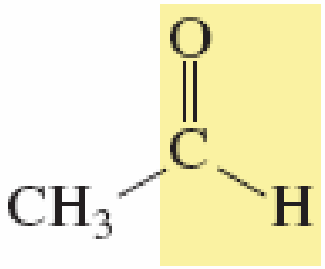

SP² carbon

# NOMENCLATURE OF ALDEHYDES

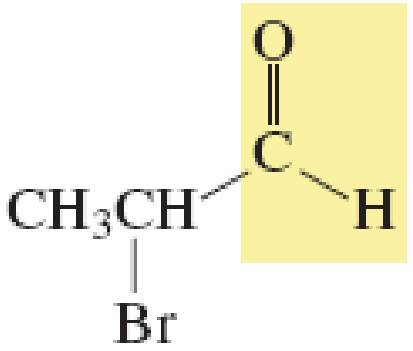
***Common names: carboxylic acid → "aldehyde" is substituted for "ic acid"***



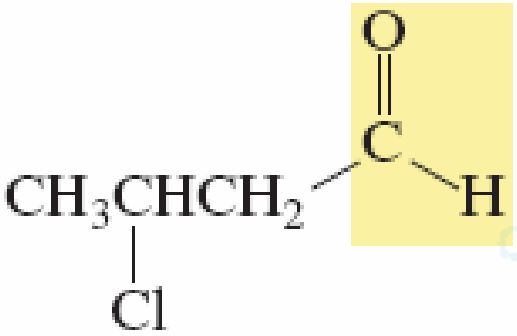
systematic name: methanal
common name: formaldehyde



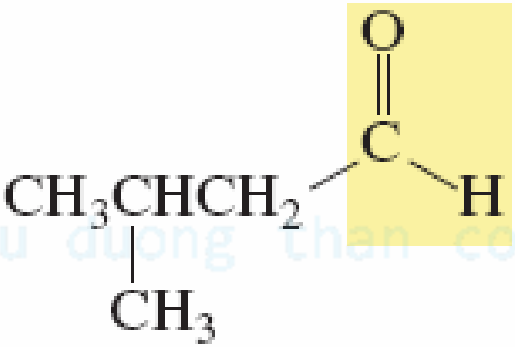
ethanal
acetaldehyde



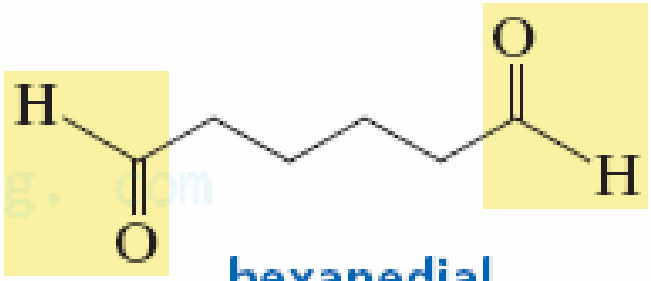
2-bromopropanal
α-bromopropionaldehyde



3-chlorobutanal
β-chlorobutyraldehyde



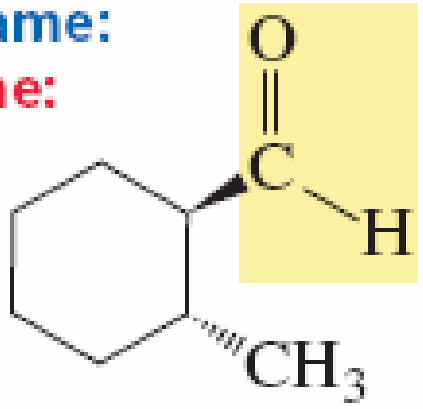
3-methylbutanal
isovaleraldehyde

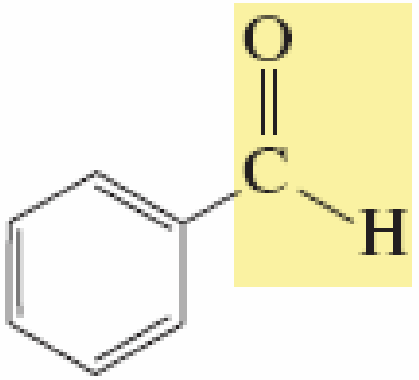


hexanedial

***IUPAC names: hydrocarbon + al***

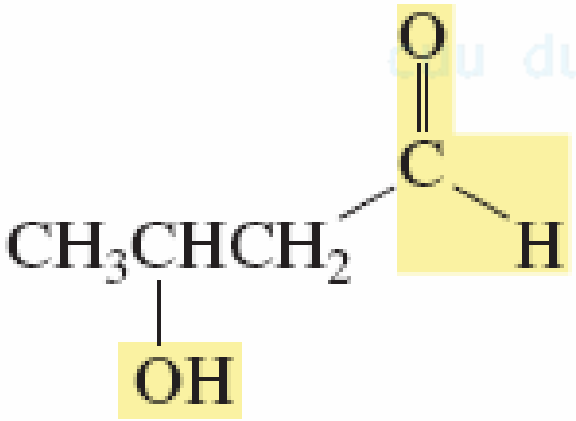
systematic name:
common name:



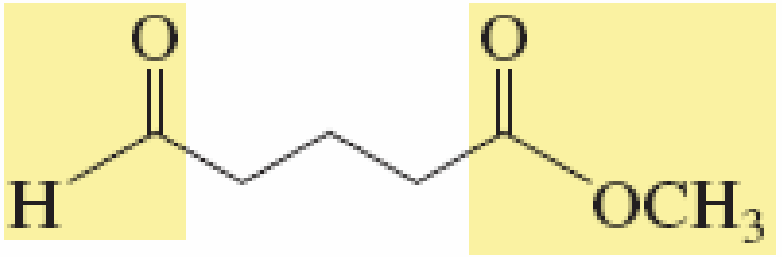


*trans*-2-methylcyclohexanecarbaldehyde

benzenecarbaldehyde
benzaldehyde



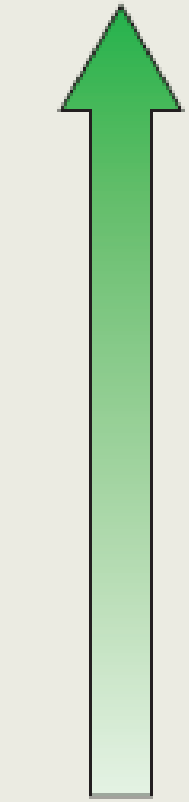
3-hydroxybutanal



methyl 5-oxopentanoate

***Lower priority than ester → "oxo" group***

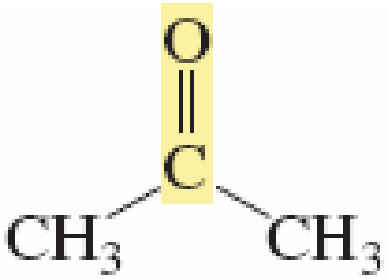
## Summary of Functional Group Nomenclature




| Class | Suffix Name | Prefix Name |
|---|---|---|
| Carboxylic acid | -oic acid | Carboxy |
| Ester | -oate | Alkoxycarbonyl |
| Amide | -amide | Amido |
| Nitrile | -nitrile | Cyano |
| Aldehyde | -al | Oxo (=O) |
| Aldehyde | -al | Formyl (—CH=O) |
| Ketone | -one | Oxo (=O) |
| Alcohol | -ol | Hydroxy |
| Amine | -amine | Amino |
| Alkene | -ene | Alkenyl |
| Alkyne | -yne | Alkynyl |
| Alkane | -ane | Alkyl |
| Ether | — | Alkoxy |
| Alkyl halide | — | Halo |

# NOMENCLATURE OF KETONES

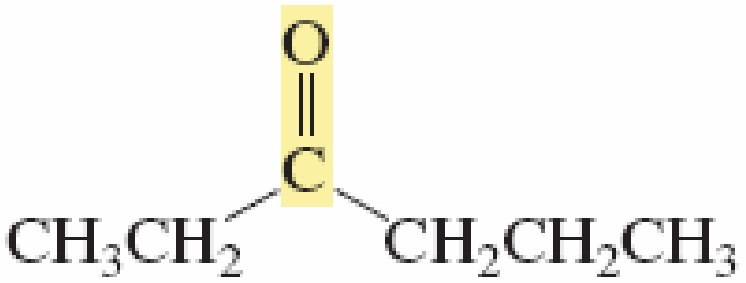
## *Derived names: alkyls + ketone*



systematic name: propanone

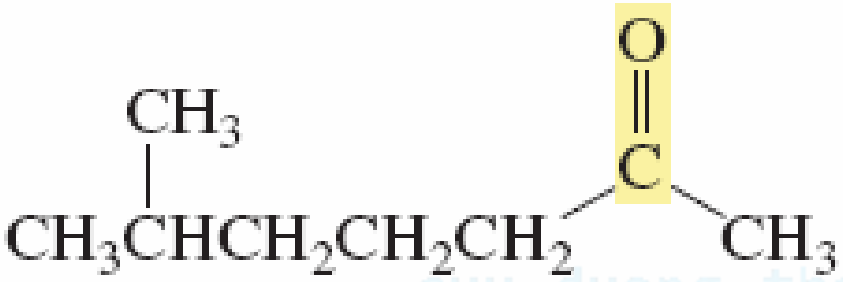
common name: acetone

derived name: dimethyl ketone



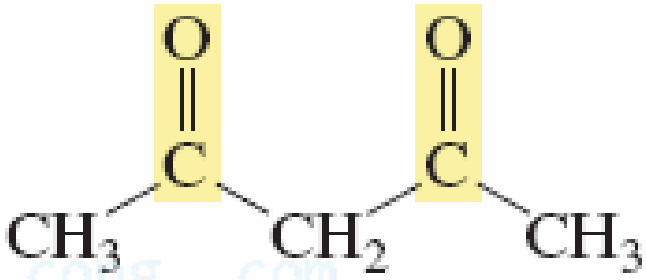
3-hexanone

ethyl propyl ketone



6-methyl-2-heptanone

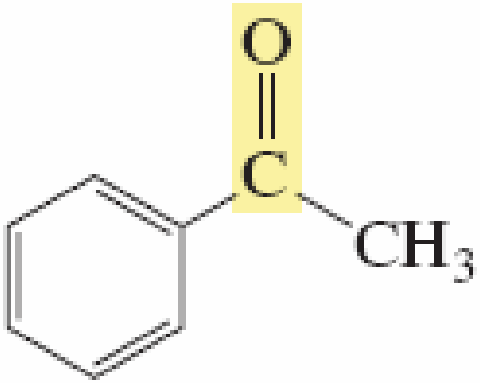
isohexyl methyl ketone



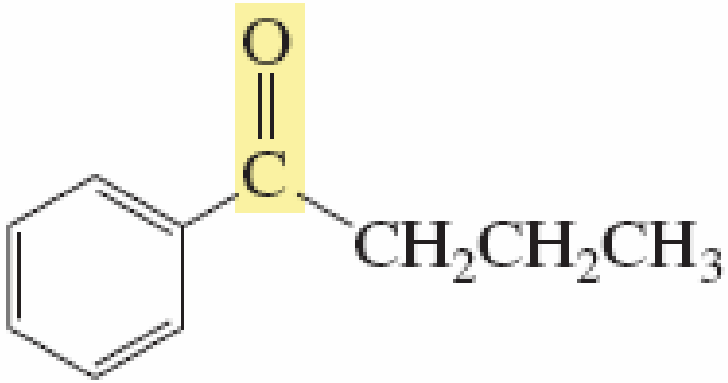
2,4-pentanedione

acetylacetone

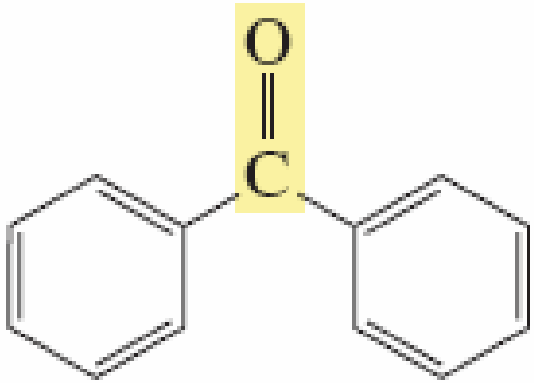
## *IUPAC names: hydrocarbon + one*



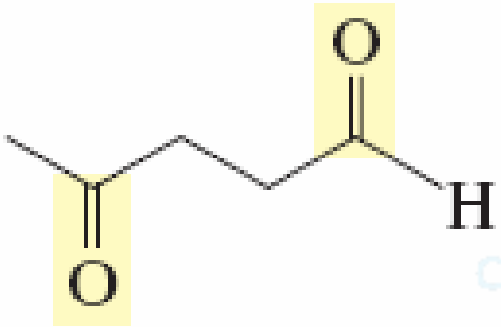

**acetophenone**
**methyl phenyl ketone**



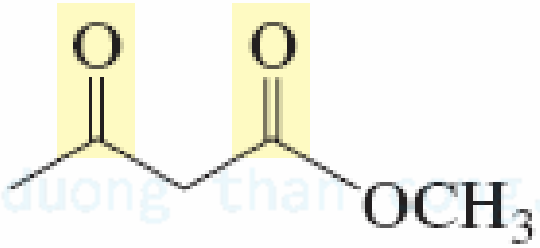

**butyrophenone**
**phenyl propyl ketone**



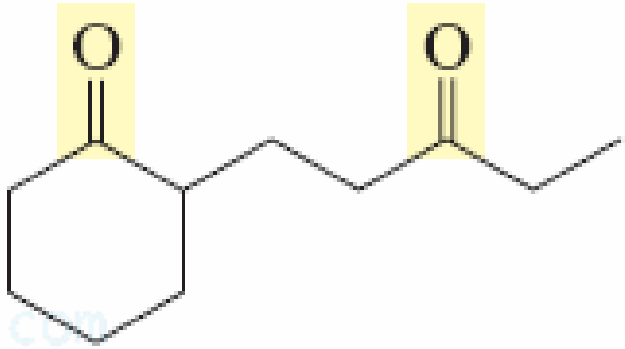

**benzophenone**
**diphenyl ketone**




**4-oxopentanal**

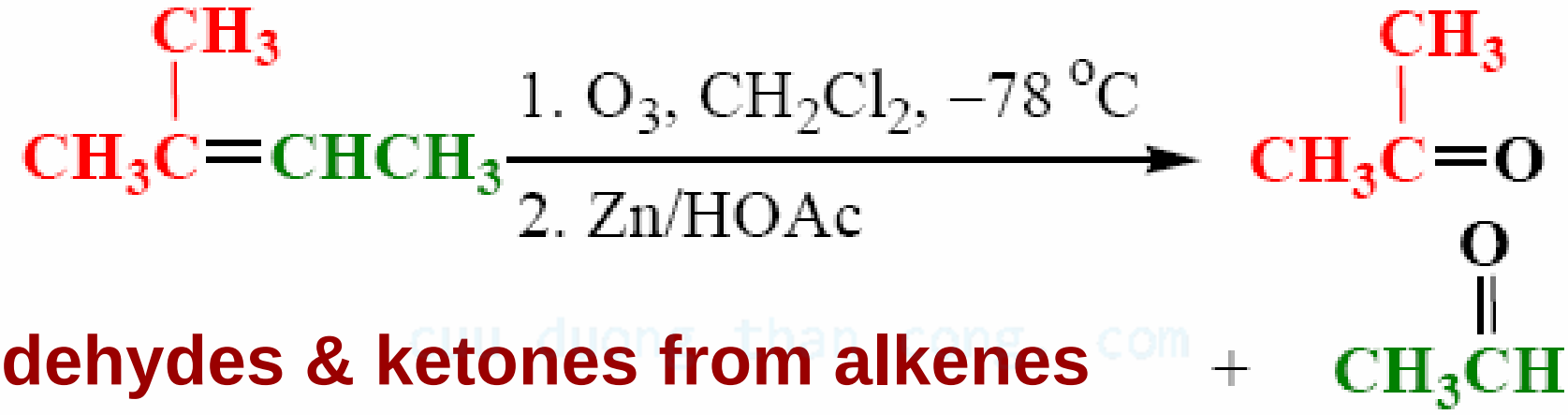



**ethyl 3-oxobutanoate**

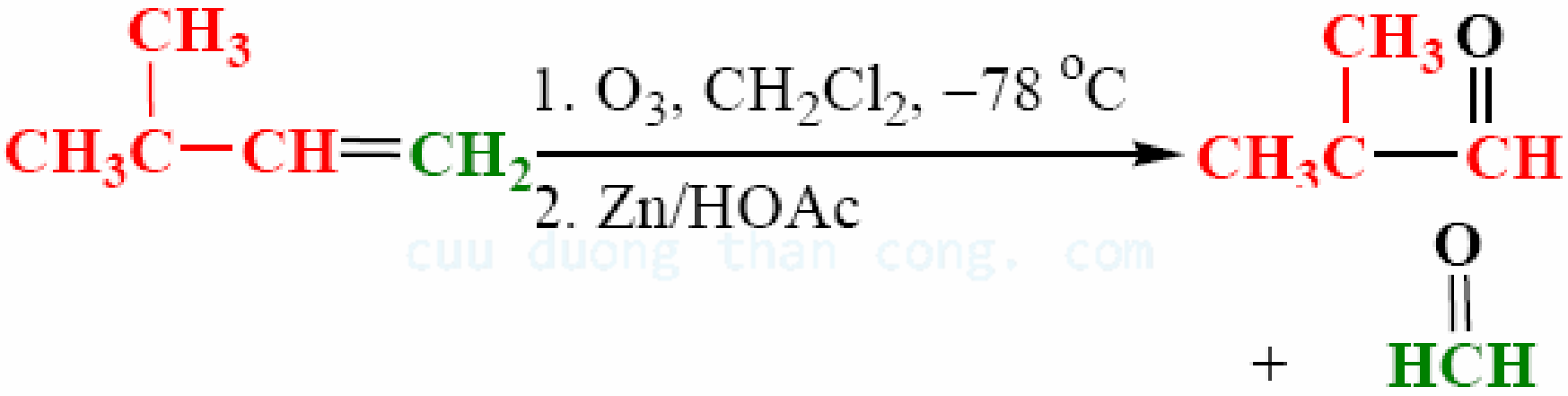



**2-(3-oxopentyl)-cyclohexanone**

# PREPARATION OF ALDEHYDES & KETONES



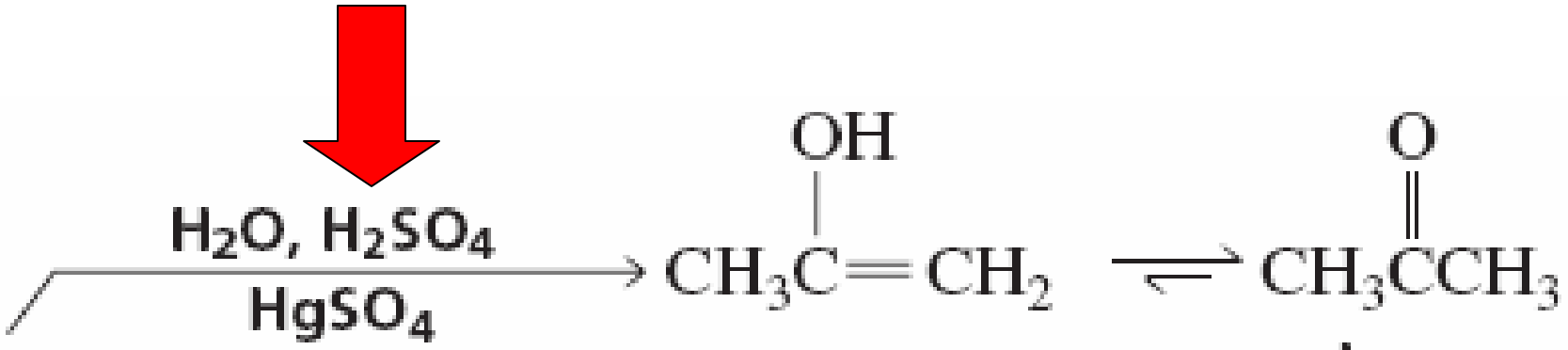

**Aldehydes & ketones from alkenes**



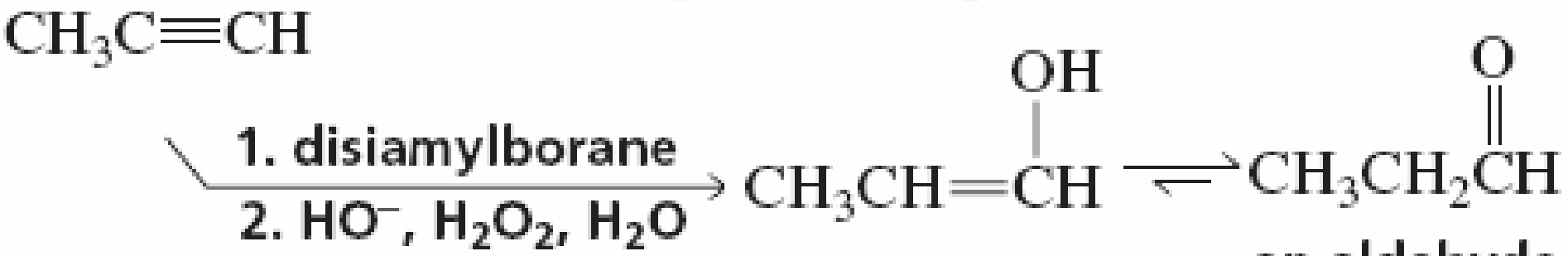

**In the presence of an *oxidizing agent*, the products will be ketones / carboxylic acids**

# Aldehydes & ketones from alkynes

***Markovnikov's rule***



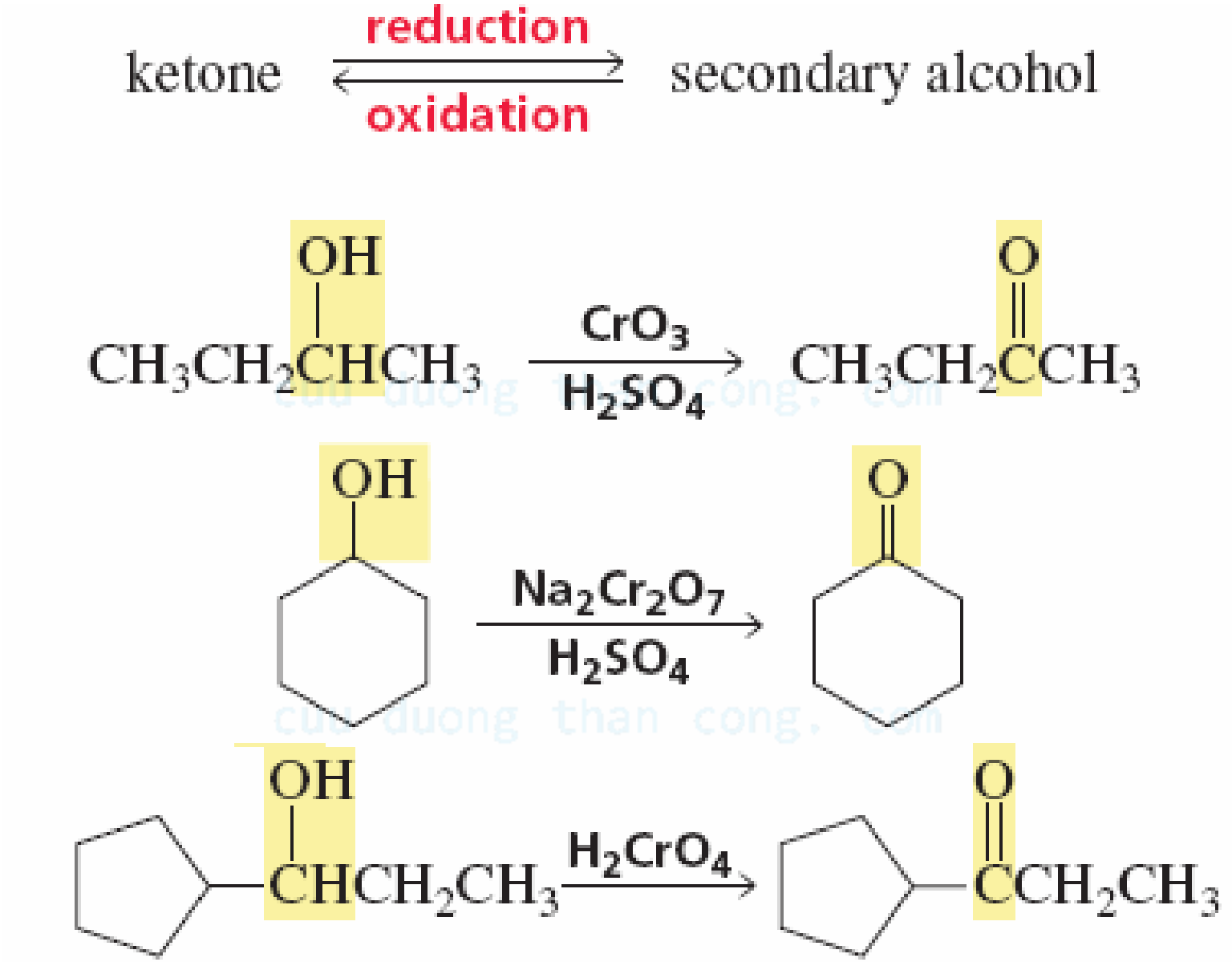


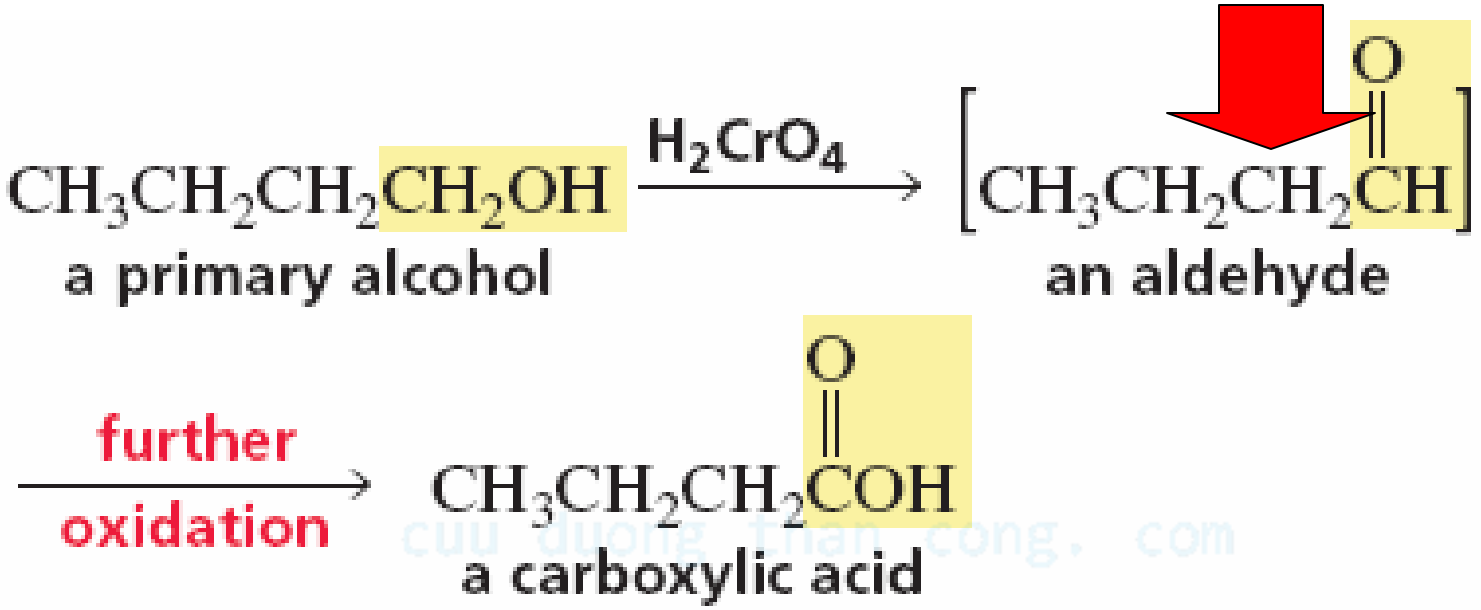


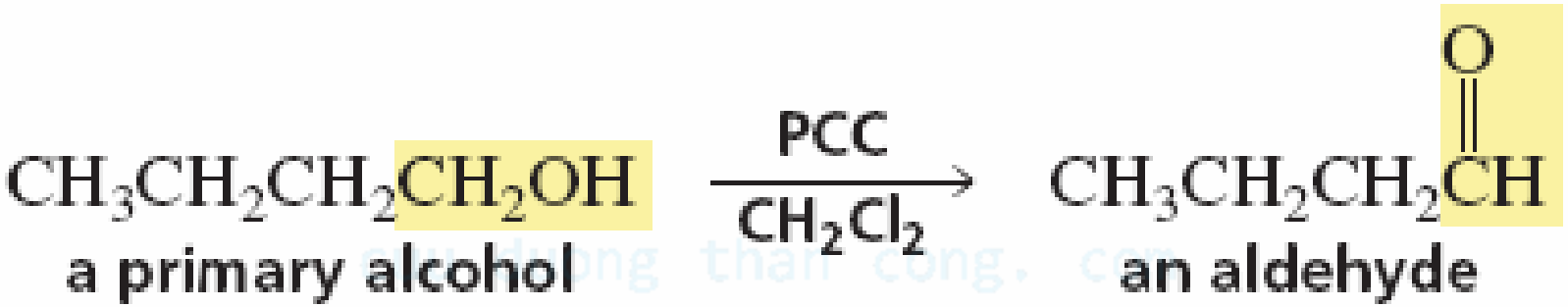

***Anti-Markovnikov***

# Aldehydes & ketones from alcohols



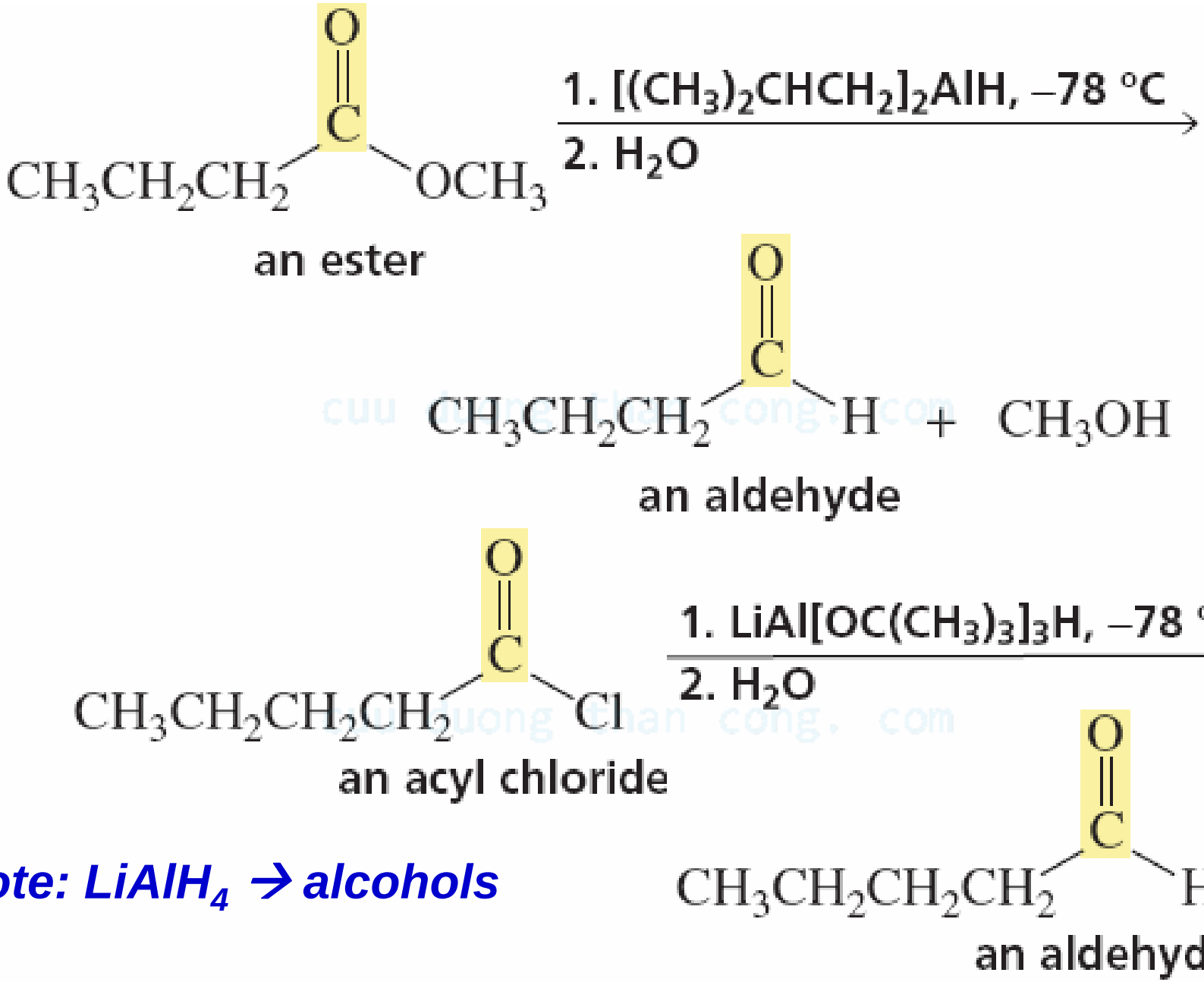
***Can NOT be isolated***



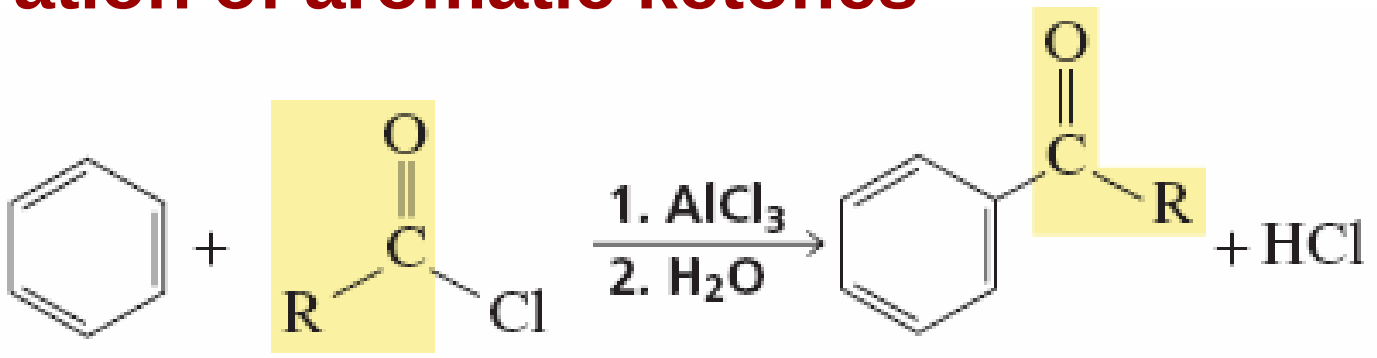

***PCC: pyridinium chlorochromate***

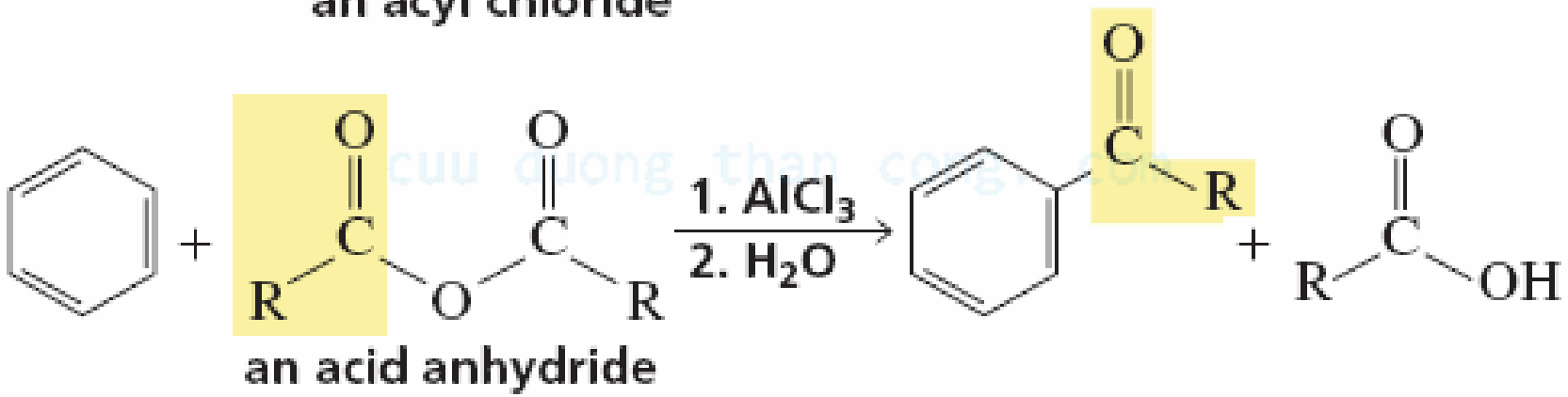
# Aldehydes from esters, acyl chlorides

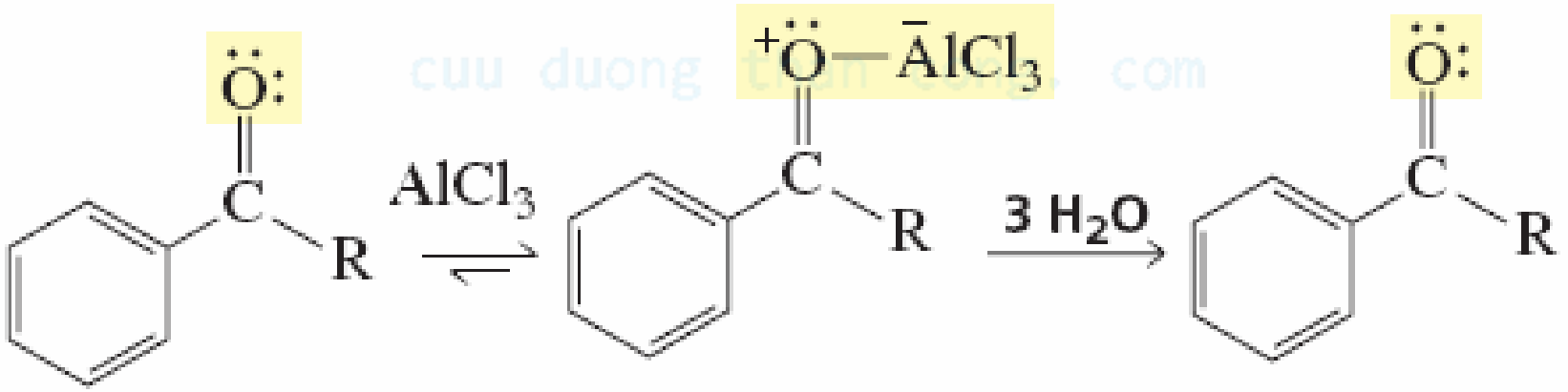



***Note: $LiAlH_4$ → alcohols***

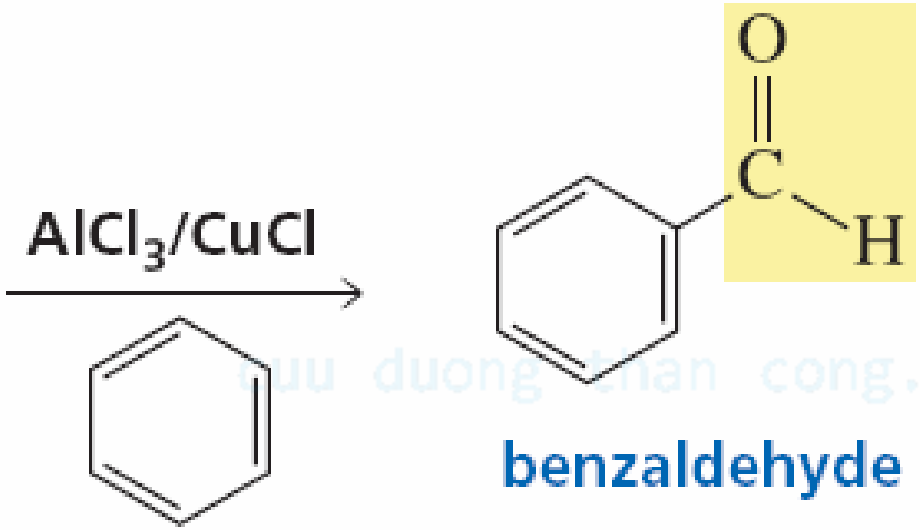
# Preparation of aromatic ketones



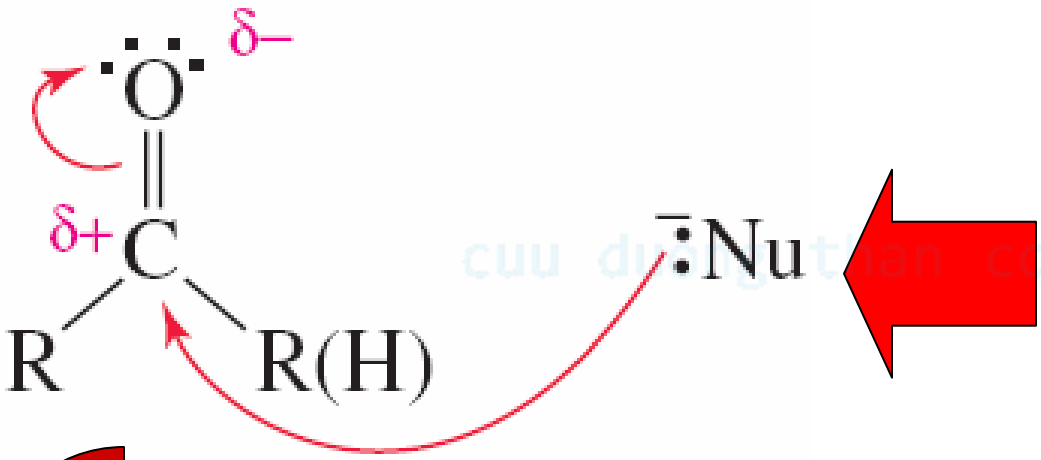



# *Gatterman-Koch synthesis of benzaldehyde*


**Can NOT be prepared & isolated**

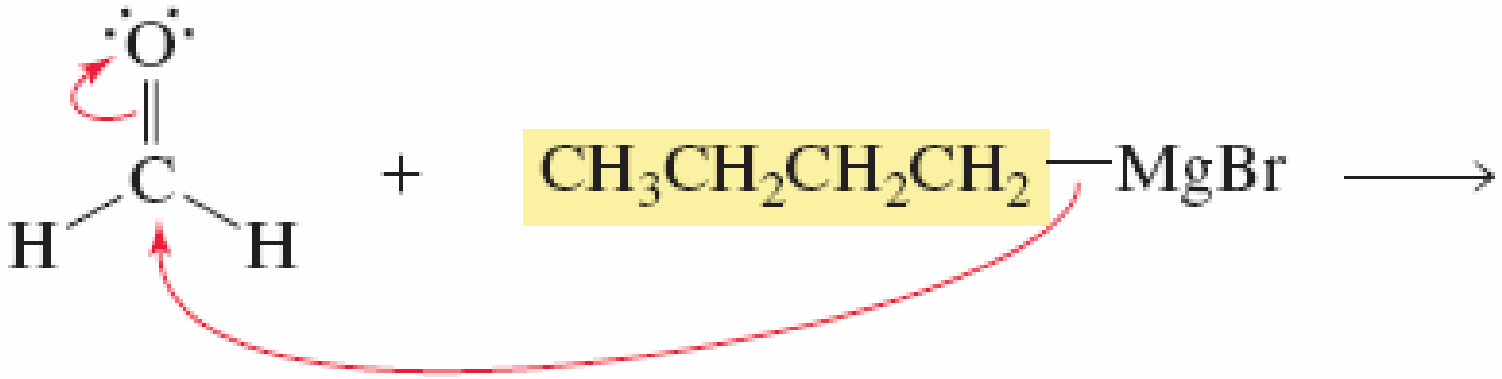
# REACTIONS OF ALDEHYDES & KETONES I




**The partial positive carbon can be attacked by nucleophiles**

***The addition of nucleophiles to the carbon atom of the carbonyl group in <u>nucleophilic addition reactions</u>***

# Reactions with Grignard reagents




formaldehyde

butylmagnesium bromide

$CH_3CH_2CH_2CH_2CH_2\ddot{O}:^{-}\ {}^{+}MgBr \xrightarrow{H_3O^+} CH_3CH_2CH_2CH_2CH_2\ddot{O}H$

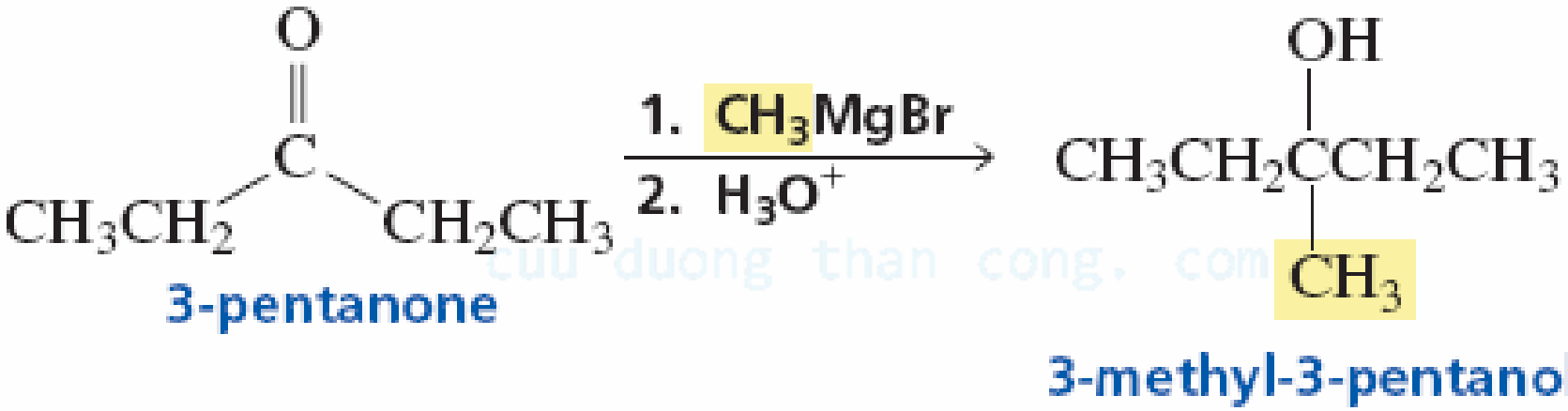
an alkoxide ion

1–pentanol

a primary alcohol

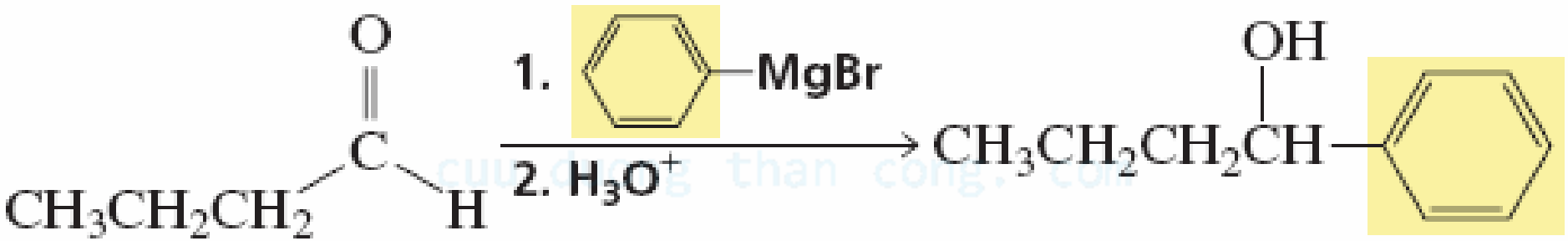
**Only for the reaction of HCHO**

***Numbers 1 & 2 are used to indicate that the acid is not added until the reaction with the Grignard reagent is complete***




3-pentanone

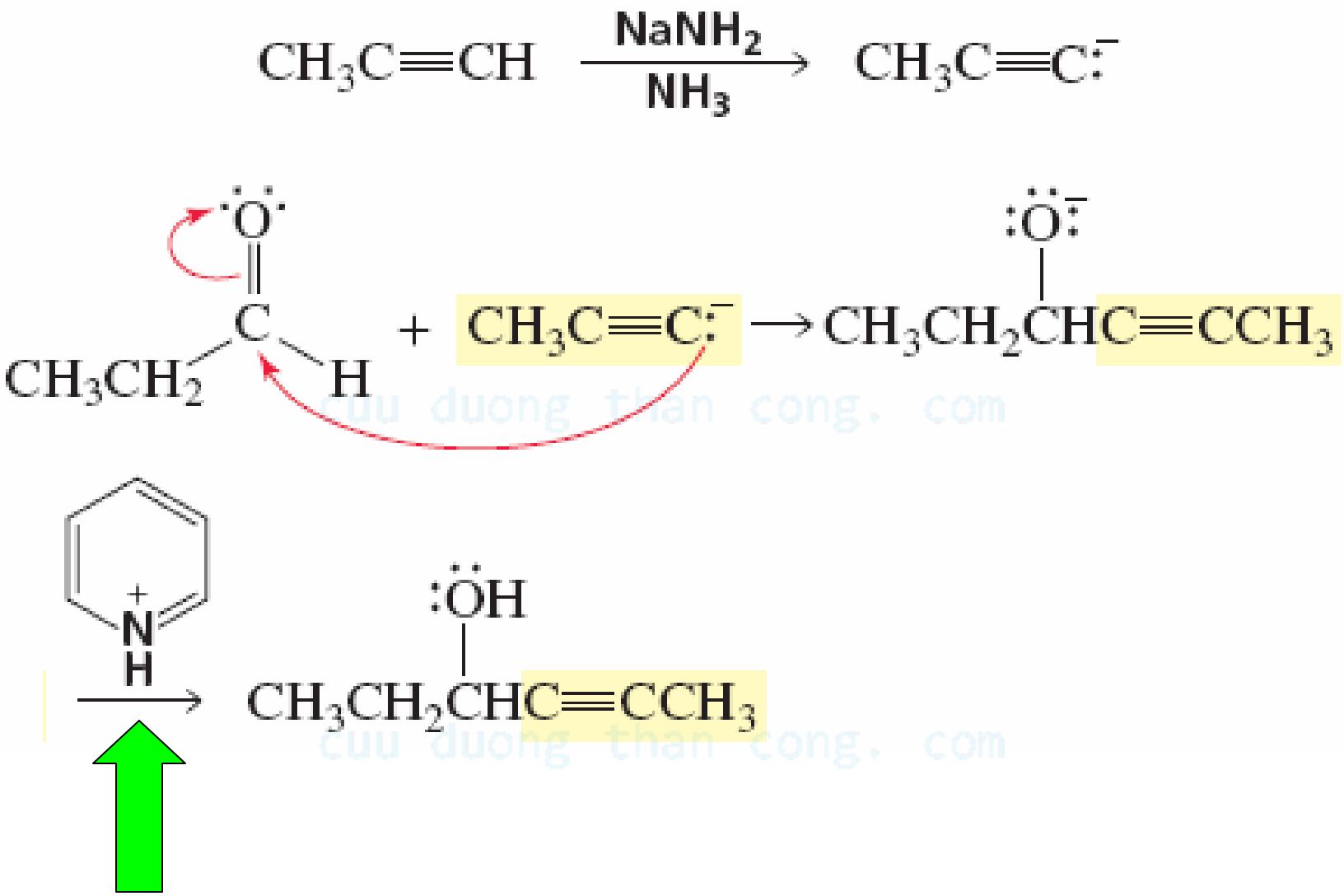
3-methyl-3-pentanol




butanal

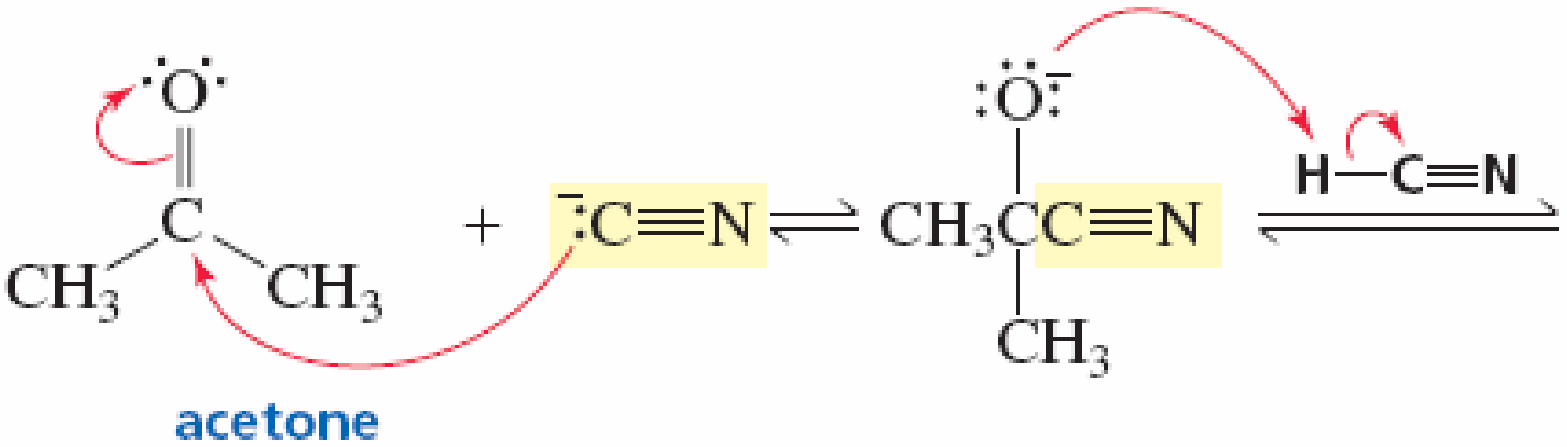
1-phenyl-1-butanol

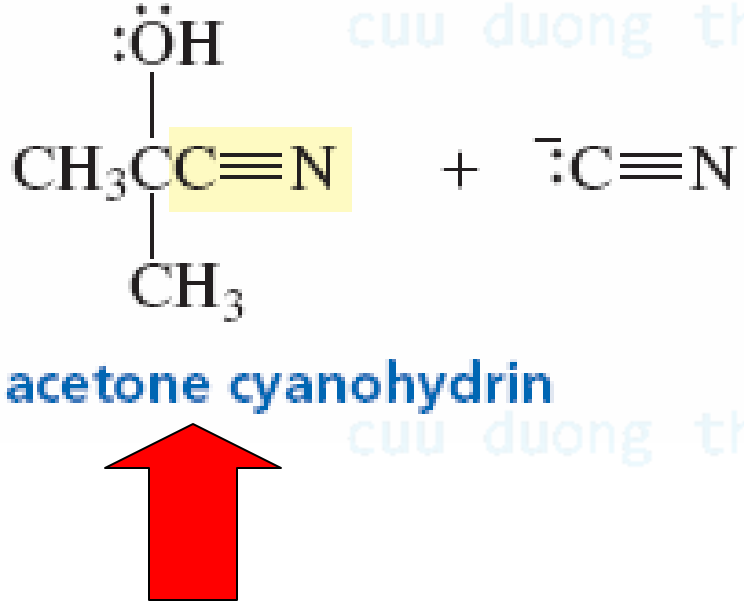
# Reactions with acetylide ions




***Weak acid, will NOT react with the triple bond***

# Reactions with hydrogen cyanide



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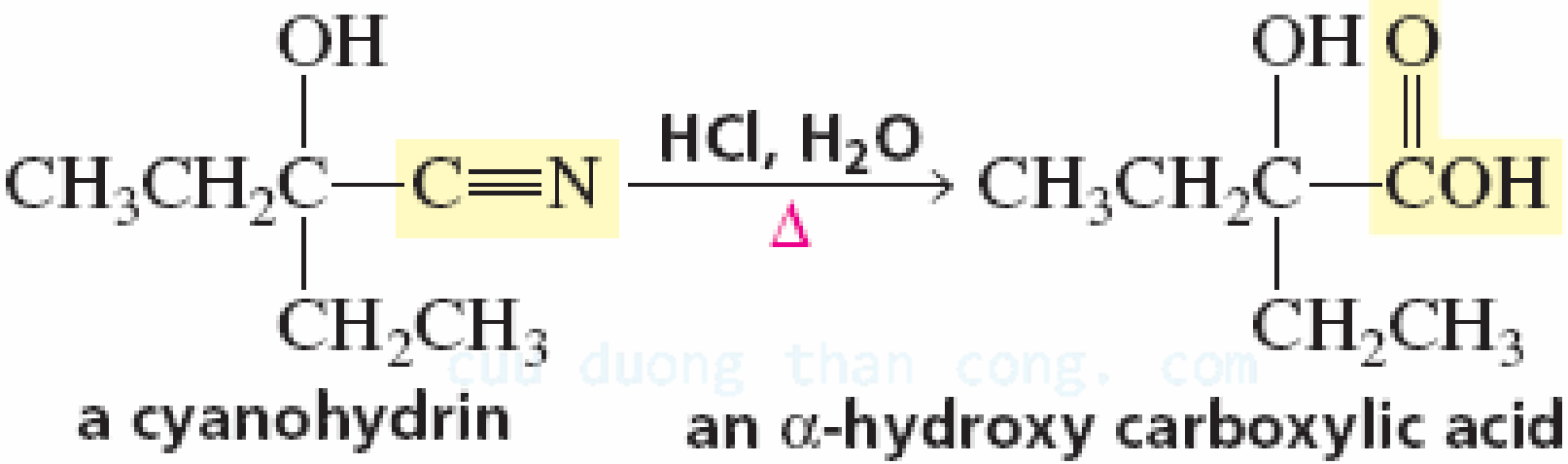
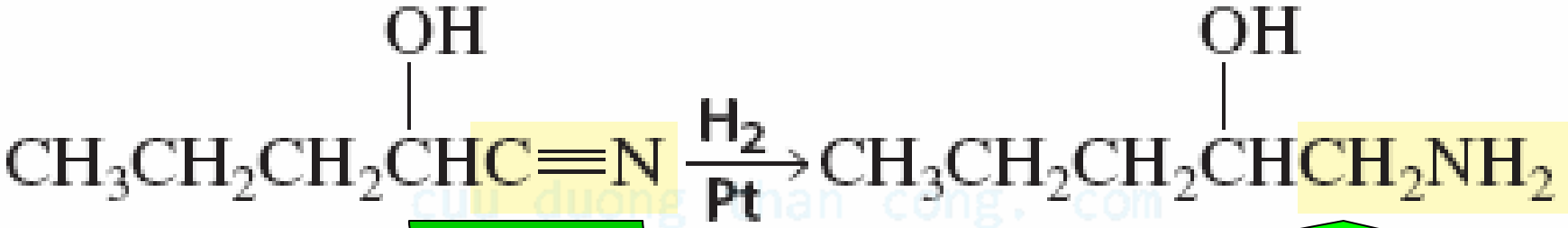
***Converted back to carbonyl in basic solutions***

## *Nitriles → carboxylic acids*



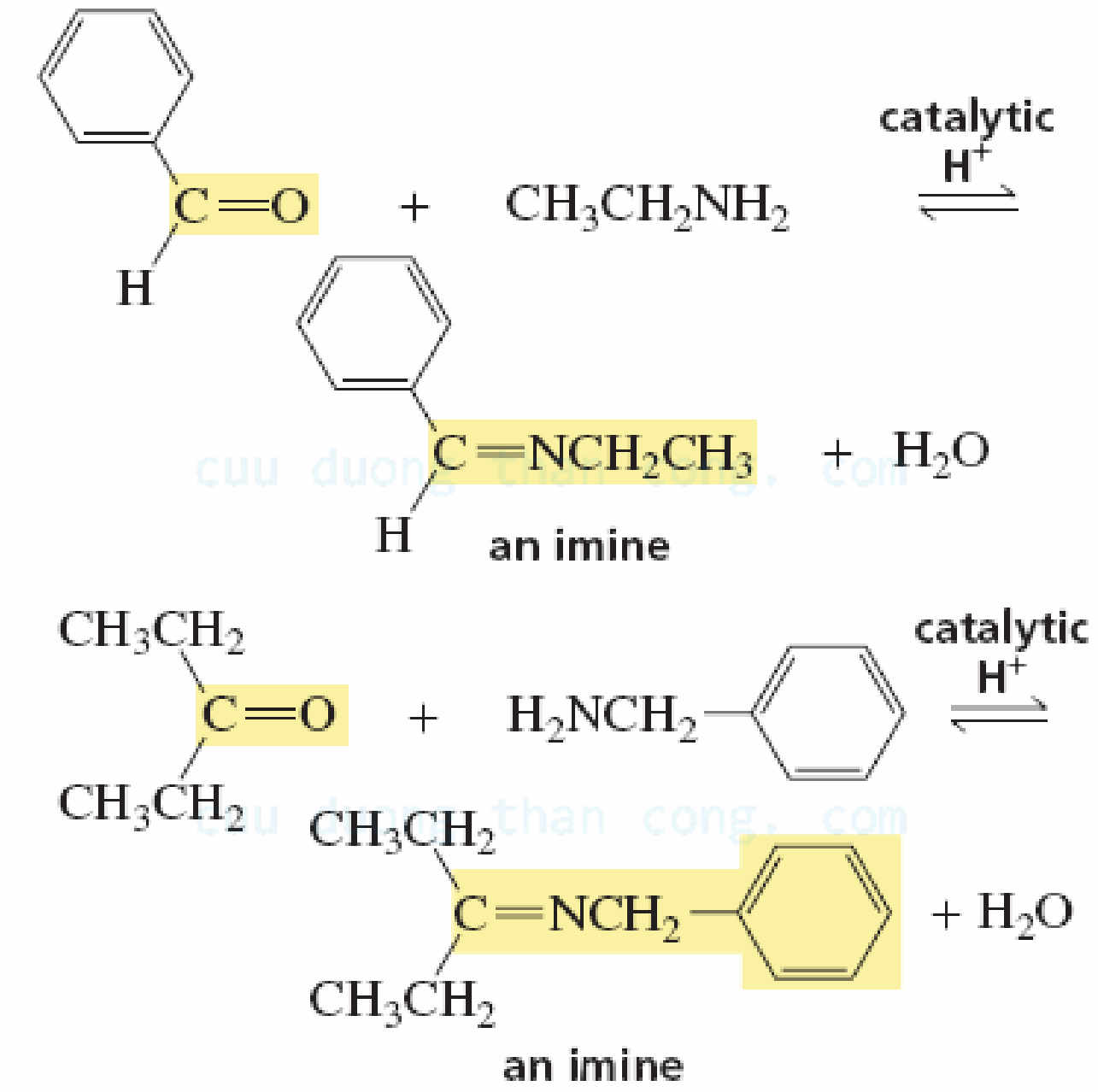

a cyanohydrin

an α-hydroxy carboxylic acid

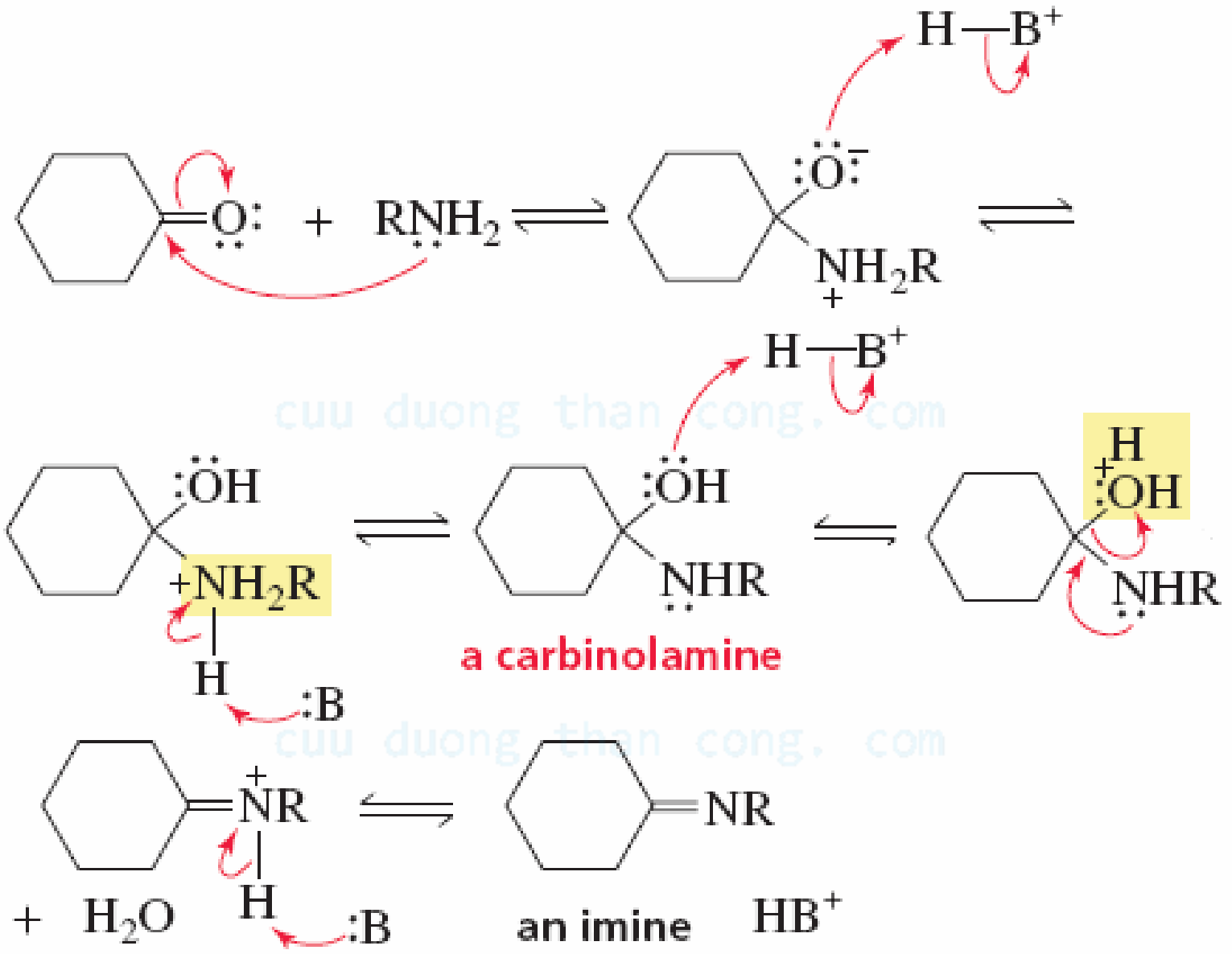



## *Nitriles → amines*

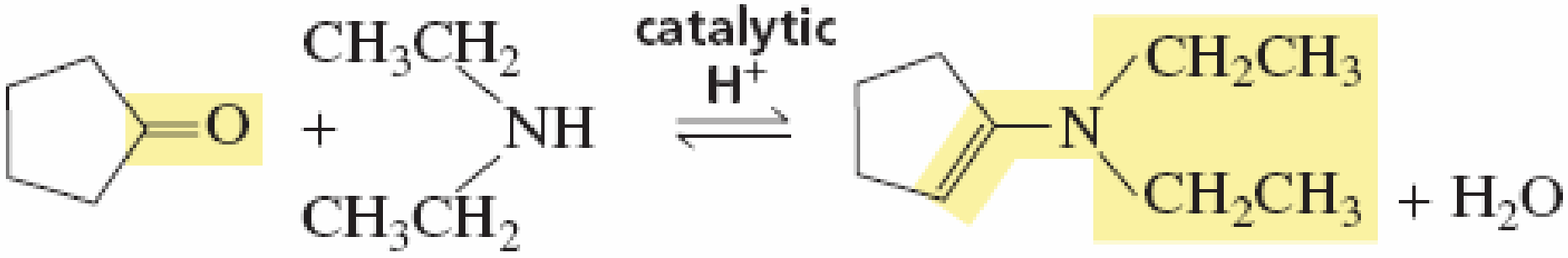
# Reactions with primary amines



# *Reaction mechanism:*



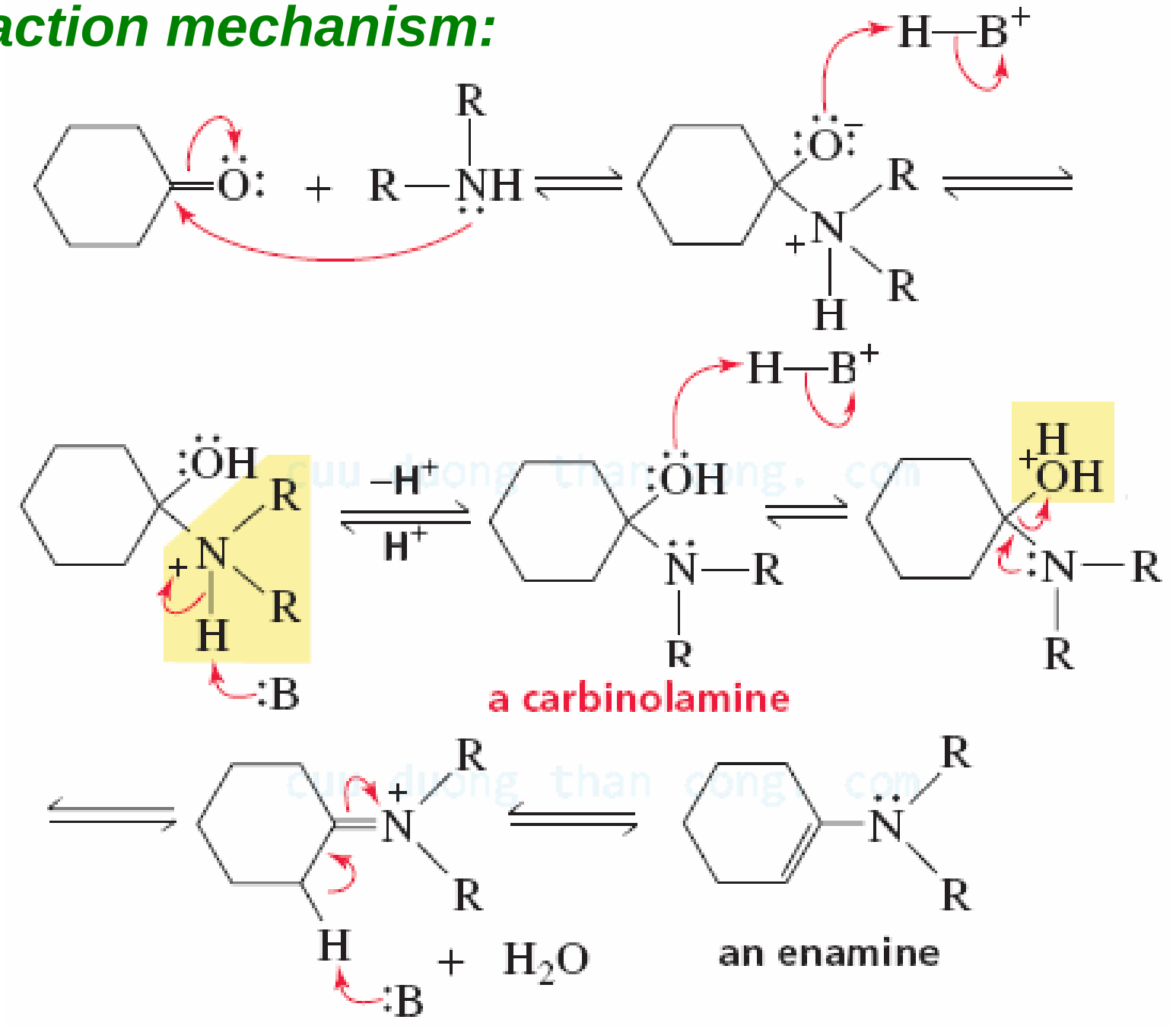
# Reactions with secondary amines



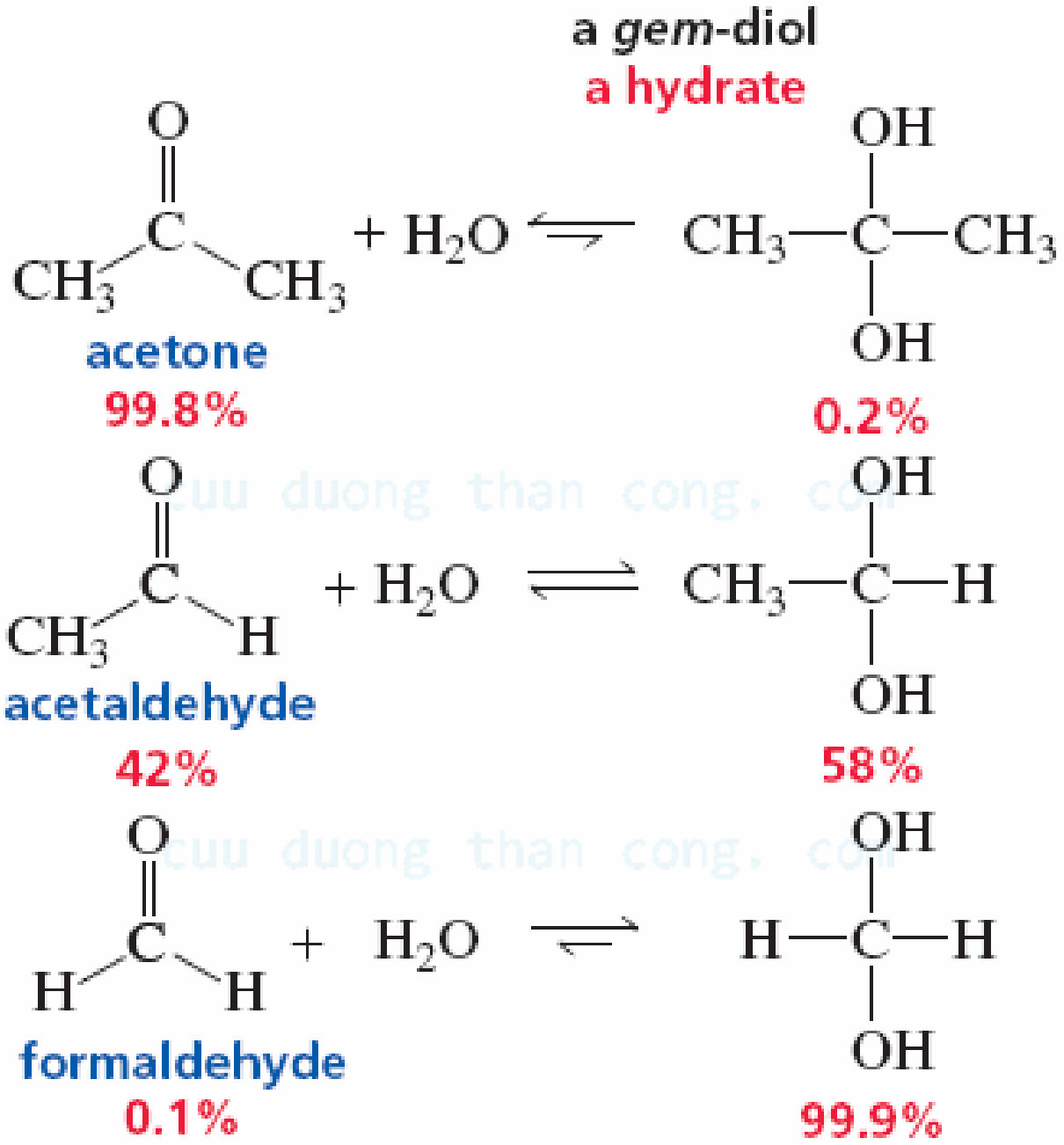

an enamine


an enamine

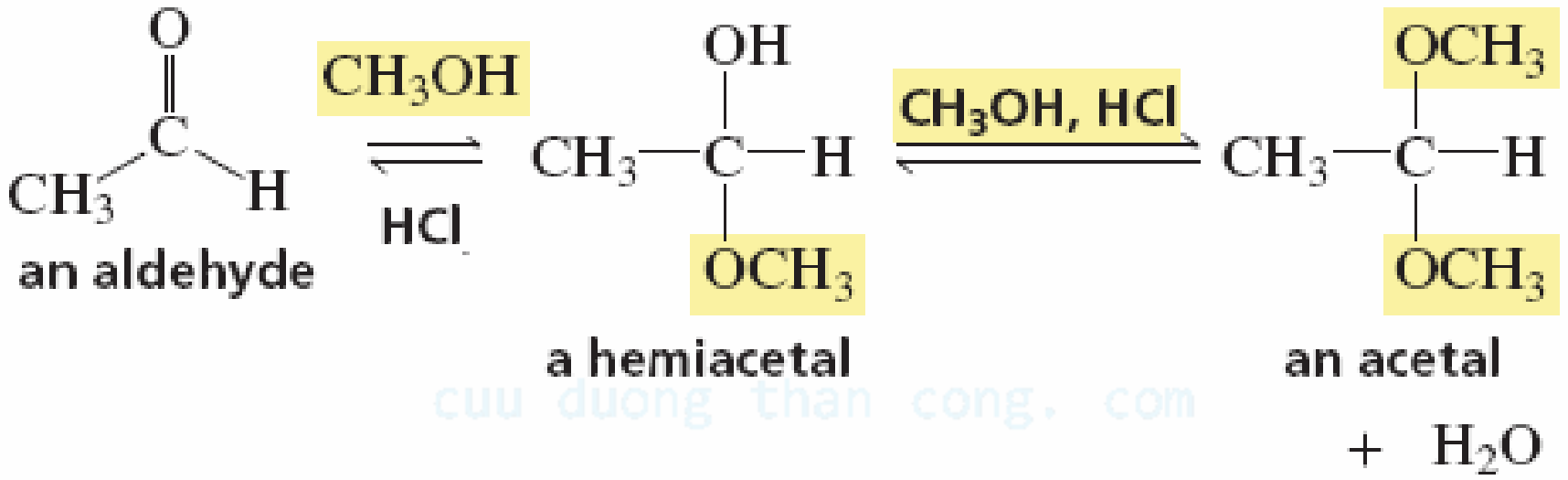
# Reaction mechanism:

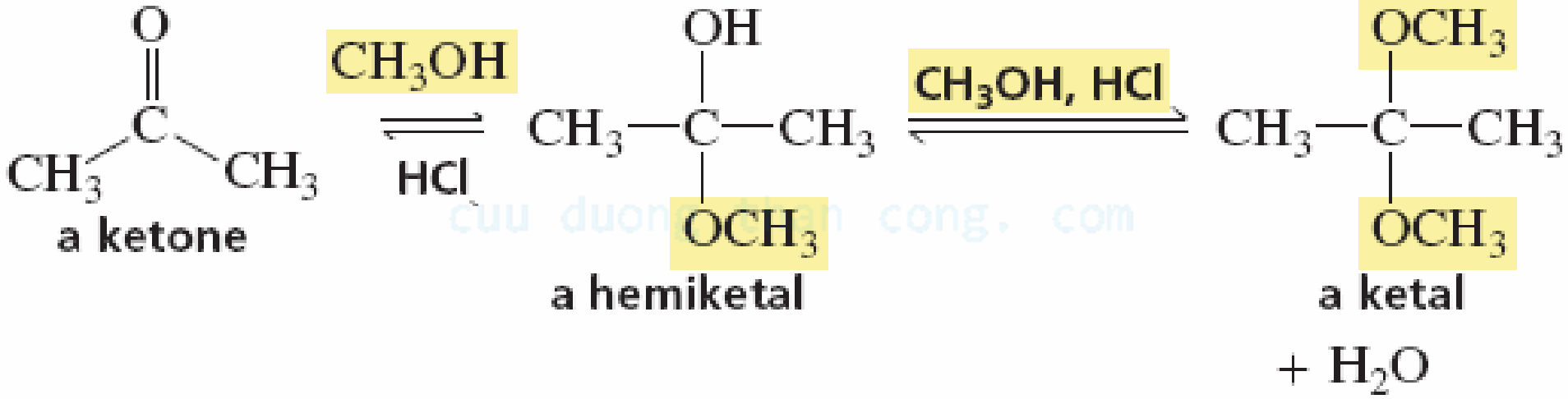


# Reactions with water

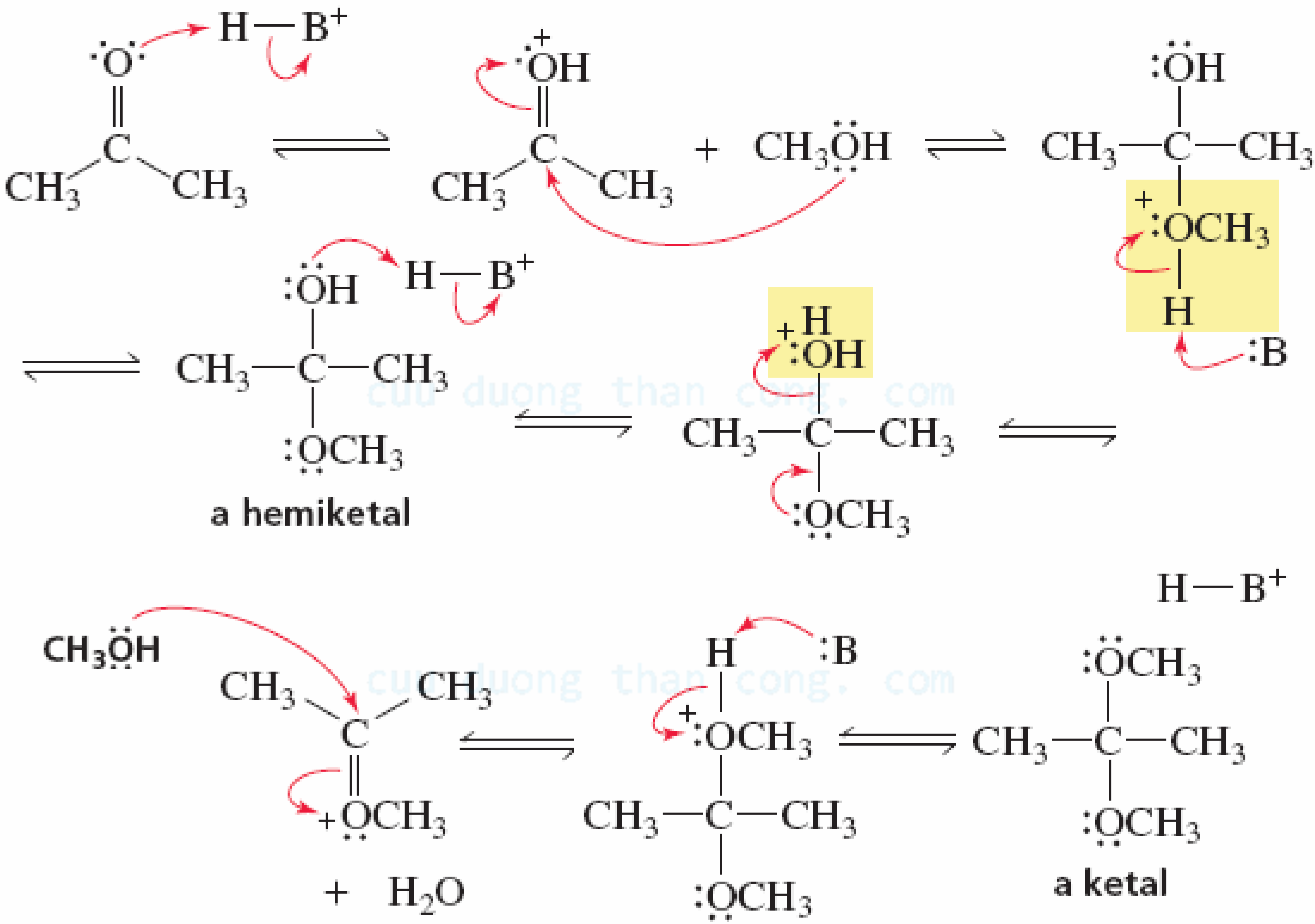


# Reactions with alcohols

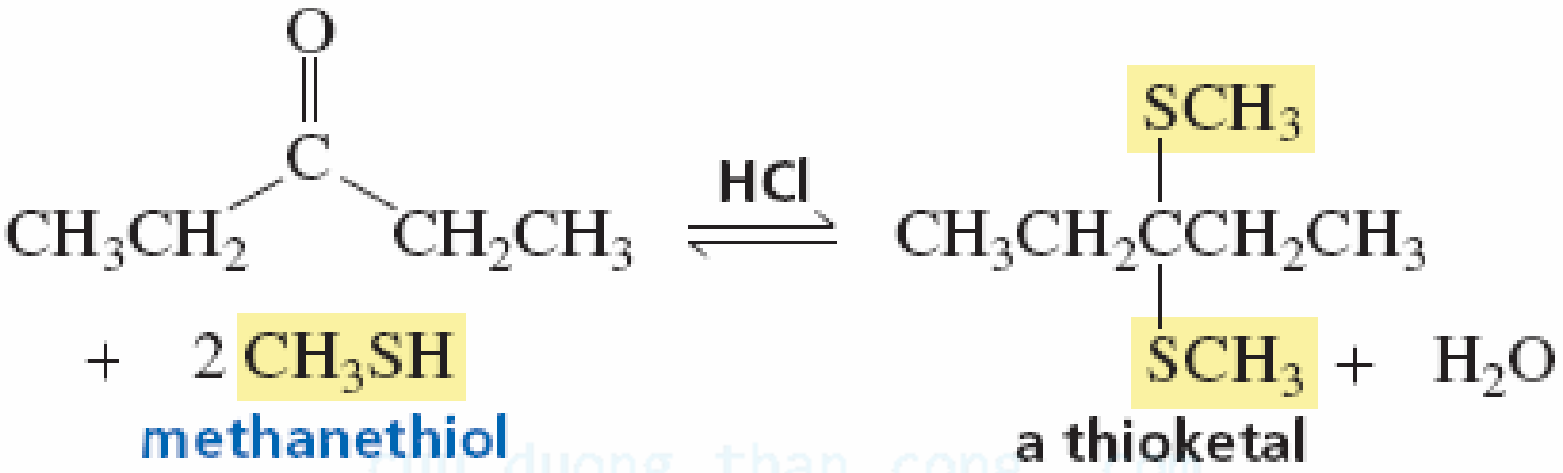


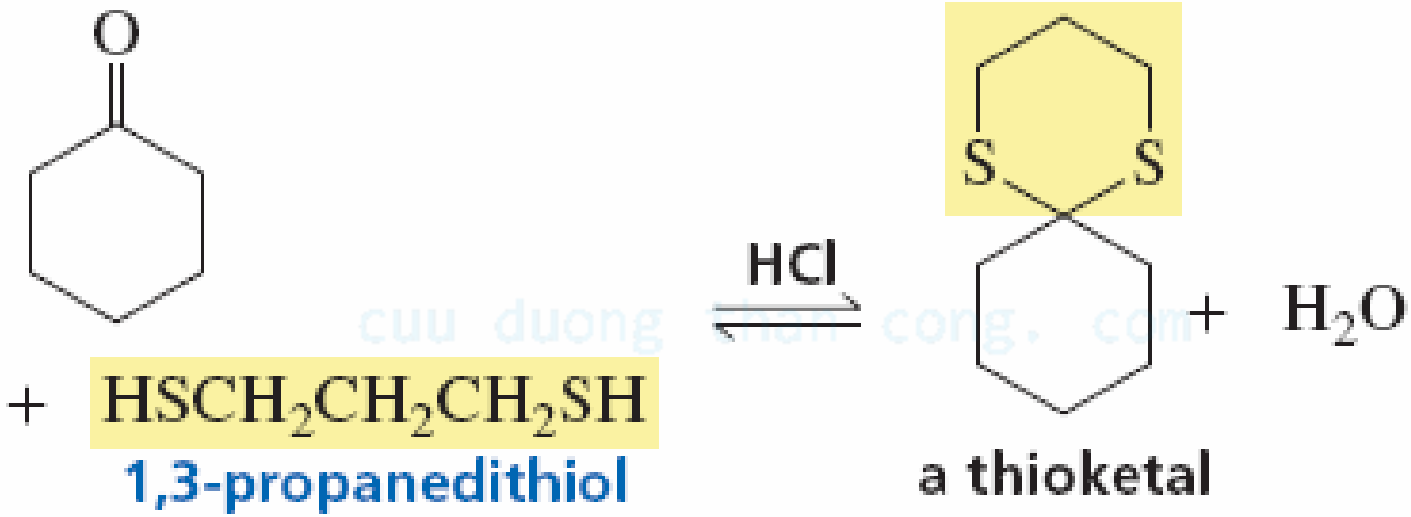



# Reaction mechanism:

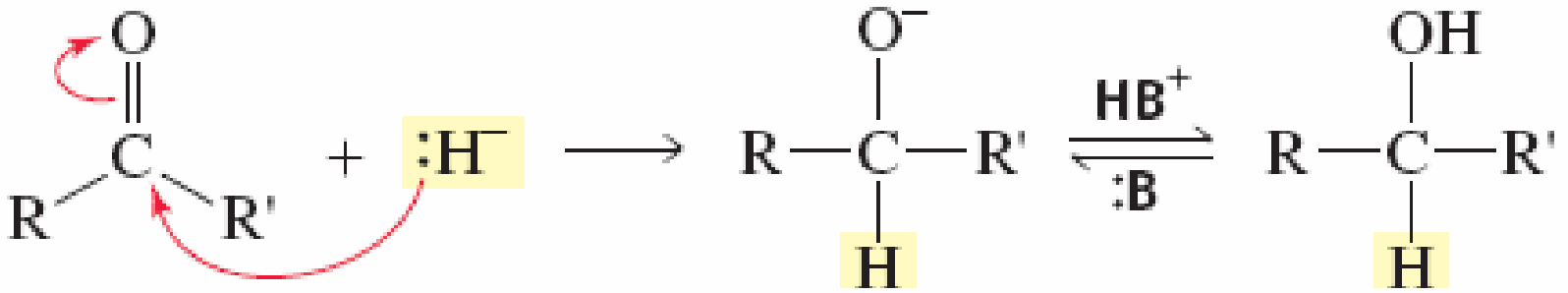


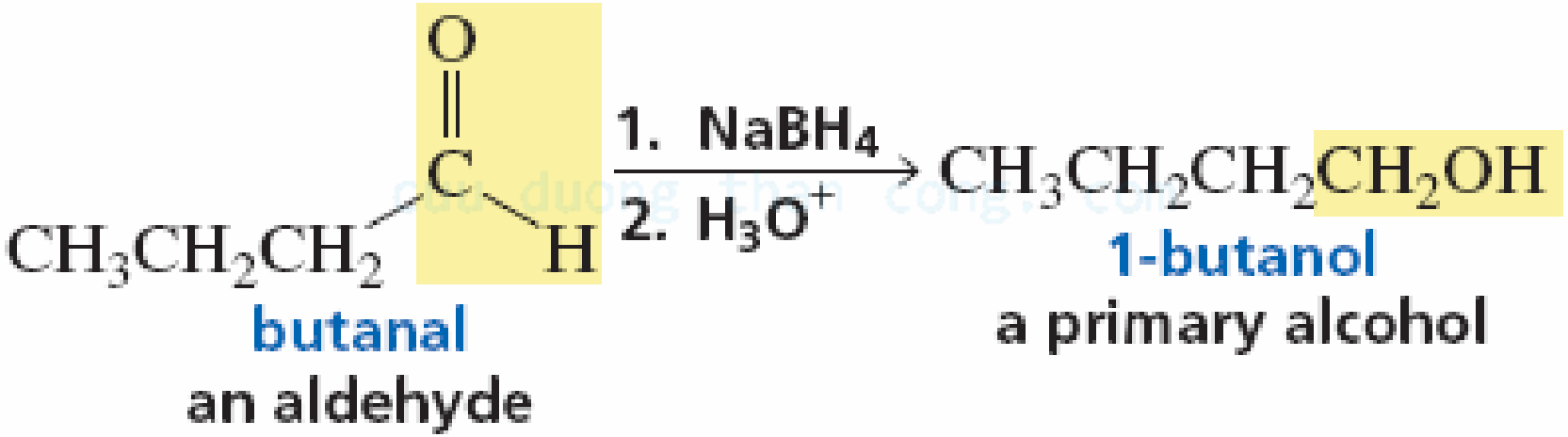
# Reactions with sulfur nucleophiles



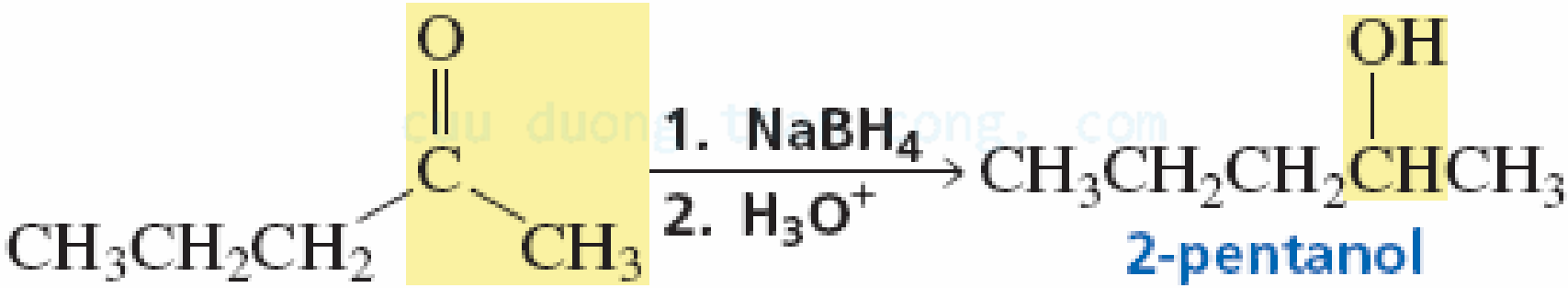
# Reduction reactions – with hydride ion




butanal
an aldehyde

1-butanol
a primary alcohol

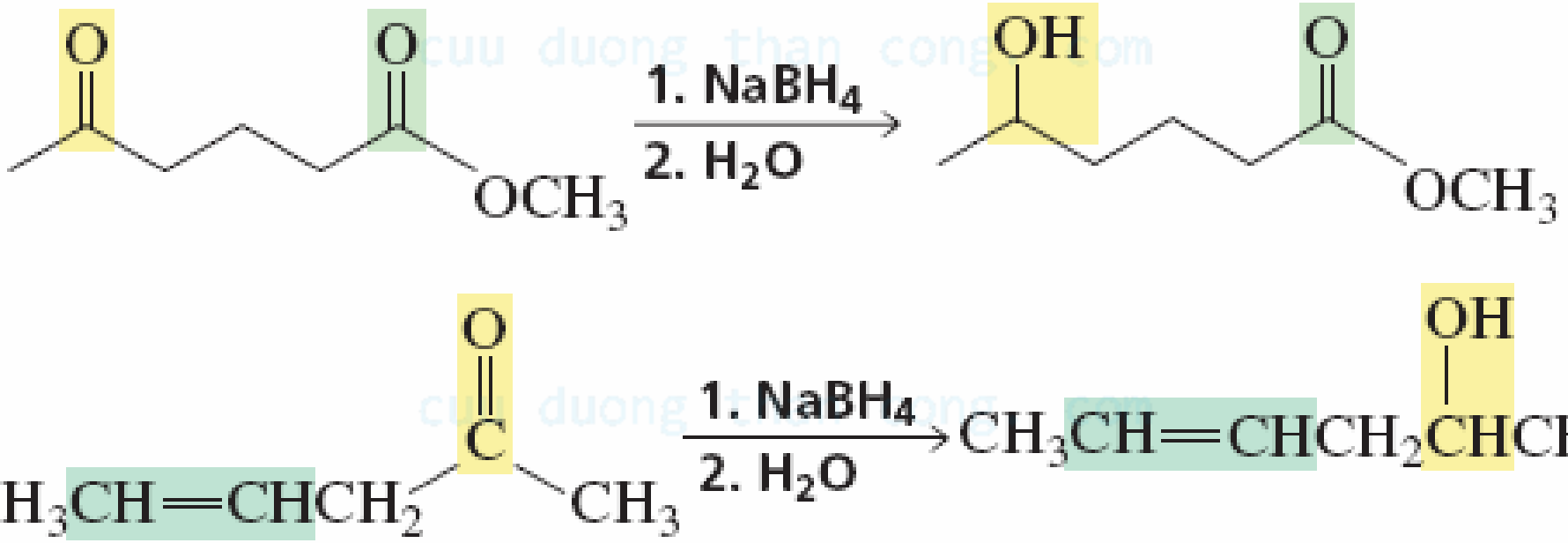



2-pentanone
a ketone

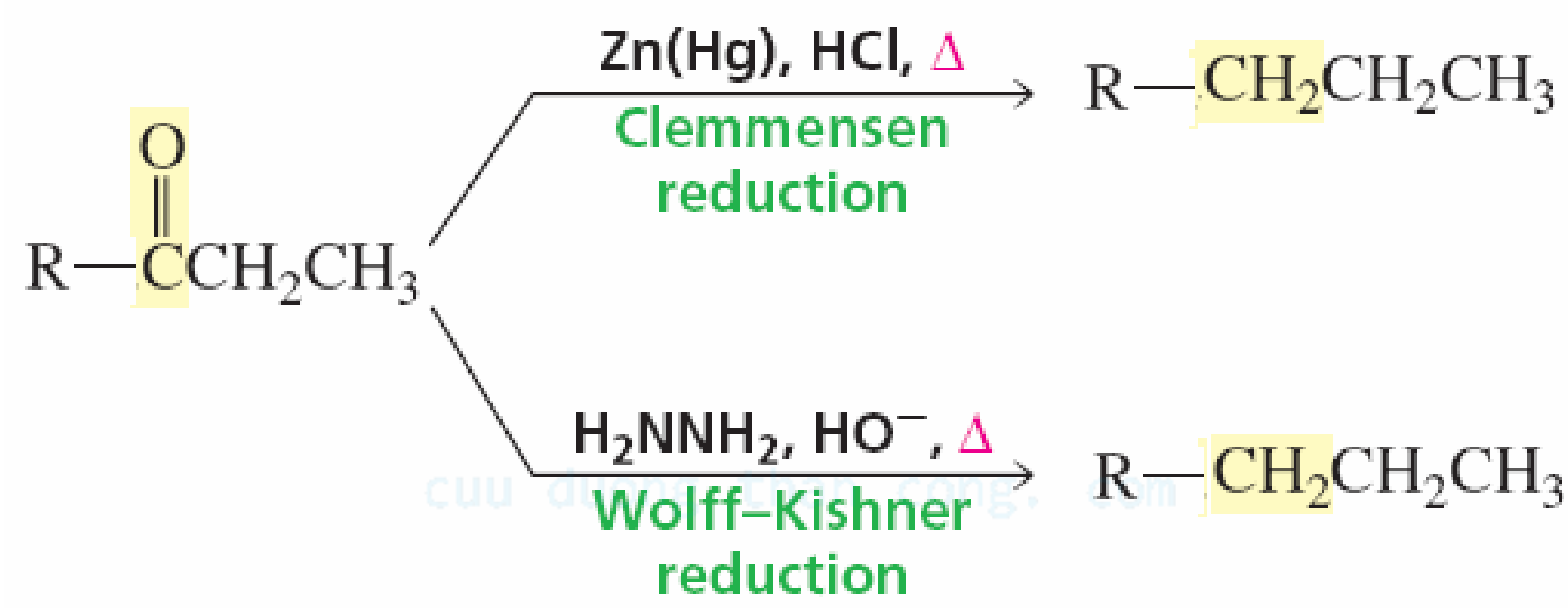
2-pentanol
a secondary alcohol

- ***$NaBH_4$ can reduce aldehyde, ketones, acyl chlorides, but NOT alkenes & alkynes***

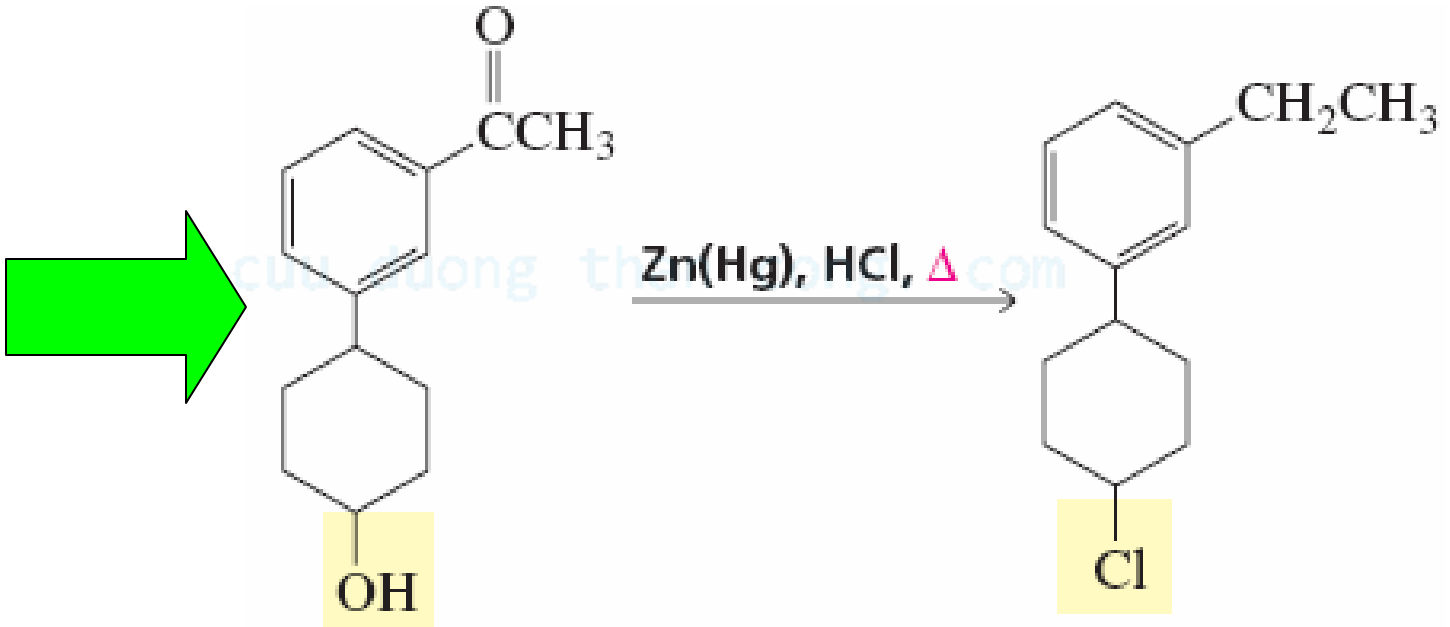
- ***$LiAlH_4$ is a stronger reducing agent than $NaBH_4$, but NOT safe to use for aldehydes & ketones***



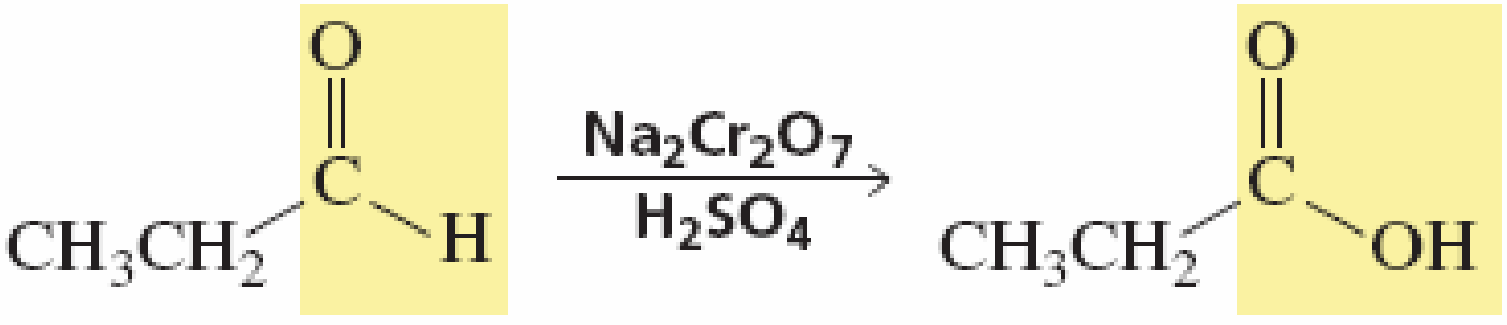
# Reduction reactions to hydrocarbons

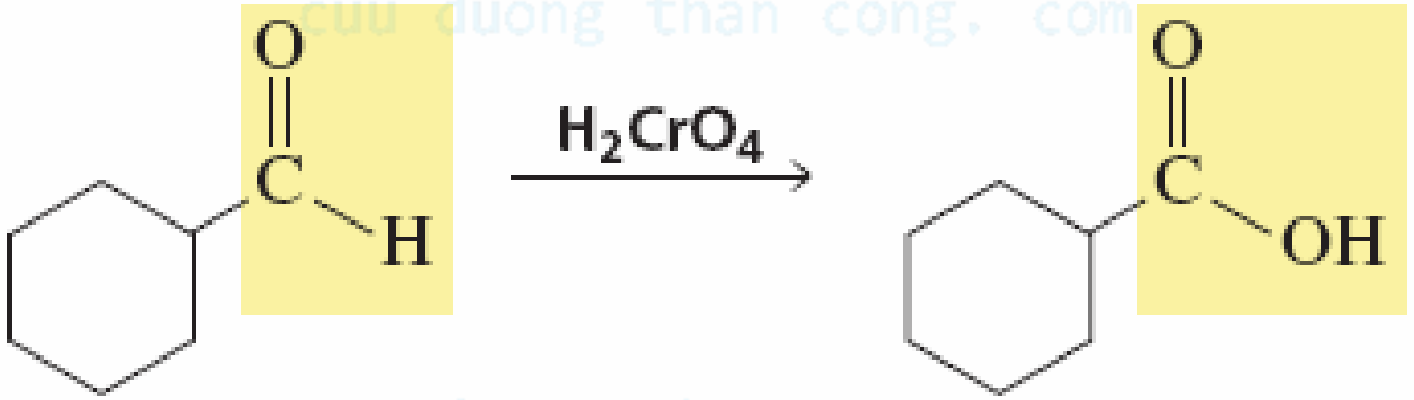



***NOTE:***



# Oxidation reactions



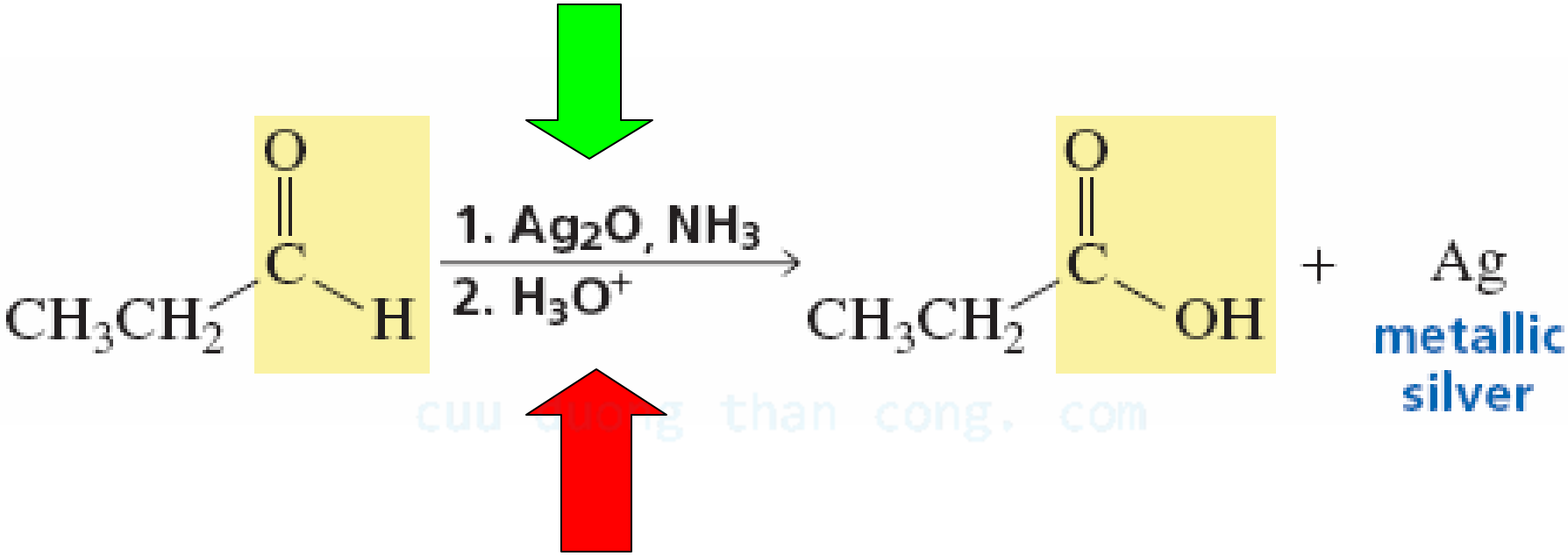




aldehydes carboxylic acids



***Aldehydes are generally easier to oxidize than primary alcohols***

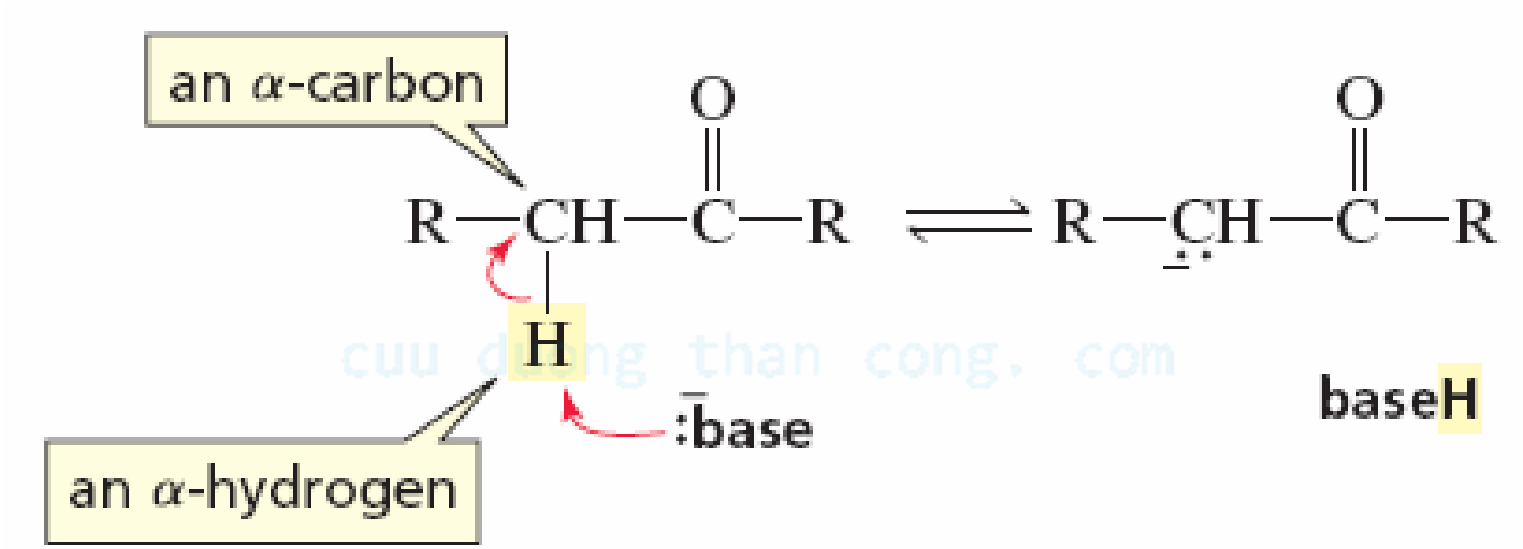
## *Tollens reagent*

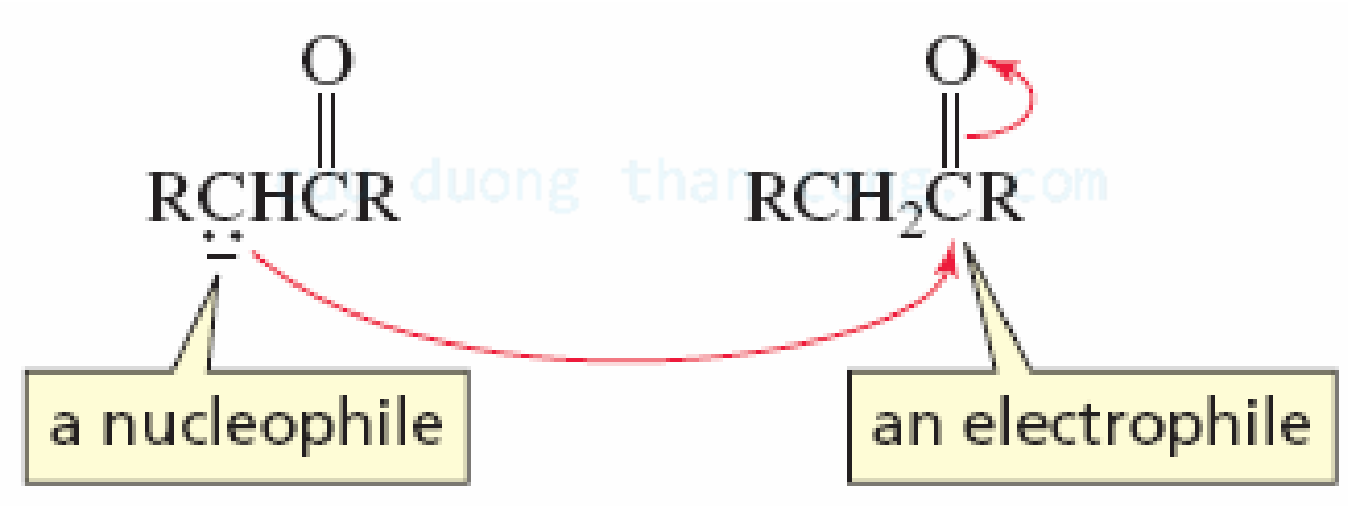



**Too weak to oxidize an alcohol or any other functional groups**

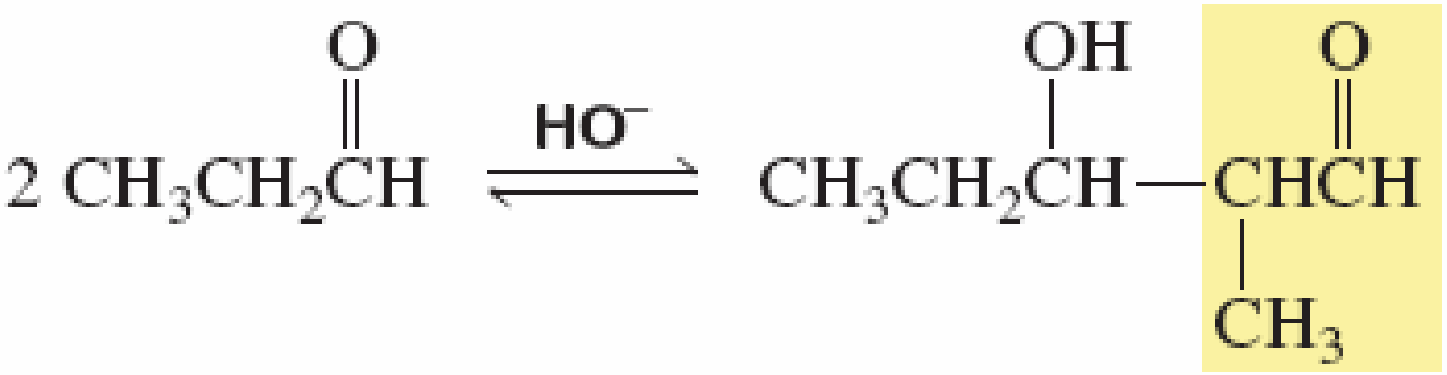
***Should be used when oxidizing aldehydes containing double bond***

# REACTIONS OF ALDEHYDES & KETONES II – REATIONS AT α-C

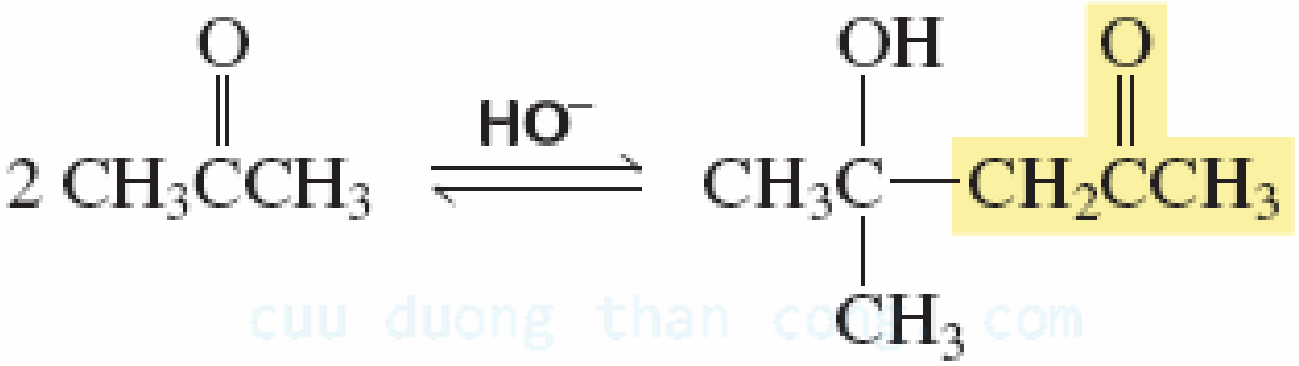


# Aldol additions



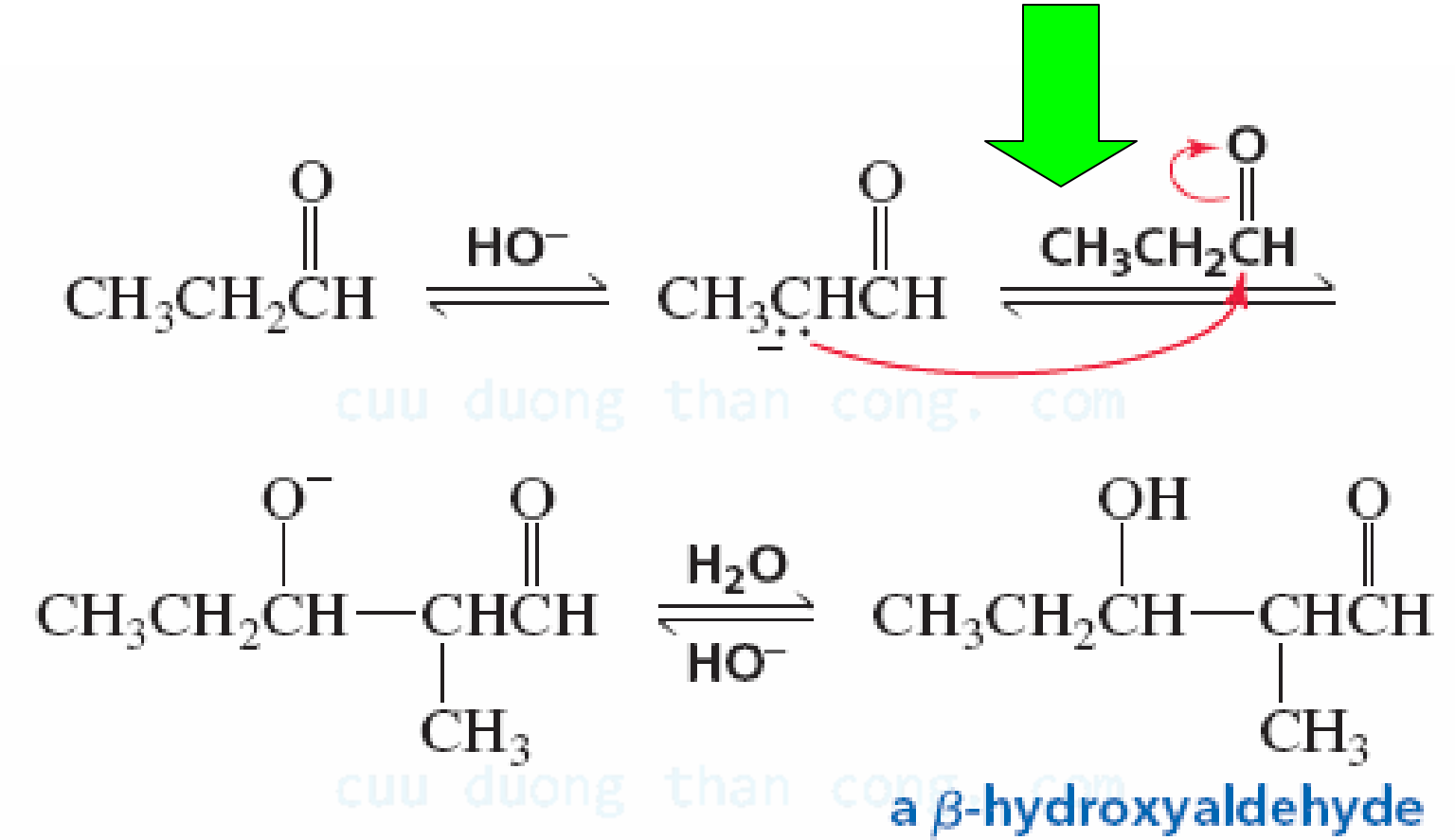

a β-hydroxyaldehyde




a β-hydroxyketone

## *Reaction mechanism:*

### *Nucleophilic additions*

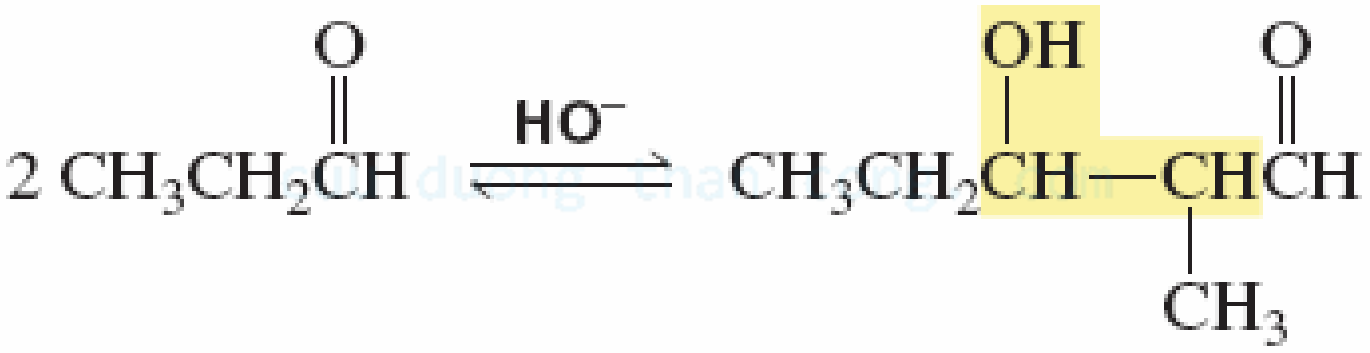




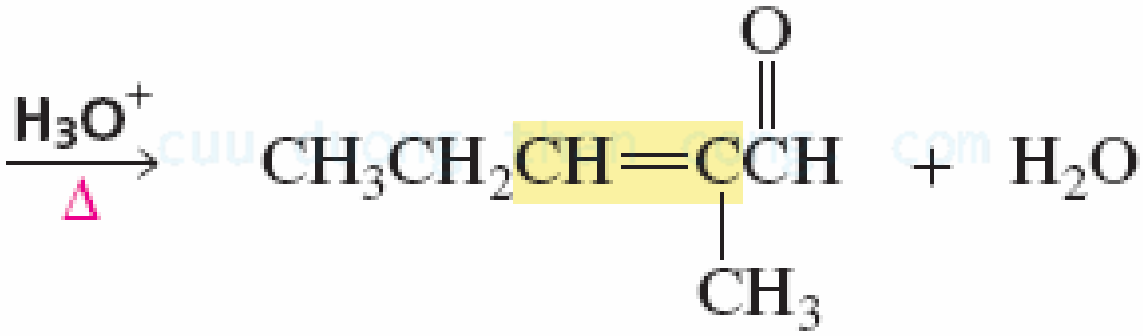

***Aldol additions occur more slowly with ketones***

# Aldol condensations = Additions + dehydrations

***Easier to dehyrate than other alcohols because the double bond is conjugated with the carbonyl group***

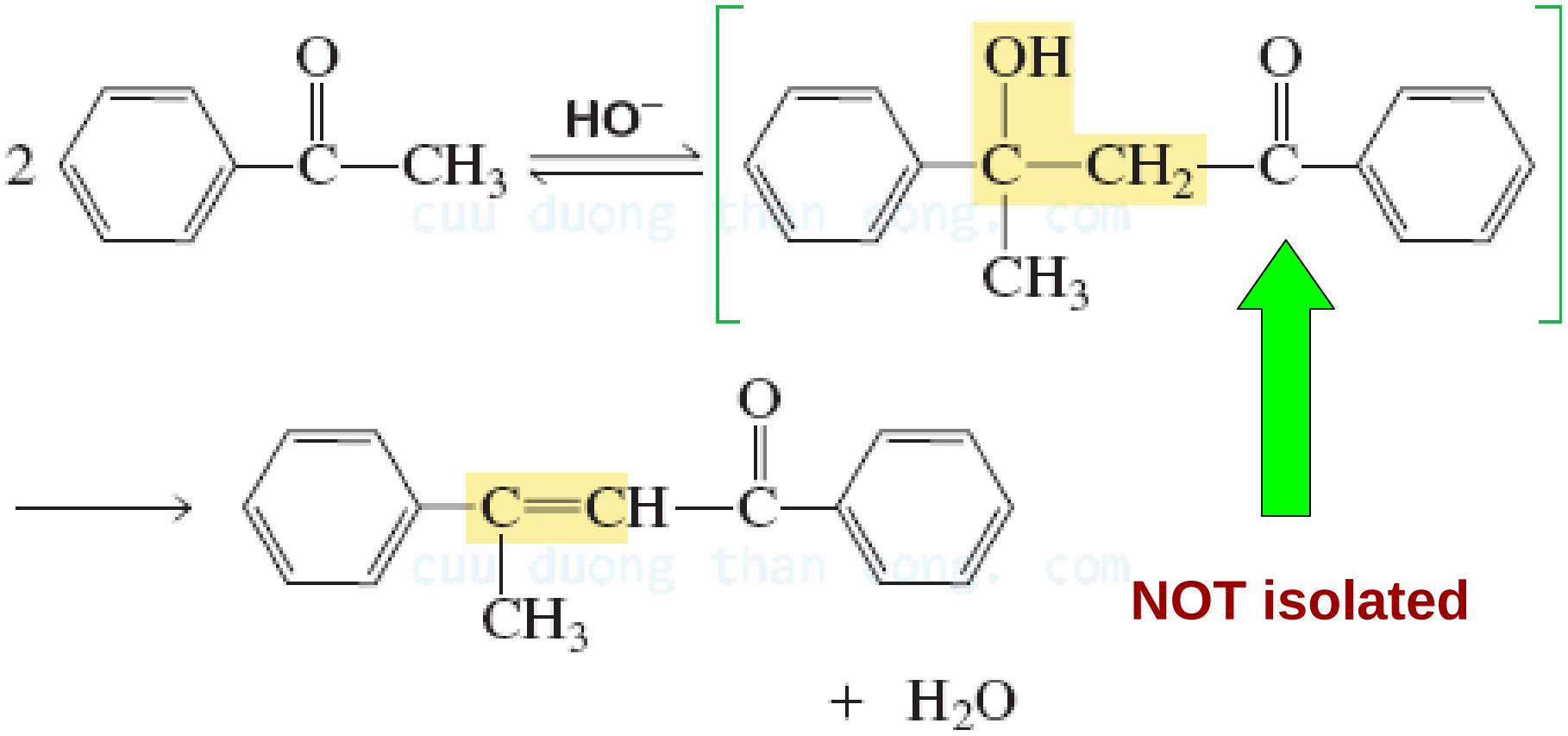



a β-hydroxyaldehyde

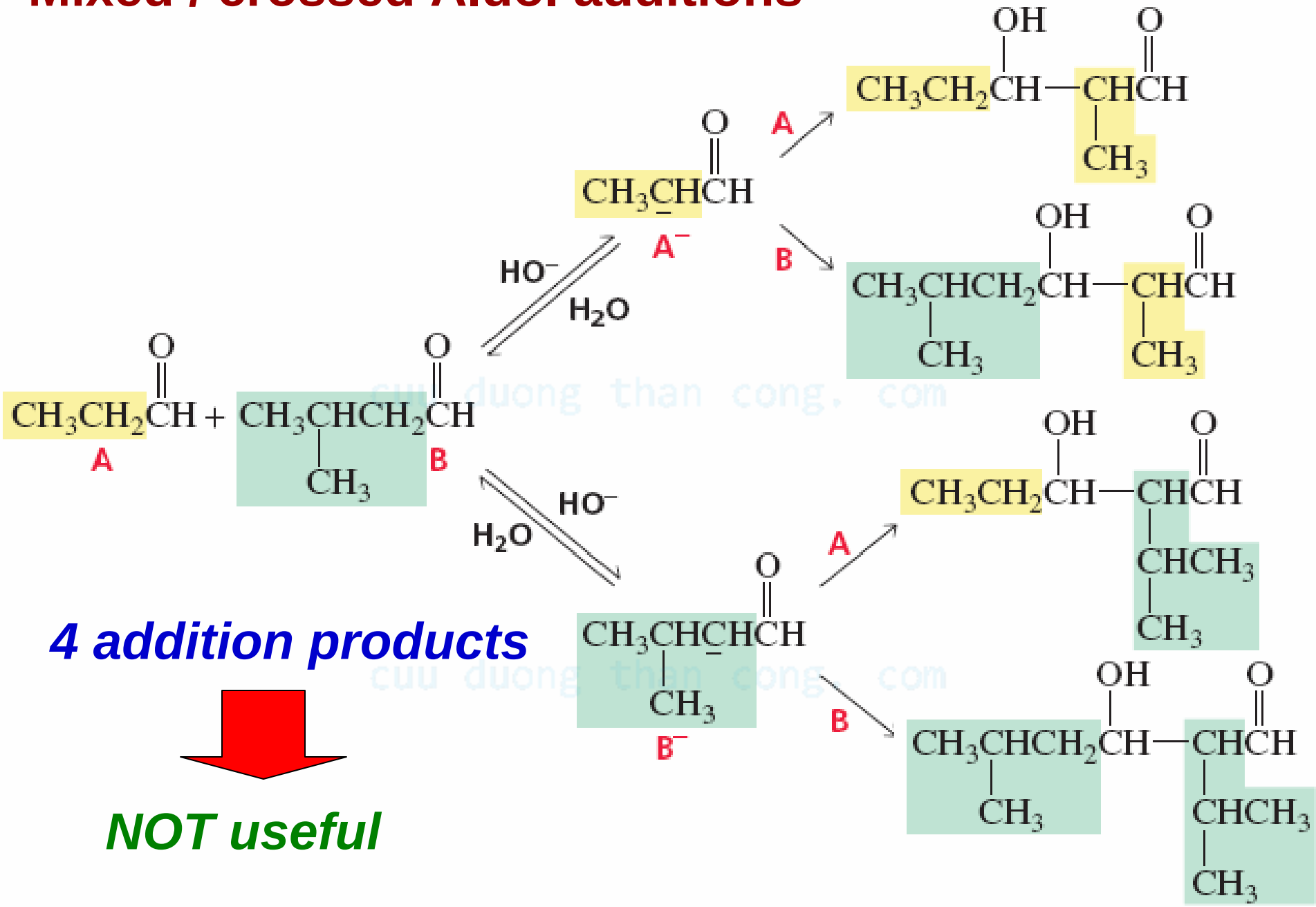


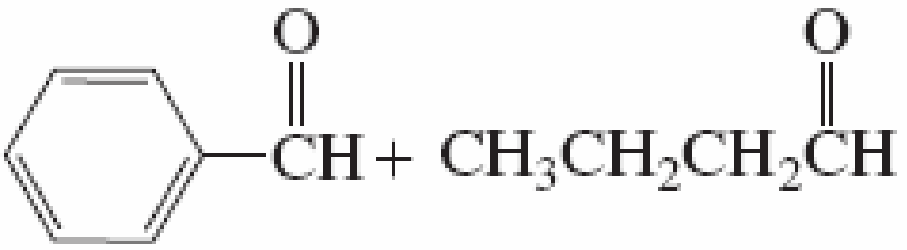

an α,β-unsaturated aldehyde

## *Aldol condensations sometimes occur under the aldol addition conditions without additional heating*



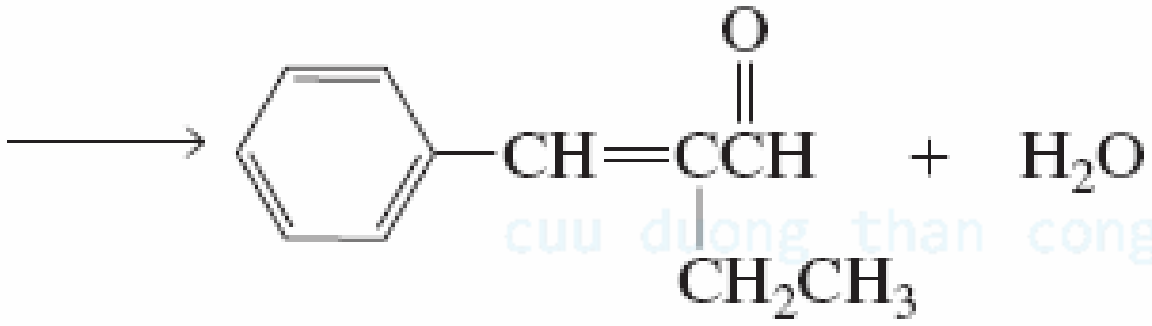
# Mixed / crossed Aldol additions



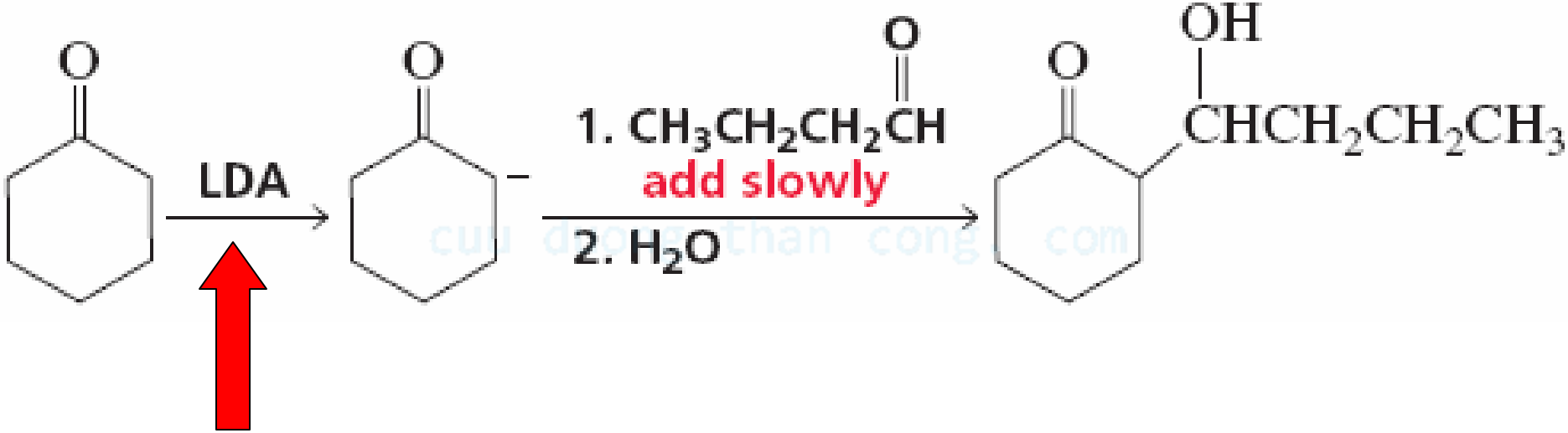



excess add slowly





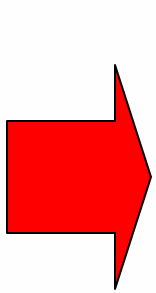



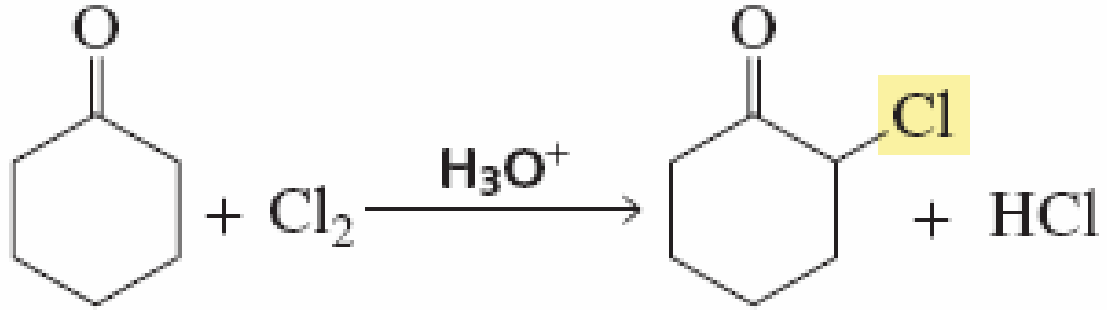


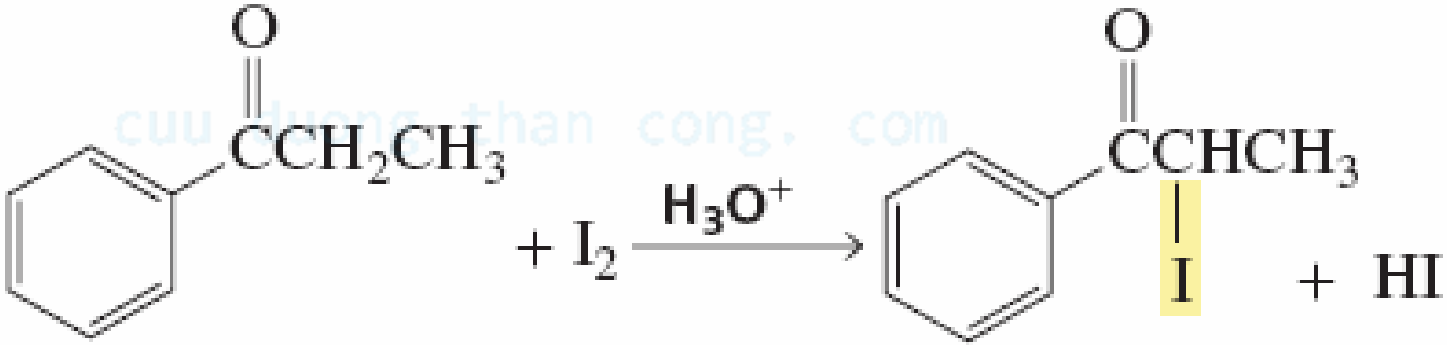

***Very strong base***

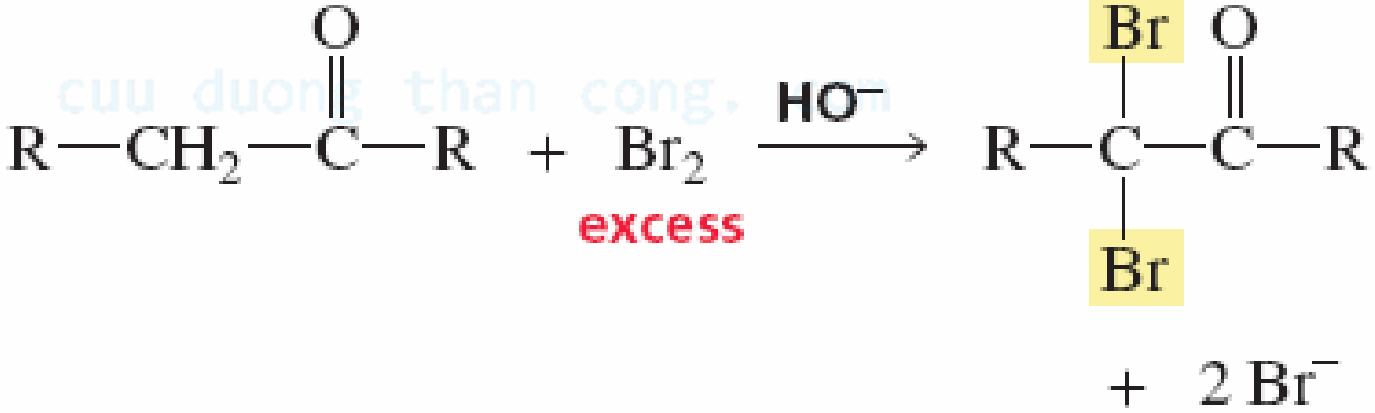
# Halogenations at α-C

***Only 1 hydrogen is replaced in acidic solution***





# The haloform reactions

***Only for methyl ketones***