ORGANIC CHEMISTRY

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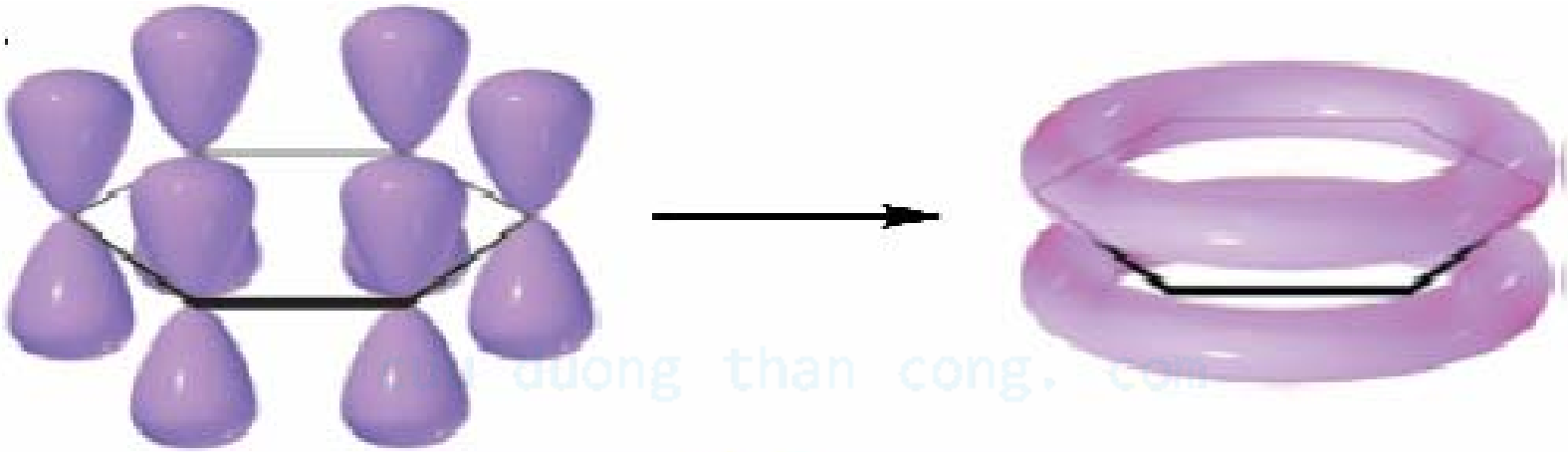
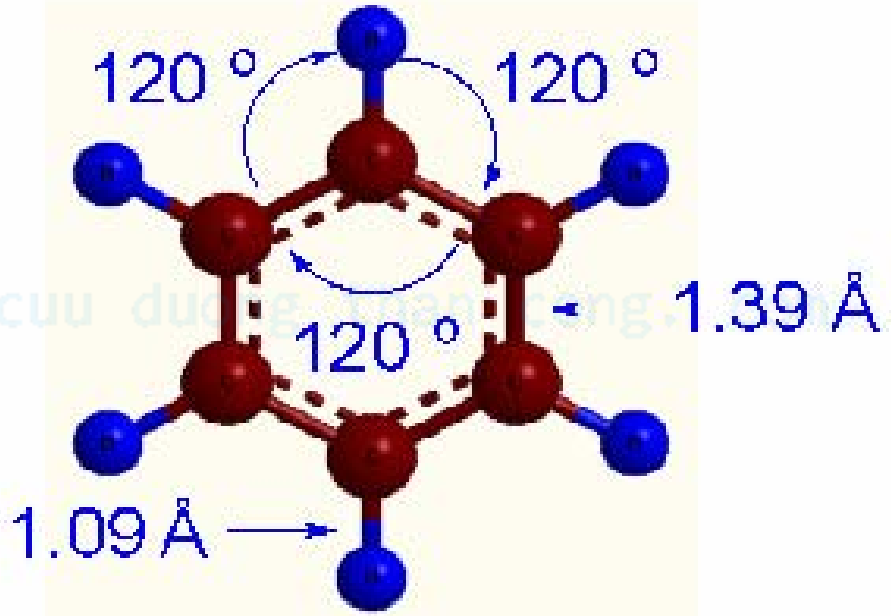
Chapter 8: ARENES



Benzene

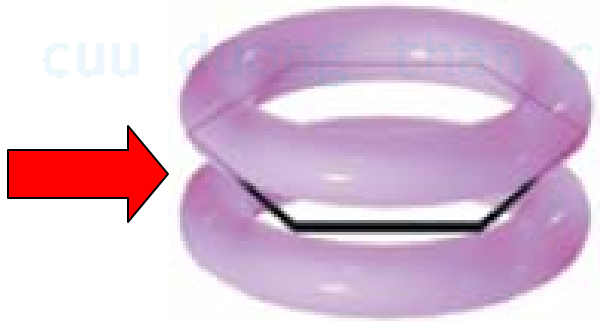


CRITERIA FOR AROMATICITY

To be classified as aromatic, a compound must meet both of the following criteria:

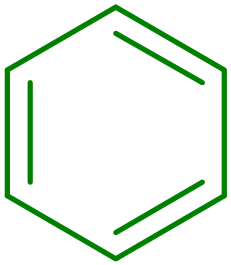
- **It must have an *un-interrupted cyclic π cloud* above & below the plane of the molecule**
- **The π cloud must contain *(4n + 2) π electrons* (n = 0, 1, 2…)**

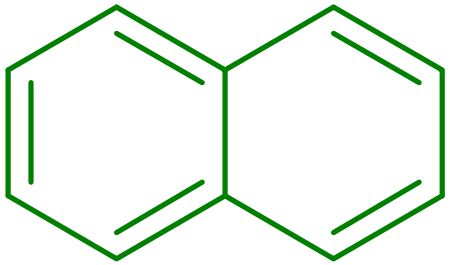
un-interrupted cyclic π cloud

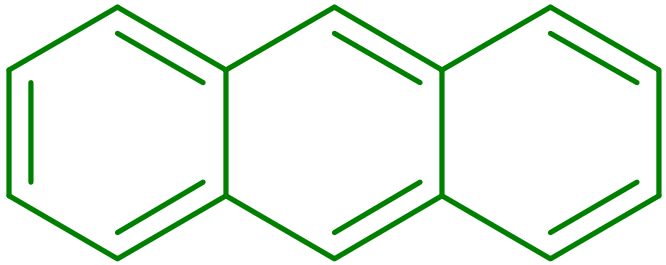


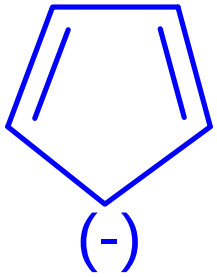
6 π e = 4 x 1 + 2

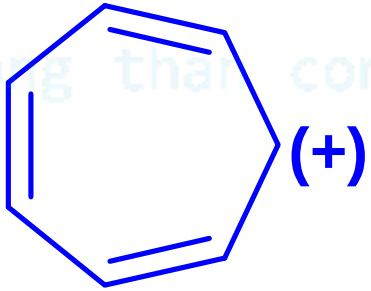
Aromatic:

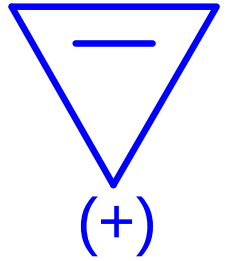


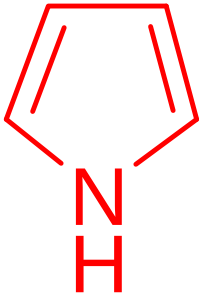


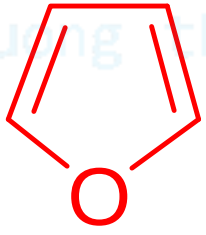


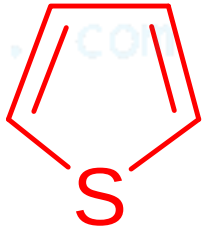






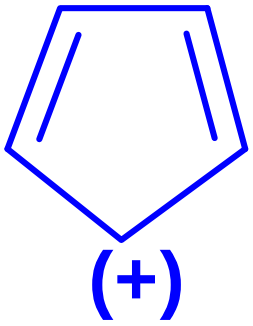




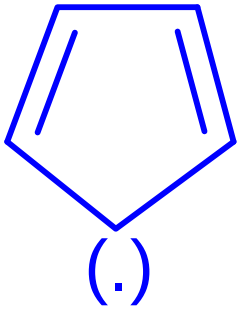


NOT aromatic:

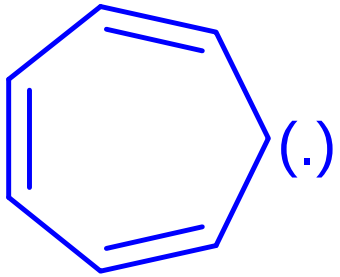
NOT (4n + 2) π e



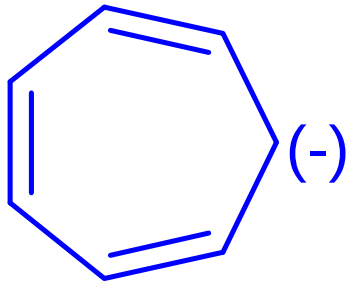
4 π e



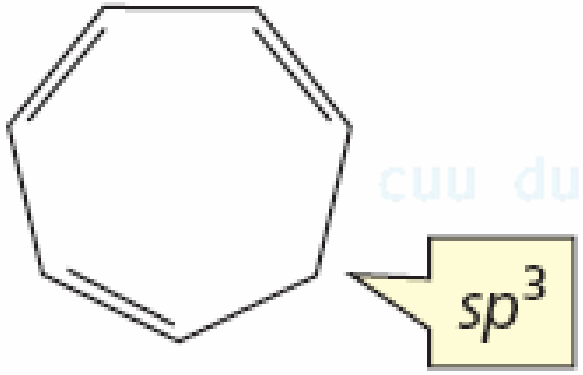
5 π e



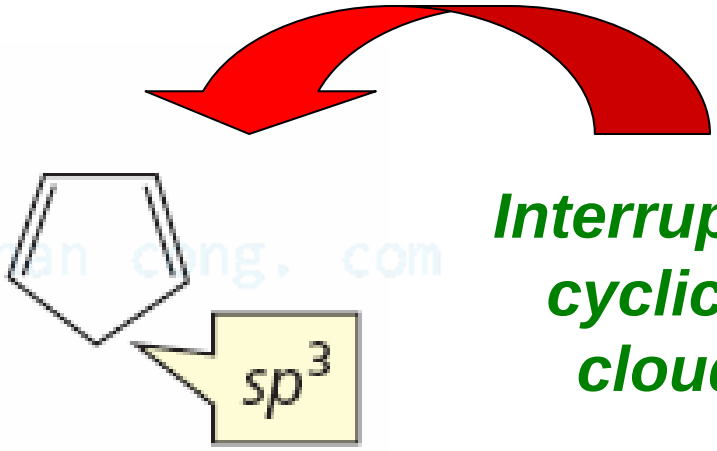
7 π e



8 π e



cycloheptatriene

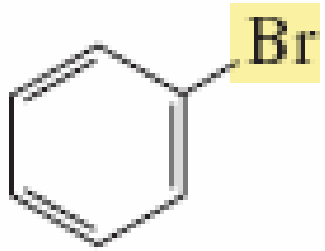


cyclopentadiene

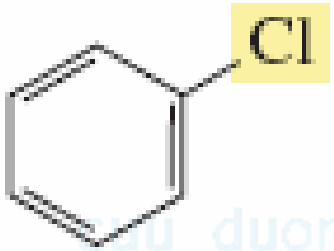
Interrupted cyclic π cloud

NOMENCLATURE OF MONOSUBSTITUTED BENZENES

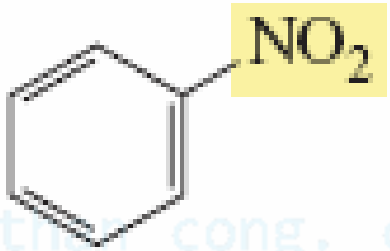
Name of substituent + benzene



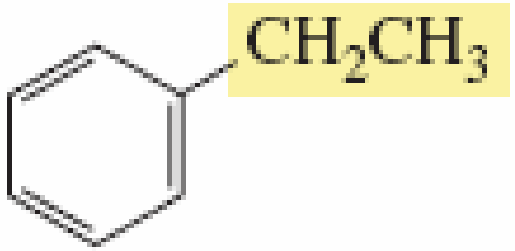
bromobenzene



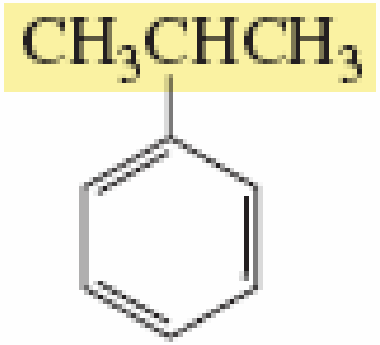
chlorobenzene



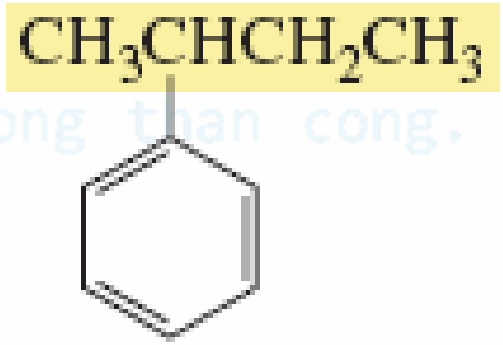
nitrobenzene



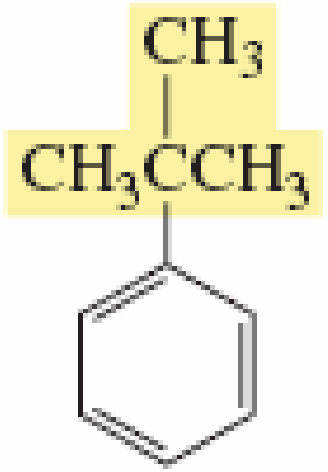
ethylbenzene



isopropylbenzene

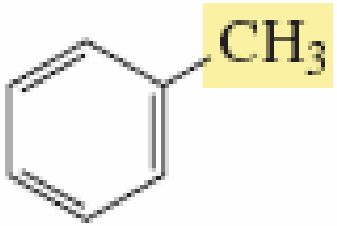


sec-butylbenzene

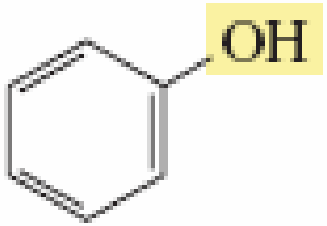


tert-butylbenzene

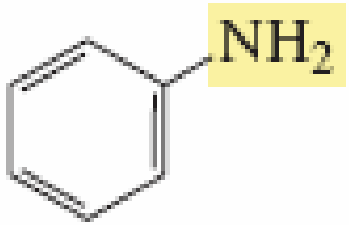
Names have to be memorized:



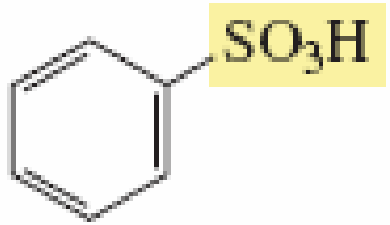
toluene



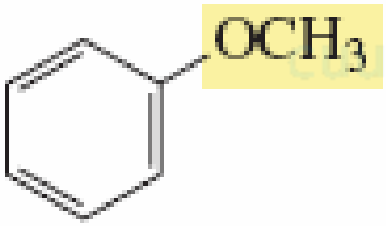
phenol



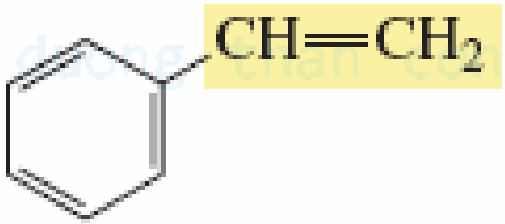
aniline



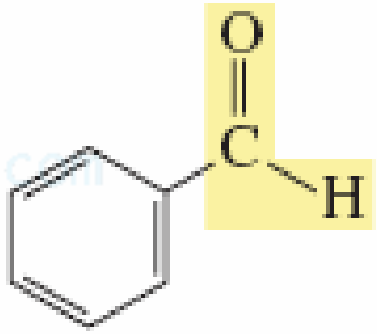
benzenesulfonic acid



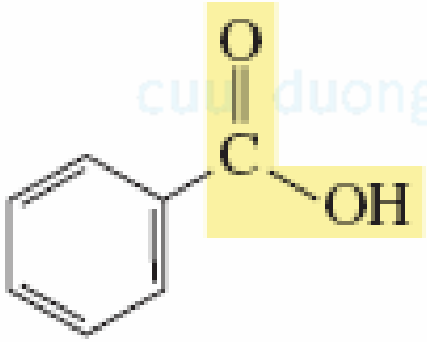
anisole



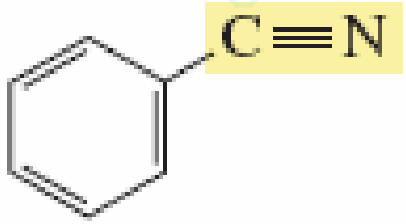
styrene



benzaldehyde

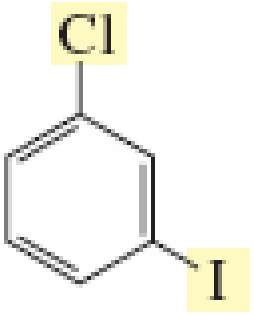


benzoic acid

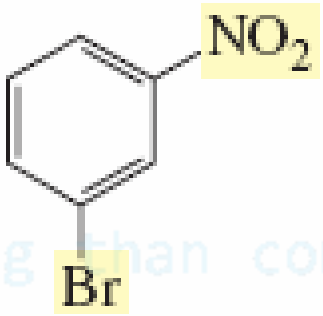


benzonitrile

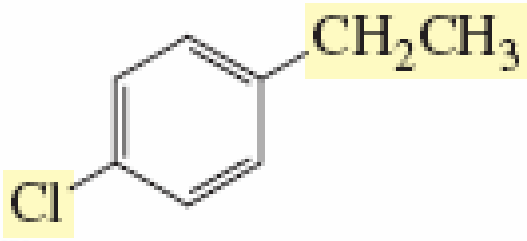
NOMENCLATURE OF DI- & POLYSUBSTITUTED BENZENES



1-chloro-3-iodobenzene
meta-chloroiodobenzene
not
1-iodo-3-chlorobenzene or
meta-iodochlorobenzene



1-bromo-3-nitrobenzene
meta-bromonitrobenzene

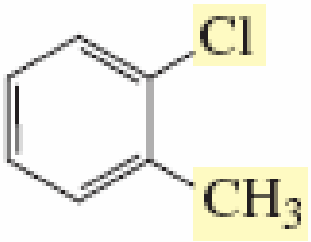


1-chloro-4-ethylbenzene
para-chloroethylbenzene

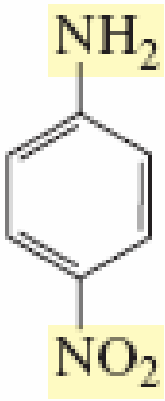
cuu duong than cong. com

Alphabetical order, 1-position for the 1st stated substituent

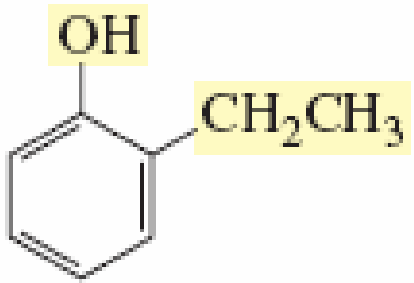
1 of the substituents can be incorporated into a name:



2-chlorotoluene
ortho-chlorotoluene
not
ortho-chloromethylbenzene

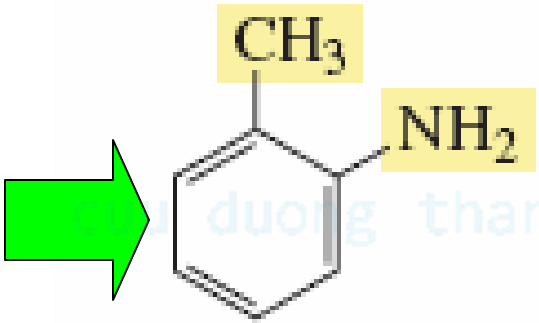


4-nitroaniline
para-nitroaniline
not
para-aminonitrobenzene

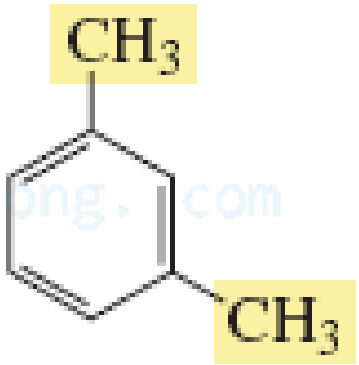


2-ethylphenol
ortho-ethylphenol
not
ortho-ethylhydroxybenzene

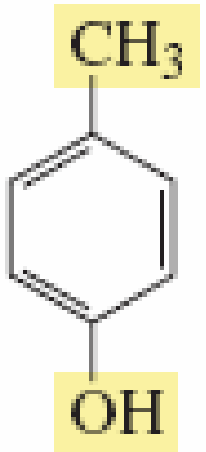
Names incorporating 2 substituents



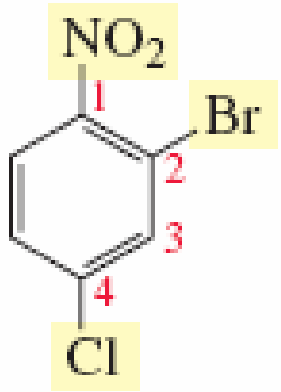
ortho-toluidine



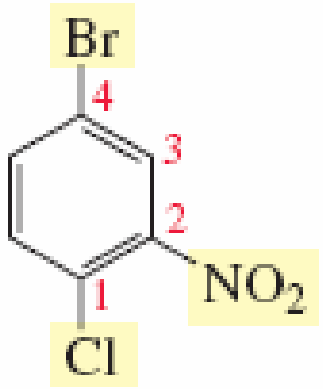
meta-xylene



para-cresol

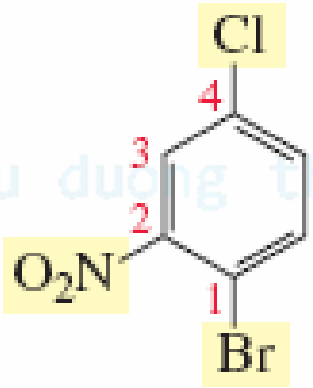


2-bromo-4-chloro-1-nitrobenzene



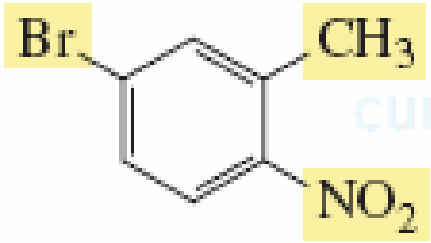
4-bromo-1-chloro-2-nitrobenzene

Alphabetical order

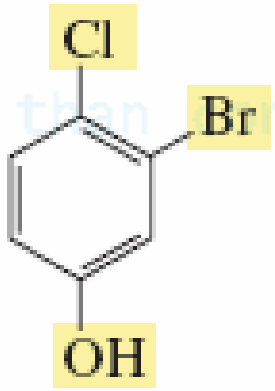


1-bromo-4-chloro-2-nitrobenzene

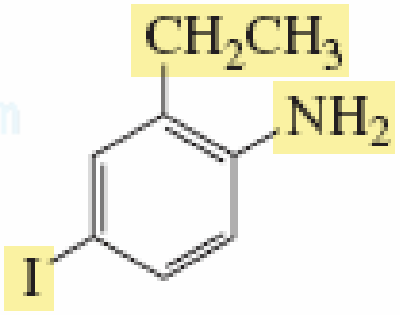
Lowest possible numbers



5-bromo-2-nitrotoluene



3-bromo-4-chlorophenol



2-ethyl-4-iodoaniline

PREPARATION OF BENZENE

$$C_6H_5CO_2H + CaO \xrightarrow{\text{heat}} C_6H_6 + CaCO_3$$

Benzoic acid Calcium oxide Benzene Calcium carbonate

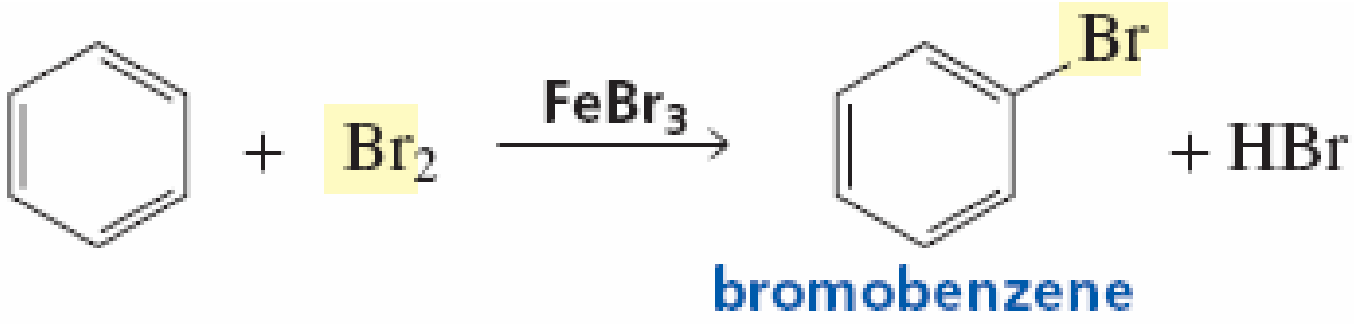
$$3\ HC{\equiv}CH \xrightarrow{\text{catalyst}} C_6H_6$$

acetylene Benzene

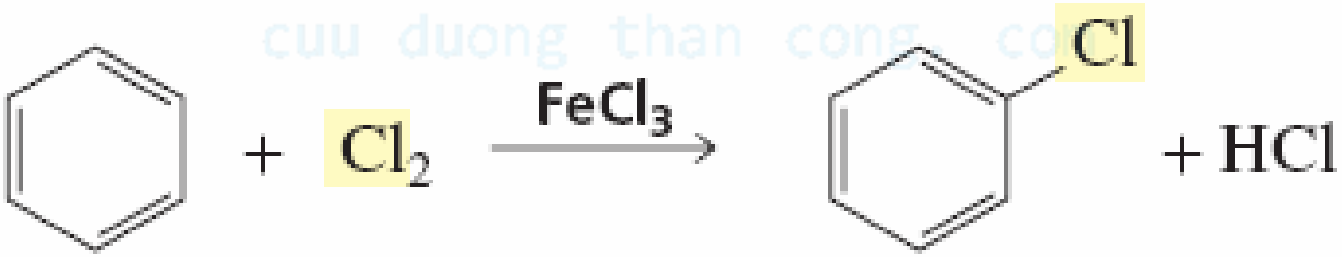
Petroleum *Bezene*

REACTIONS OF BENZENE

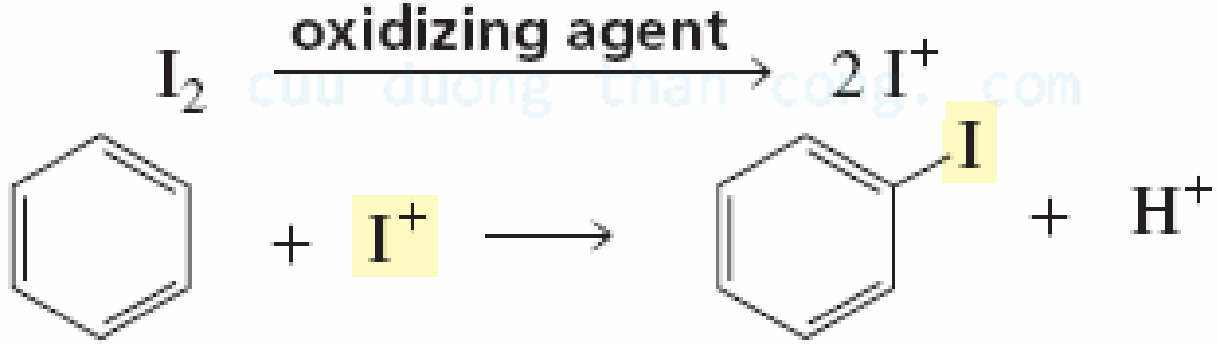
Halogenations of benzene



bromobenzene

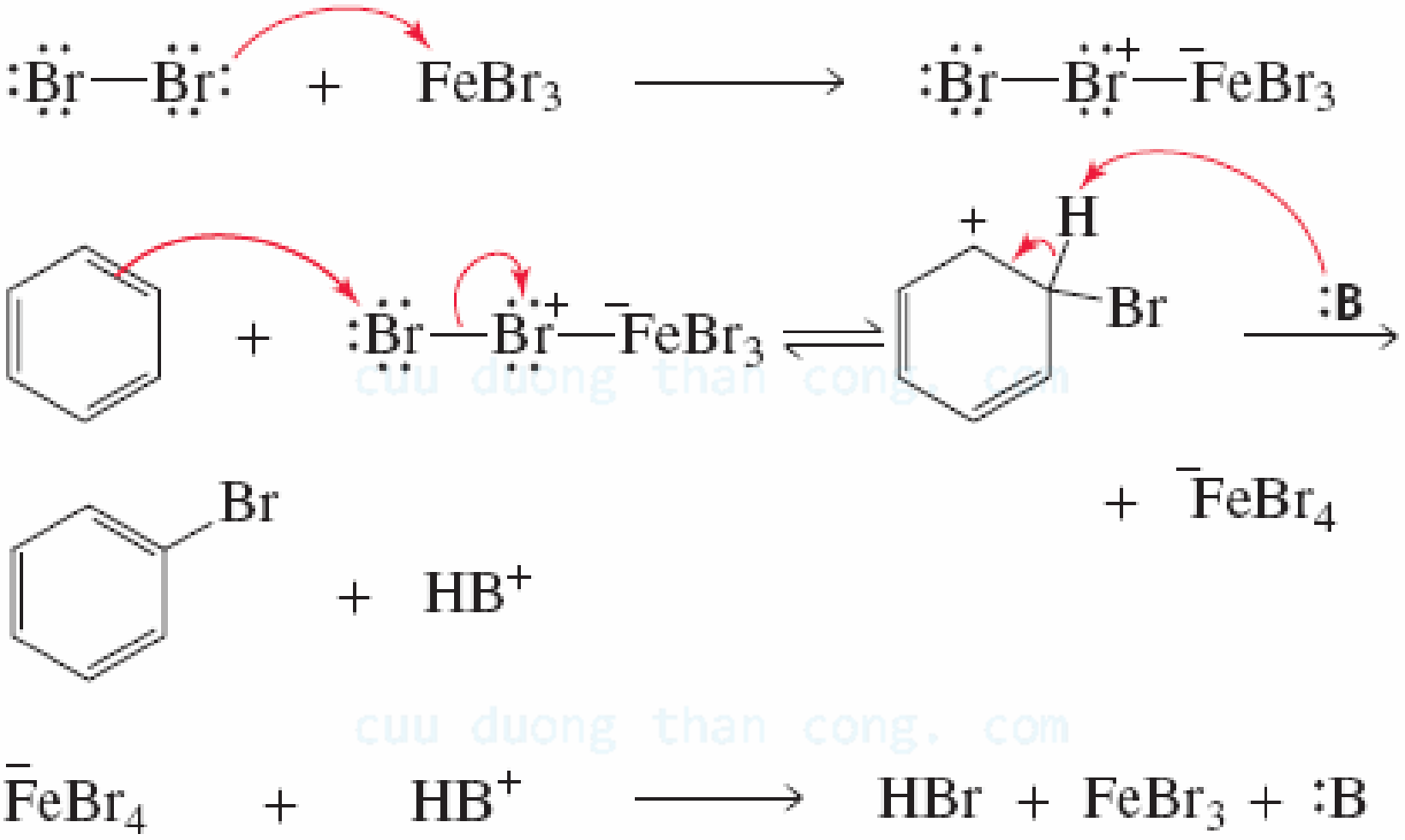


chlorobenzene

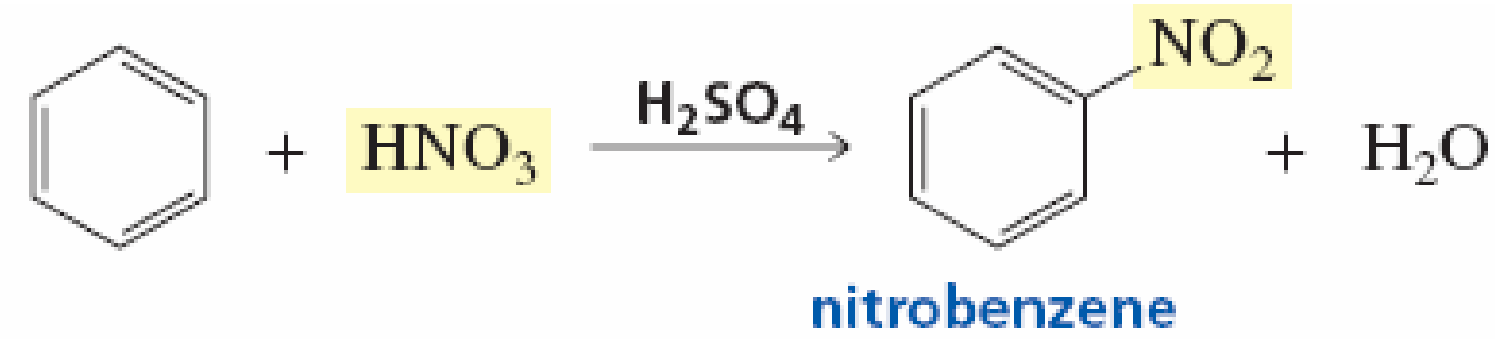


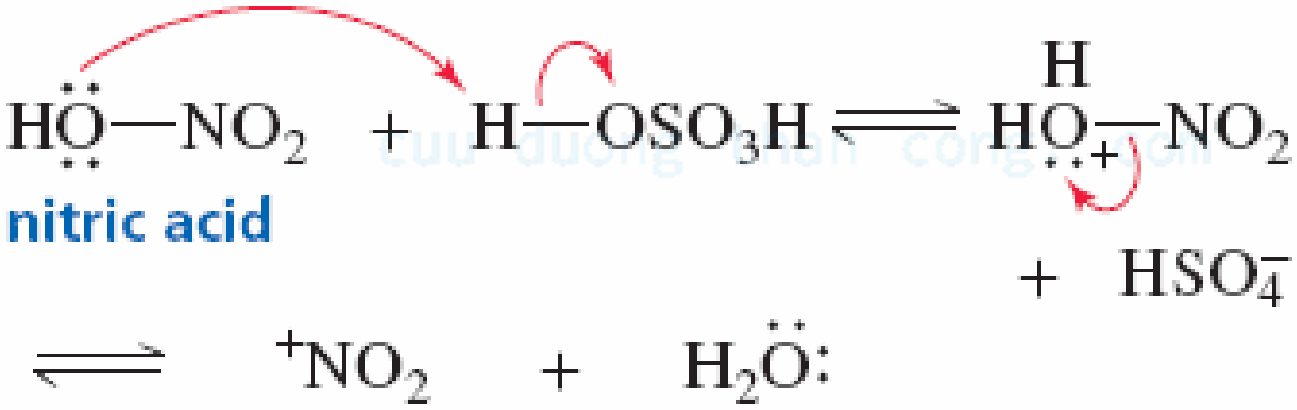
iodobenzene

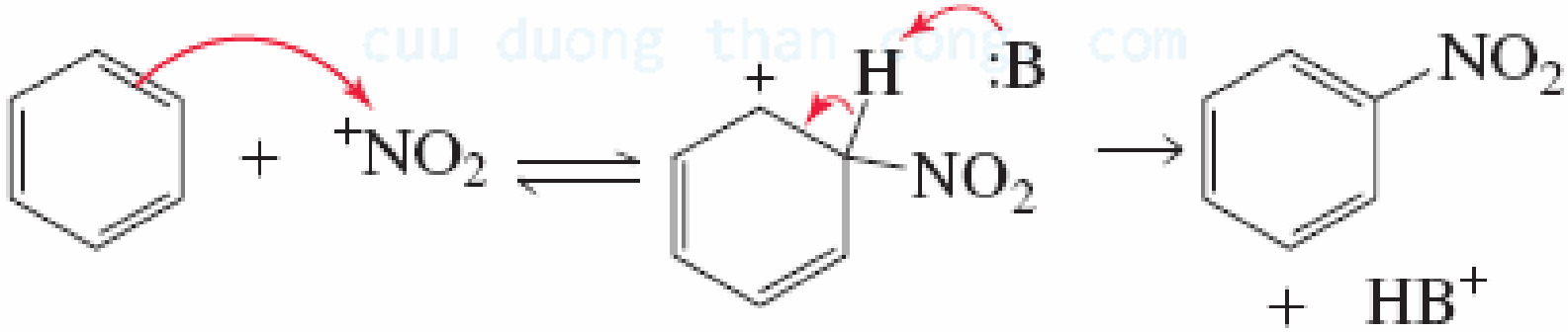
Reaction mechanism: electrophilic substitution



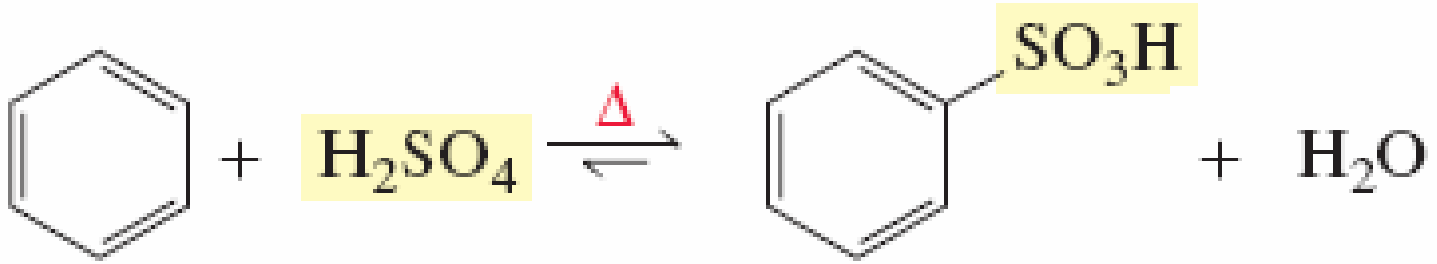
Nitration of benzene



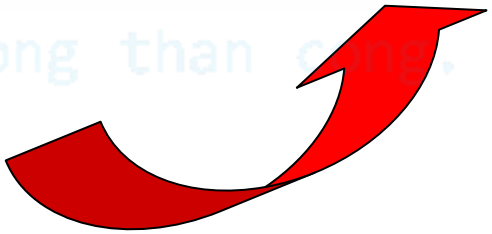




Sulfonation of benzene

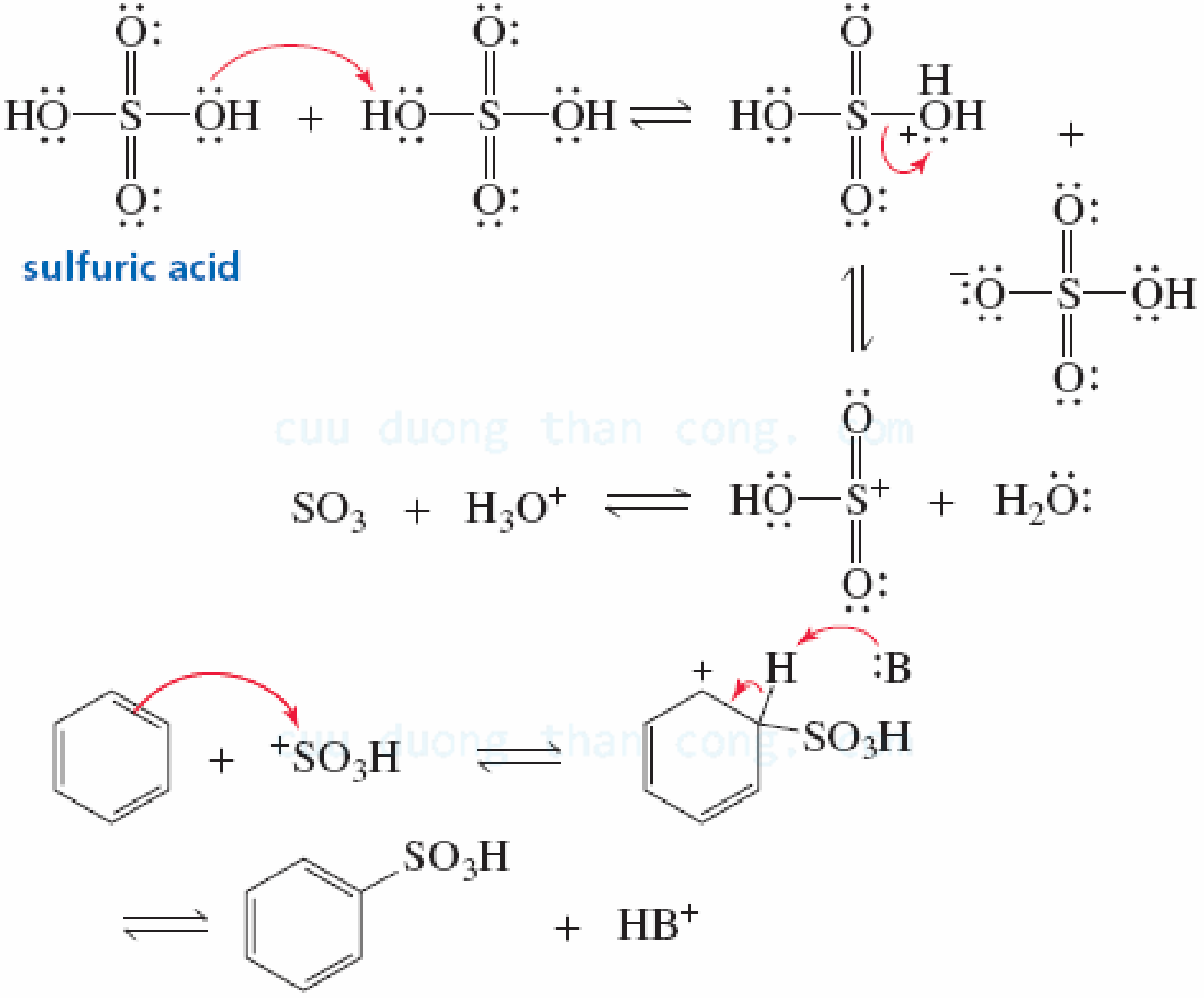


benzenesulfonic acid

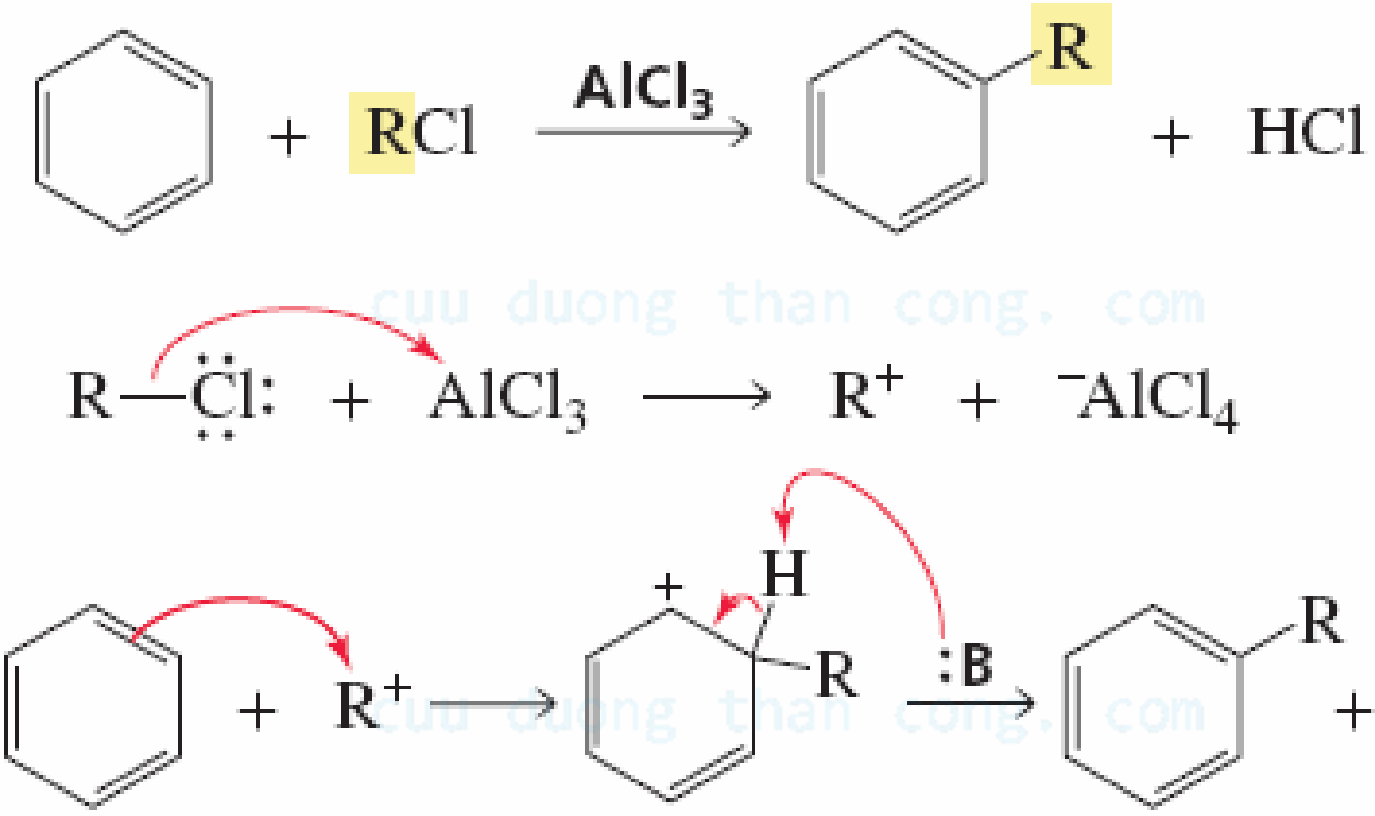


Reversible reaction

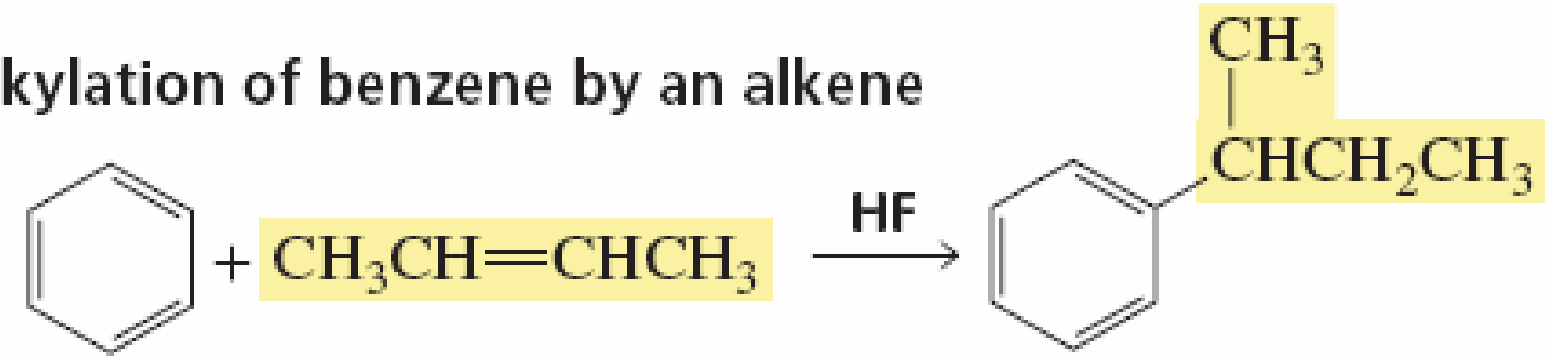
Reaction mechanism: electrophilic substitution



Friedel-Crafts Alkylations of benzene

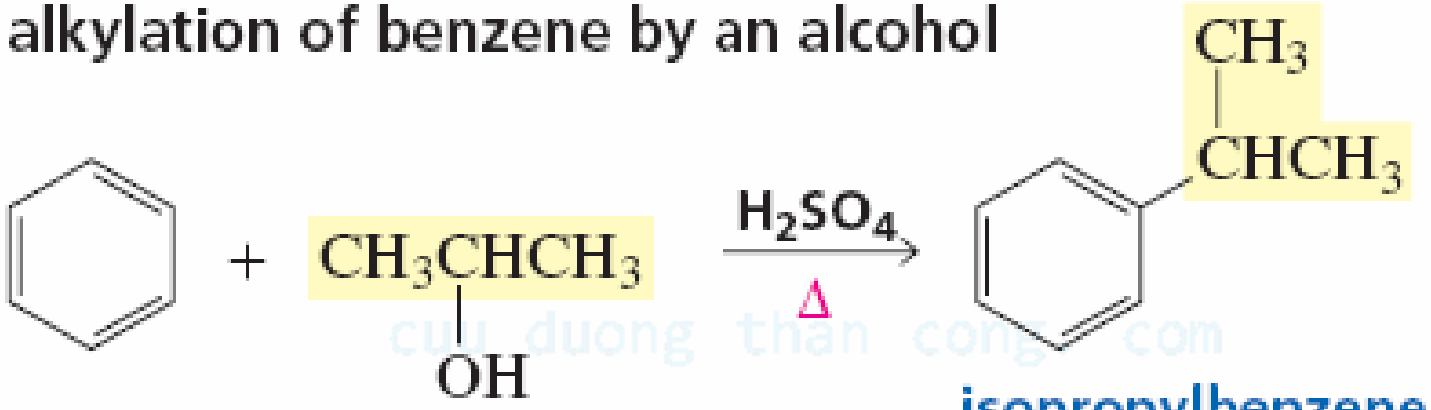


alkylation of benzene by an alkene



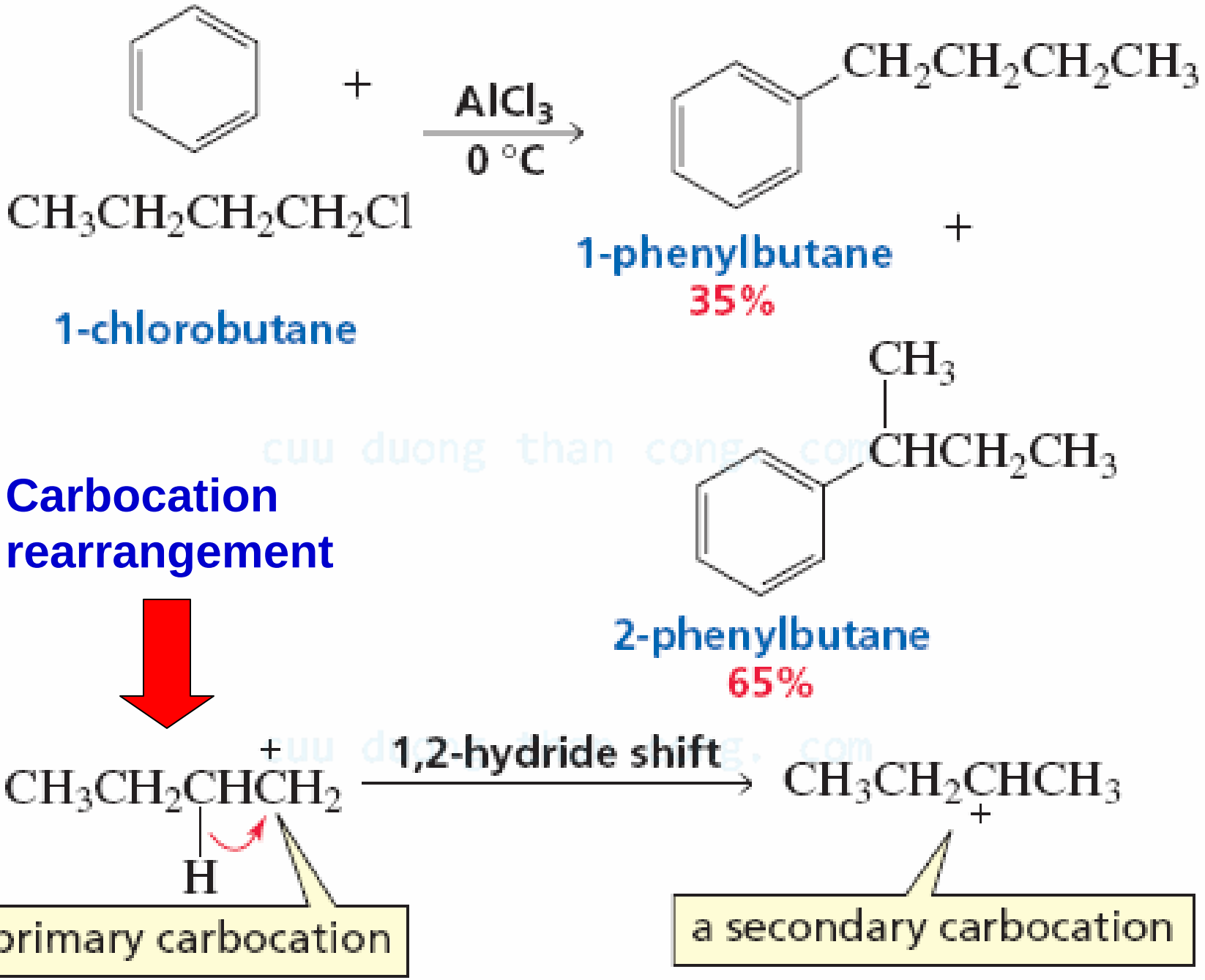
sec-butylbenzene

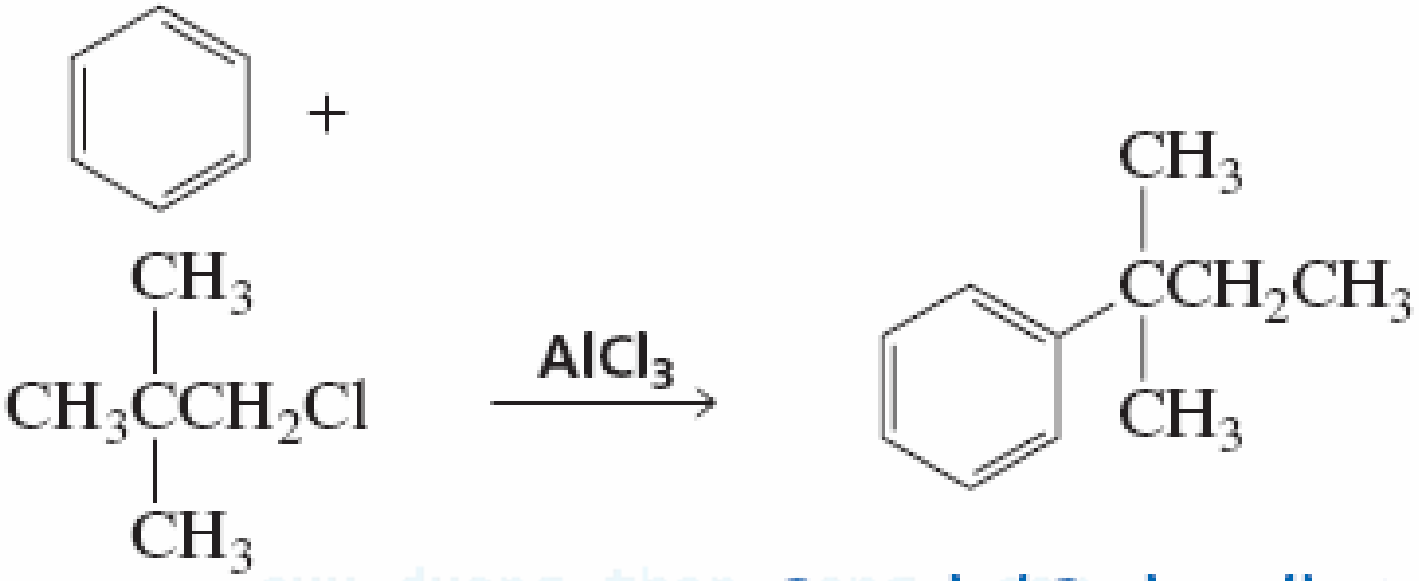
alkylation of benzene by an alcohol



isopropylbenzene

cumene

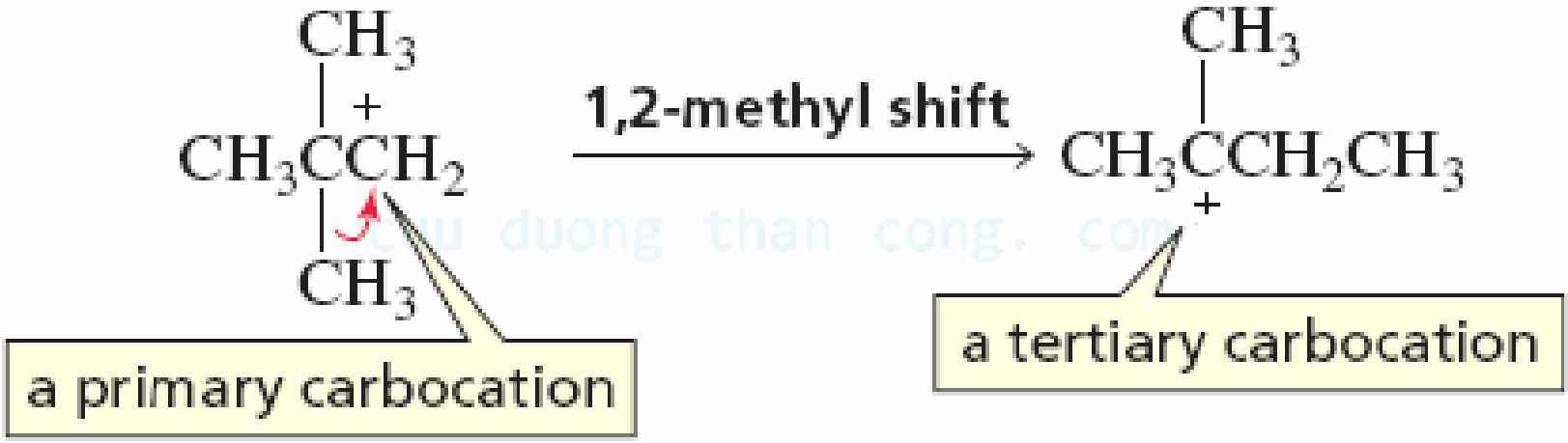

+
AlCl3
0 °C
CH3CH2CH2CH2Cl
1-chlorobutane
CH2CH2CH2CH3
1-phenylbutane
35%
+
CH3
CHCH2CH3
2-phenylbutane
65%
Carbocation rearrangement
CH3CH2CHCH2
H
1,2-hydride shift
CH3CH2CHCH3
a primary carbocation
a secondary carbocation



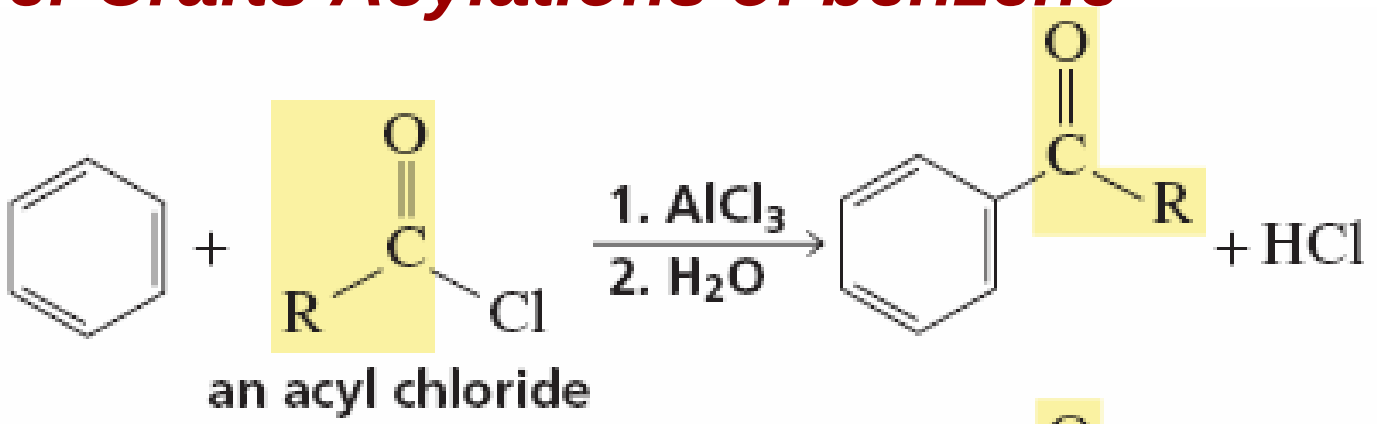
1-chloro-2,2-dimethylpropane

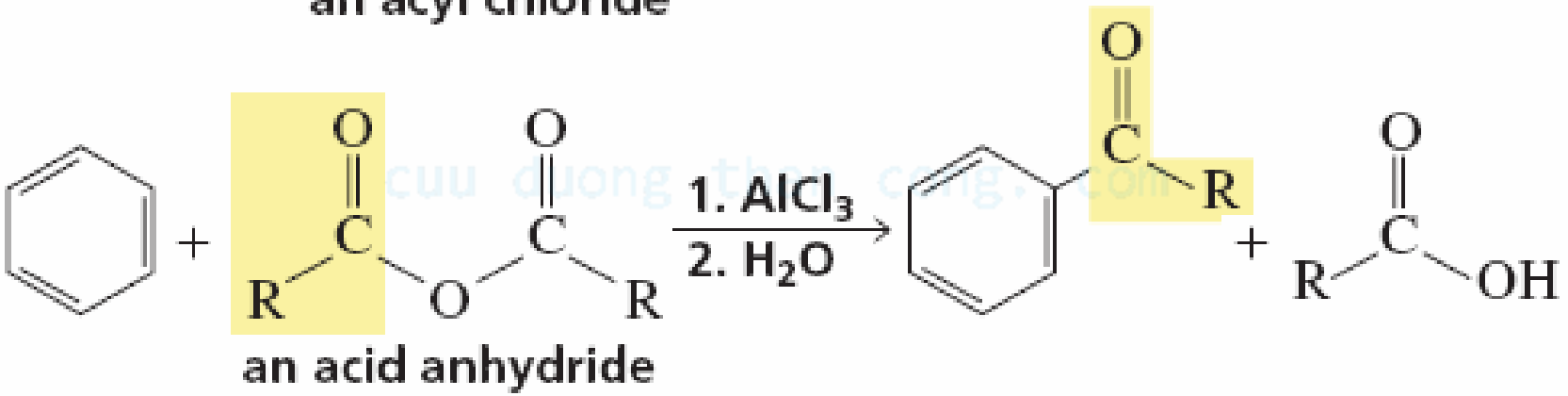
2-methyl-2-phenylbutane

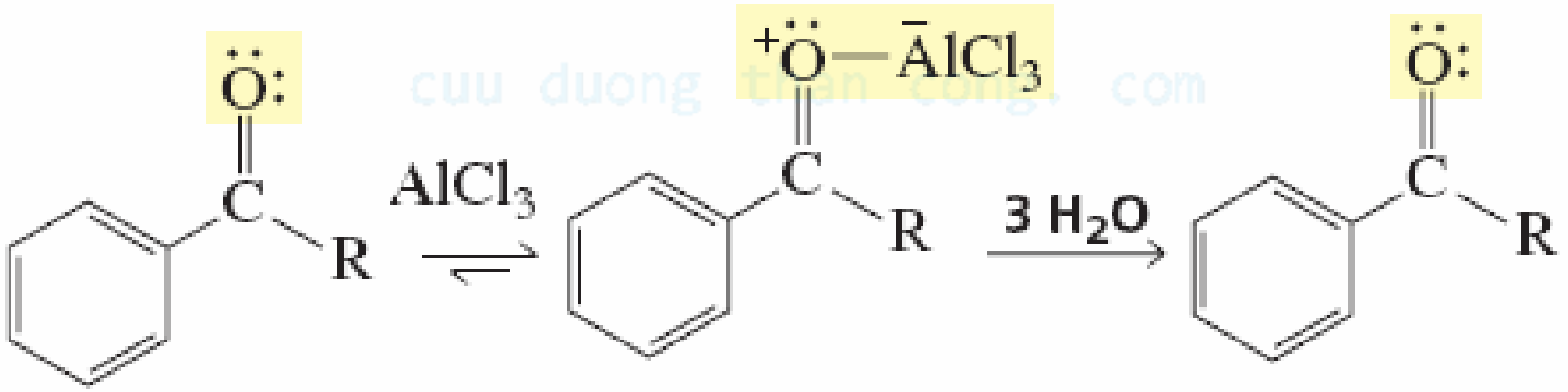
100%



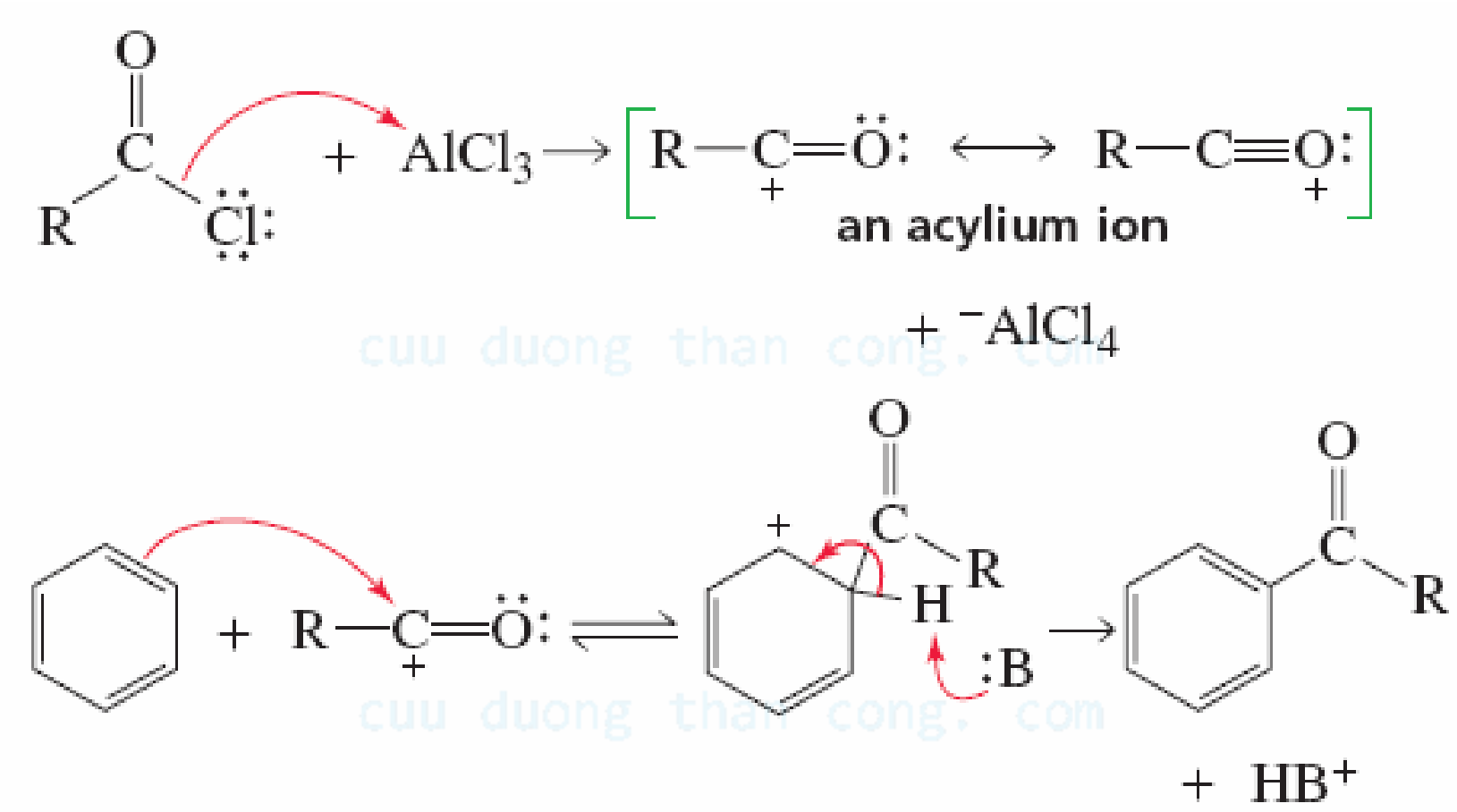
Friedel-Crafts Acylations of benzene

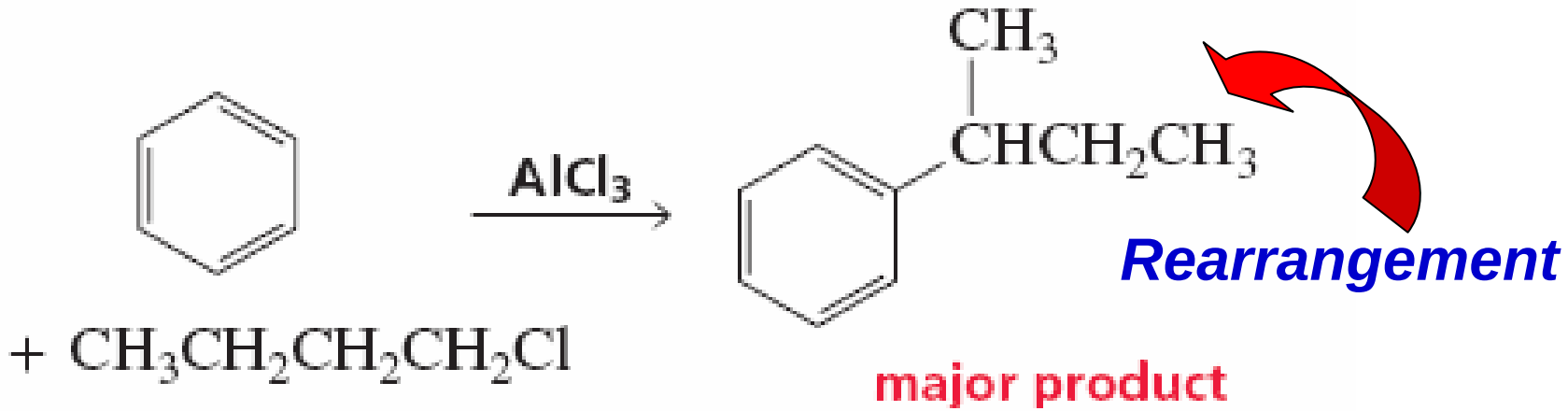


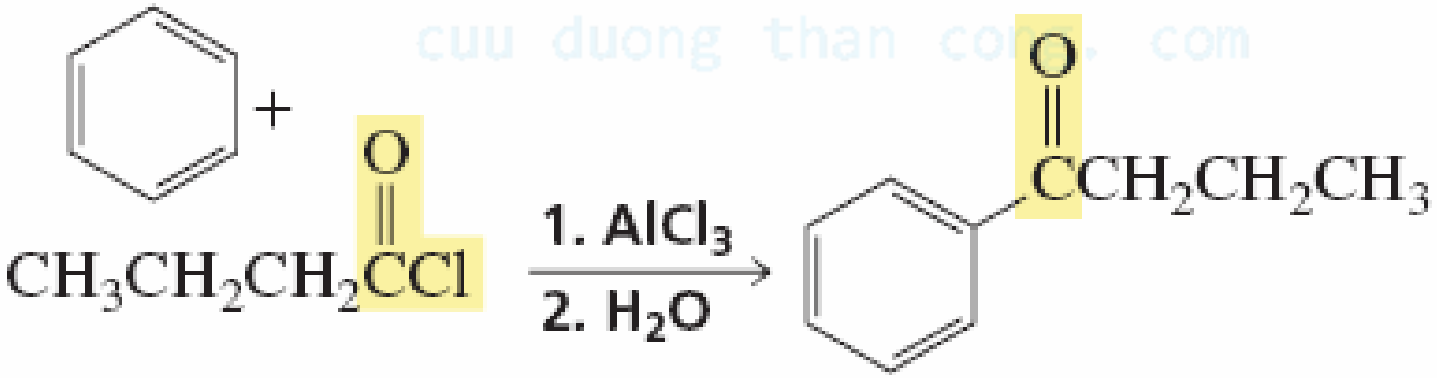


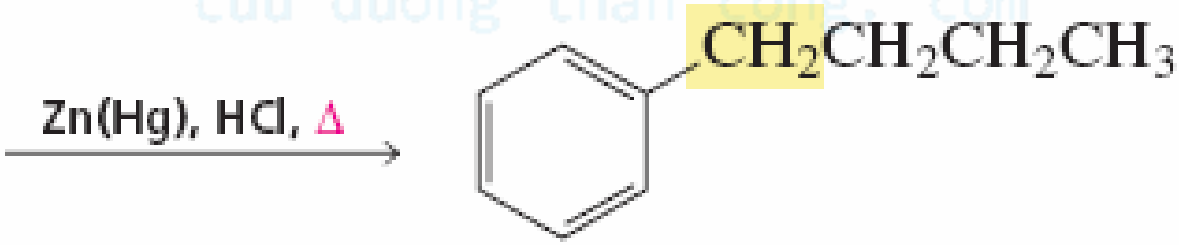


Reaction mechanism: electrophilic substitution



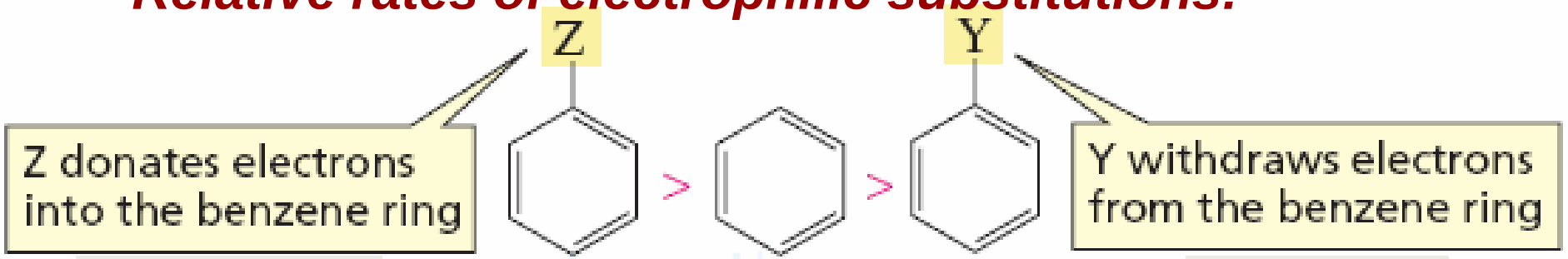




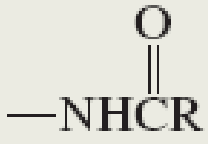


REACTIONS OF SUBSTITUTED BENZENES

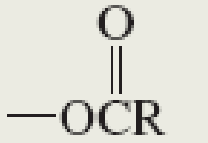
Relative rates of electrophilic substitutions:



—NH_2
—NHR
—NR_2
—OH
—OR



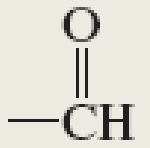
—NHCR



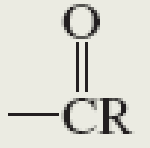
—OCR
—R

Electron-donating

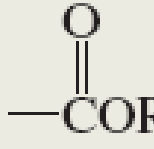
Electron-withdrawing



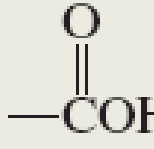
—CH



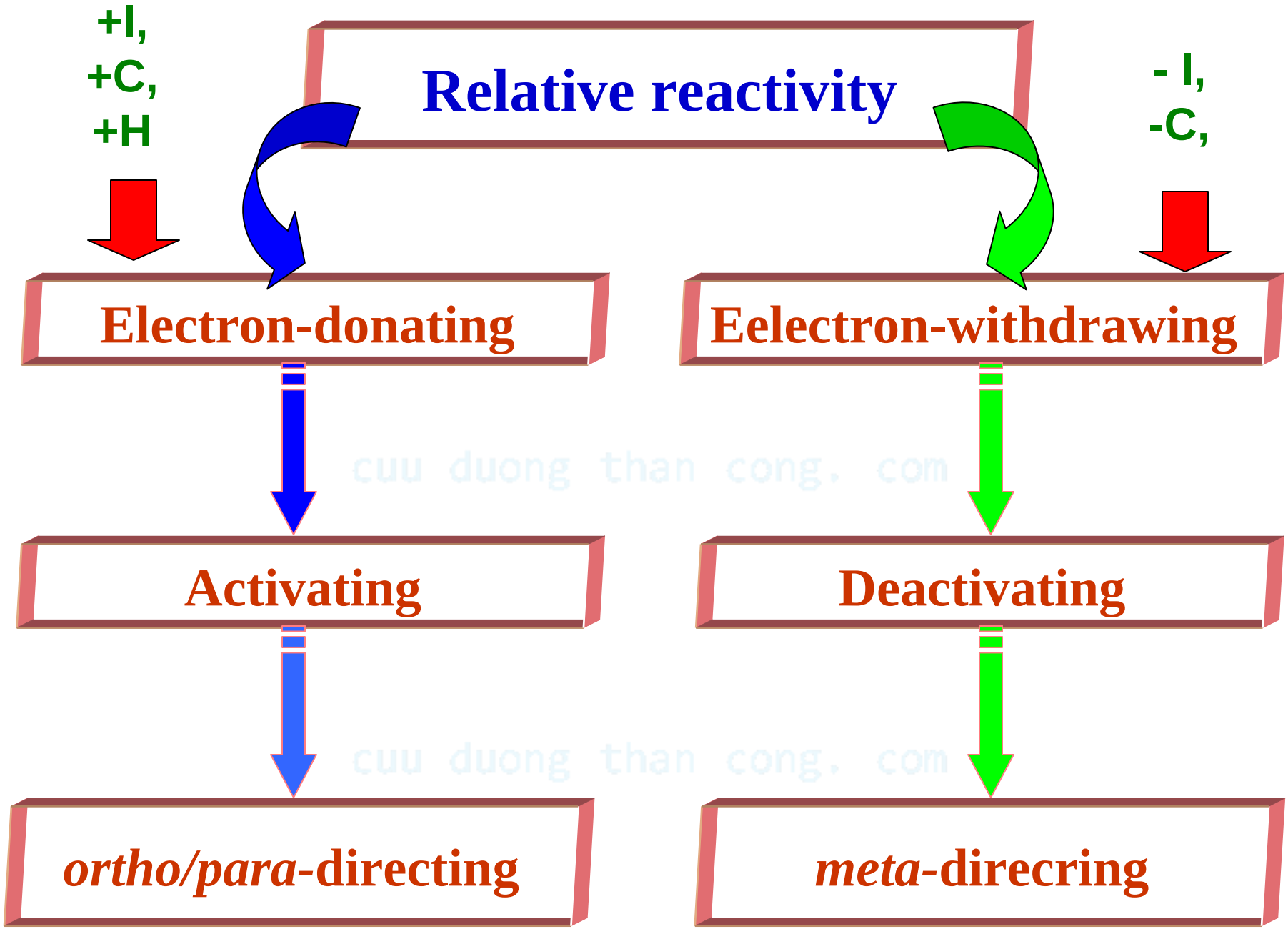
—CR



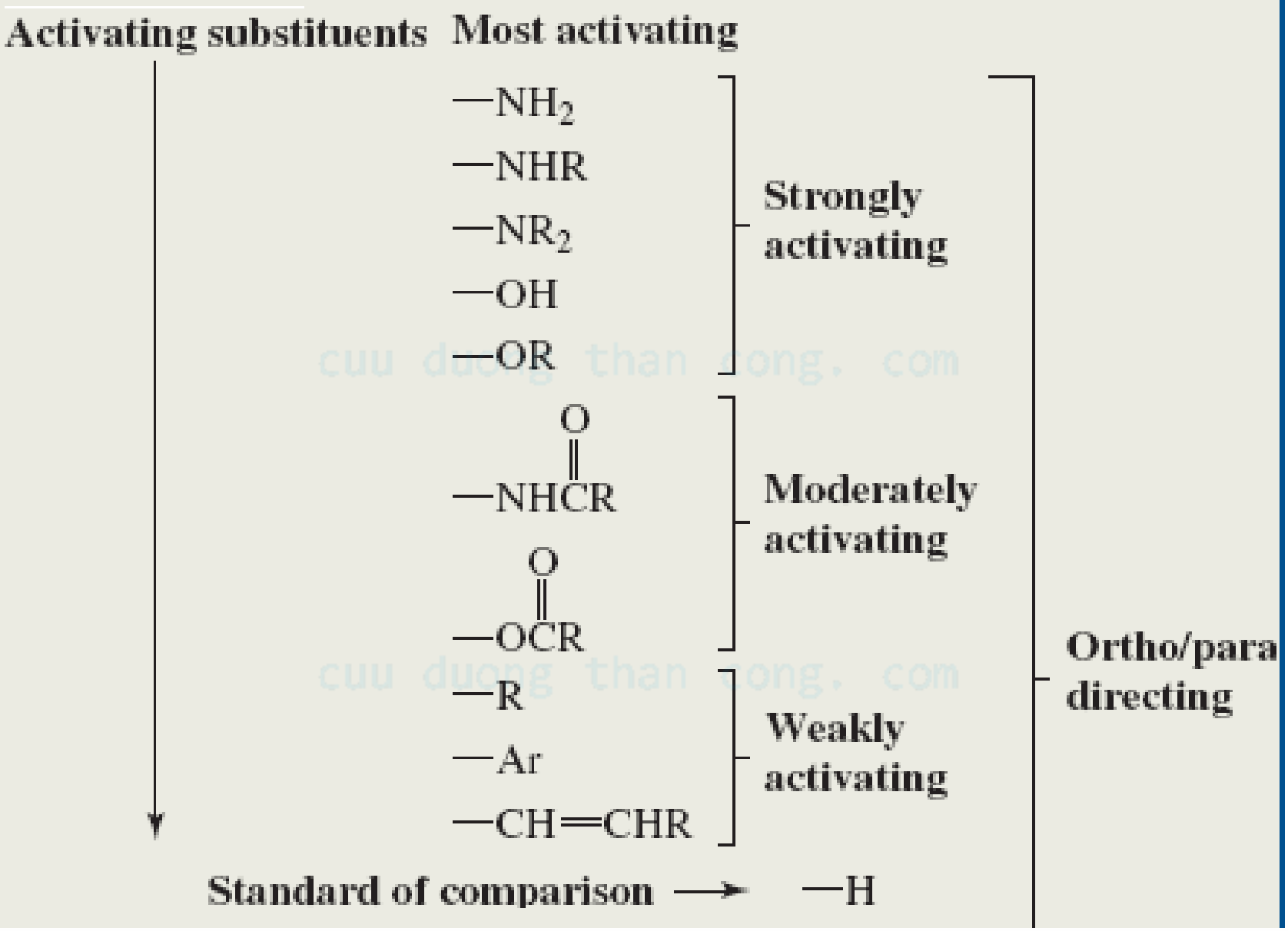
—COR

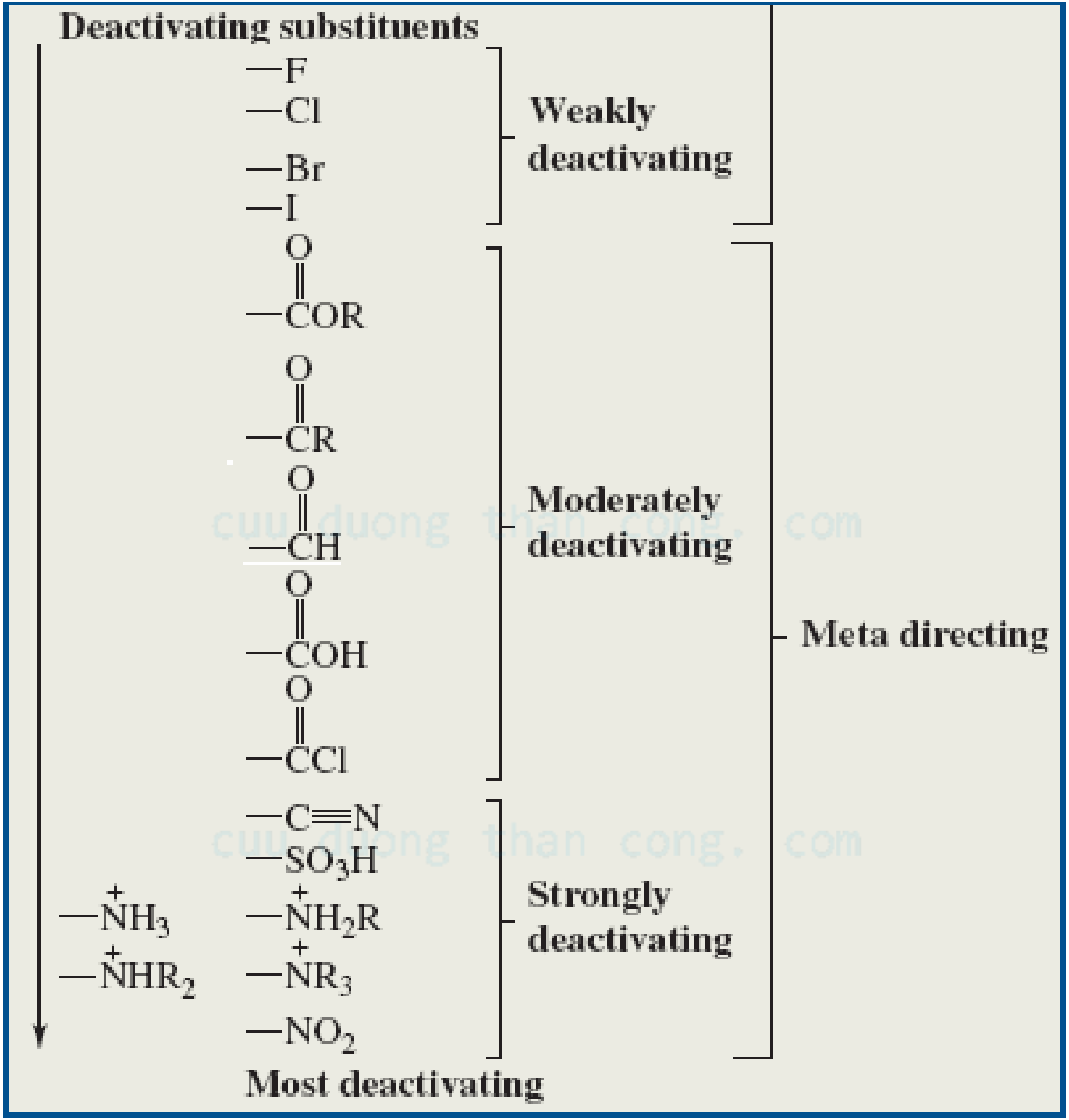


—COH
—NO_2



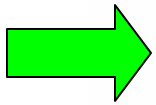
The Effects of Substituents on the Reactivity of a Benzene Ring Toward Electrophilic Substitution

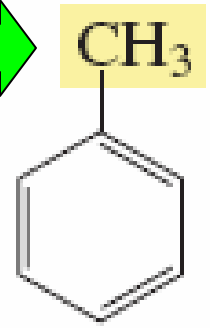



Deactivating substituents
—F
—Cl
—Br
—I
Weakly deactivating
—COR
—CR
—CH
—COH
—CCl
Moderately deactivating
Meta directing
—C≡N
—SO3H
—NH2R
—NR3
—NO2
Strongly deactivating
—NH3
—NHR2
Most deactivating

EFFECTS OF SUBSTITUENTS ON ORIENTATION

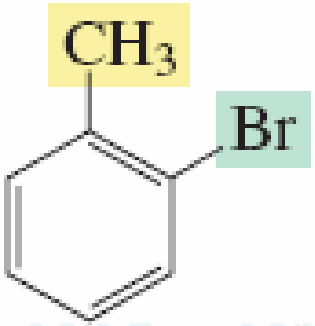
E/D group





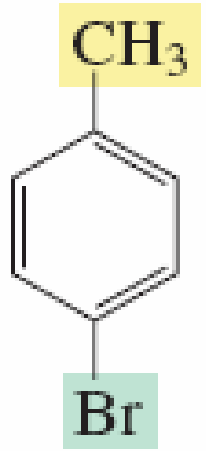
toluene

Br_2 / $FeBr_3$



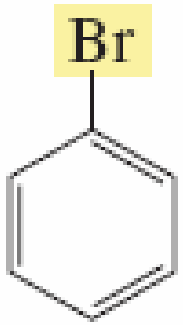
o-bromotoluene

+



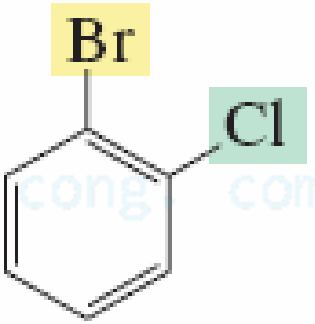
p-bromotoluene

Only for halogen group



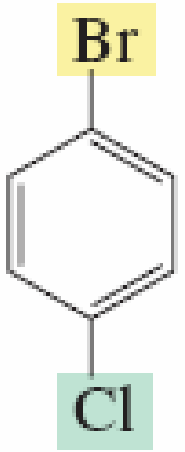
bromobenzene

Cl_2 / $FeCl_3$



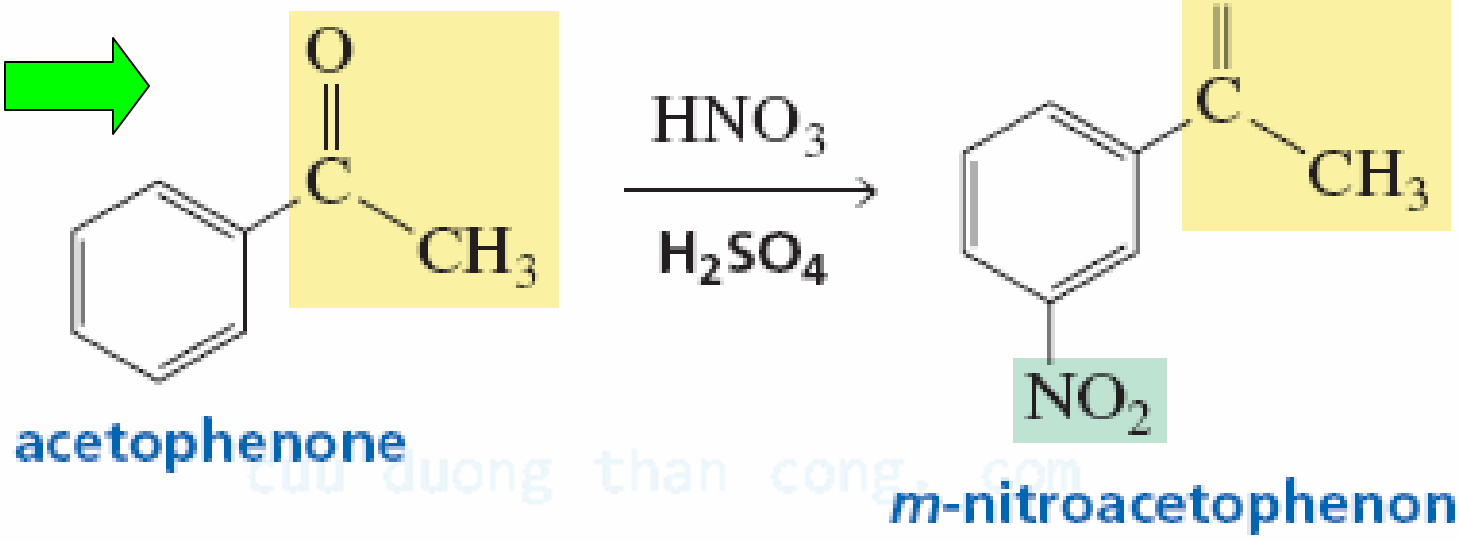
o-bromochlorobenzene

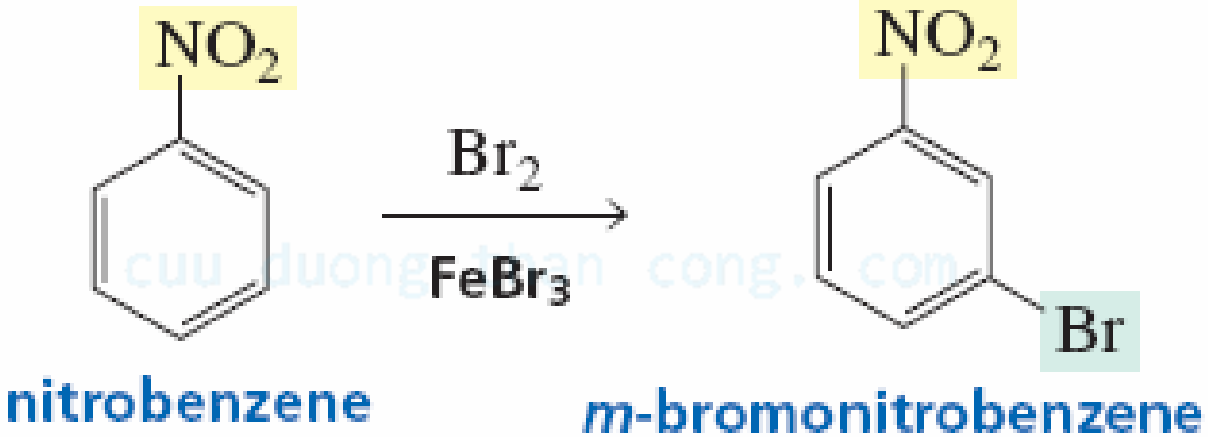
+

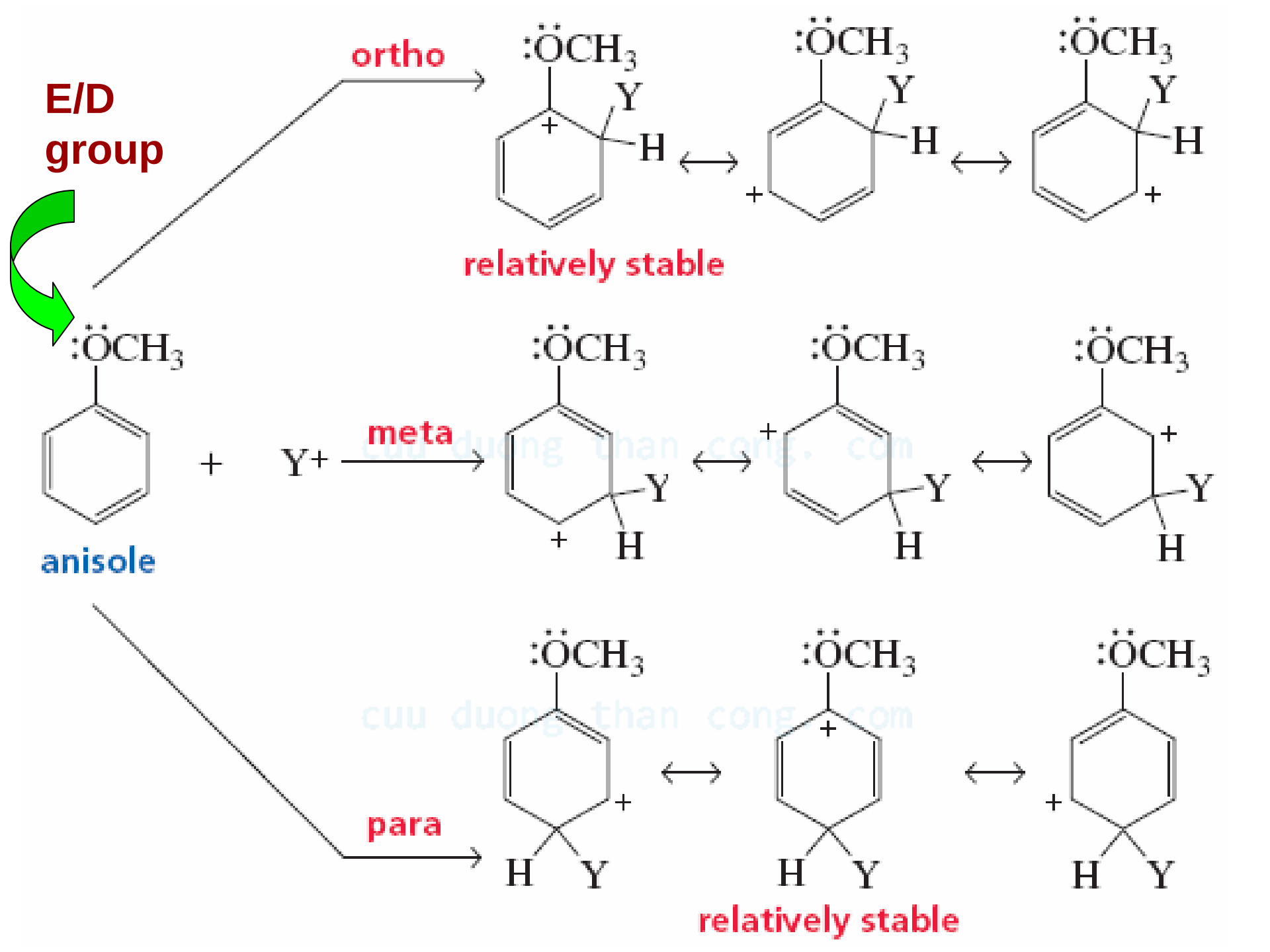


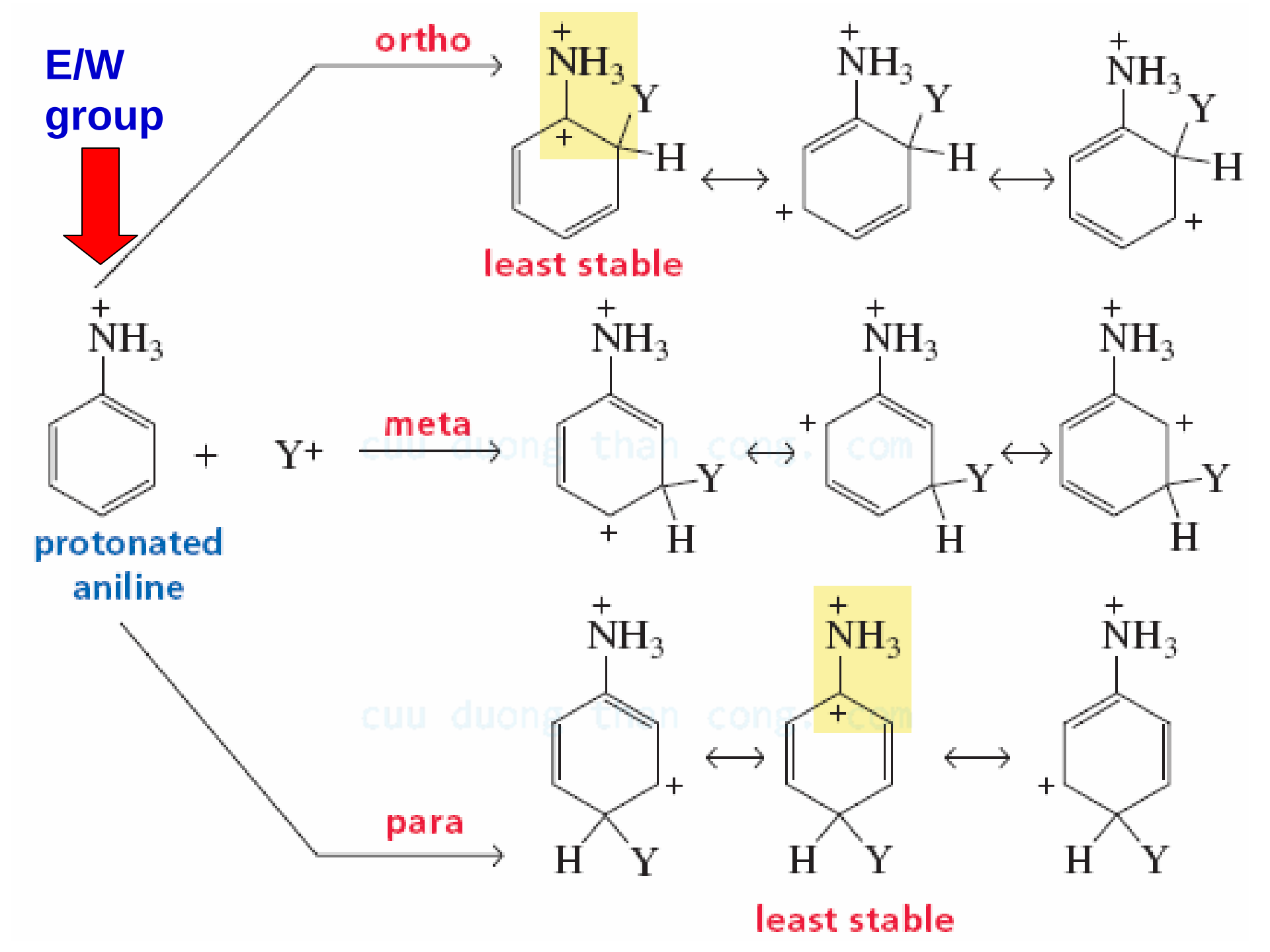
p-bromochlorobenzene

E/W group

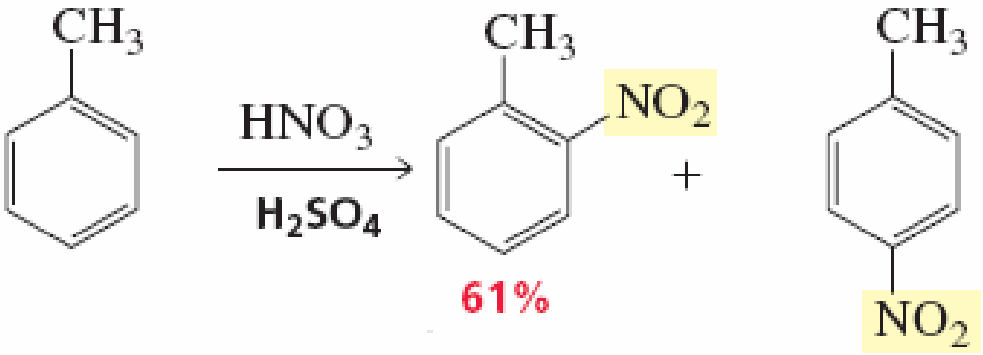




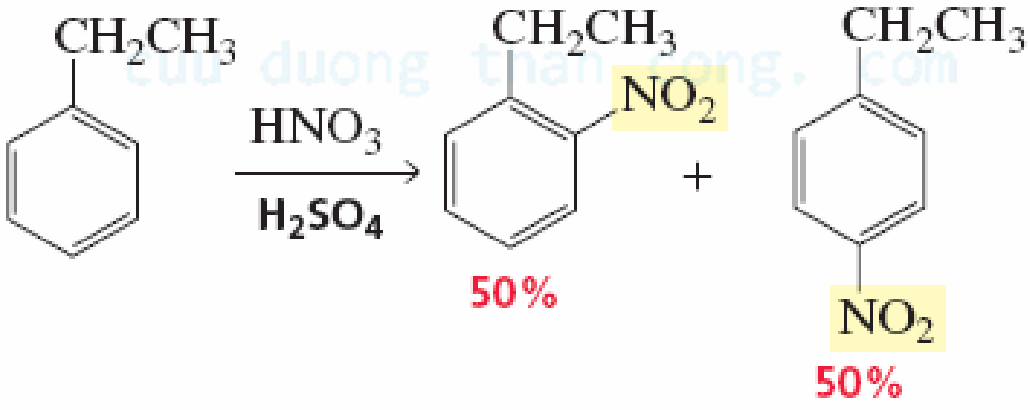

E/D group
ortho
meta
para
anisole
relatively stable
relatively stable

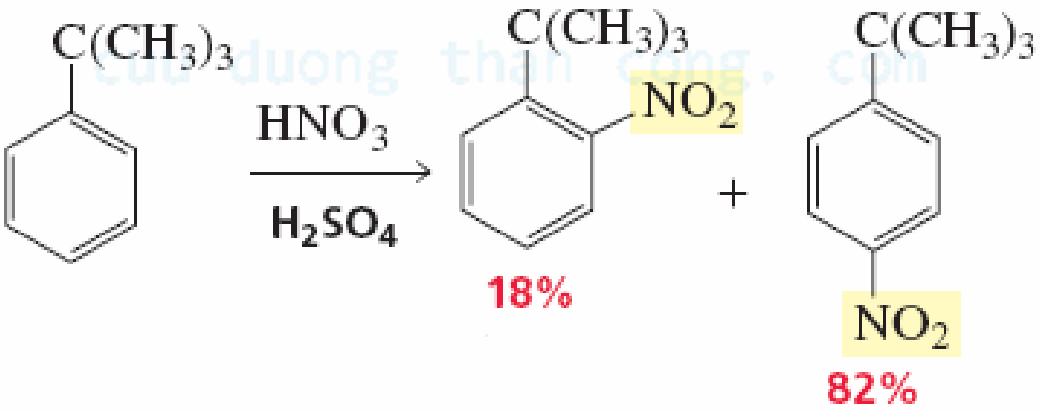

E/W group
ortho
meta
para
protonated aniline
Y+
least stable
least stable

THE *ORTHO-PARA* RATIO



Increase in the size of substituents

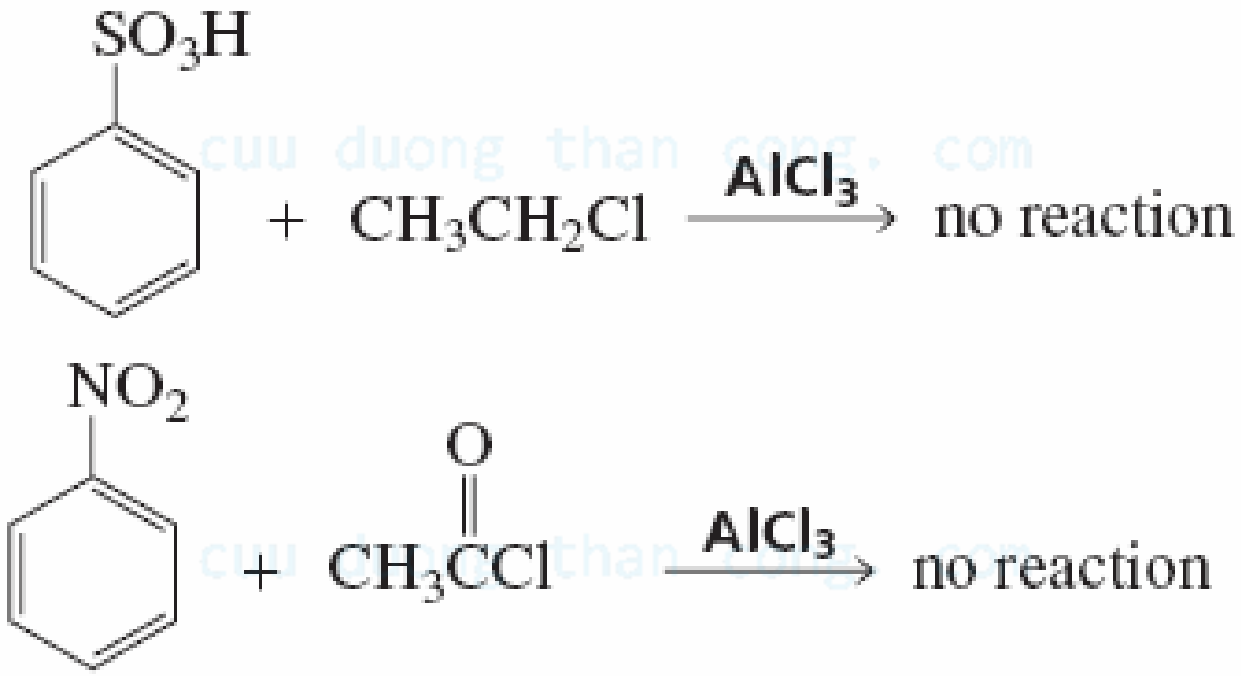




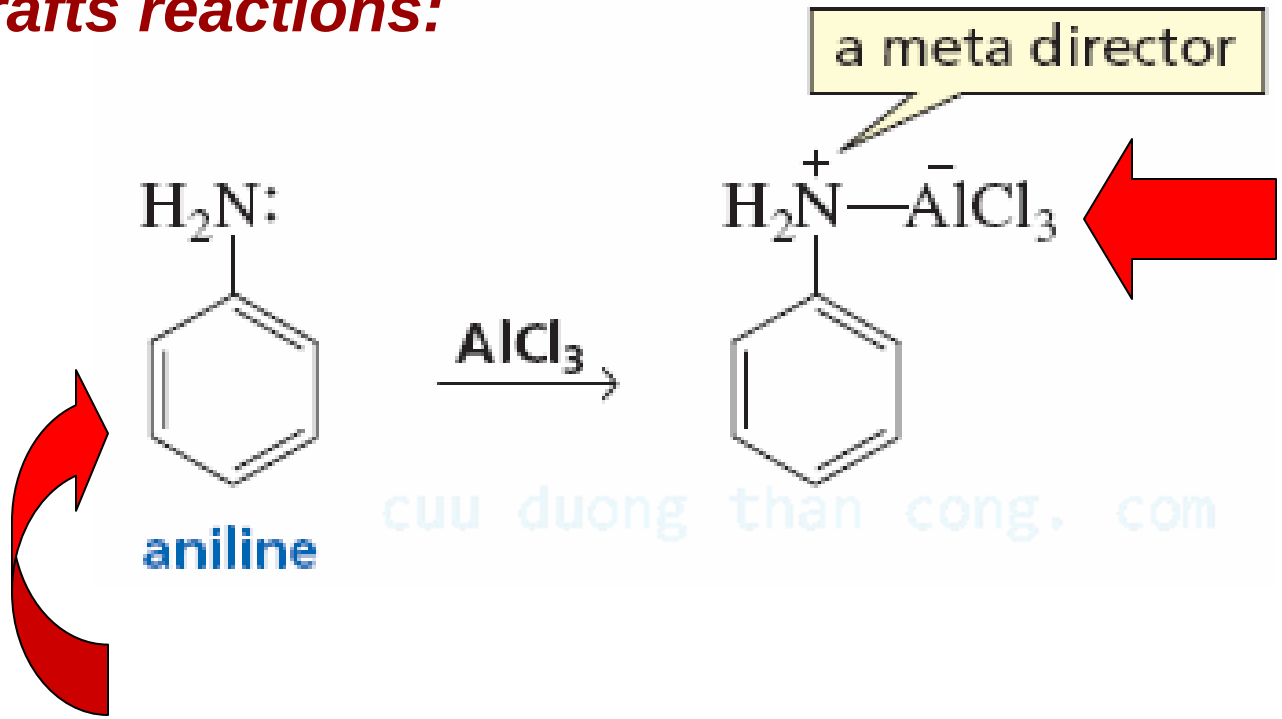
Decrease in the o/p ratio

ADDITIONAL CONSIDERATIONS

More deactivating than halogen, the ring is too unreactive for (only) Friedel-Crafts alkylations & acylations



Aniline & N-substituted anilines <u>do NOT</u> undergo Friedel-Crafts reactions:



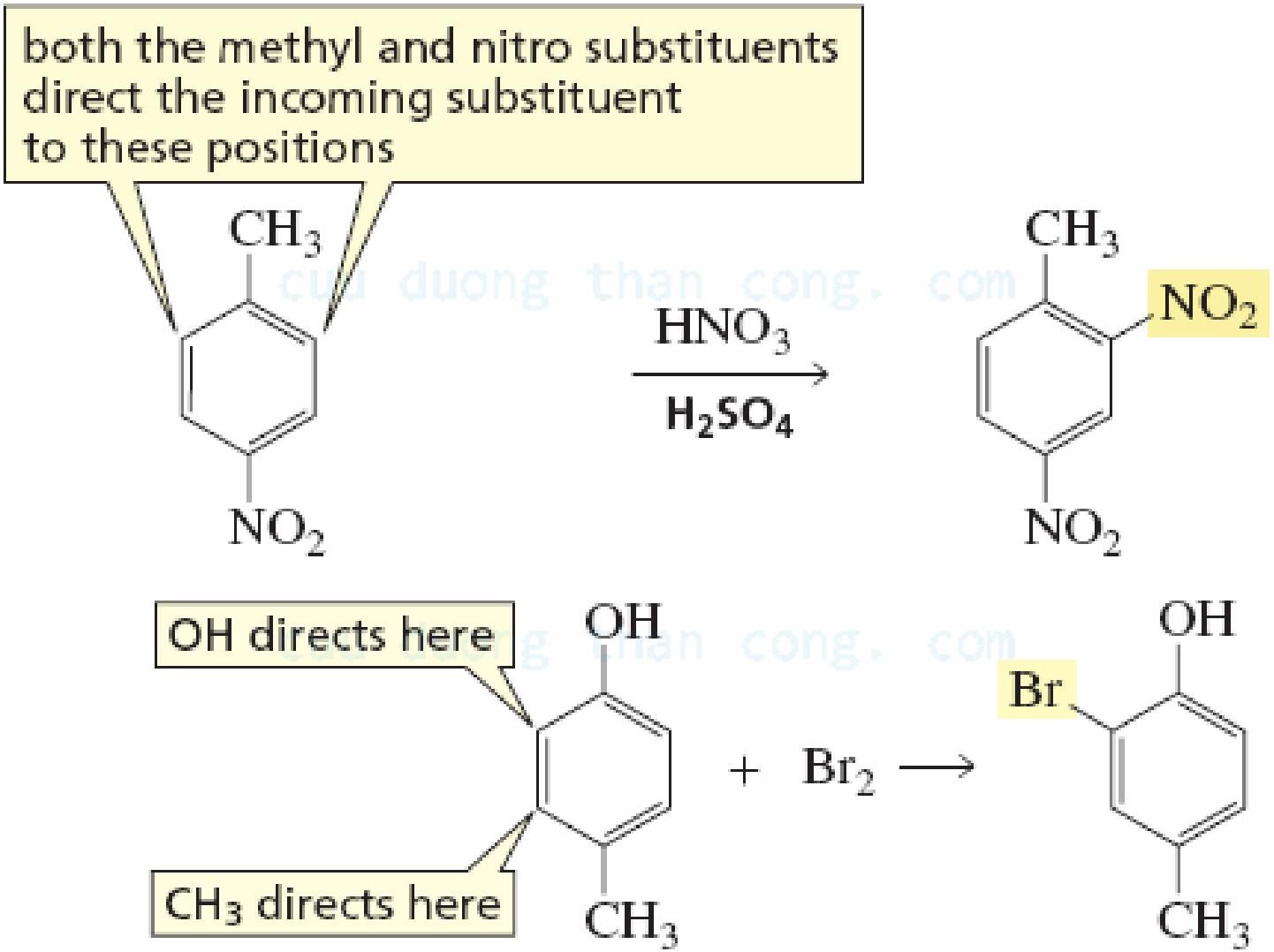
More deactivating than halogen

Also can NOT undergo nitration – primary amines are easily oxidized

Phenol & anisole do undergo Friedel-Crafts reactions, orienting ortho & para – oxygen does NOT complex with the Lewis acid

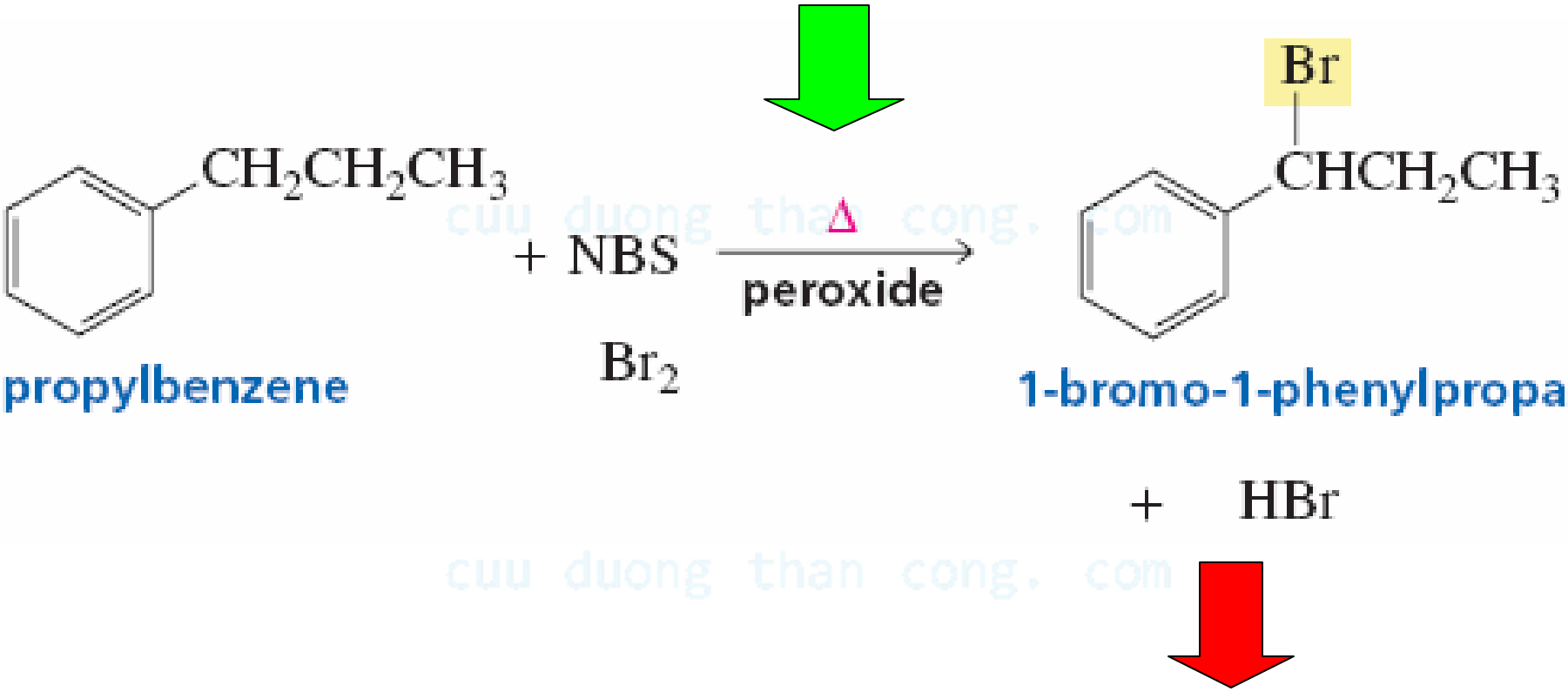
SYNTHESIS OF TRISUBSTITUTED BENZENES

More activating substituent controls the regioselectivity



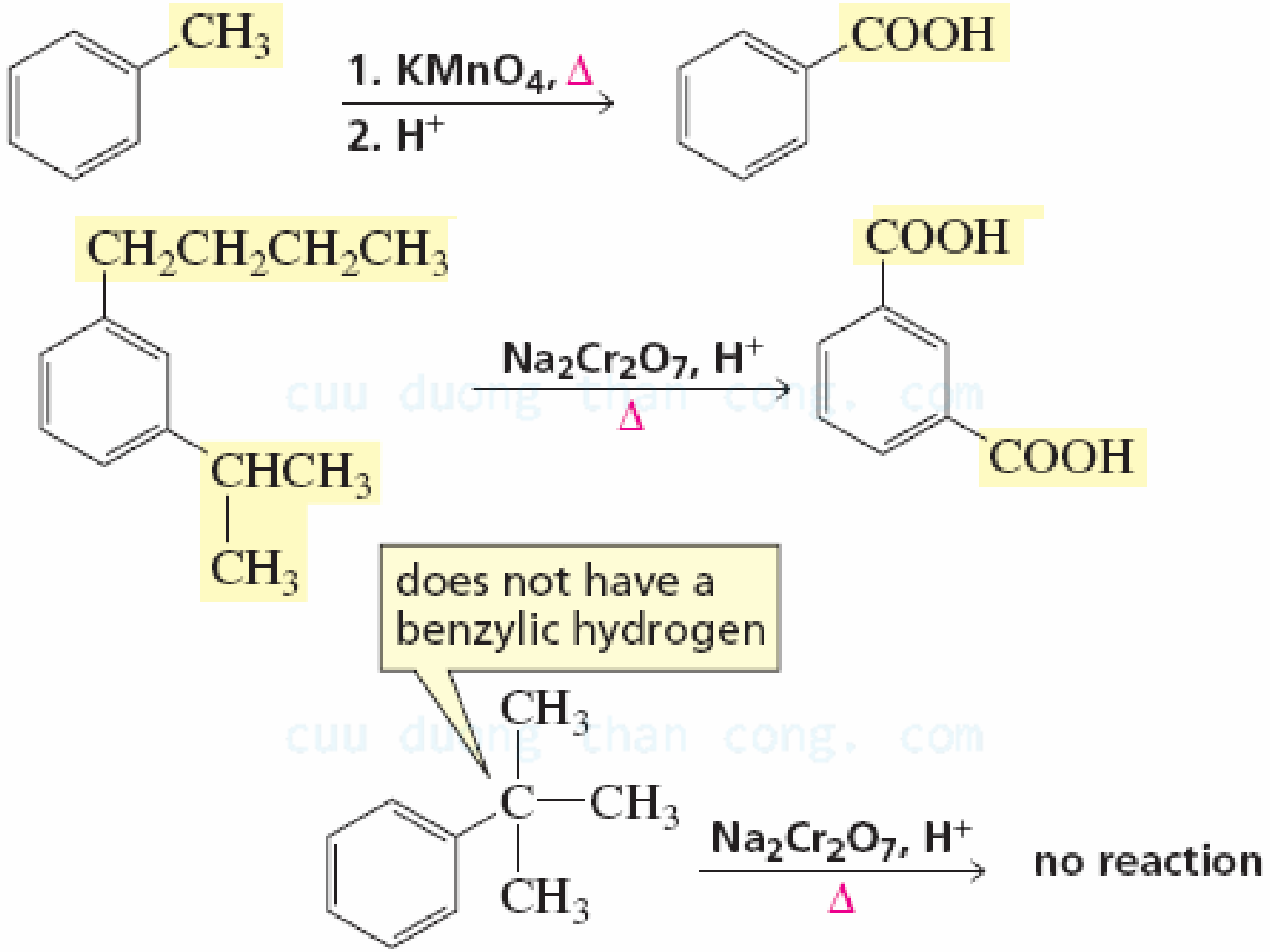
HALOGENATIONS OF ALKYL SUBSTITUENTS

NOT Lewis acid

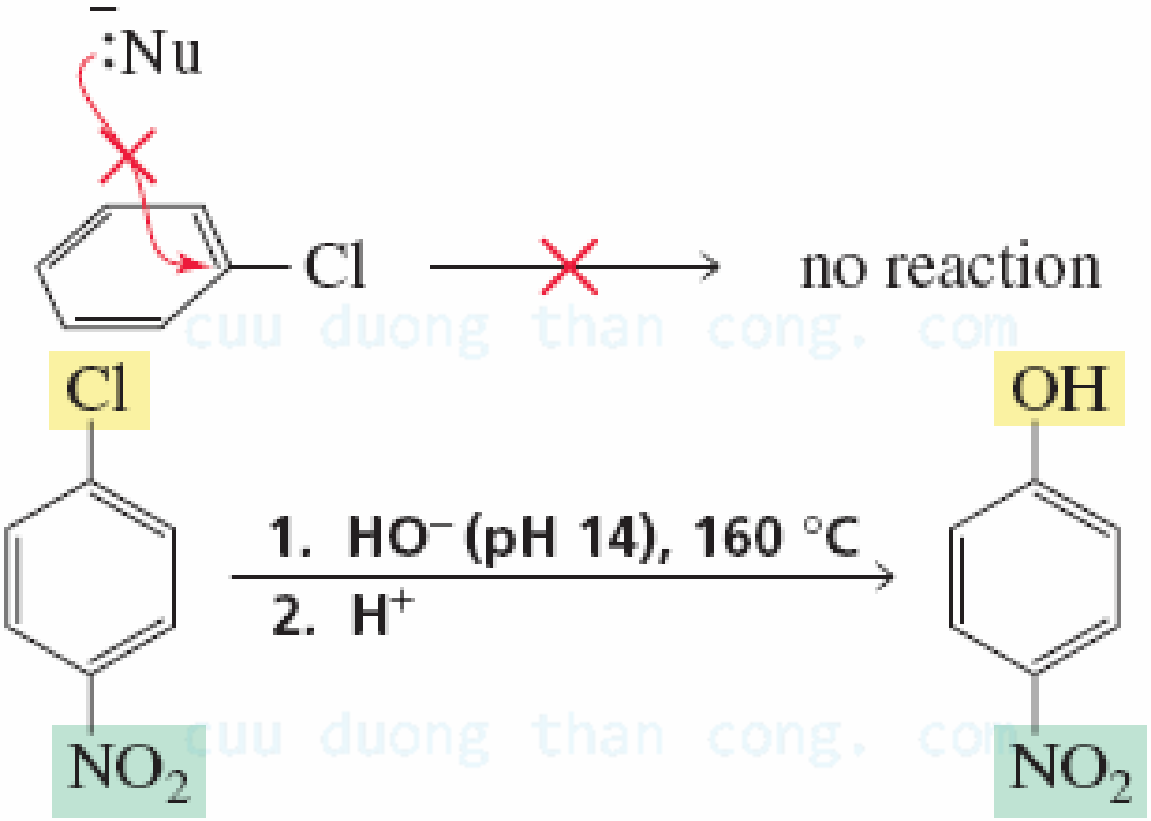


Can undergo E1 & E2, S_N1 & S_N2 reactions as usual

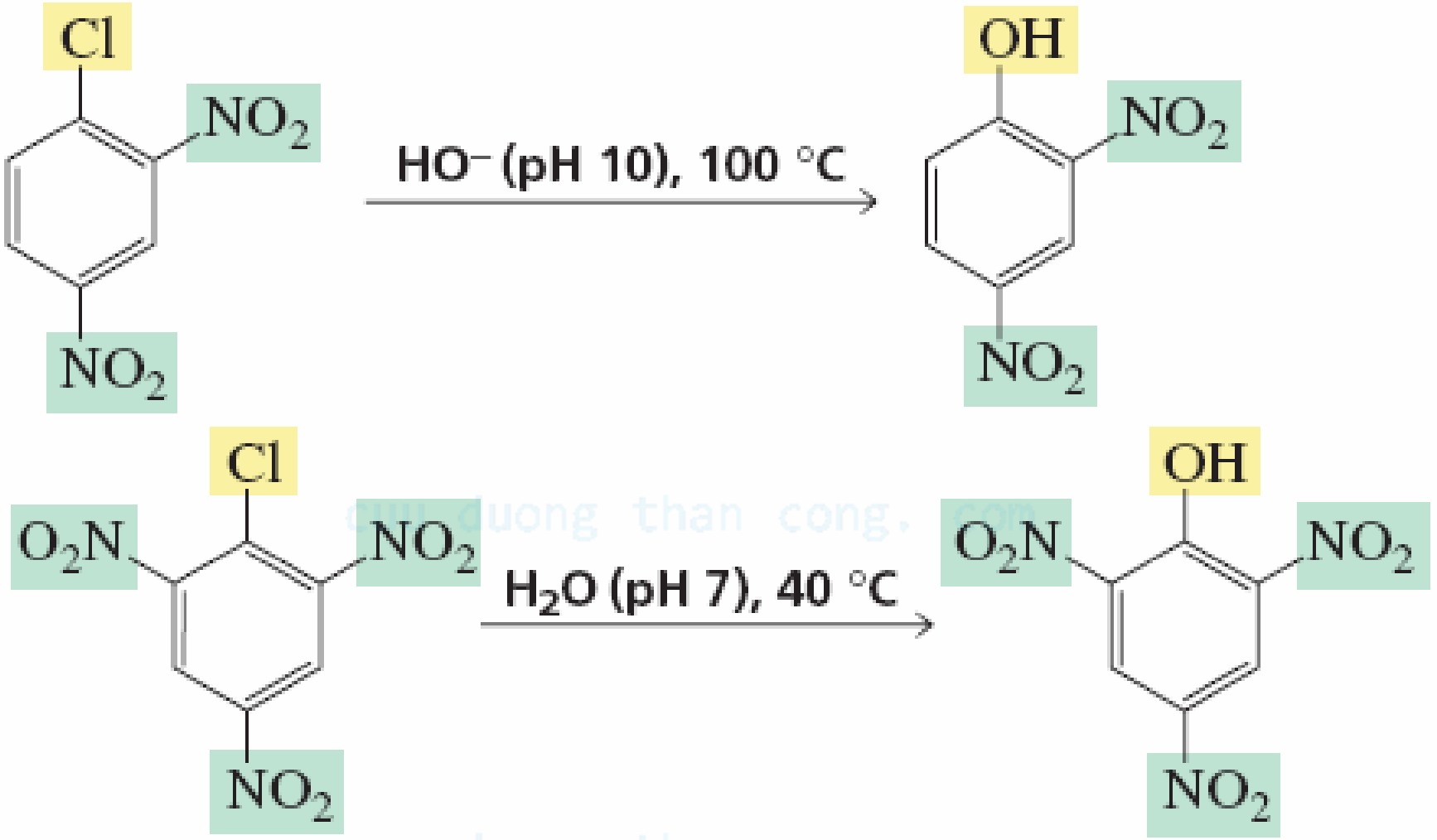
OXIDATIONS OF ALKYL SUBSTITUENTS



NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS



E/W groups must be positioned <u>ortho / para</u> to the halogen



The greater the number of E/W substituents, the easier it is to carry out the reaction