ORGANIC CHEMISTRY

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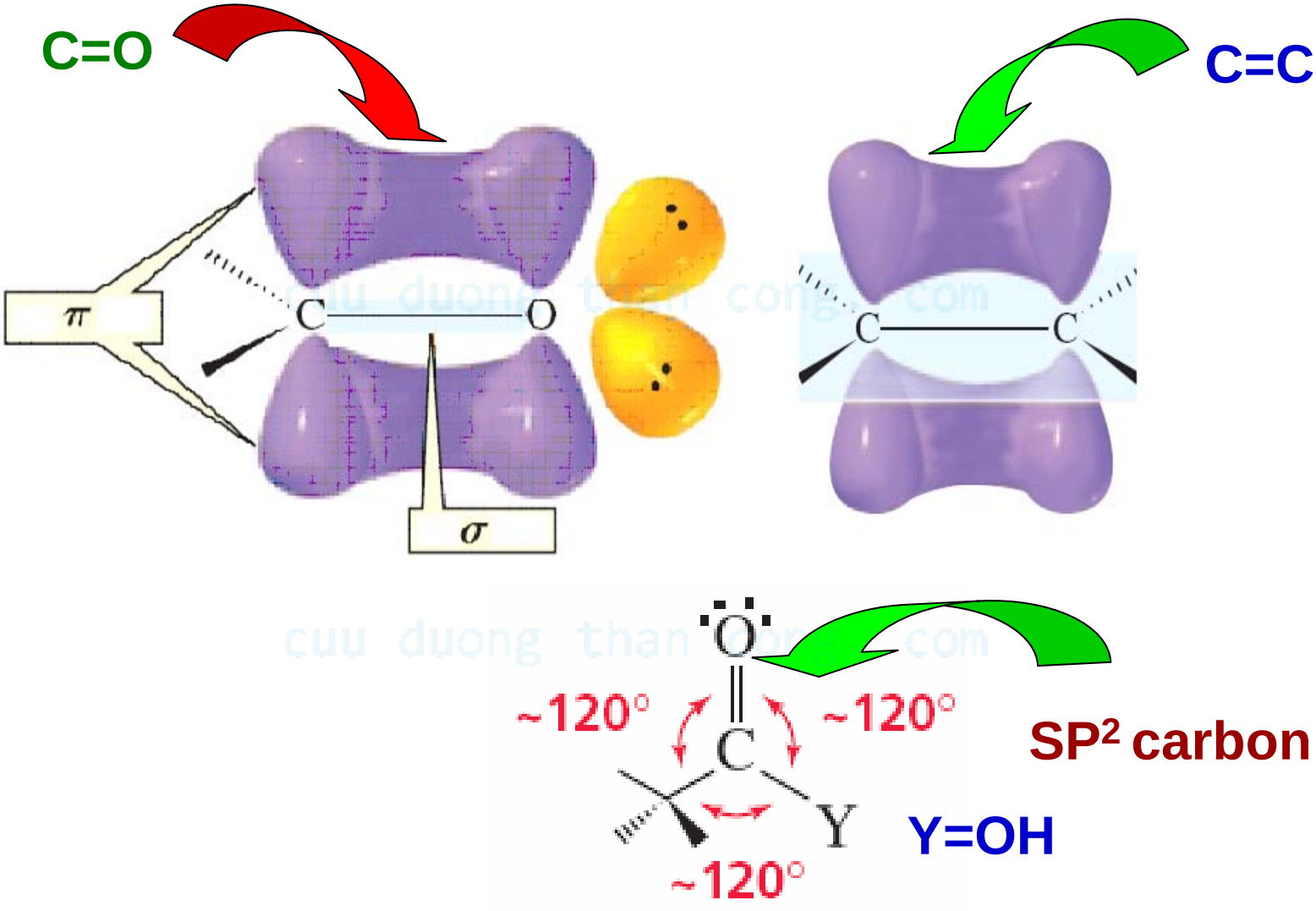
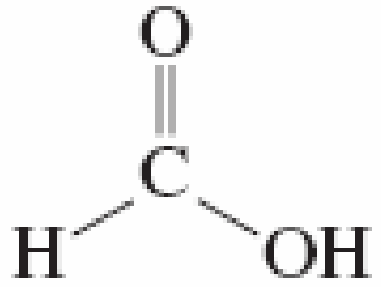
Chapter 12: CARBOXYLIC ACIDS

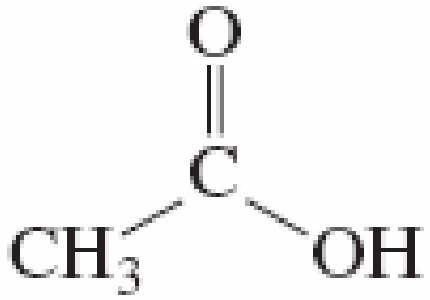


NOMENCLATURE OF CARBOXYLIC ACIDS



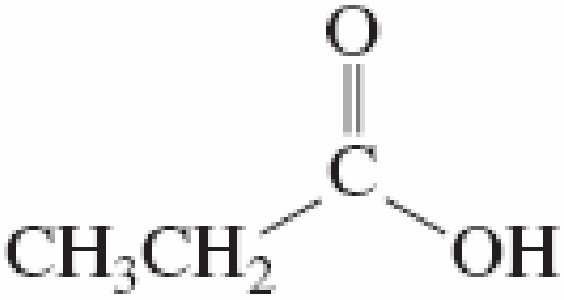
systematic name: methanoic acid

common name: formic acid



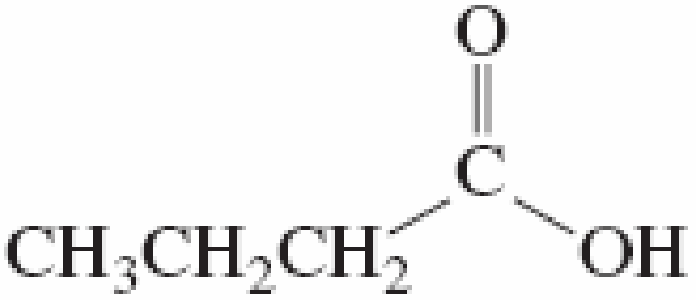
ethanoic acid

acetic acid



propanoic acid

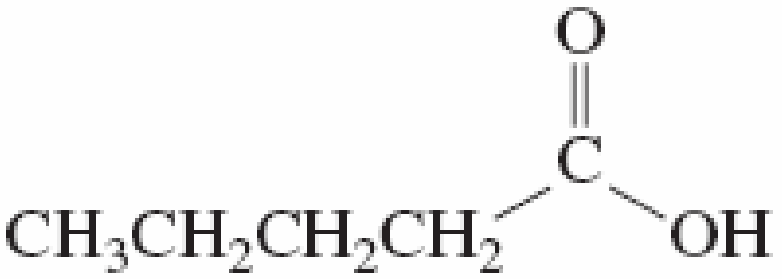
propionic acid



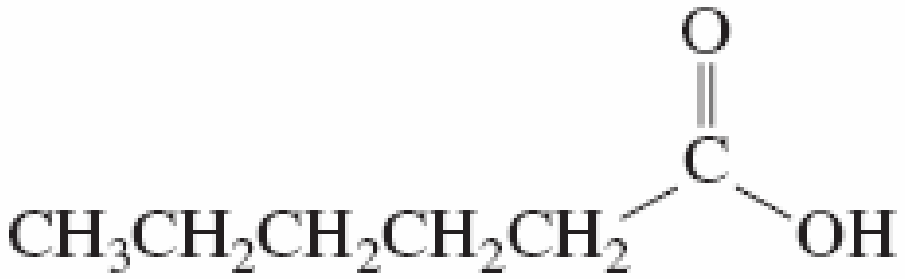
butanoic acid

butyric acid

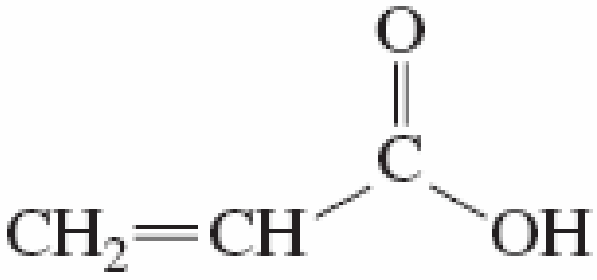
IUPAC names: hydrocarbon + "oic acid"



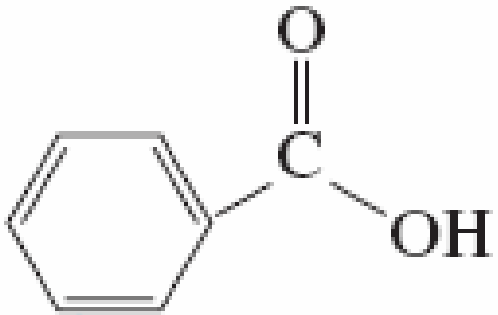
pentanoic acid
valeric acid



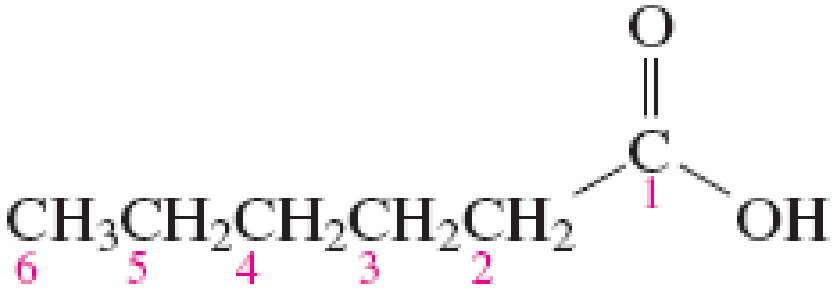
hexanoic acid
caproic acid



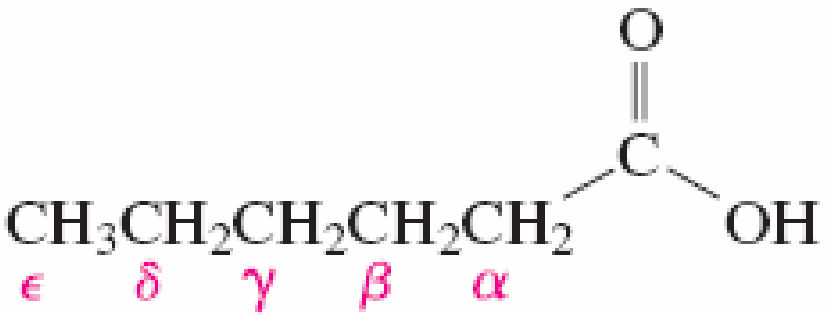
propenoic acid
acrylic acid



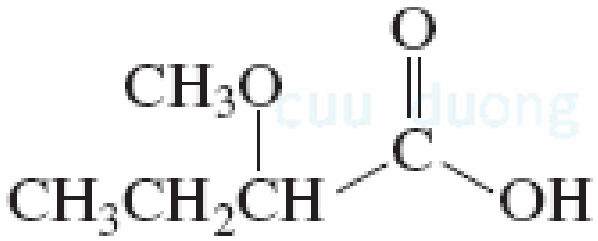
benzenecarboxylic acid
benzoic acid



systematic nomenclature

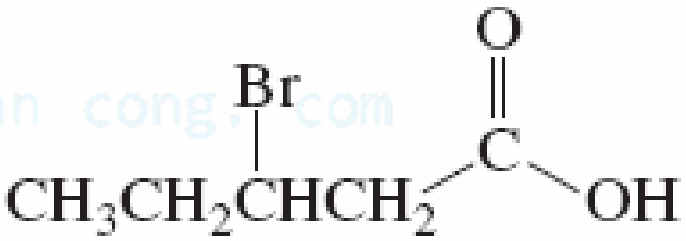


common nomenclature



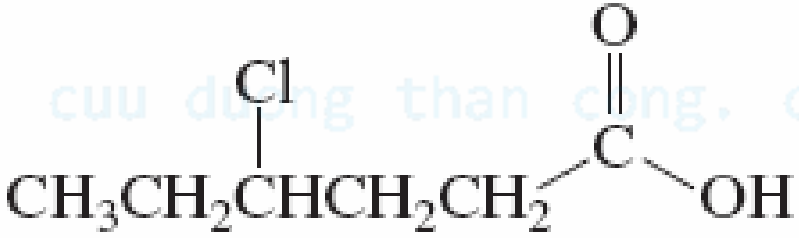
2-methoxybutanoic acid

α-methoxybutyric acid



3-bromopentanoic acid

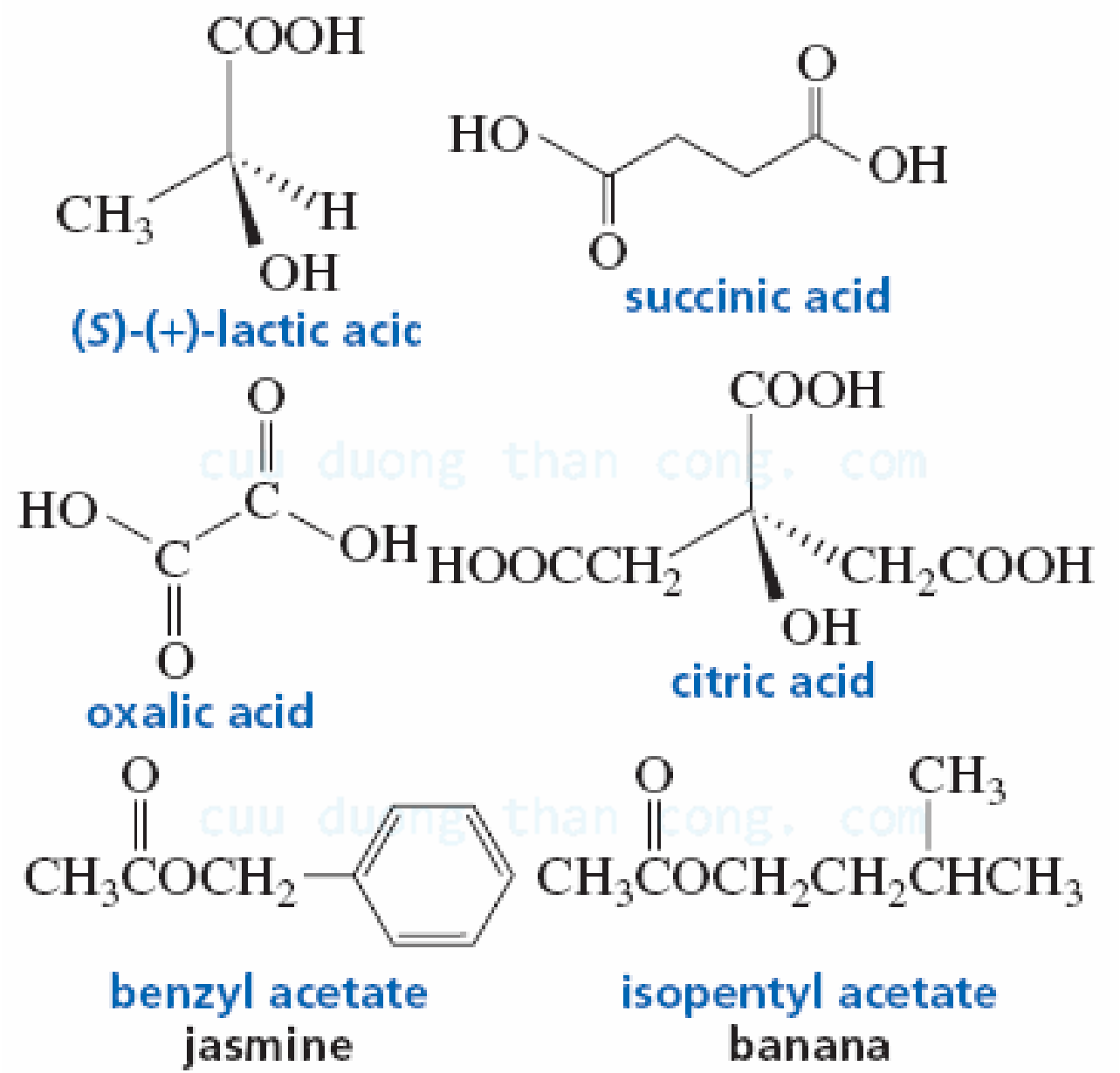
β-bromovaleric acid



4-chlorohexanoic acid

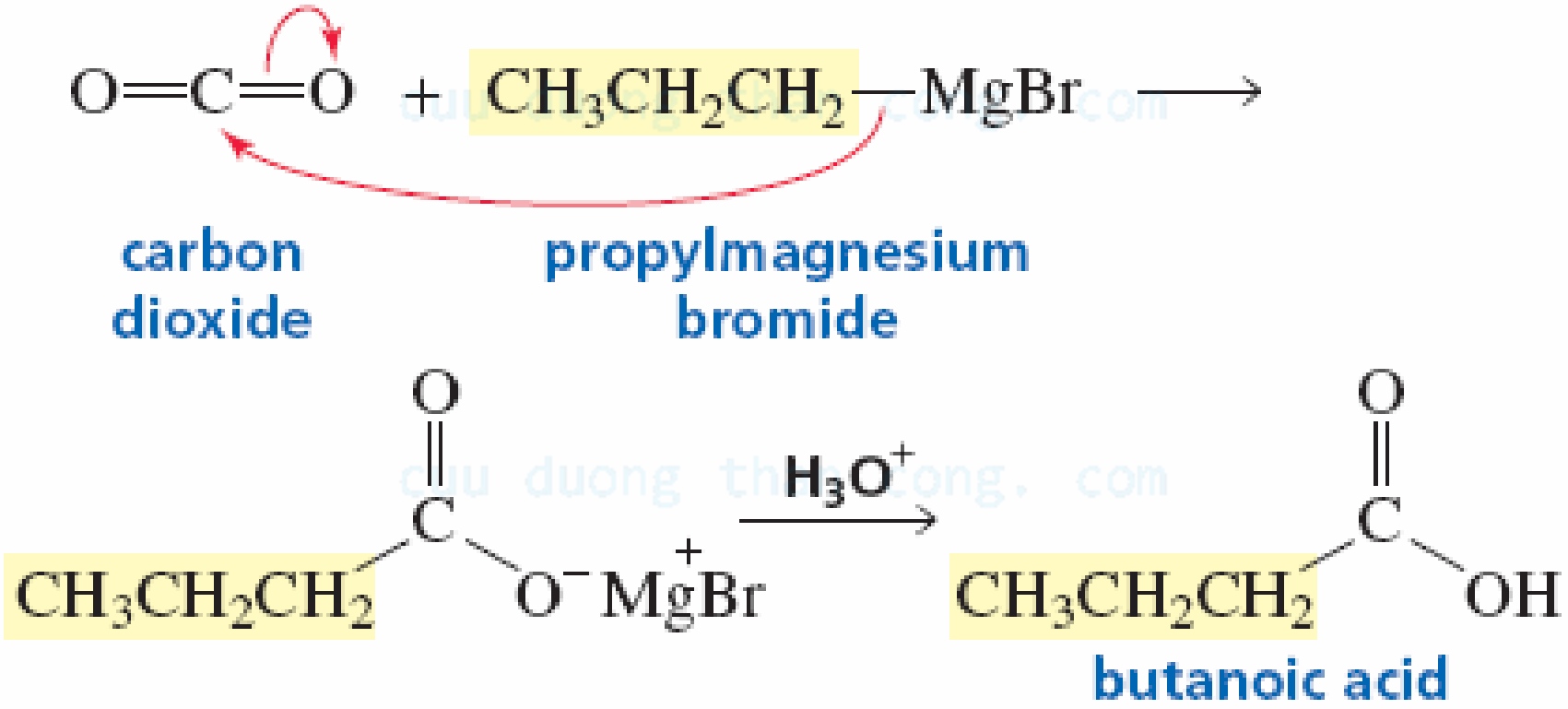
γ-chlorocaproic acid

Some natural occurring acids & derivatives

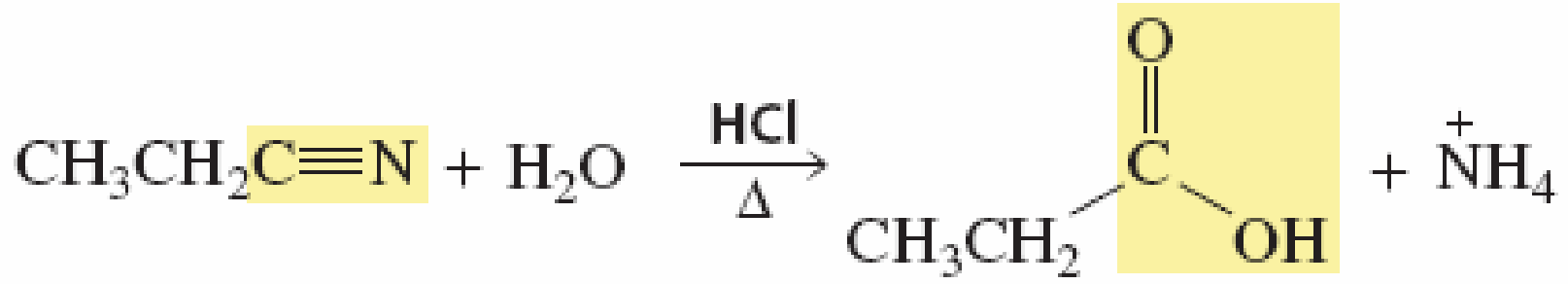


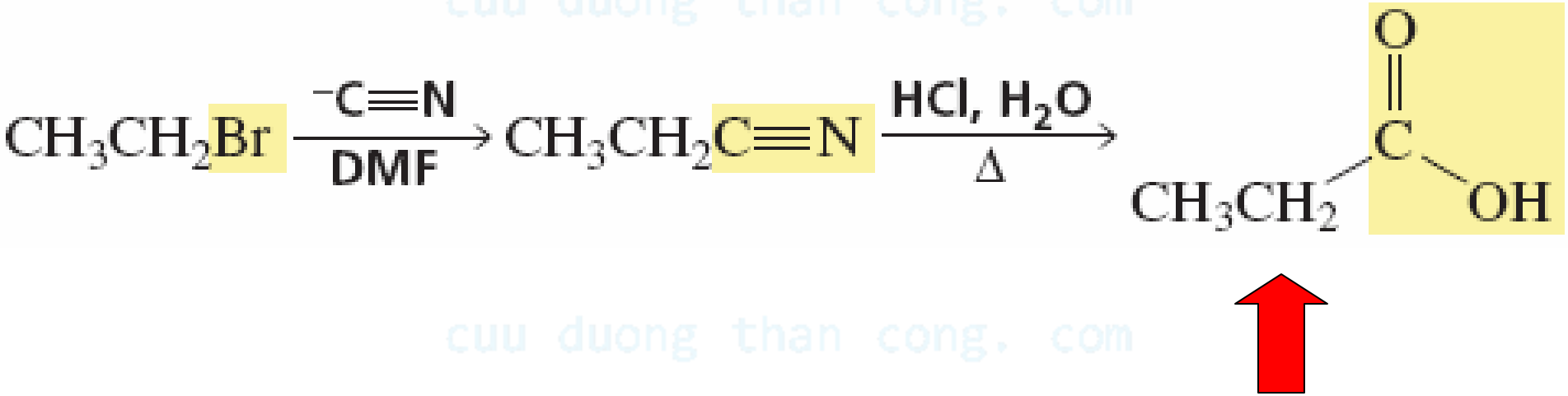
PREPARATIONS OF CARBOXYLIC ACIDS

From Grignard reagents



From nitriles

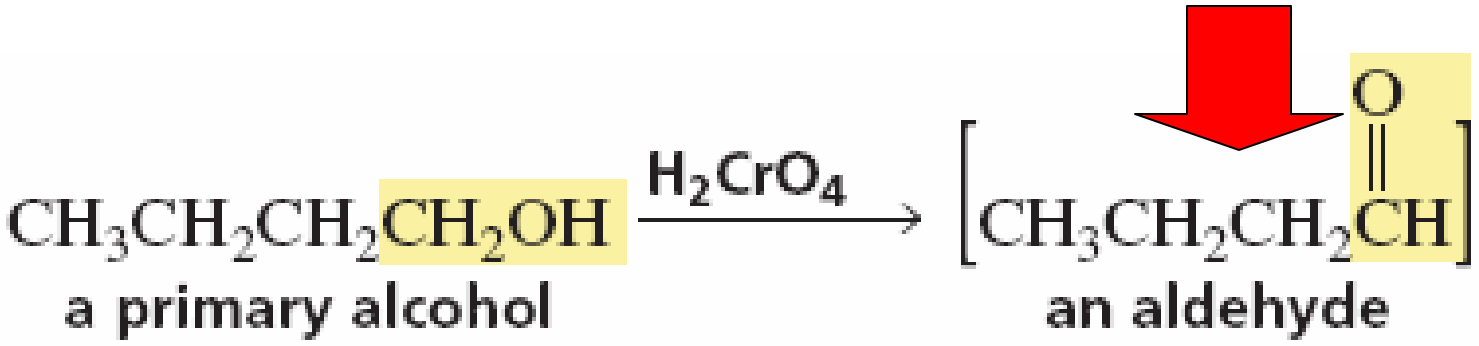


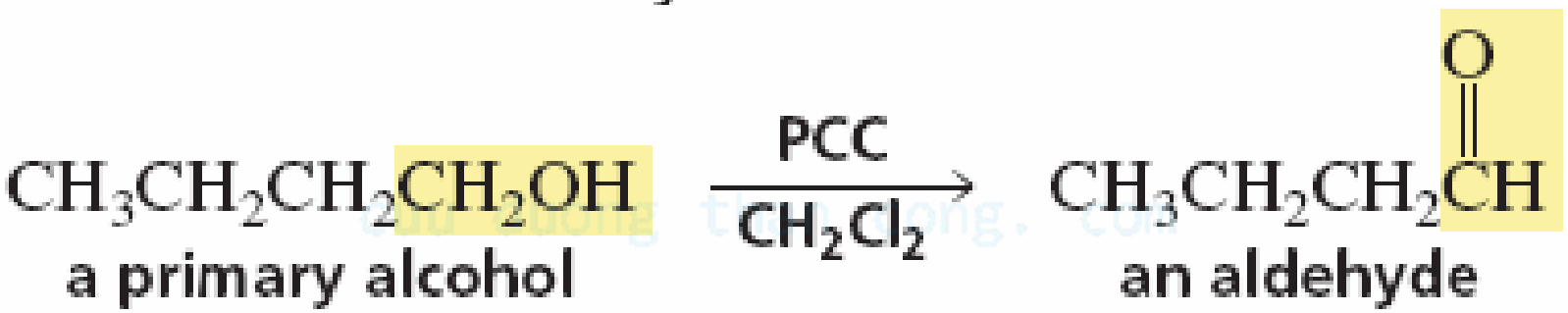


Have 1 more carbon as compared to the halide

From primary alcohols

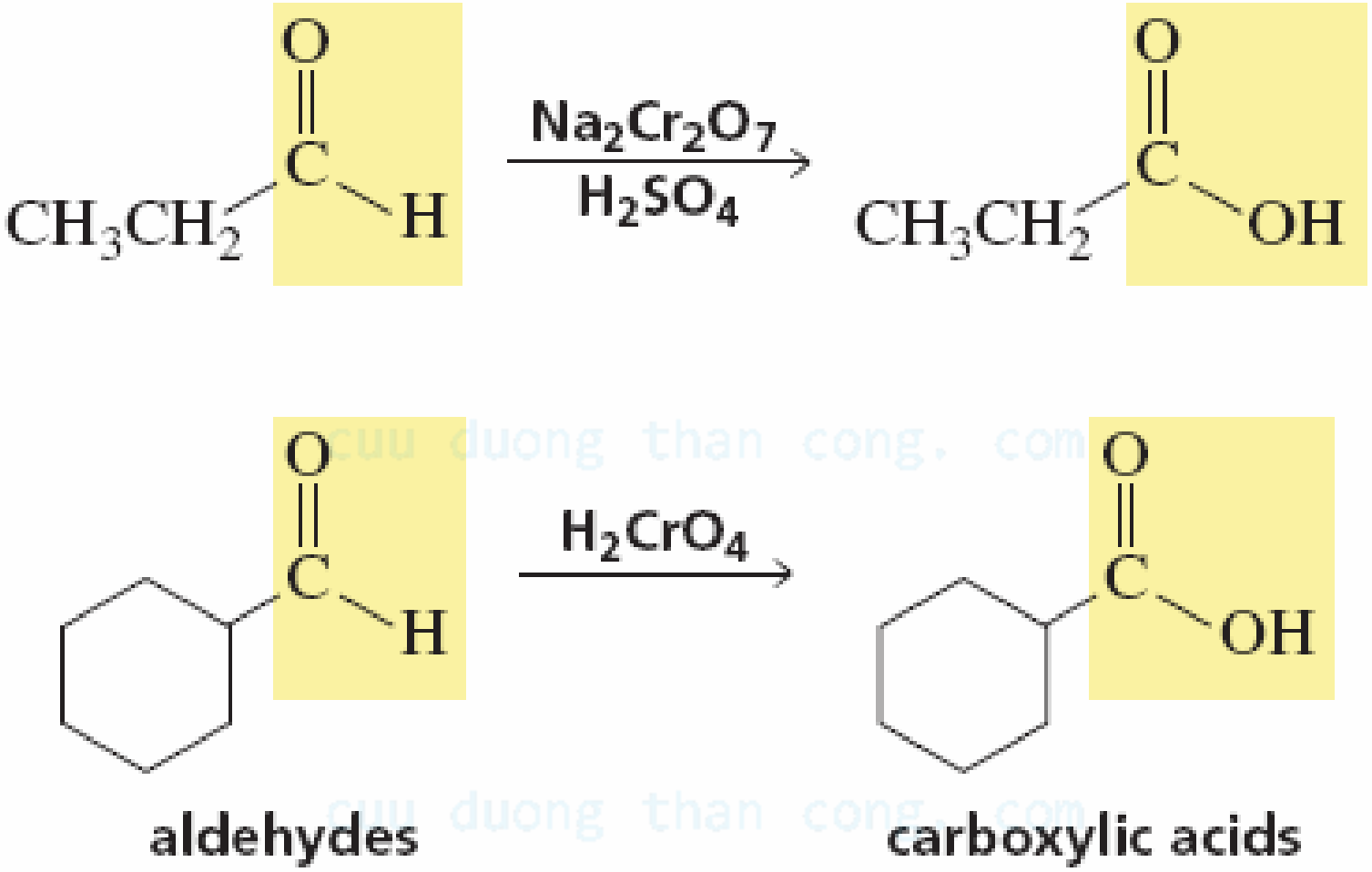
Can NOT be isolated





PCC: pyridinium chlorochromate

From aldehydes

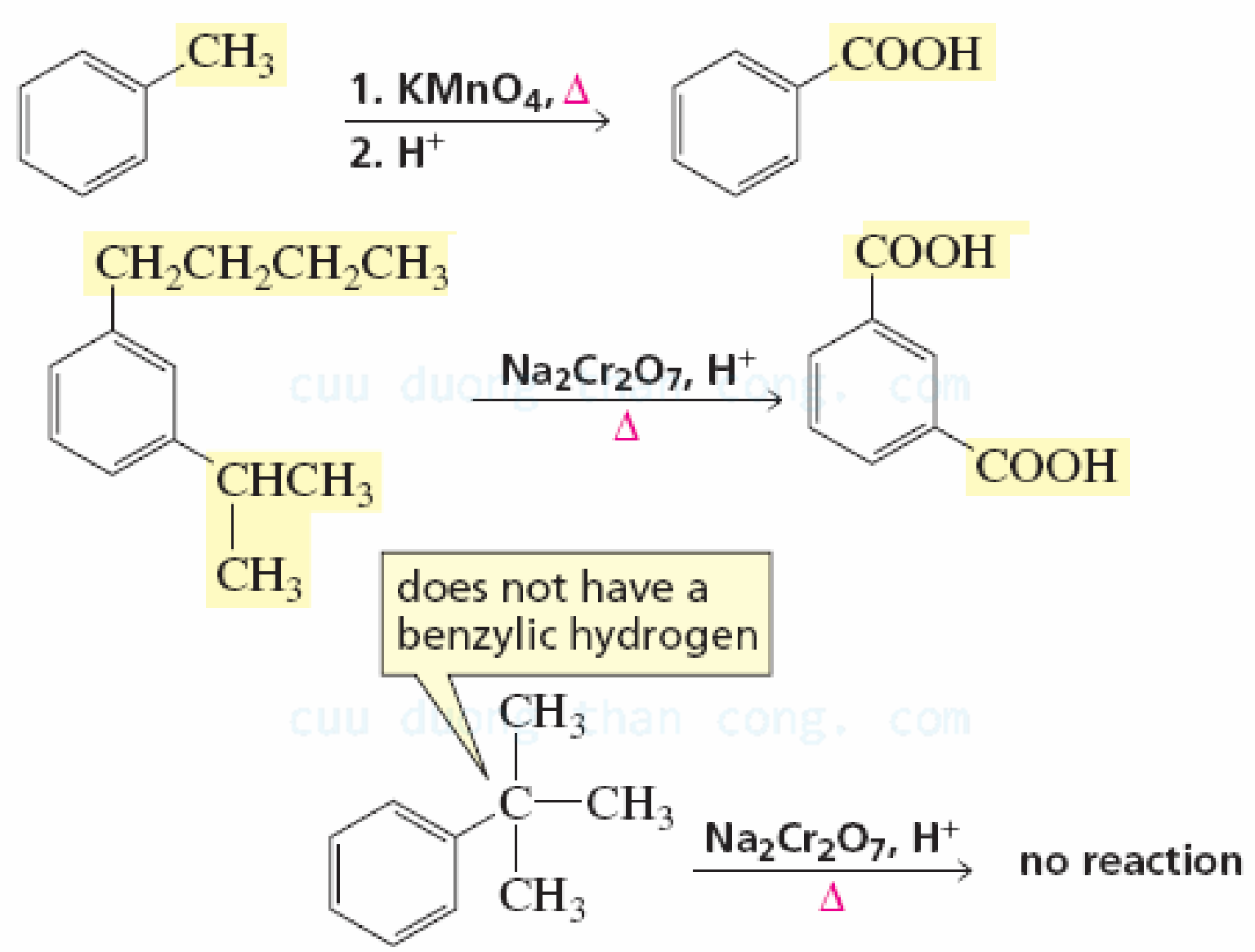


aldehydes

carboxylic acids

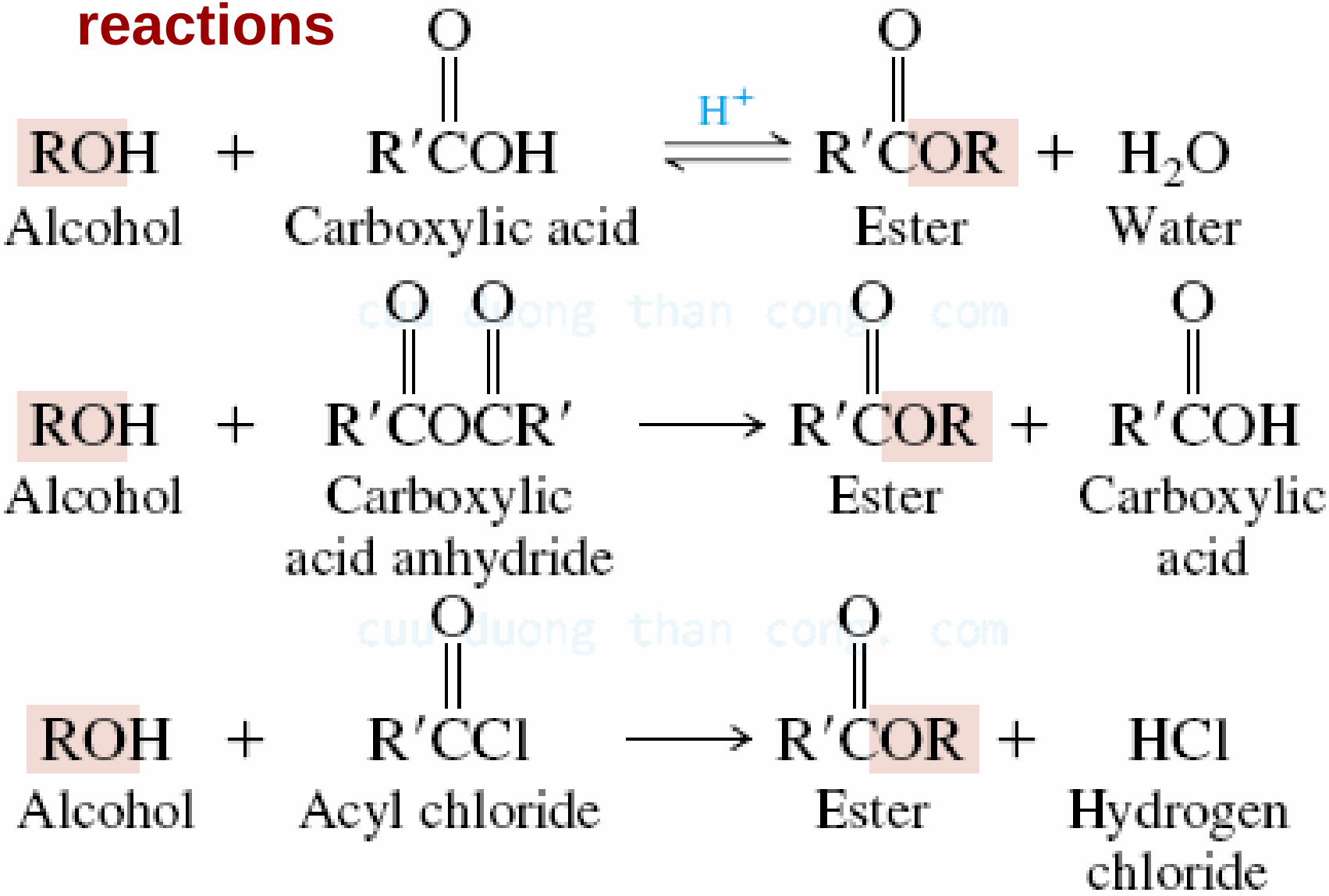
Aldehydes are generally easier to oxidize than primary alcohols

From alkylbenzenes

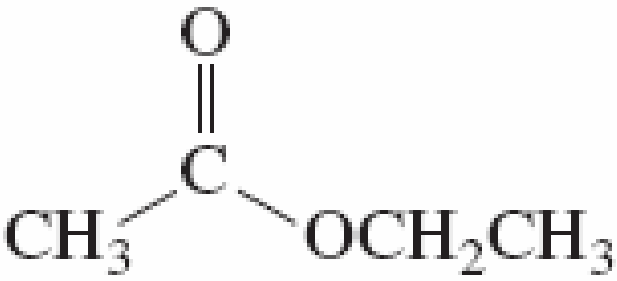


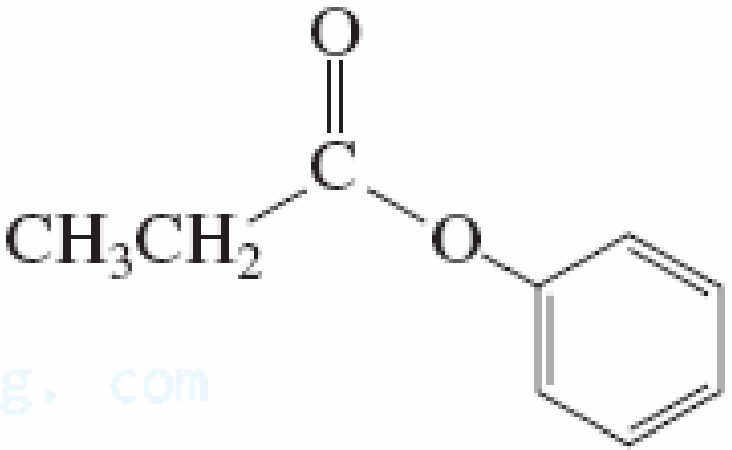
REACTIONS OF CARBOXYLIC ACIDS

Esterification reactions



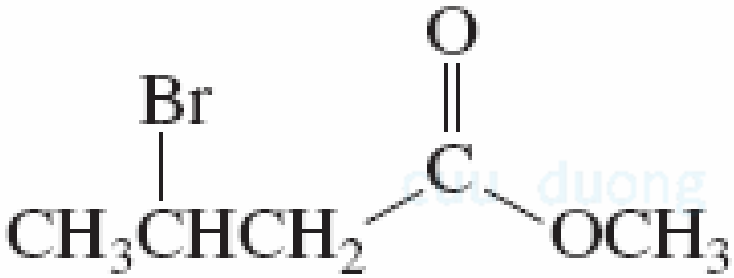
IUPAC names: alkyl + carboxylate

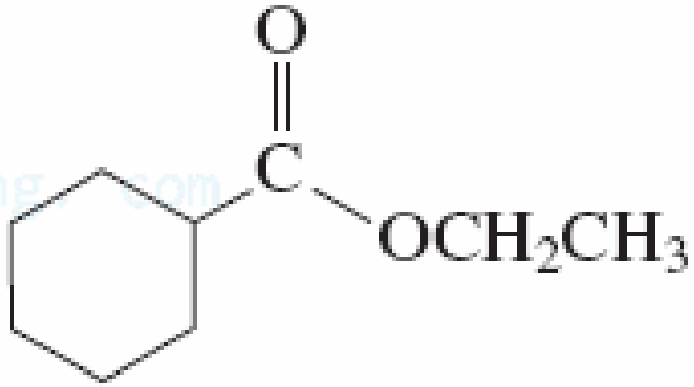




systematic name: ethyl ethanoate
common name: ethyl acetate

phenyl propanoate
phenyl propionate

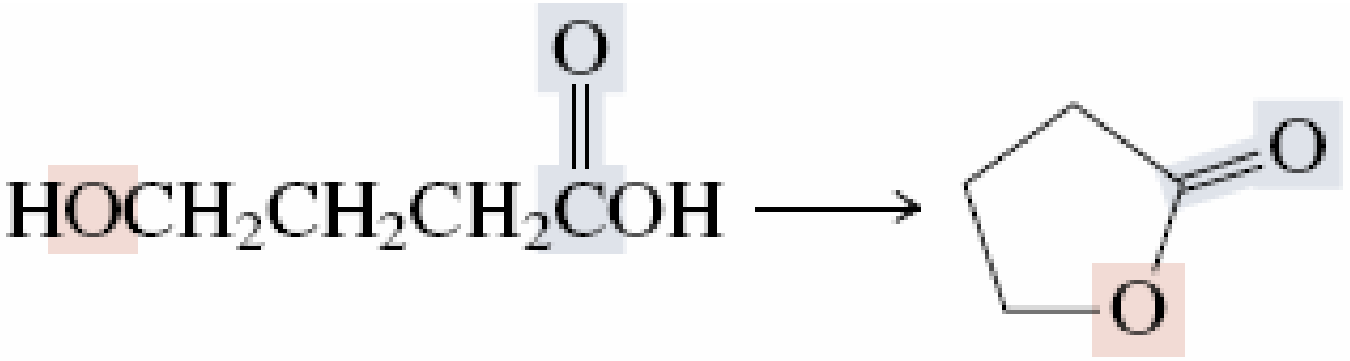




methyl 3-bromobutanoate
methyl β-bromobutyrate

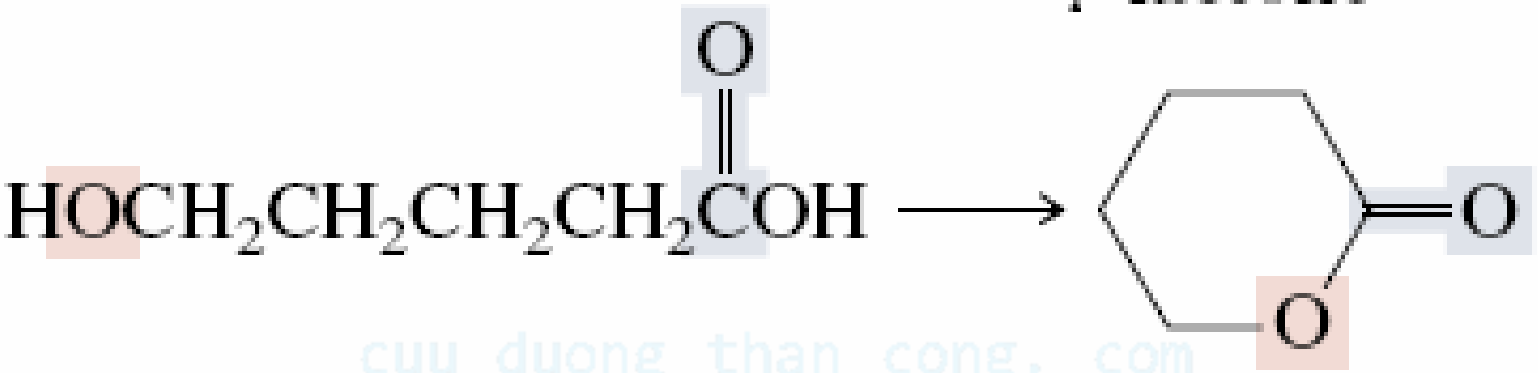
ethyl cyclohexanecarboxylate

Intramolecular ester formation: Lactones



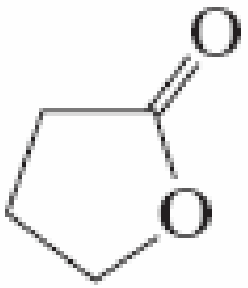
4-Hydroxybutanoic acid

4-Butanolide
γ-lactone

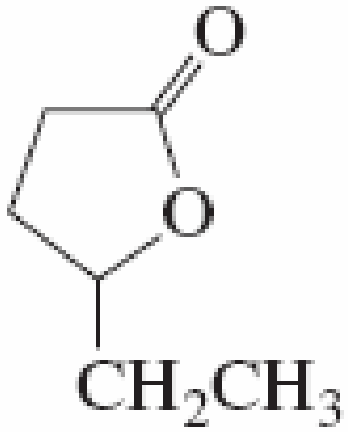


5-Hydroxypentanoic acid

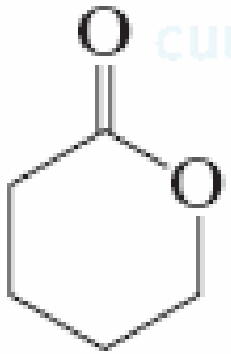
5-Pentanolide
δ-lactone



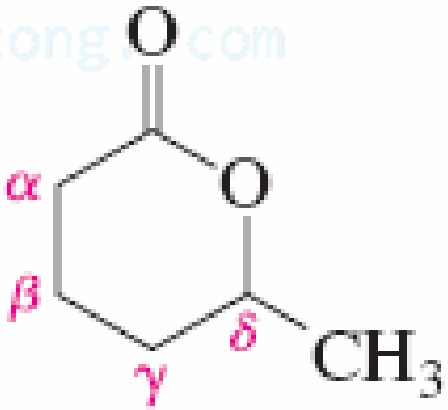
2-oxacyclopentanone
γ-butyrolactone



3-ethyl-2-oxacyclopentanone
γ-caprolactone



2-oxacyclohexanone
δ-valerolactone

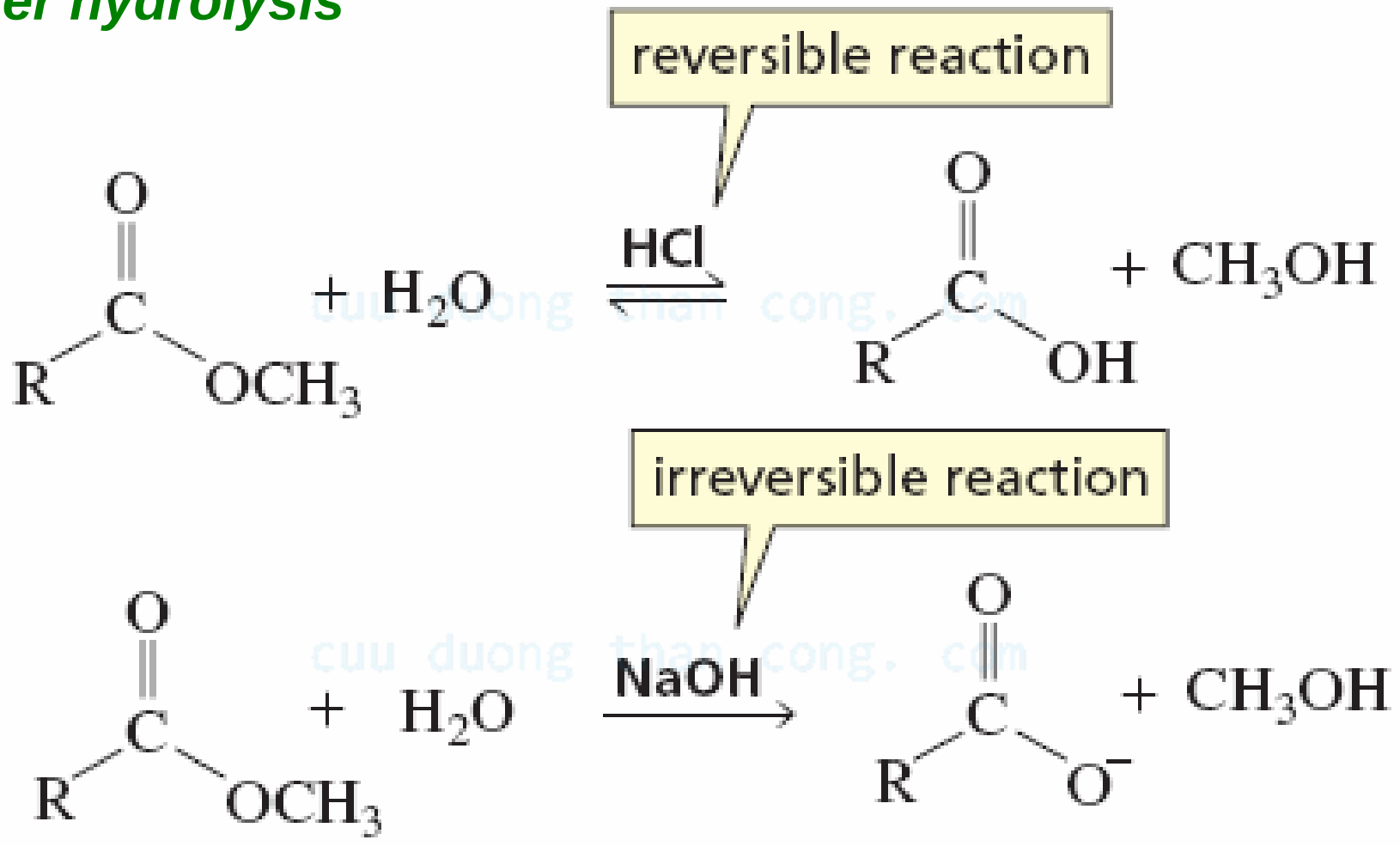


3-methyl-2-oxacyclohexanone
δ-caprolactone

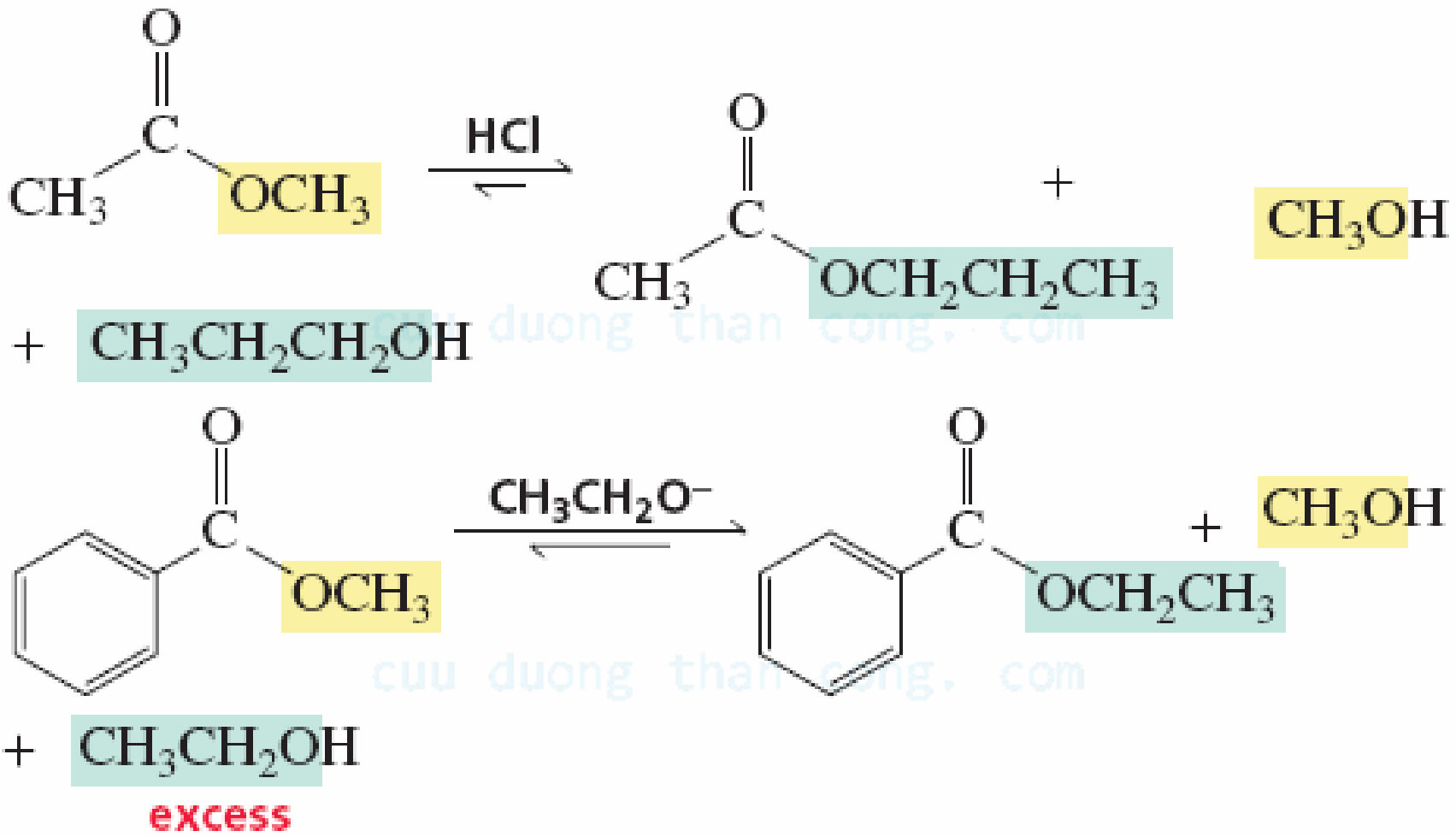
IUPAC names: 2-oxacycloalkanone

Reactions of esters

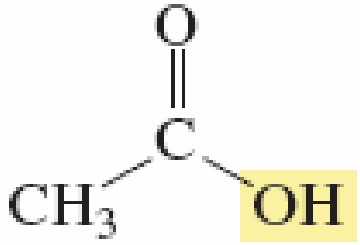
Ester hydrolysis



Transesterification reactions



Acyl chloride formation

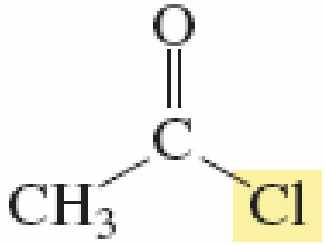


acetic acid

+ $SOCl_2$

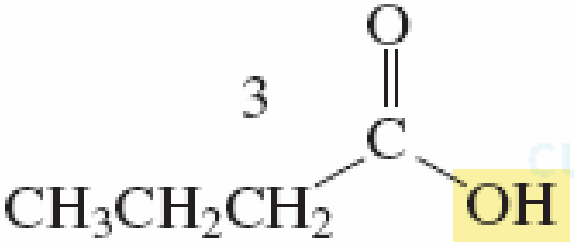
thionyl chloride

$\xrightarrow{\Delta}$



acetyl chloride

+ SO_2 + HCl

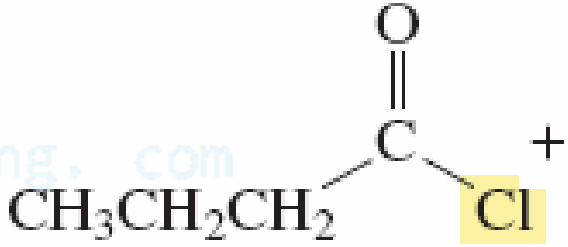


butanoic acid

+ PCl_3

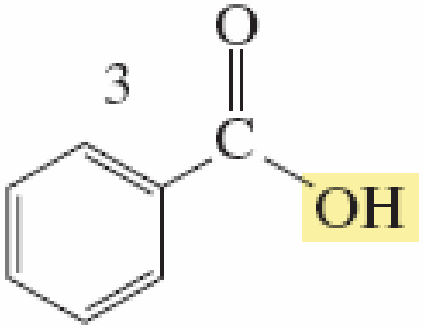
phosphorus trichloride

$\xrightarrow{\Delta}$ 3



butanoyl chloride

+ H_3PO_3

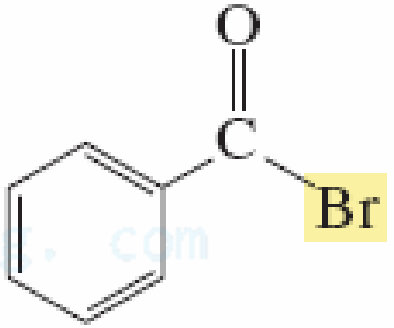


benzoic acid

+ PBr_3

phosphorus tribromide

$\xrightarrow{\Delta}$ 3

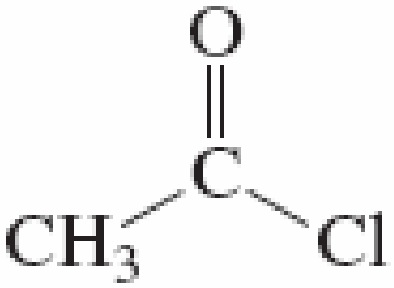


benzoyl bromide

+ H_3PO_3

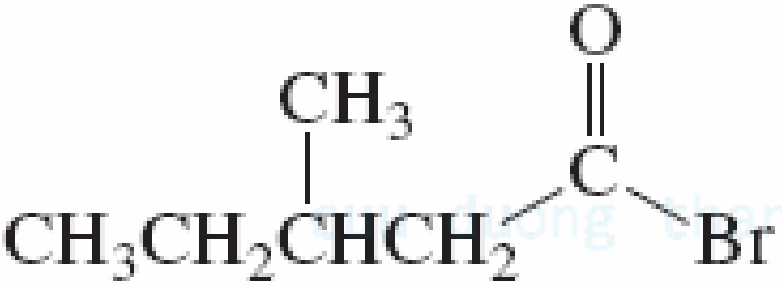
phosphorous acid

IUPAC names: replace "ic acid" with "yl halide" / "carboxylic acid" with "carbonyl halide"



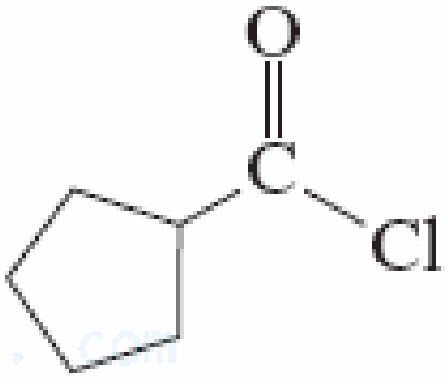
systematic name: ethanoyl chloride

common name: acetyl chloride



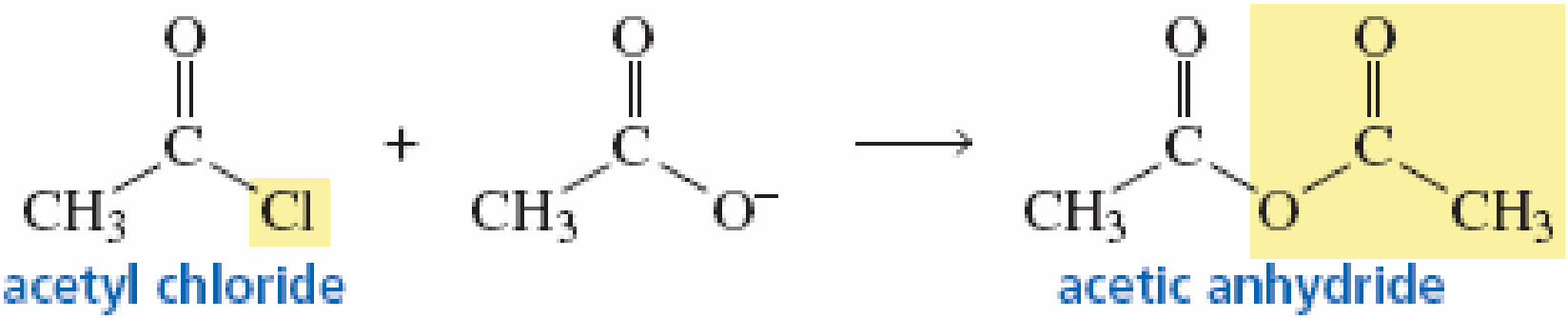
3-methylpentanoyl bromide

β-methylvaleryl bromide



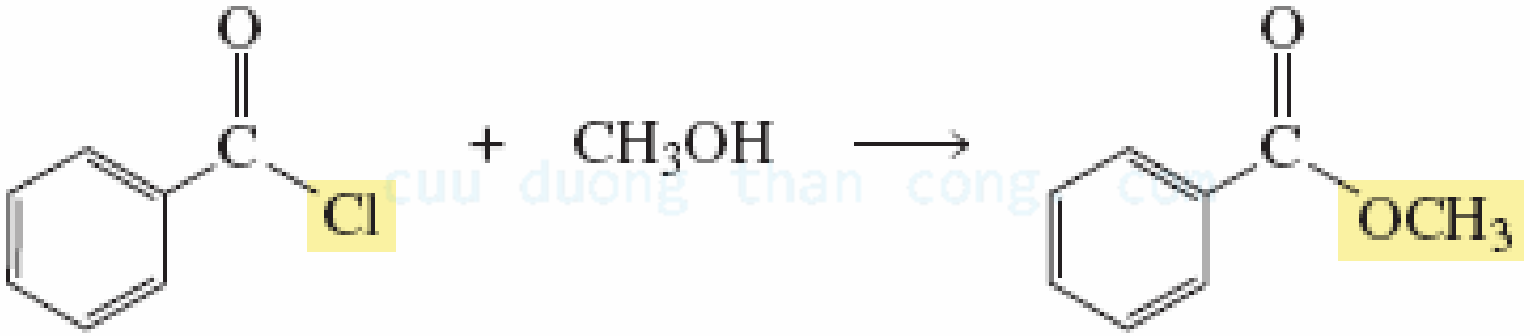
cyclopentanecarbonyl chloride

Reactions of acyl chlorides



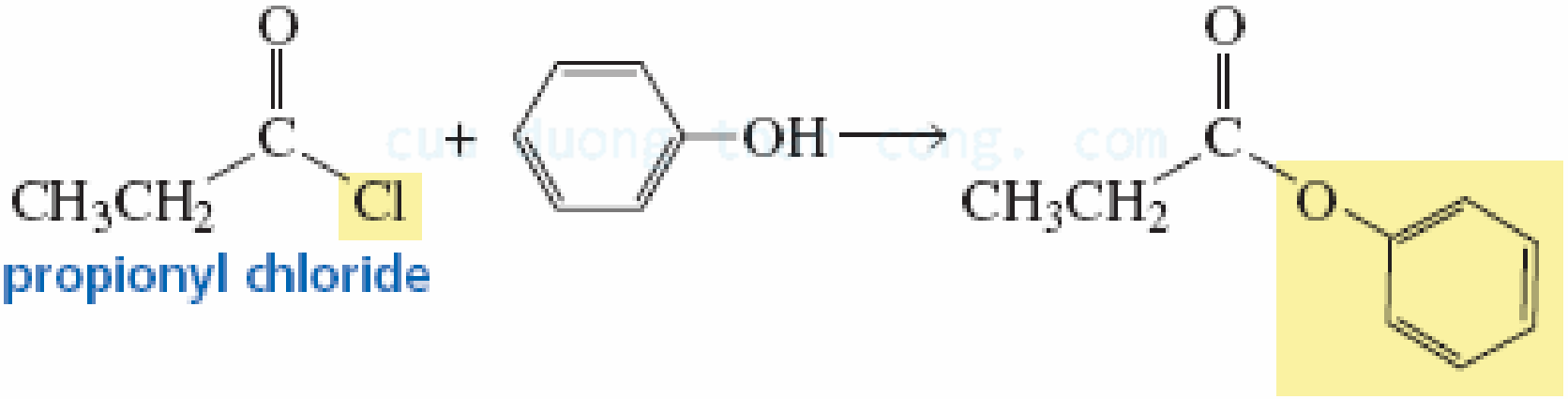
acetyl chloride

acetic anhydride



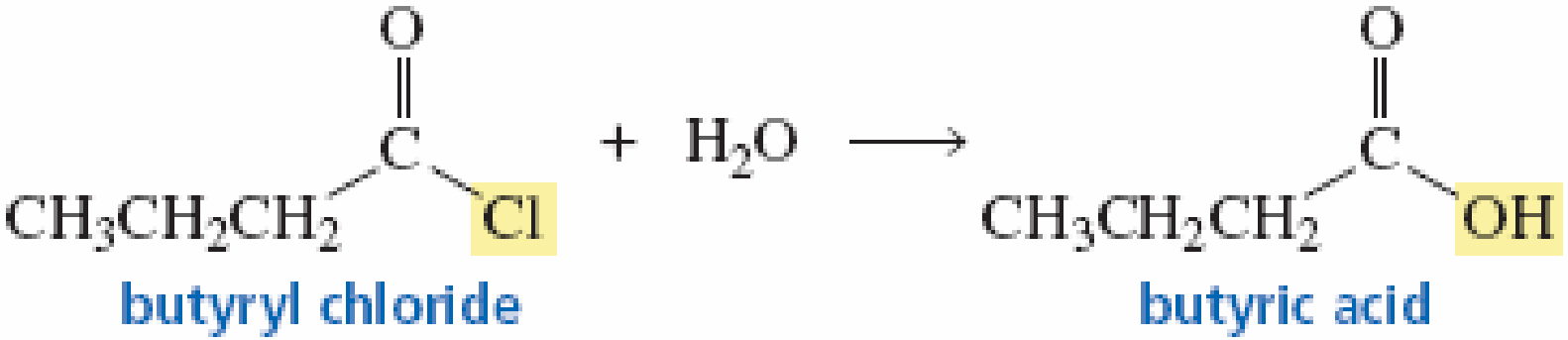
benzoyl chloride

methyl benzoate



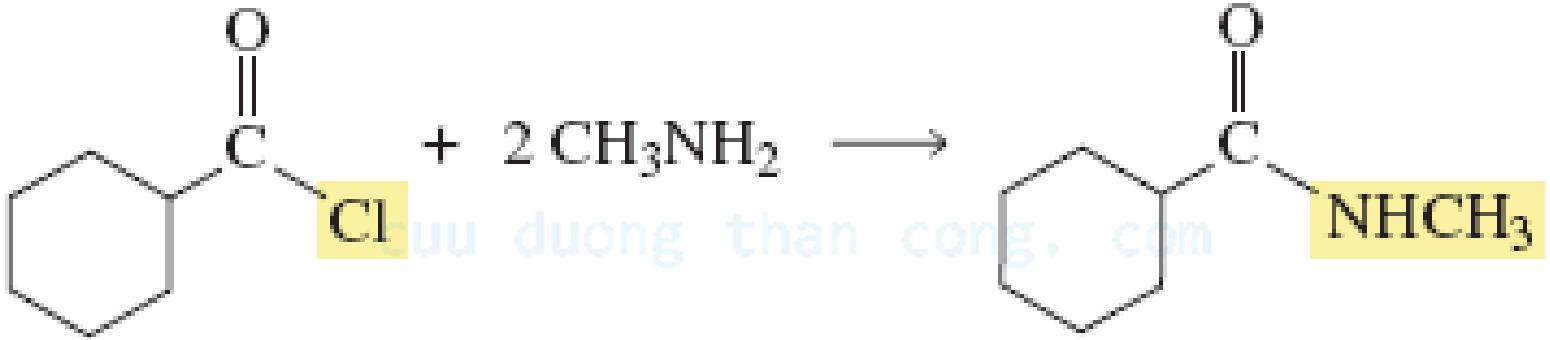
propionyl chloride

phenyl propionate



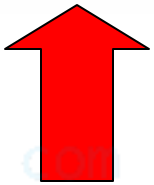
butyryl chloride

butyric acid

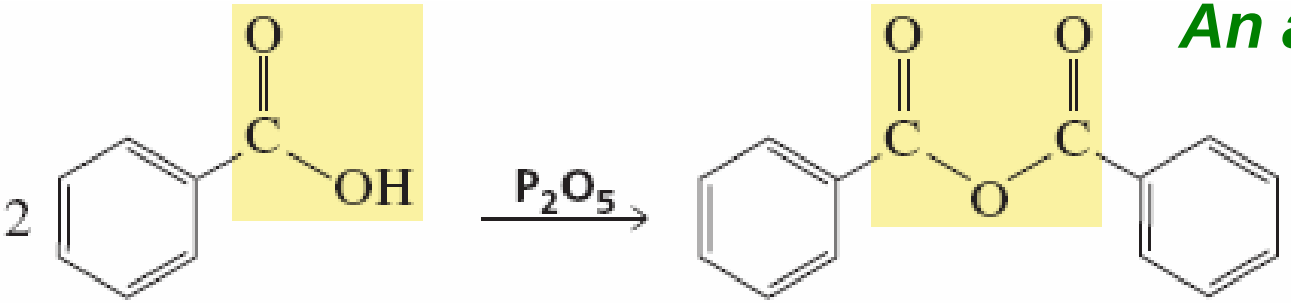


cyclohexanecarbonyl chloride

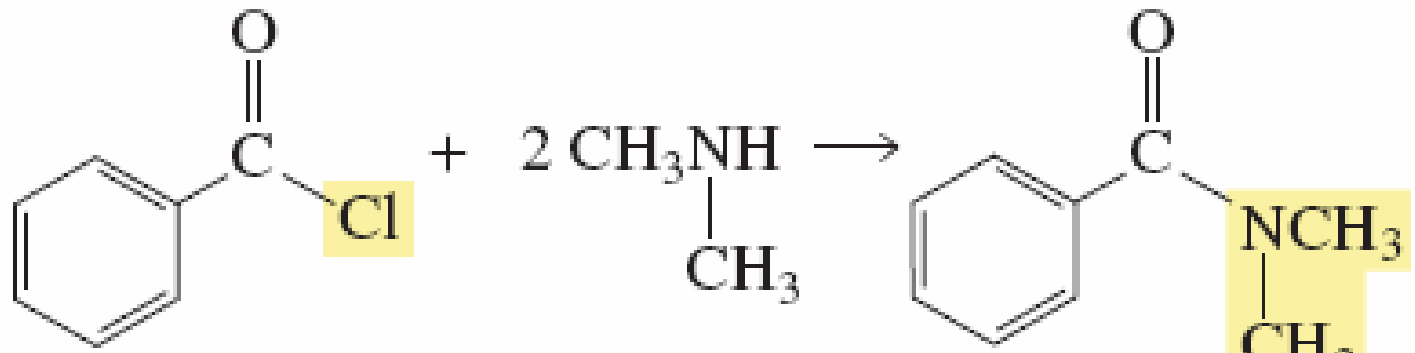
N-methylcyclohexanecarboxamide



An amide

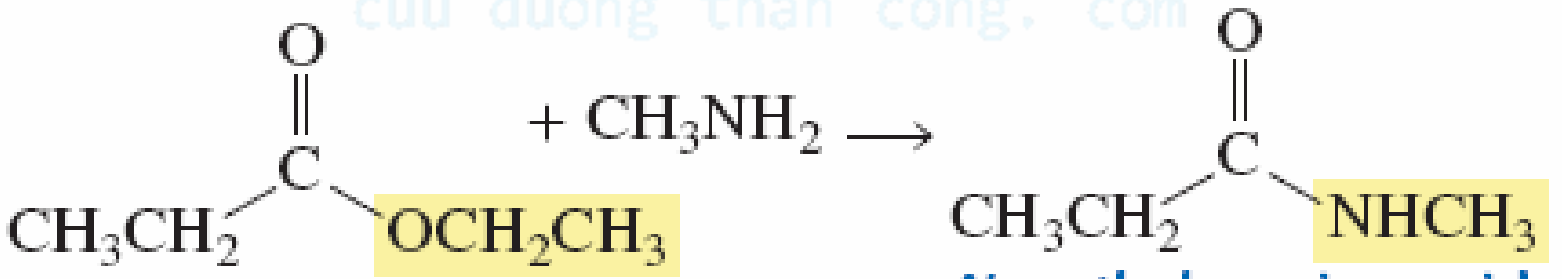


Amide formation



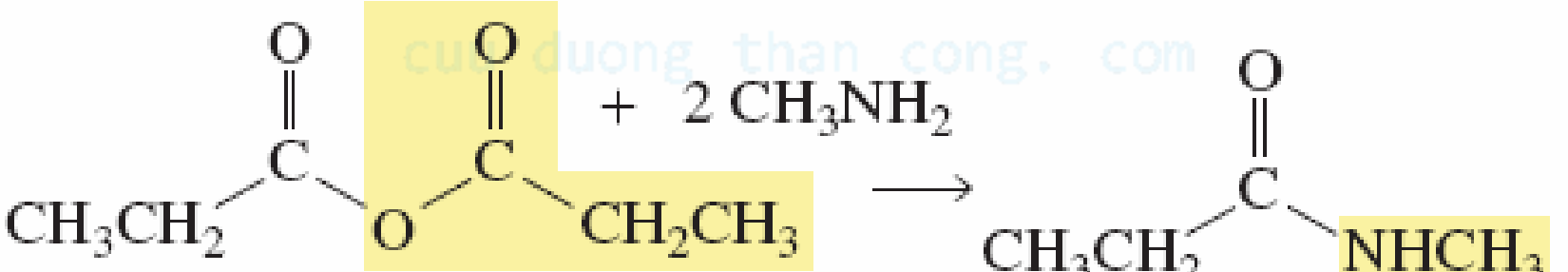
cyclohexanecarbonyl chloride

N-methylcyclohexanecarboxamide



ethyl propionate

N-methylpropionamide



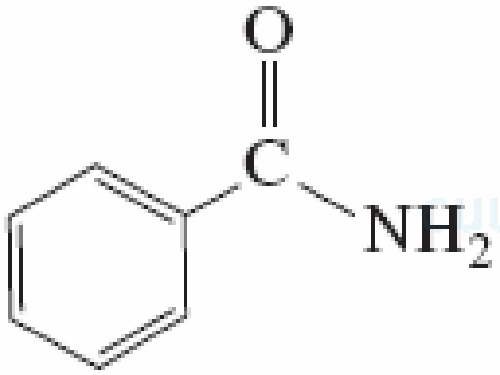
propionic anhydride

N-methylpropionamide

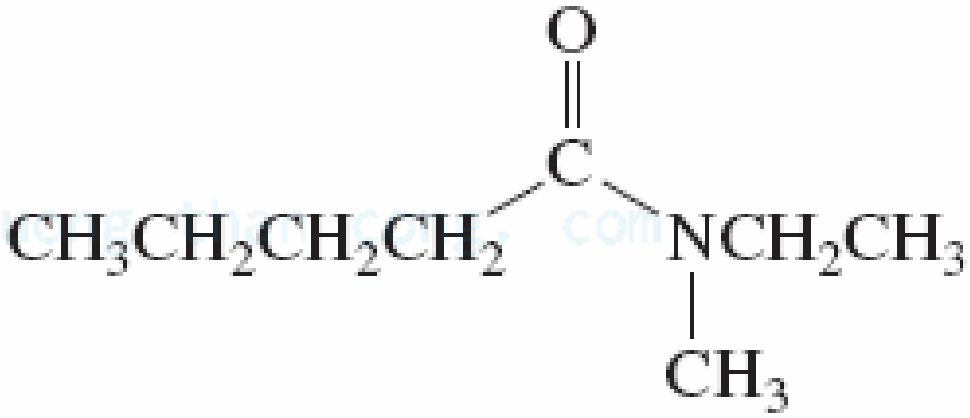
IUPAC names: replace "ic acid", "oic acid", "ylic acid" with "amide"

systematic name: ethanamide
common name: acetamide

4-chlorobutanamide
γ-chlorobutyramide

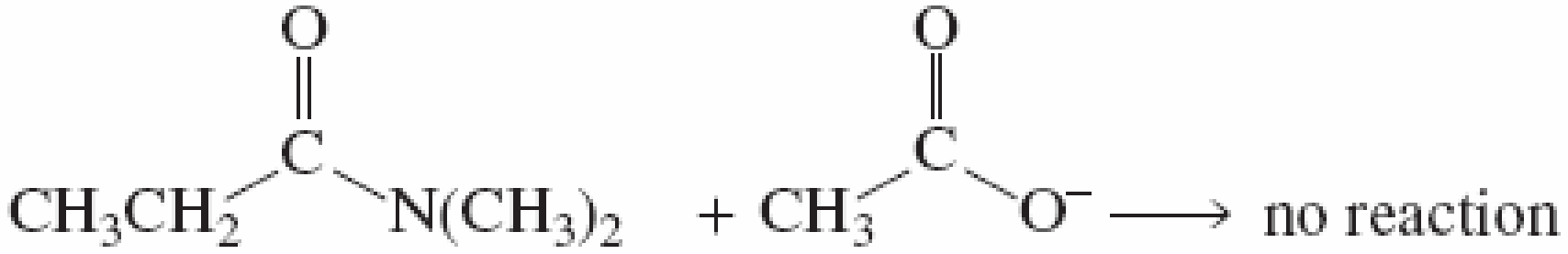


benzenecarboxamide
benzamide

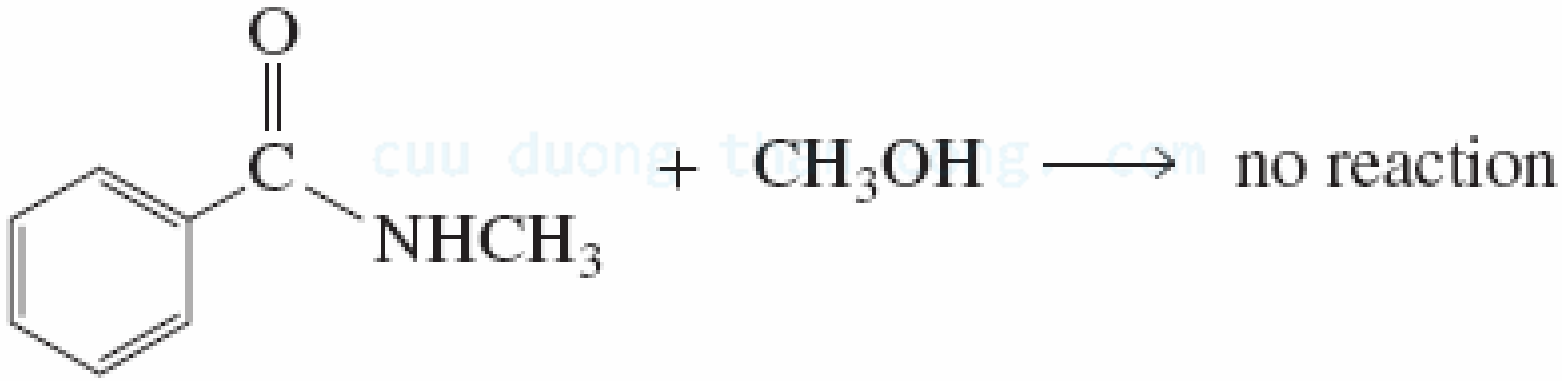


N-ethyl-*N*-methylpentanamide

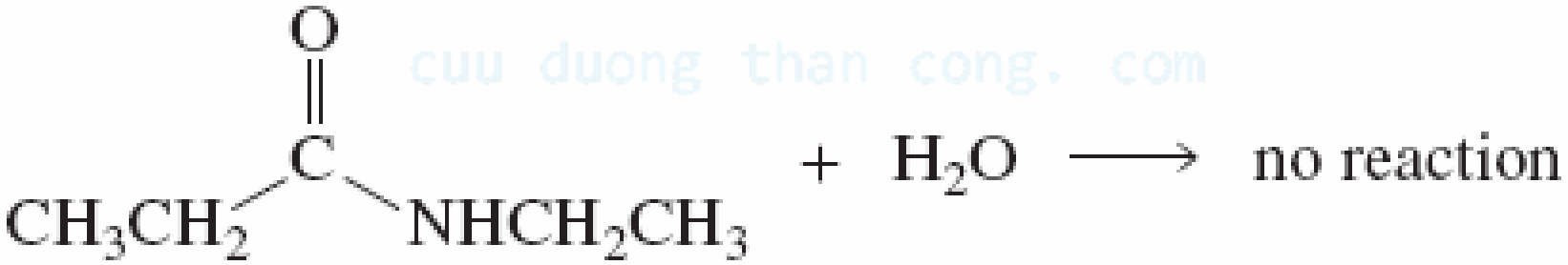
Reactions of amides



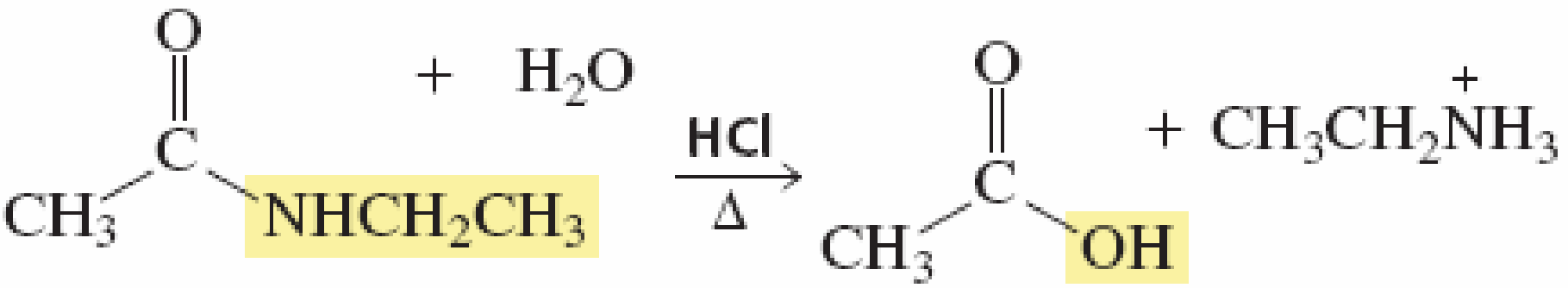
N,N-dimethylpropionamide



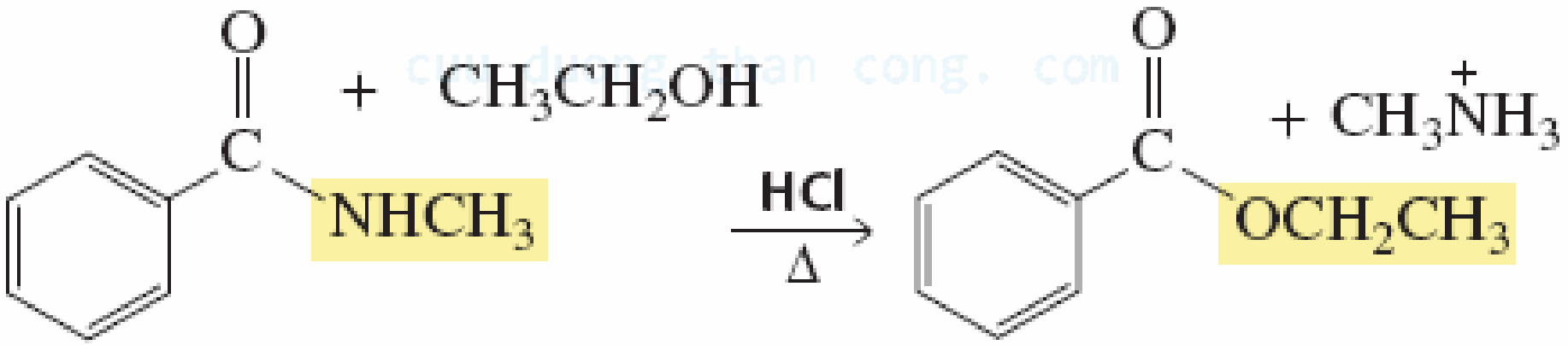
N-methylbenzamide



N-ethylpropanamide



N-ethylacetamide

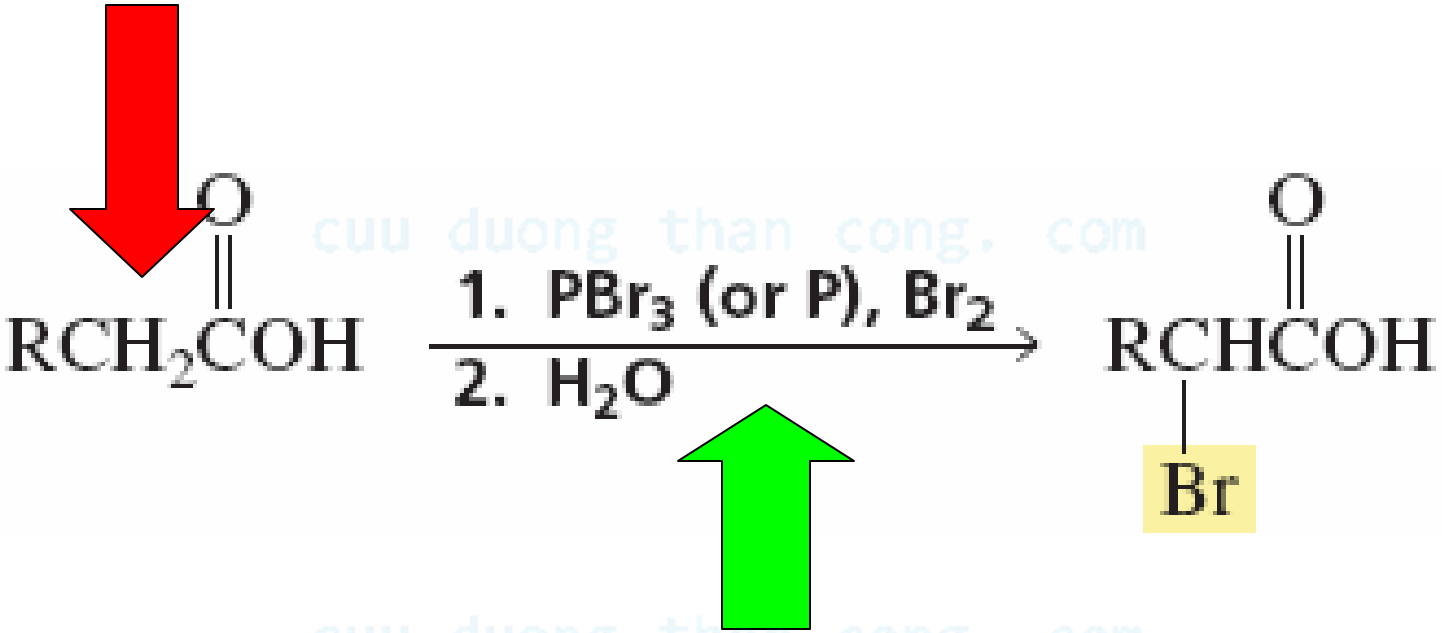


N-methylbenzamide

Reaction only in the presence of an acid

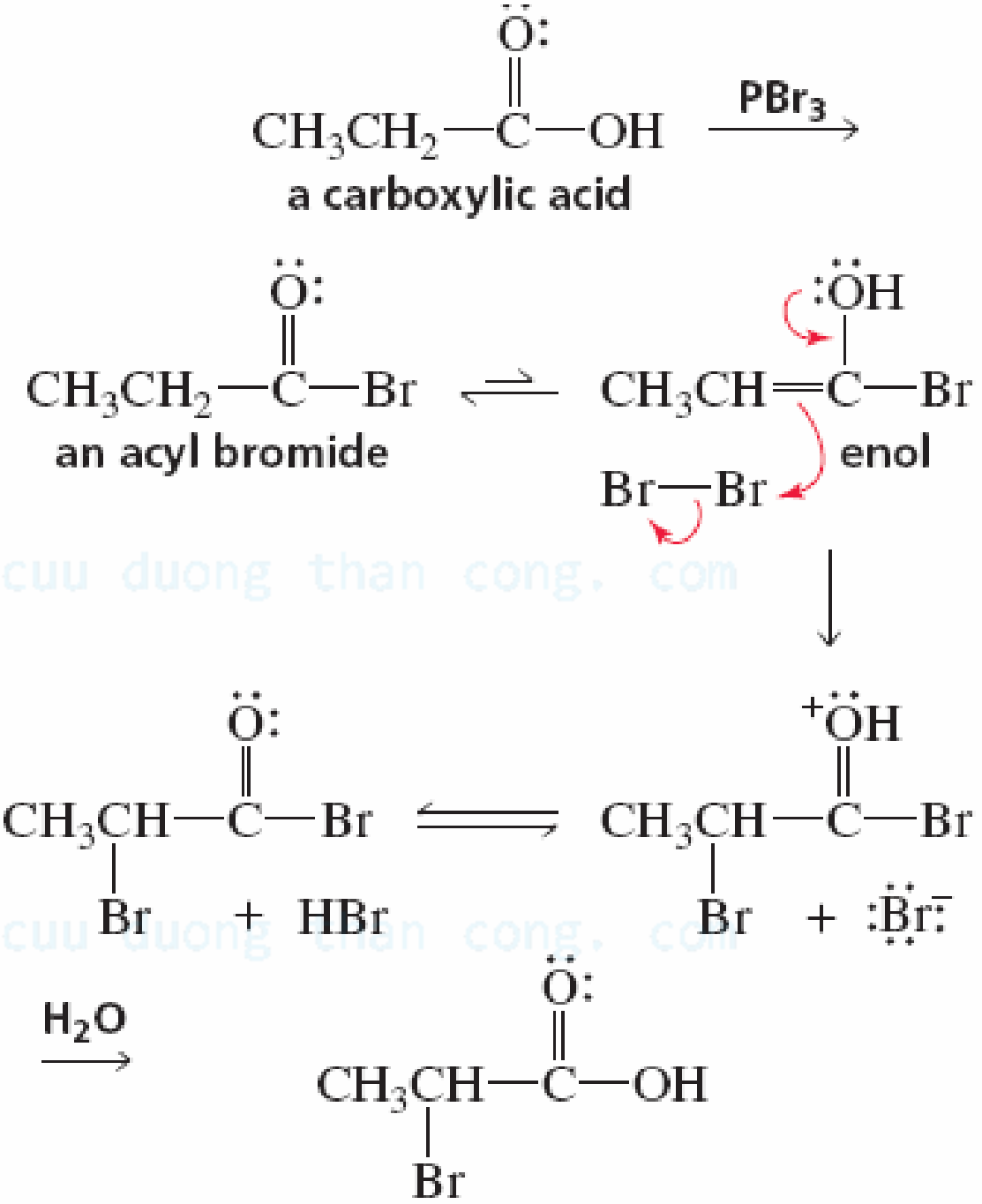
The Hell-Vohard-Zelinski reaction

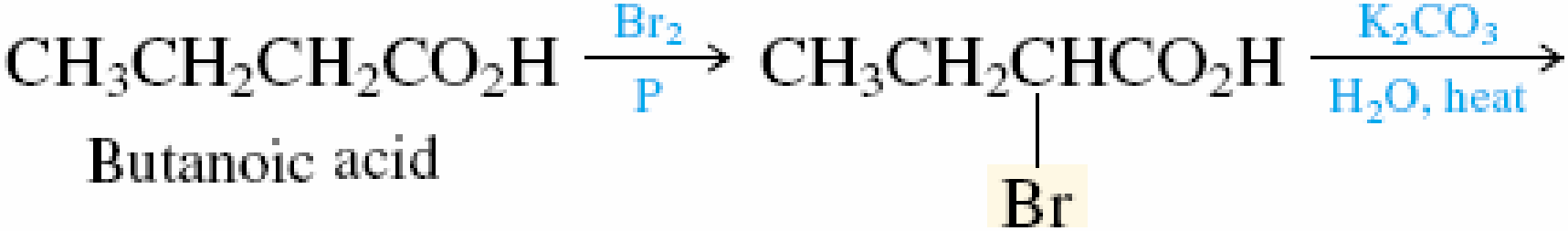
Only for α-hydrogens



Radical substitution (halogenation) will occurs in the absence of PBr_3, P

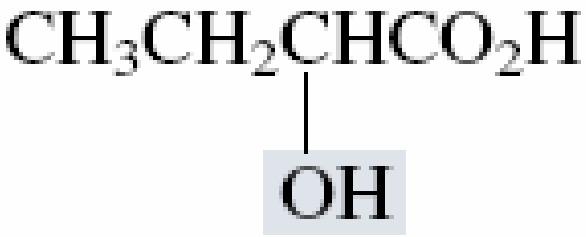
Reaction mechanism:



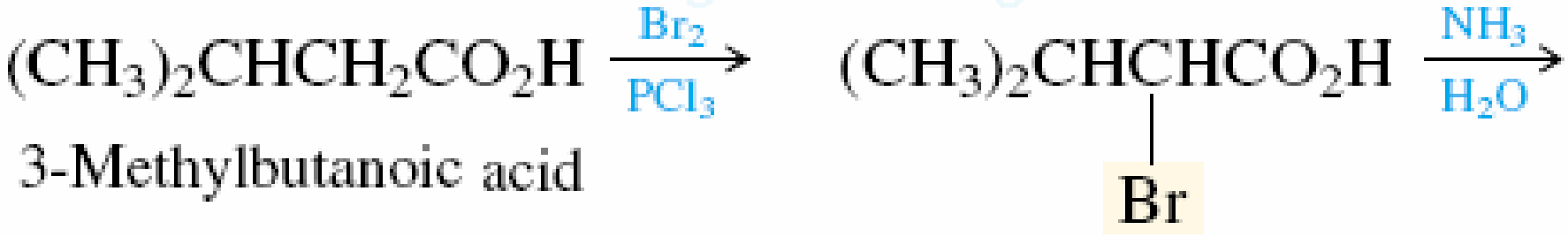


Butanoic acid

2-Bromobutanoic acid (77%)

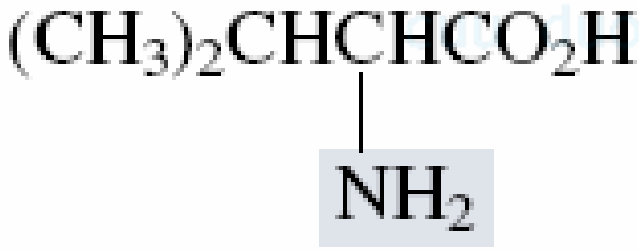


2-Hydroxybutanoic acid (69%)



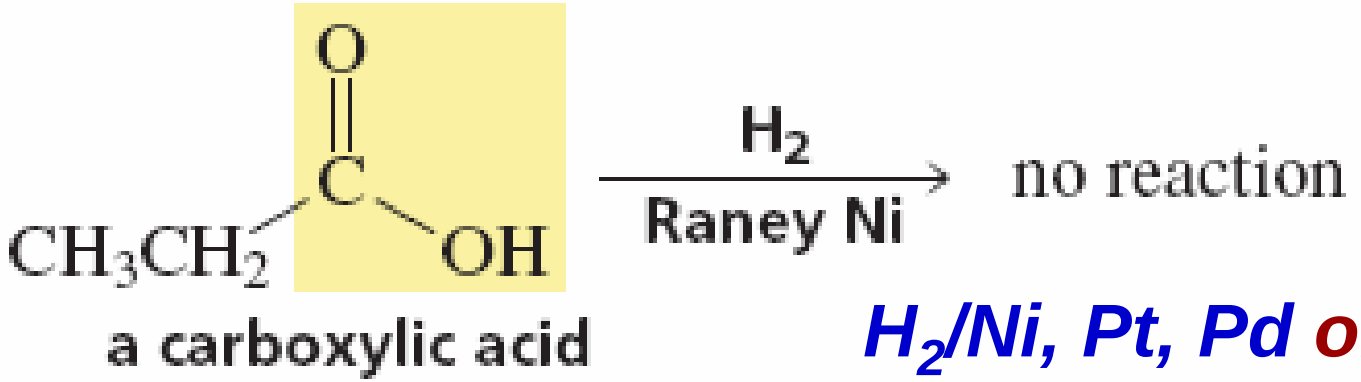
3-Methylbutanoic acid

2-Bromo-3-methylbutanoic acid (88%)



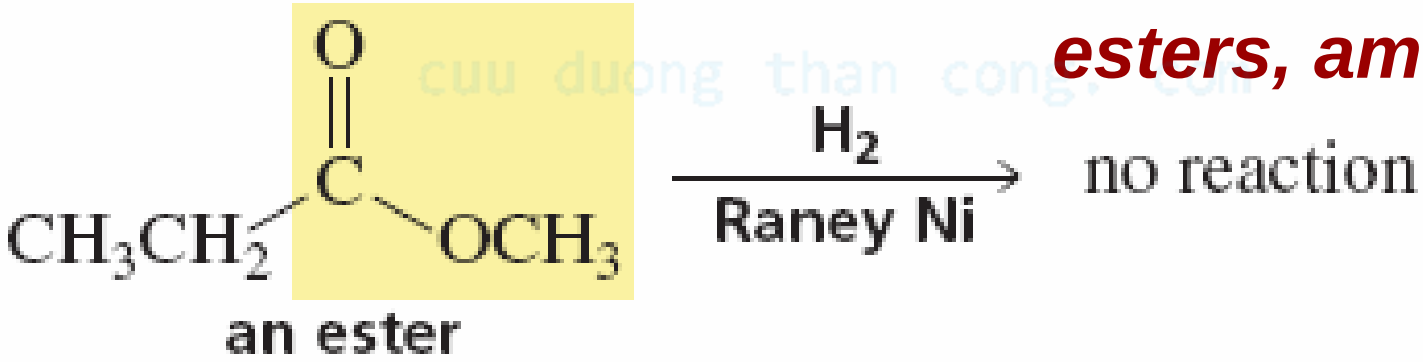
2-Amino-3-methylbutanoic acid (48%)

Reduction reactions

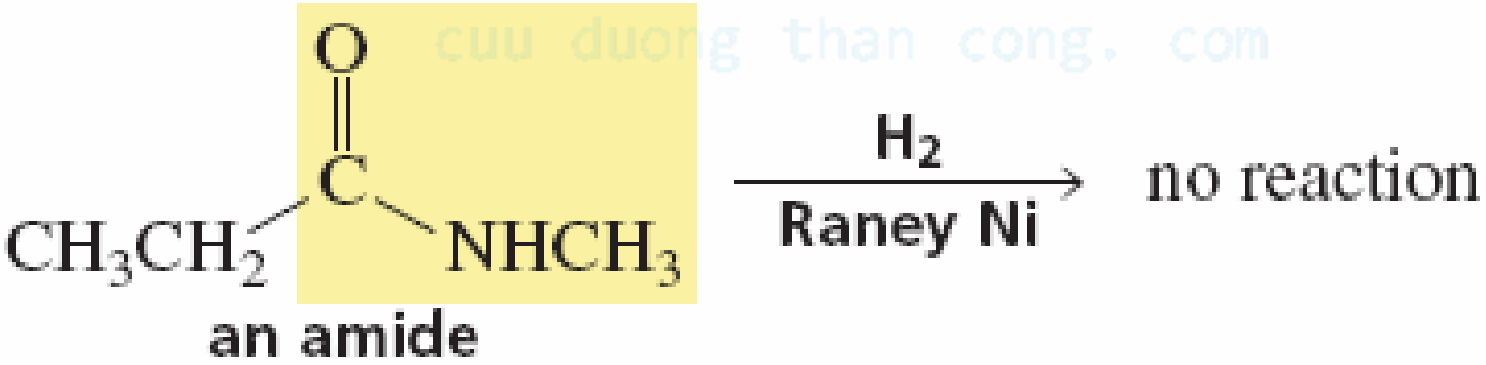


a carboxylic acid

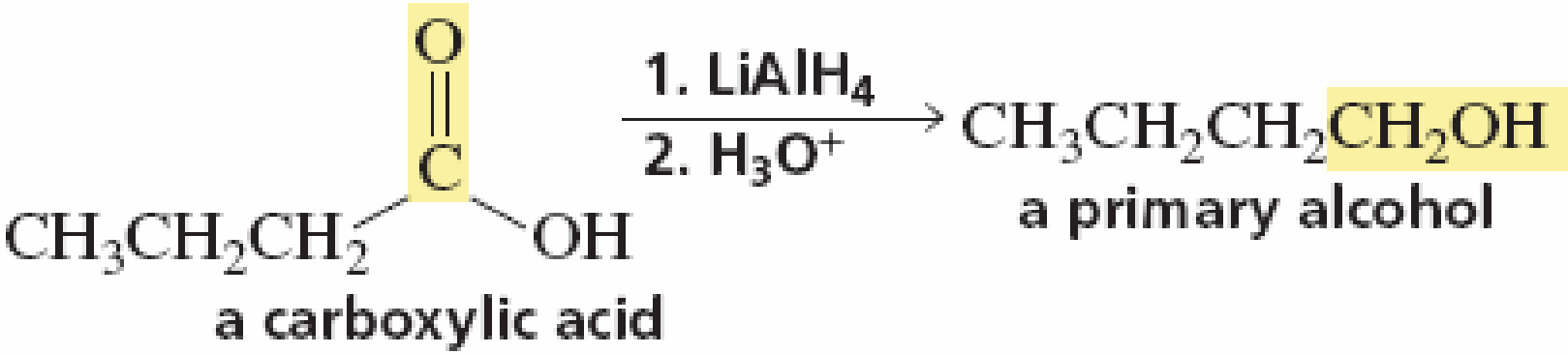
H_2/Ni, Pt, Pd or $NaBH_4$ can NOT reduce acids, esters, amides

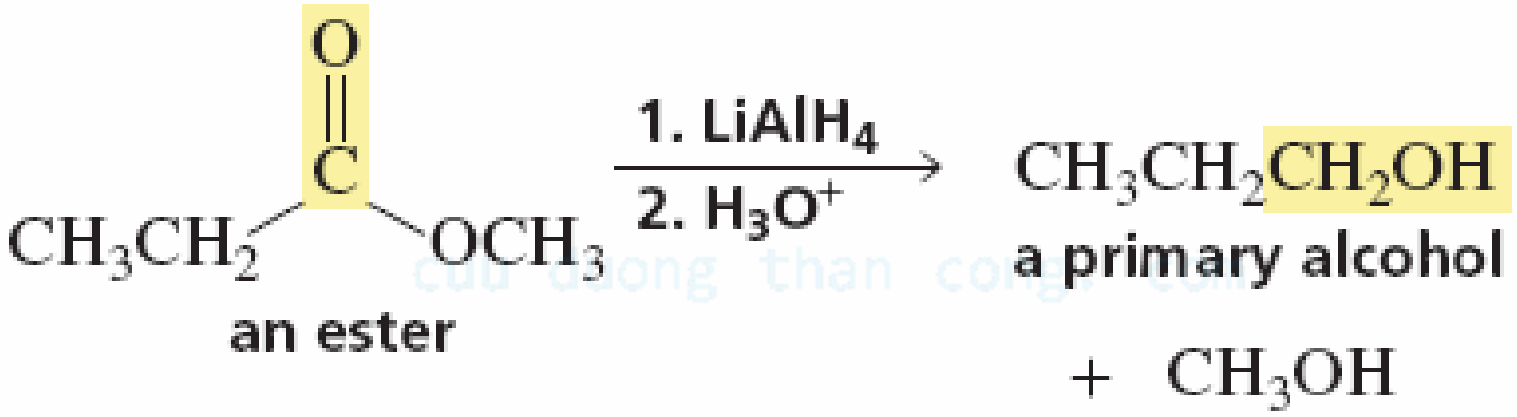


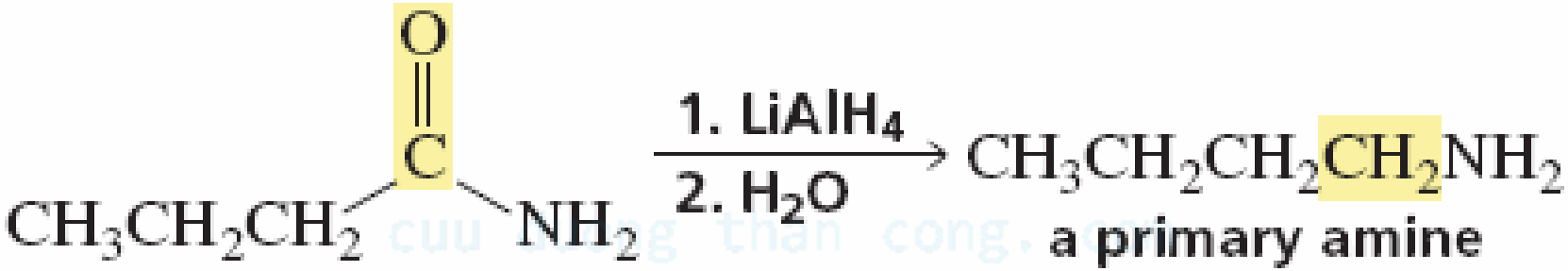
an ester



an amide







$LiAlH_4$ is used to reduce only compounds such as acids, esters, amides that can NOT be reduced by milder agents