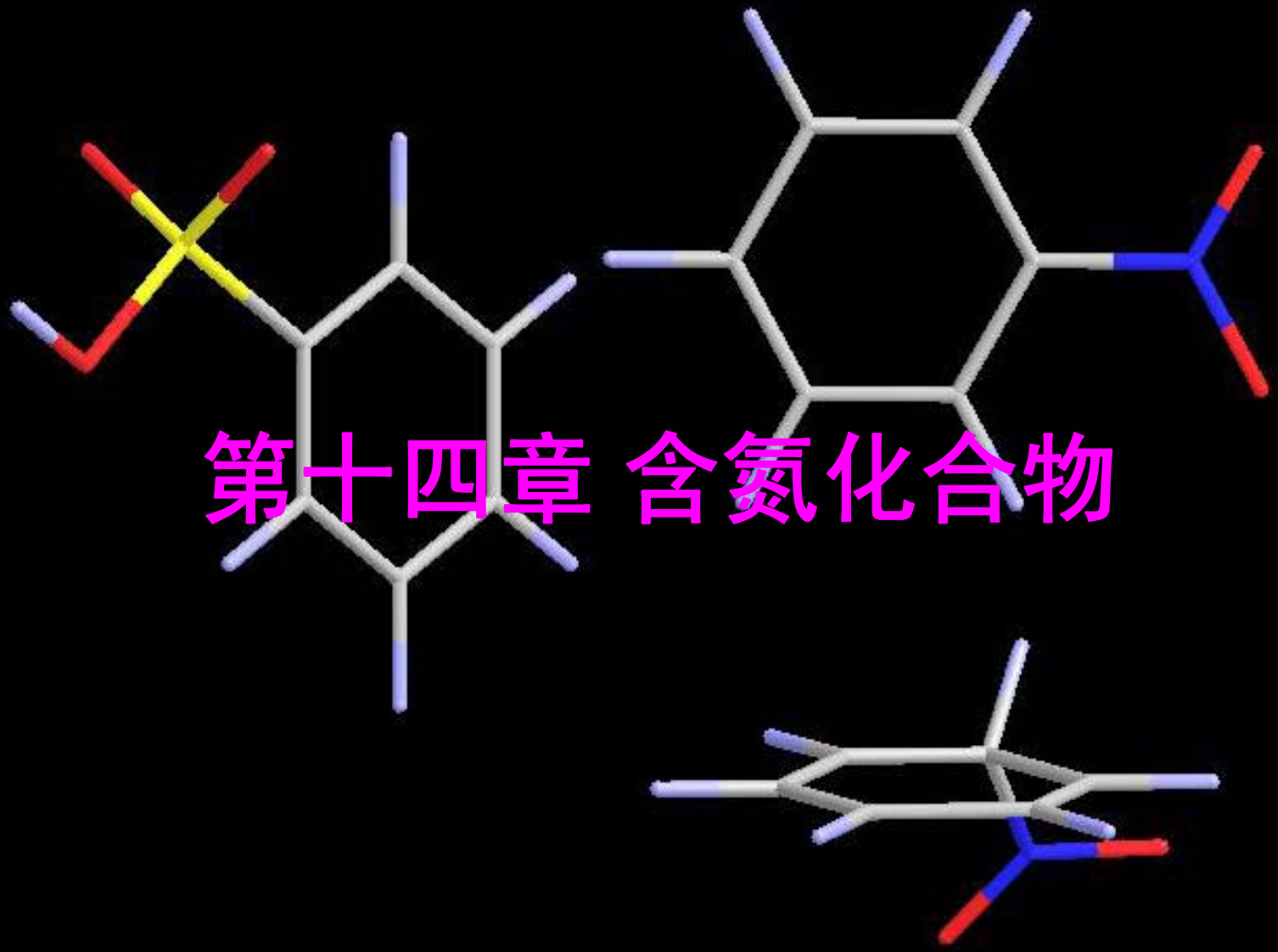
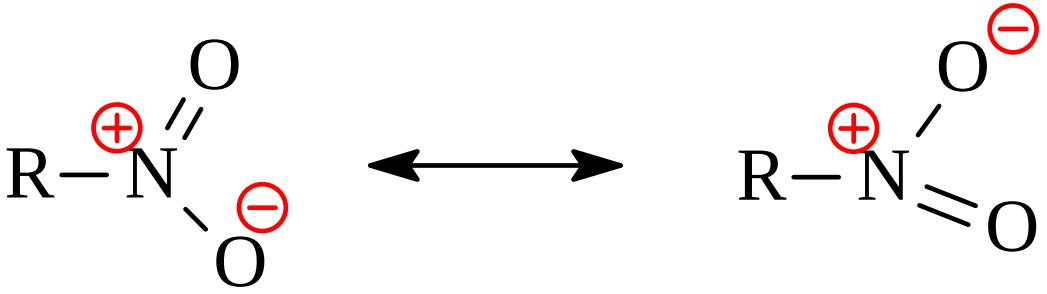
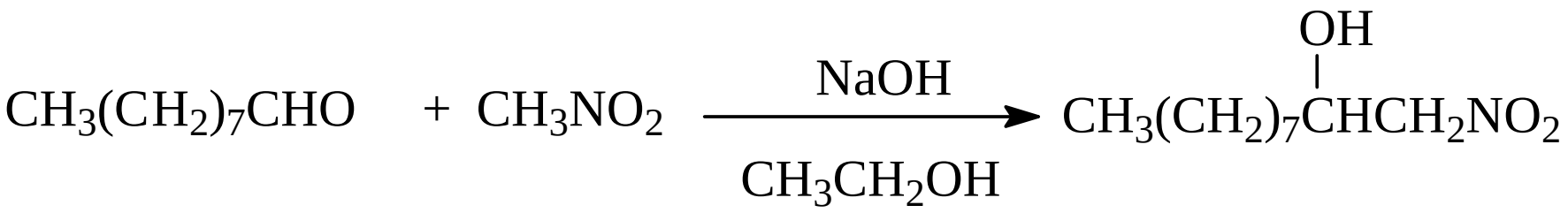


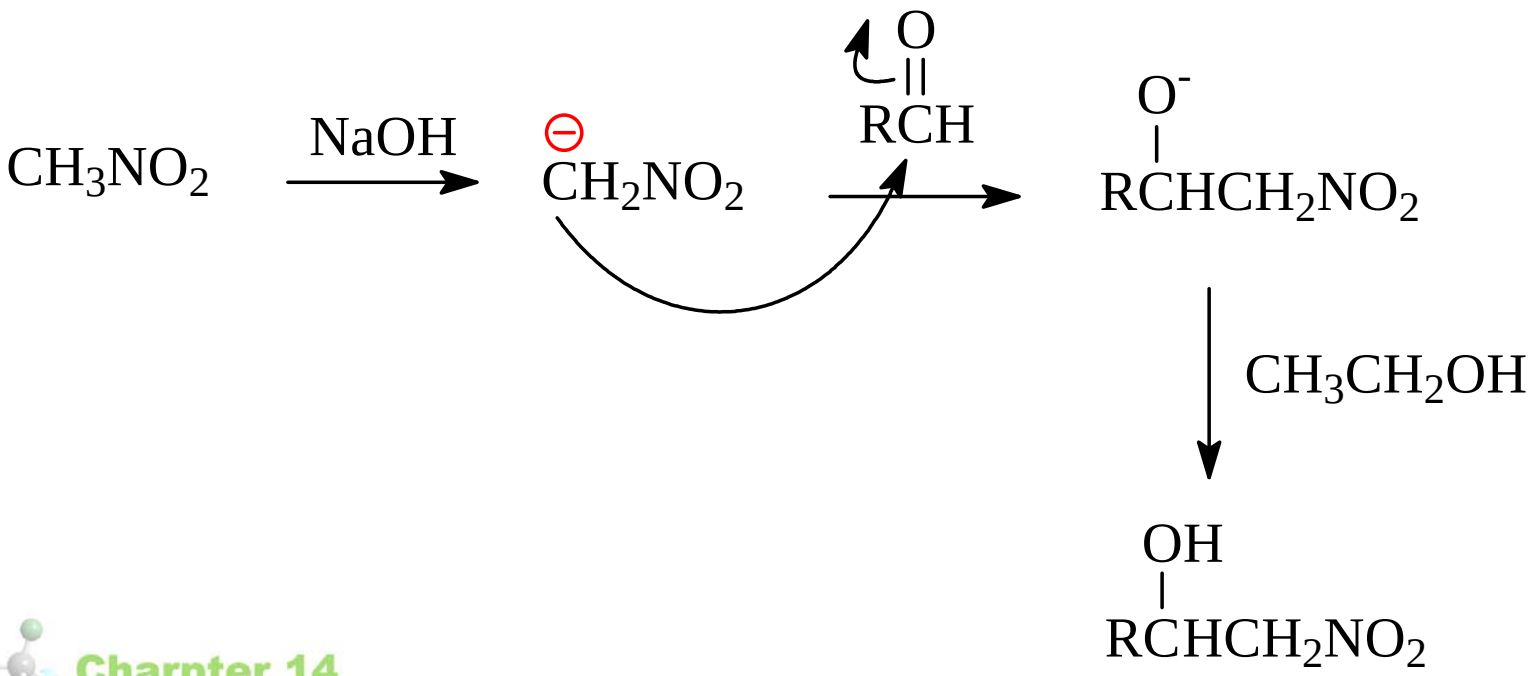
第十四章 含氮化合物

14.1 硝基化合物

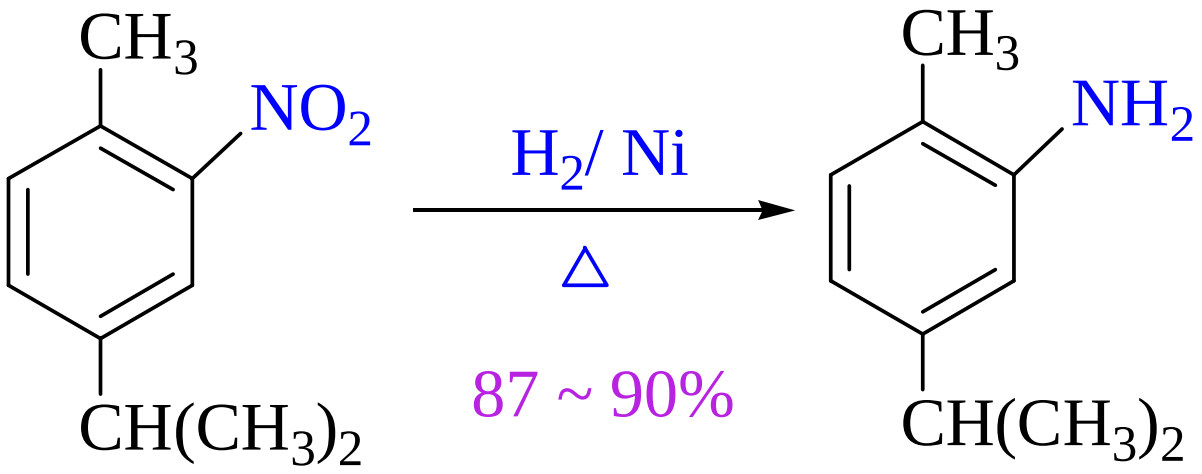


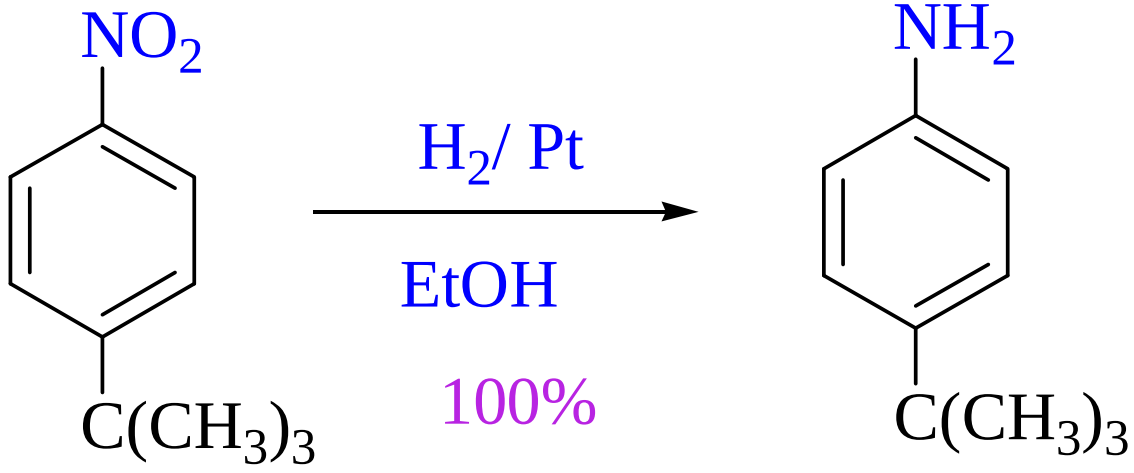
14.1.1 α-H的反应

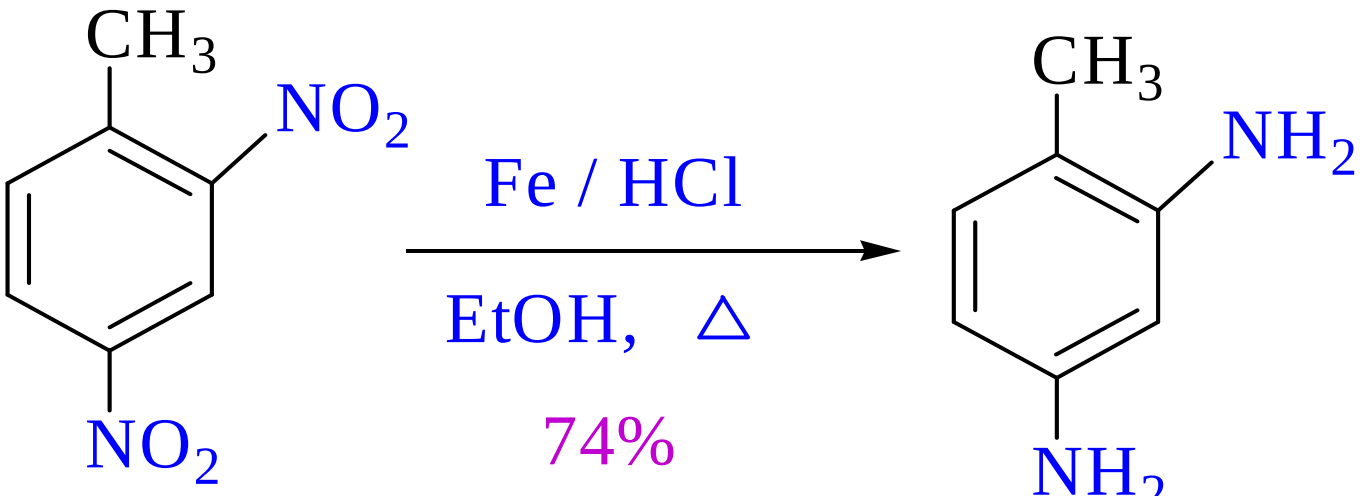

CH3(CH2)7CHO + CH3NO2
NaOH
CH3CH2OH
OH
CH3(CH2)7CHCH2NO2


CH3NO2
NaOH
CH2NO2
O
RCH
O-
RCHCH2NO2
CH3CH2OH
OH
RCHCH2NO2

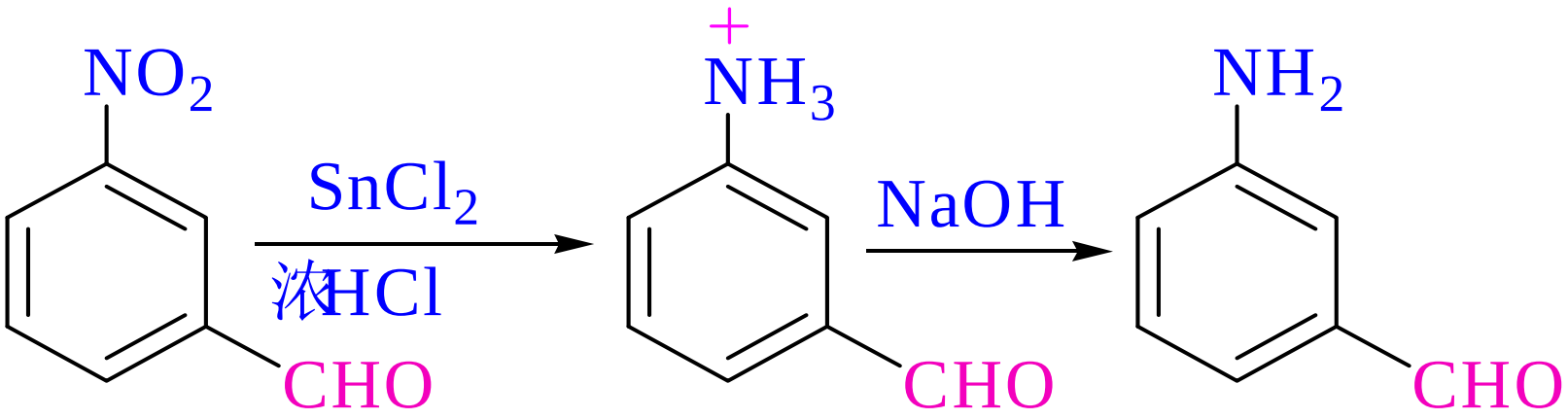
14.1.2 硝基化合物的还原反应



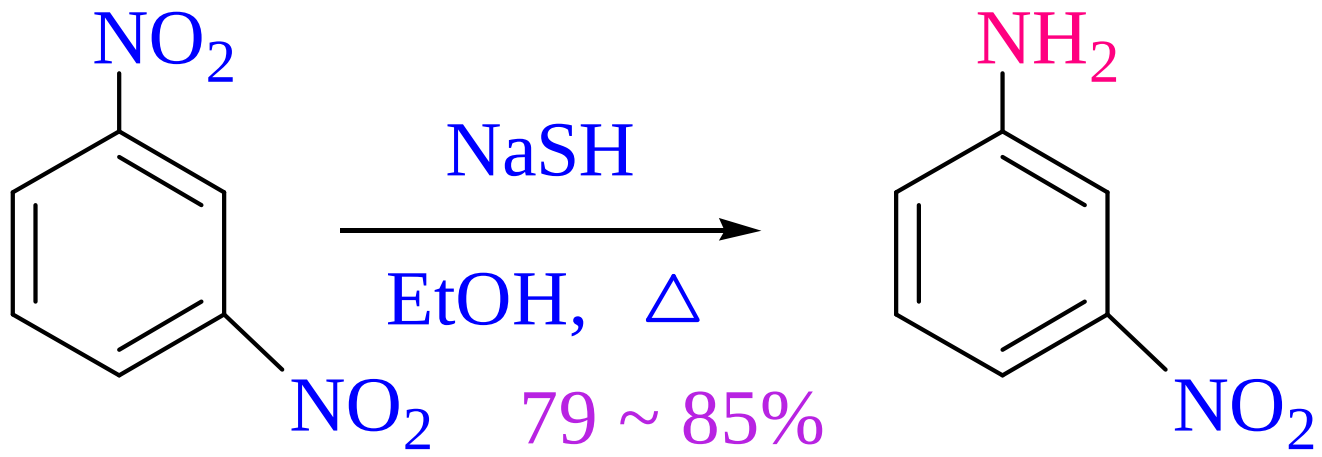


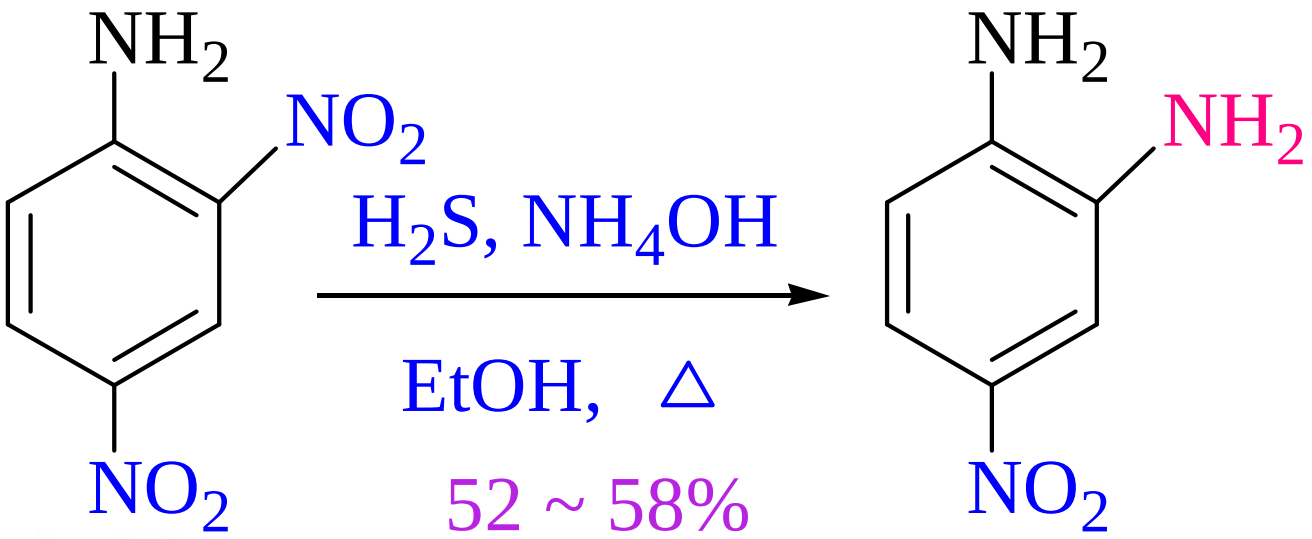


常用:
Fe / HCl
Zn / HCl

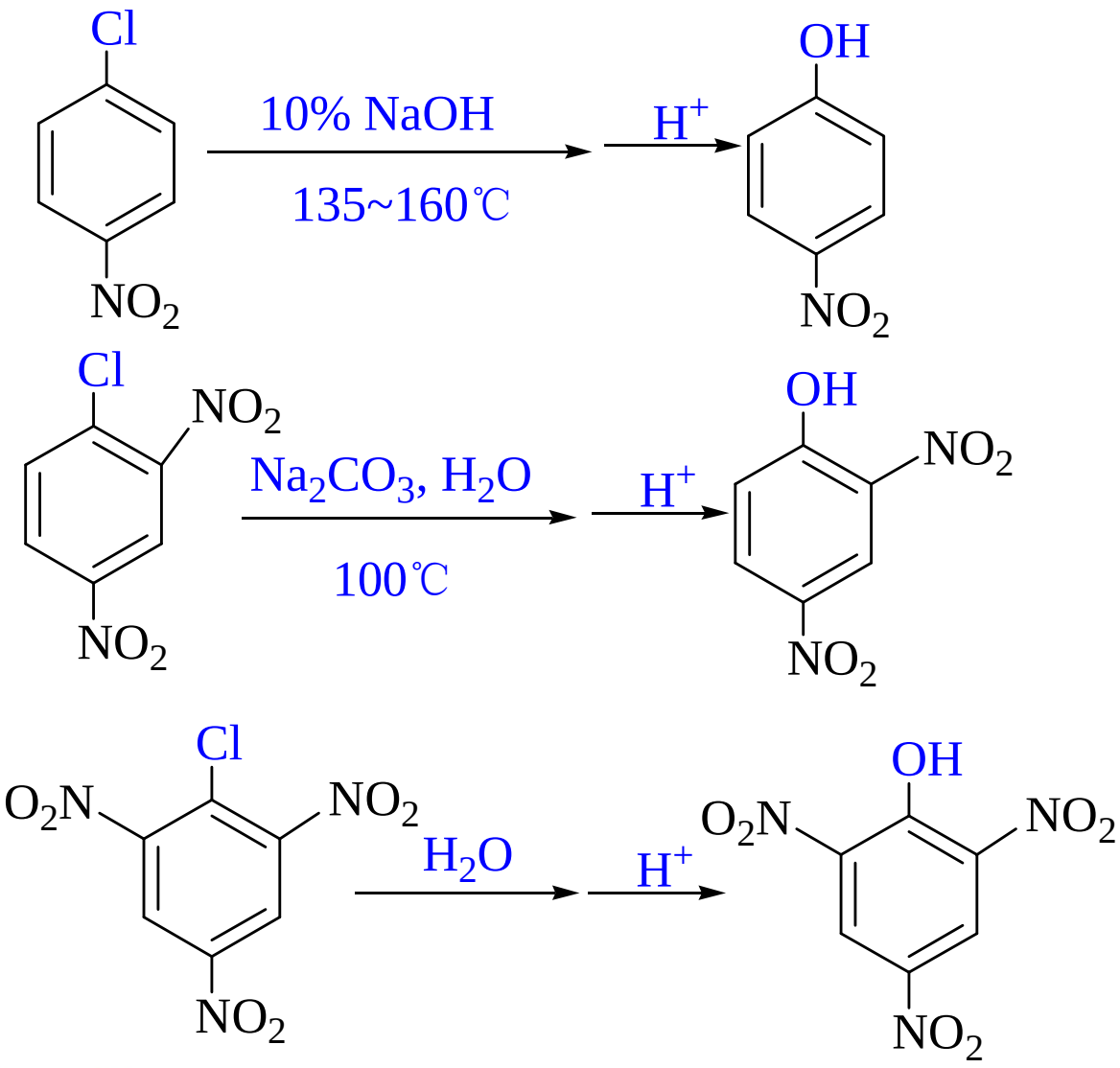


Na_2S, NaSH, $(NH_4)_2S$, NH_4SH

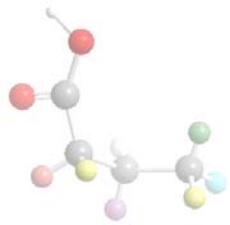




14.1.3 硝基对苯环上邻、对位取代基的影响



14.2 胺的结构命名和物理性质

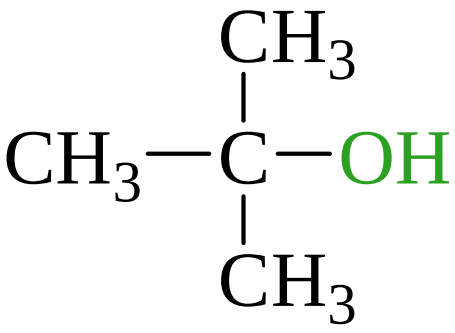


14.2.1 胺的结构

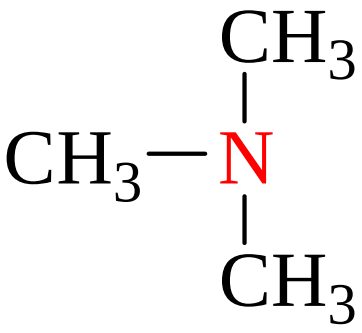
H_2O　　ROH　　R_2O

NH_3　　RNH_2　R_2NH　R_3N

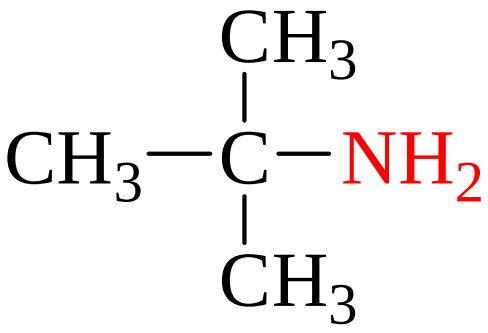
胺



叔醇



叔胺

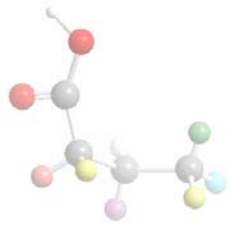


伯胺

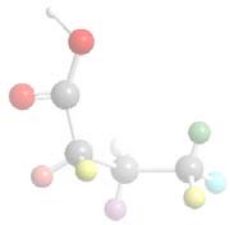
CH_3NH_2 $(CH_3)_2NH$ $(CH_3)_3N$

伯胺(一级胺) 仲胺(二级胺) 叔胺(三级胺)

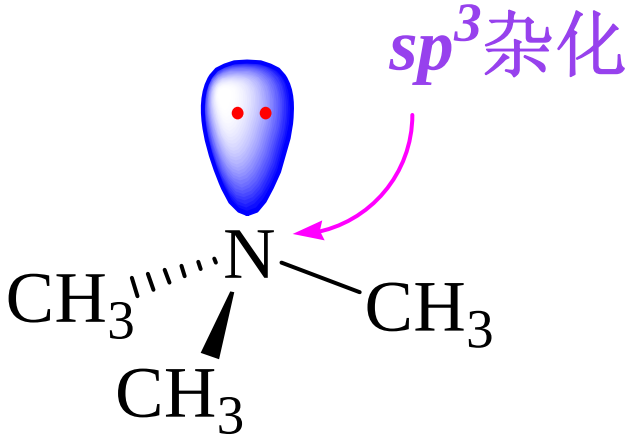
14.2.2 胺的命名和物理性质（自学）



14.3 胺的化学性质



1. 胺的碱性



胺	pK_b
甲胺	3.38
二甲胺	3.27
三甲胺	4.21
NH_3	4.76
苯胺	9.37
对甲苯胺	8.92
对氯苯胺	9.85
对硝基苯胺	13.0

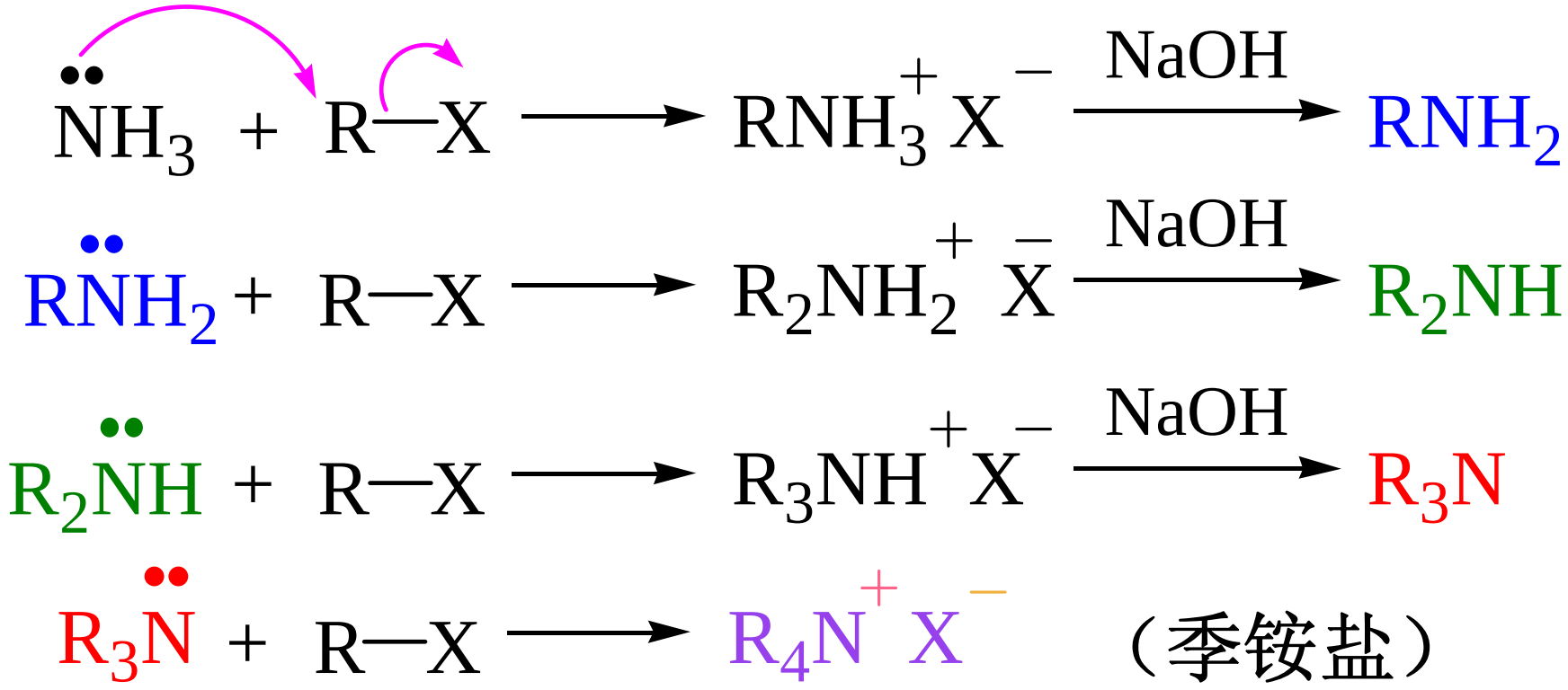
$$CH_3(CH_2)_9NH_2 + HCl \longrightarrow CH_3(CH_2)_9\overset{+}{N}H_3\ Cl^-$$

无色固体　可溶于水

↓ NaOH

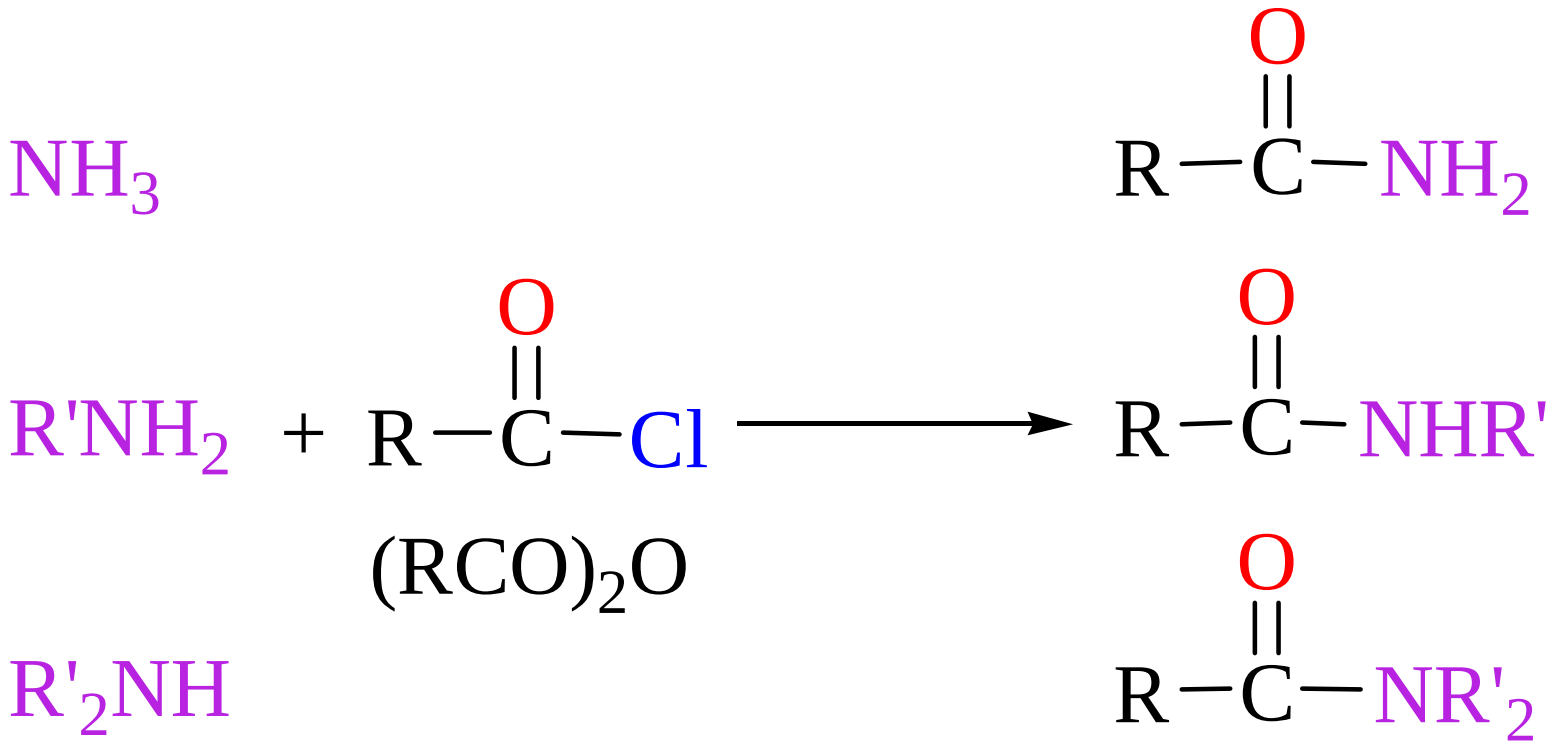
胺

2. 胺的烃基化

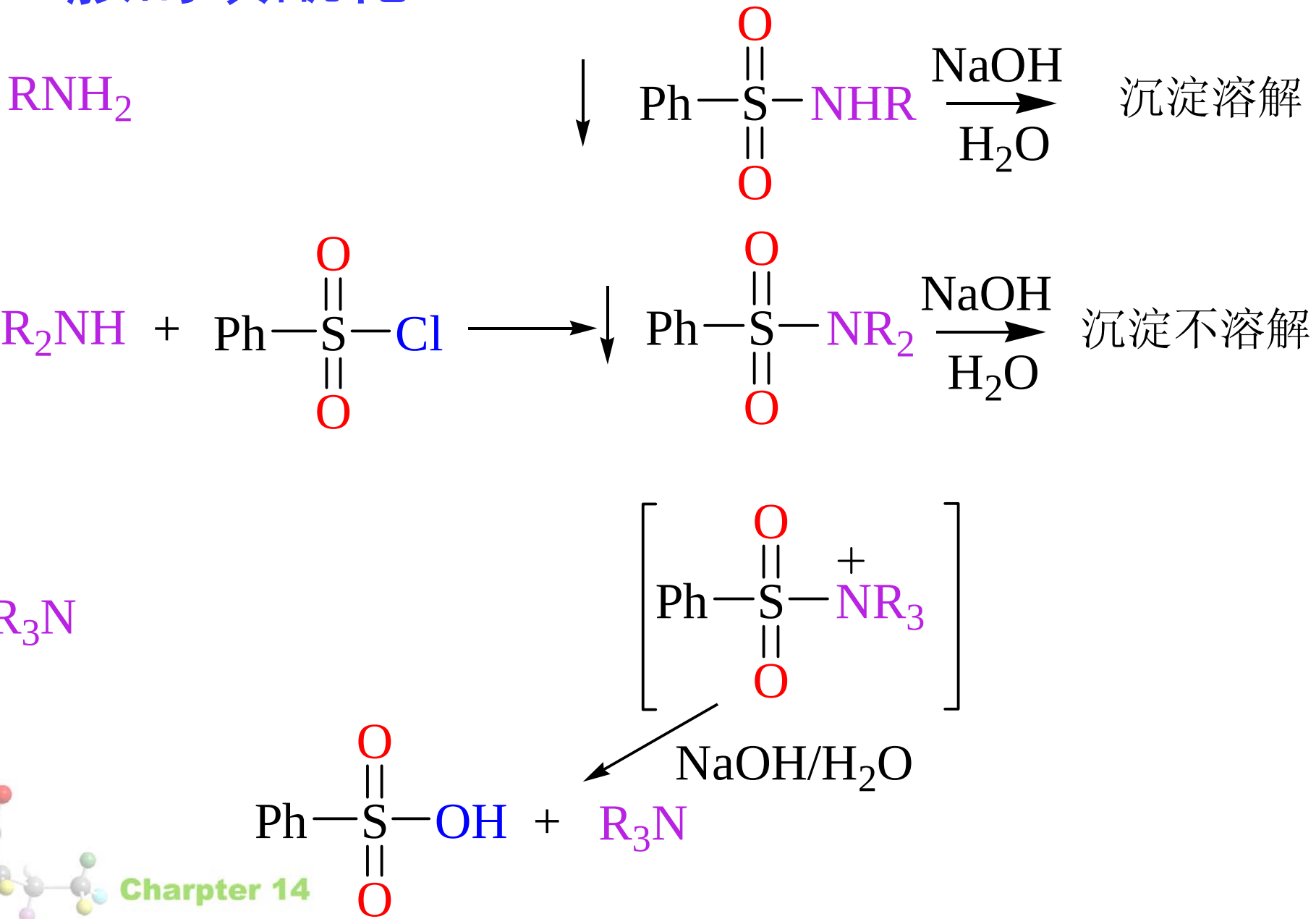


RI > RBr > RCl　　1°RX > 2°RX

3. 胺的酰基化



4. 胺的磺酰化


RNH2
Ph—S(=O)2—NHR
NaOH
H2O
沉淀溶解
R2NH + Ph—S(=O)2—Cl
Ph—S(=O)2—NR2
NaOH
H2O
沉淀不溶解
R3N
[Ph—S(=O)2—+NR3]
NaOH/H2O
Ph—S(=O)2—OH + R3N

5. 与亚硝酸反应

(1) 脂肪族胺

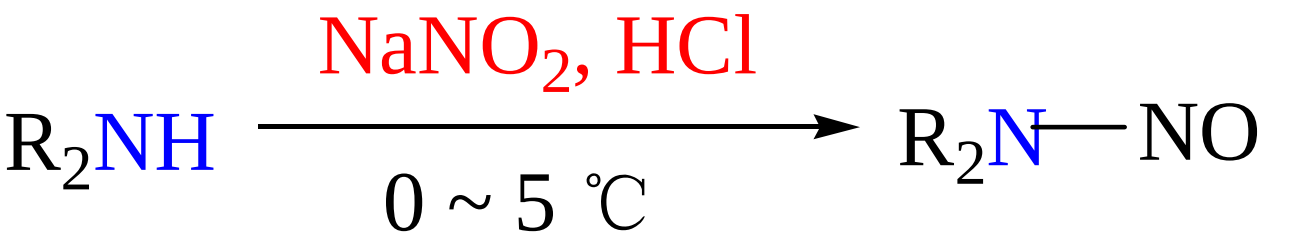
一级胺生成重氮盐

$$RNH_2 \xrightarrow[0\sim5\ ^\circ C]{NaNO_2,\ HCl} \left[R-\overset{+}{N}\equiv N\right]Cl^-$$

重氮盐

$$\xrightarrow{-N_2} R^+ \longrightarrow ROH + RX + \text{>C=C<} \quad .....$$

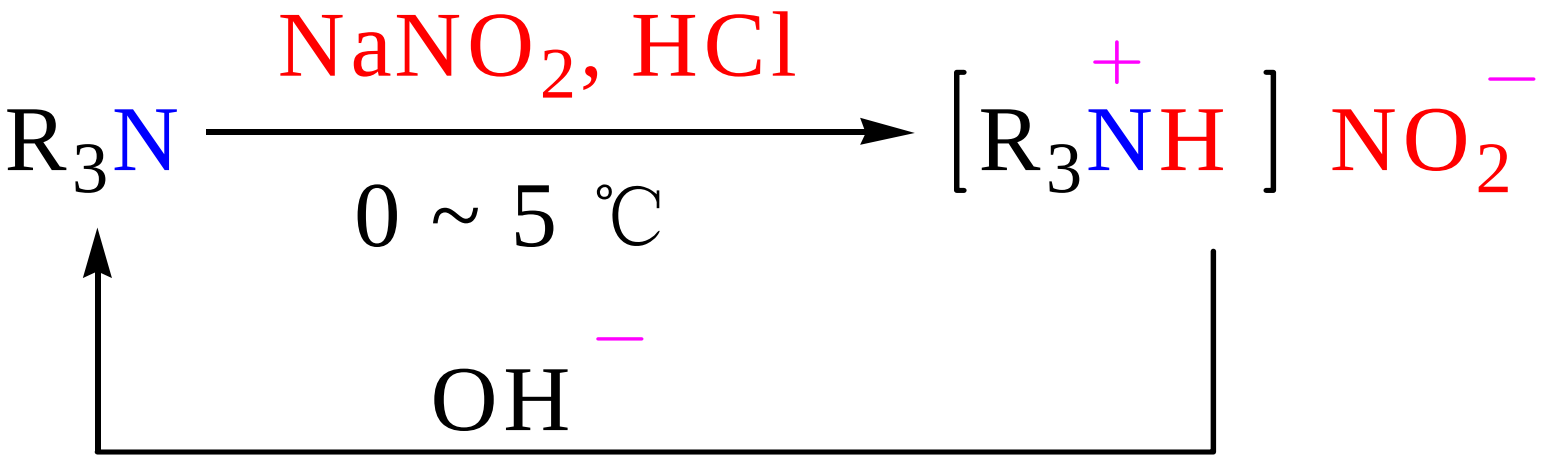
二级胺生成N-亚硝胺



N-亚硝基胺

黄色油状物

三级胺成盐



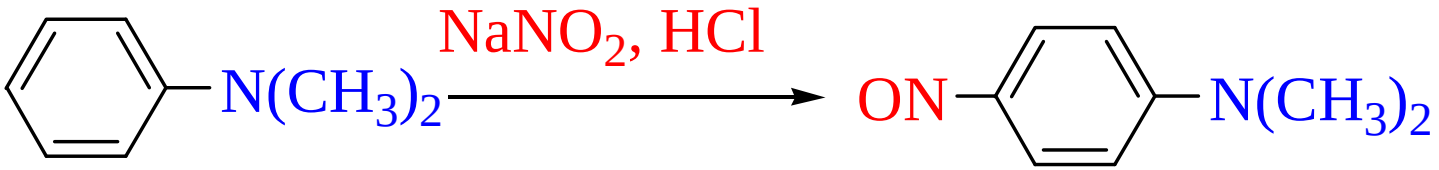
（2）芳香胺

$$ArNH_2 \xrightarrow[0\sim5\ ℃]{NaNO_2,\ HCl} [Ar\text{-}\overset{+}{N}\equiv N]\ Cl^-$$

芳香重氮盐

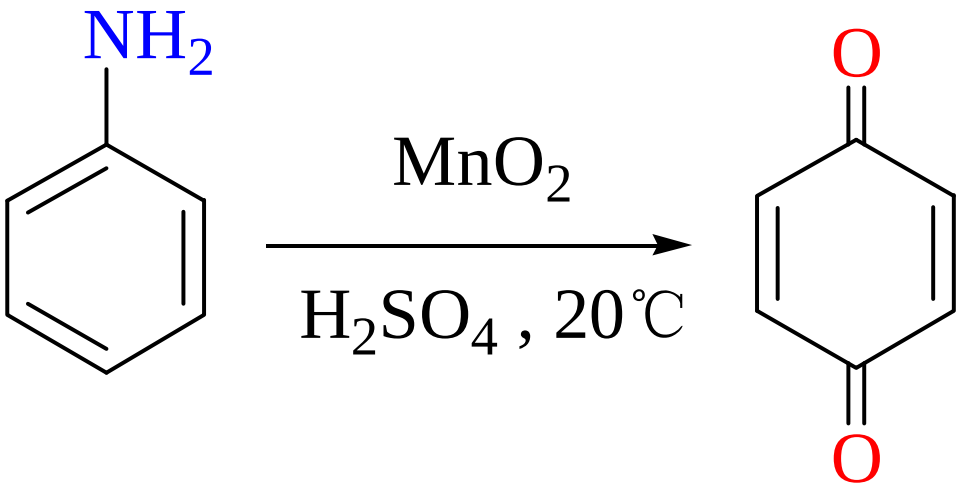
$$Ar_2NH \xrightarrow[0\sim5\ ℃]{NaNO_2,\ HCl} Ar_2N\text{—}N{=}O$$

黄色沉淀



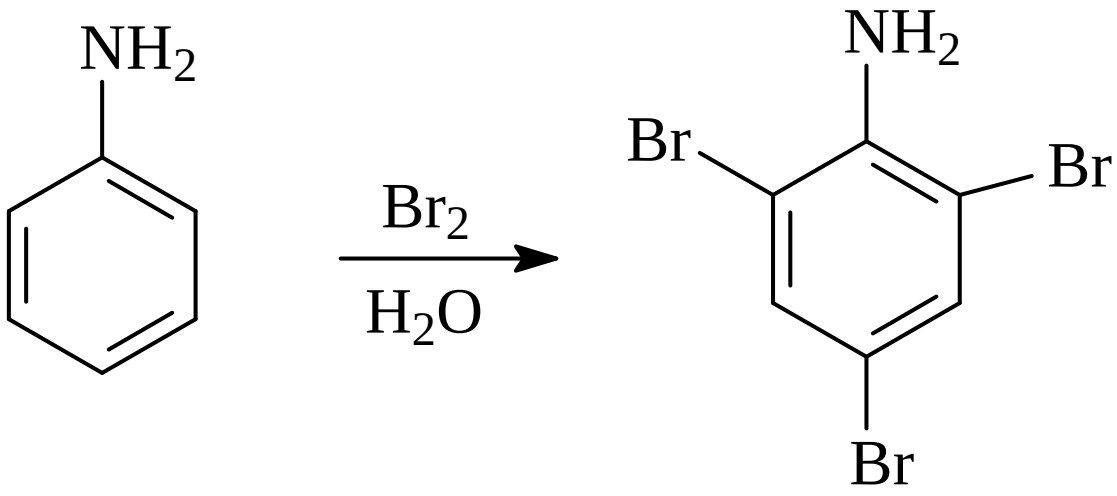
绿色晶体

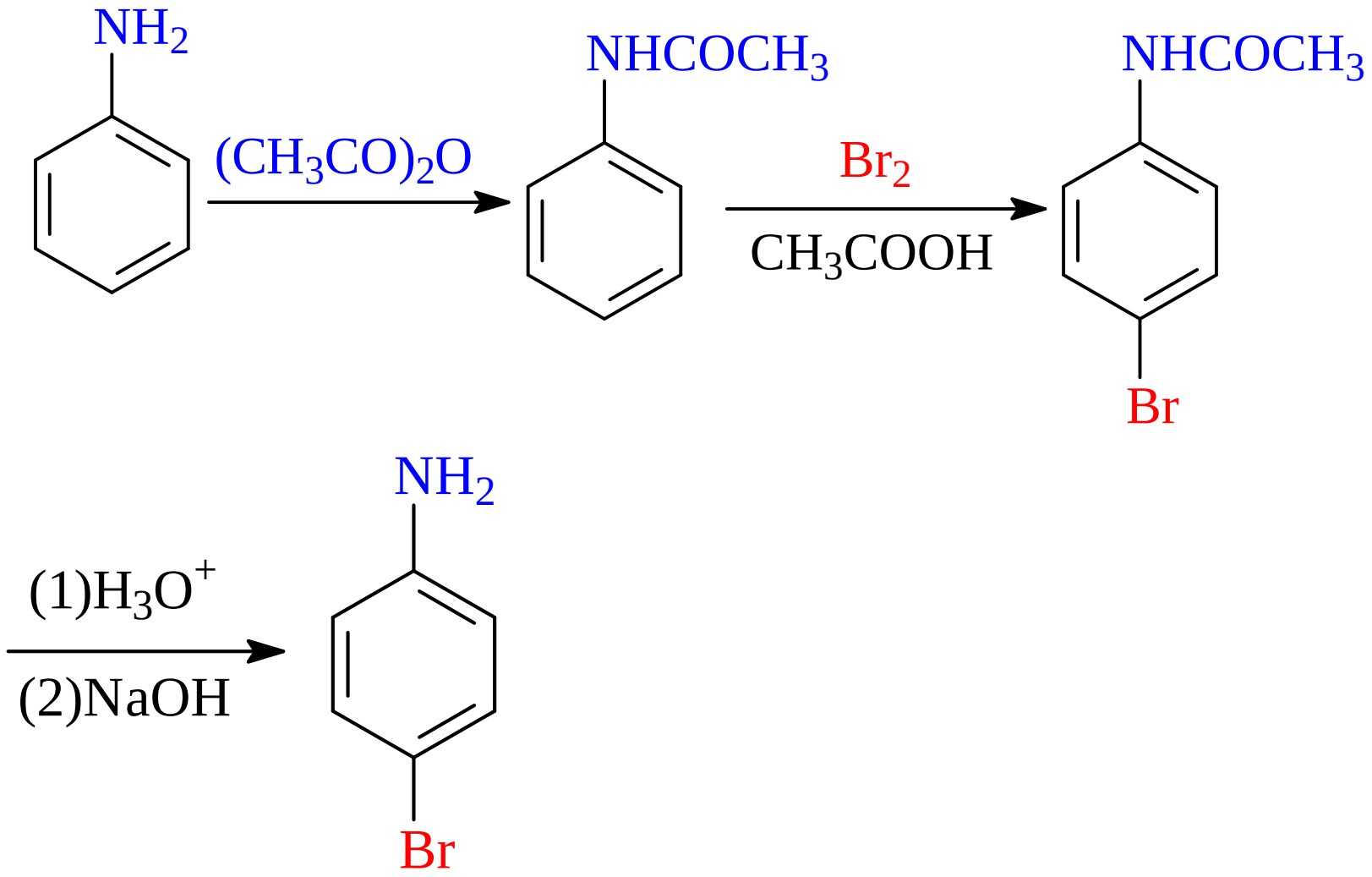
6. 氧化反应



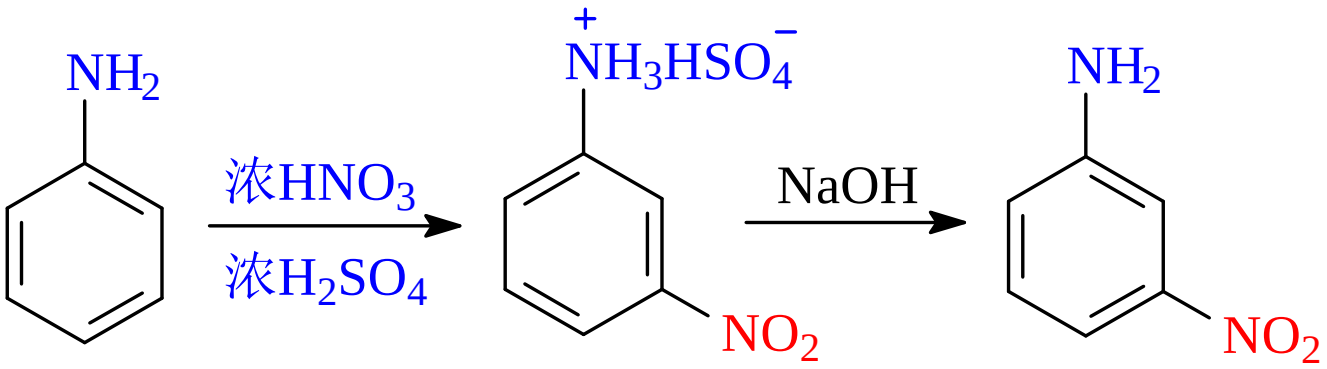
7. 芳胺的亲电取代反应

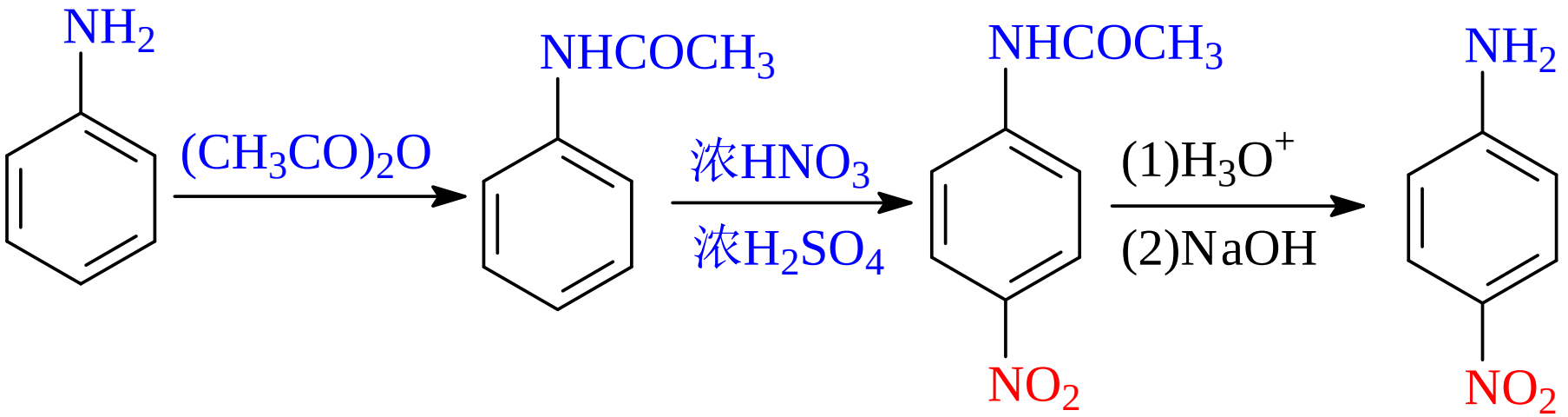
（1）卤化

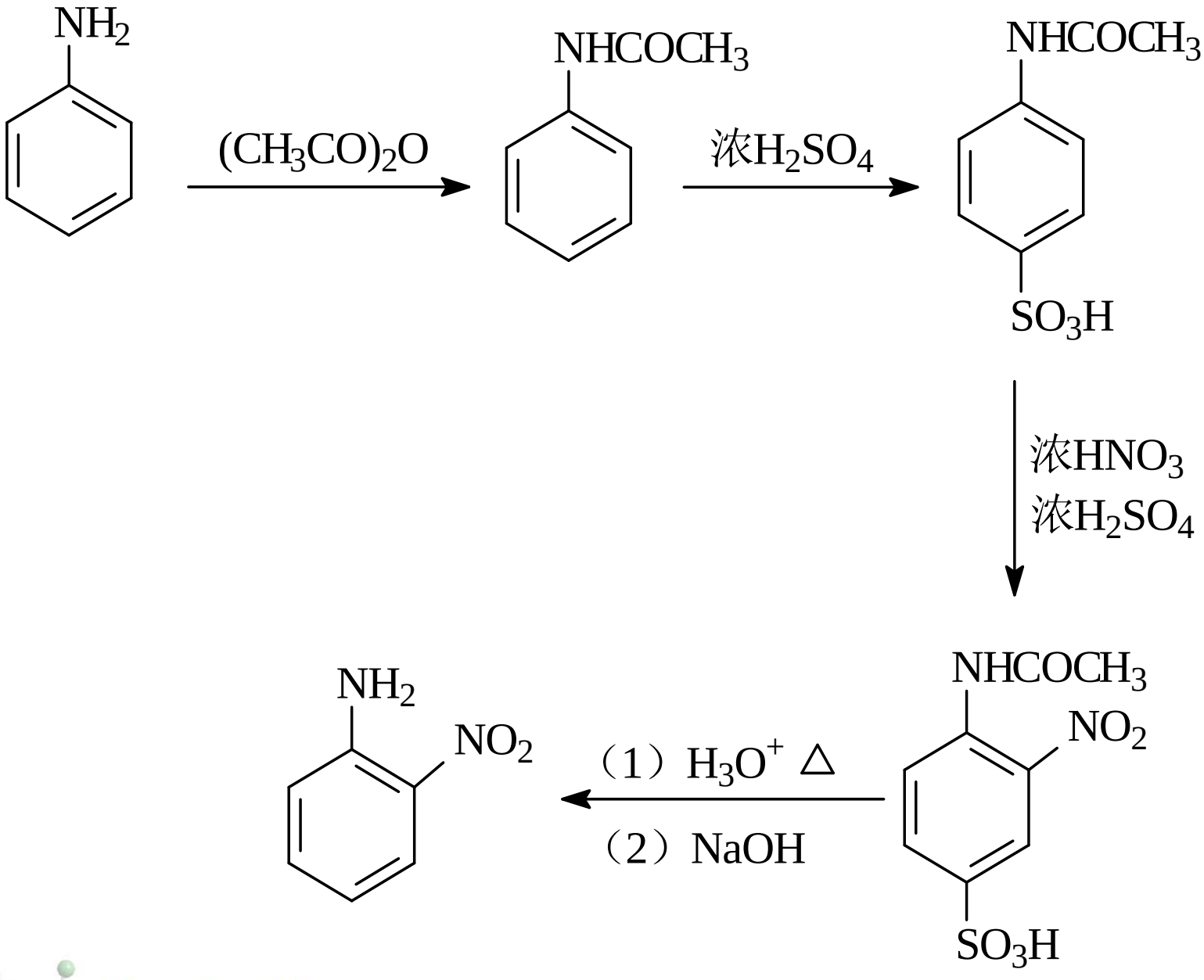



NH2
(CH3CO)2O
NHCOCH3
Br2
CH3COOH
NHCOCH3
Br
(1)H3O+
(2)NaOH
NH2
Br

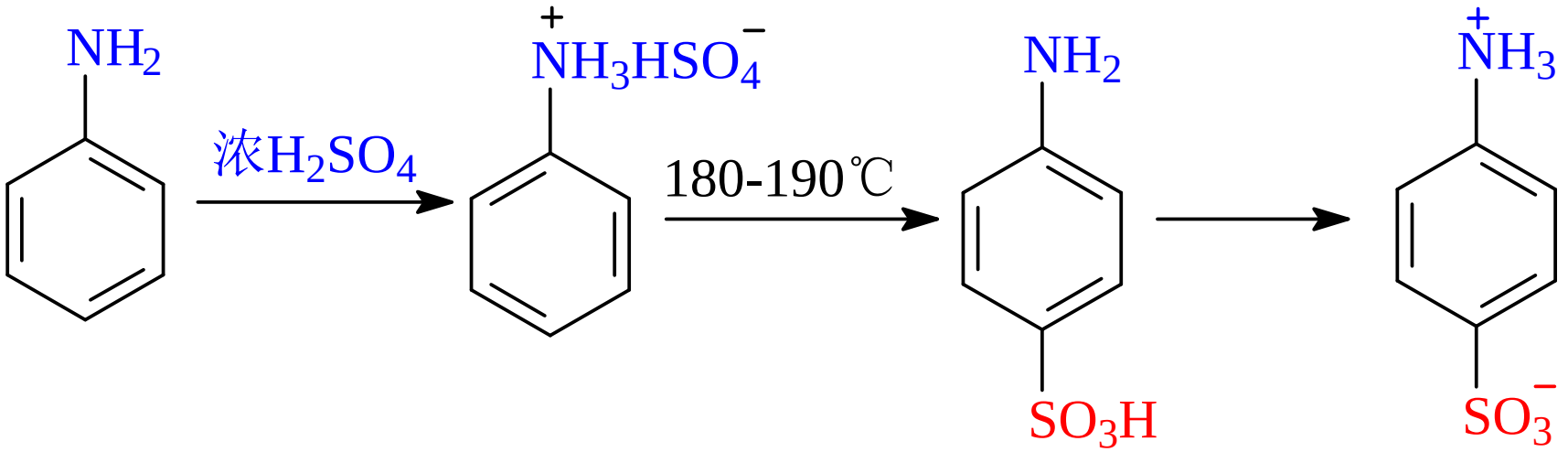
(2) 硝化反应


NH2
浓HNO3
浓H2SO4
+
NH3HSO4−
NO2
NaOH
NH2
NO2

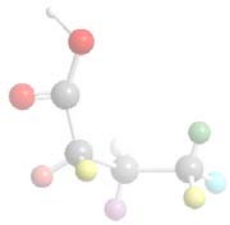

NH2
(CH3CO)2O
NHCOCH3
浓HNO3
浓H2SO4
NHCOCH3
NO2
(1)H3O+
(2)NaOH
NH2
NO2


NH2
(CH3CO)2O
NHCOCH3
浓H2SO4
NHCOCH3
SO3H
浓HNO3
浓H2SO4
NHCOCH3
NO2
SO3H
（1）H3O+ △
（2）NaOH
NH2
NO2

(3) 磺化反应



14.5 四级铵盐化合物



$$(C_2H_5)_3N + CH_3I \xrightarrow[\text{醚}]{25℃} (C_2H_5)_3N^+CH_3\ I^-$$

四级铵盐
(季铵盐)

$$(C_2H_5)_3N^+CH_3\ I^- \xrightarrow{Ag_2O} (C_2H_5)_3N^+CH_3\ OH^-$$

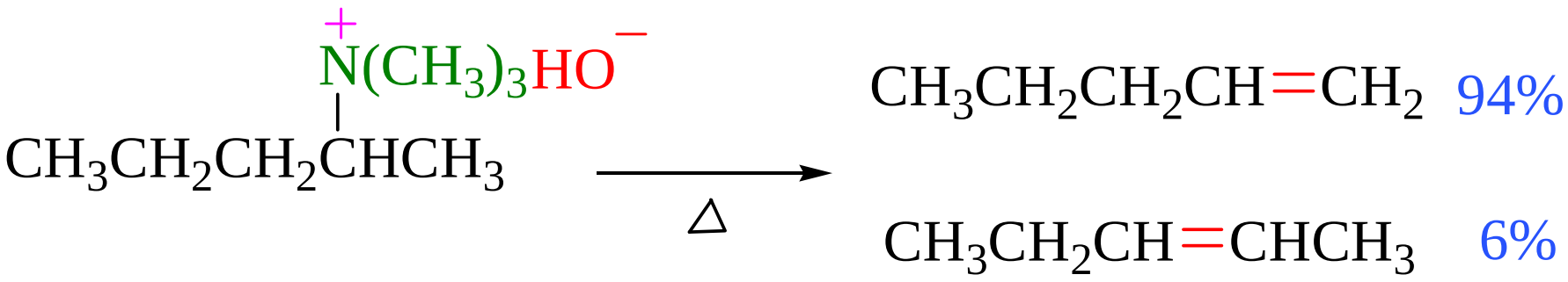
四级铵碱
(季铵碱)

四级铵碱受热分解反应

$$CH_3(CH_2)_5NH_2 \xrightarrow{CH_3I} CH_3(CH_2)_5\overset{+}{N}(CH_3)_3\ I^-$$

$$\xrightarrow{Ag_2O} CH_3(CH_2)_5\overset{+}{N}(CH_3)_3\ OH^- \xrightarrow{\triangle}$$

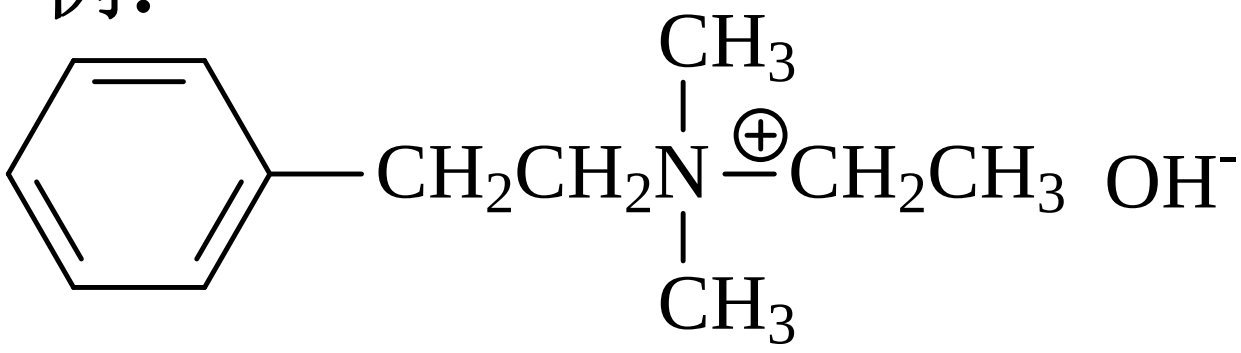
$$CH_3CH_2CH_2CH_2CH{=}CH_2 + (CH_3)_3N$$

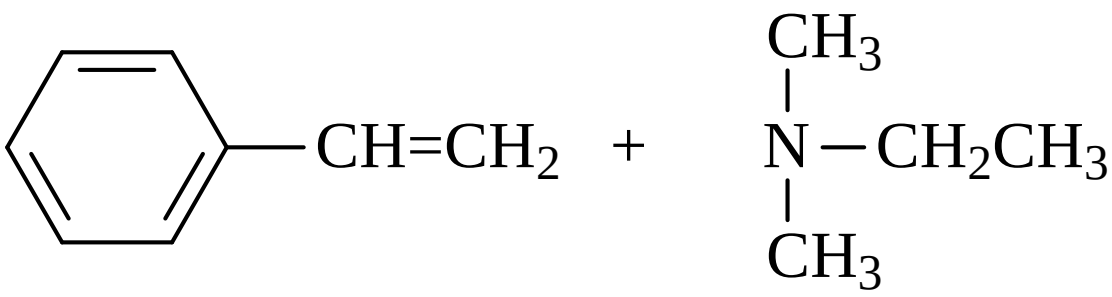


霍夫曼（**Hofmann**）规律：

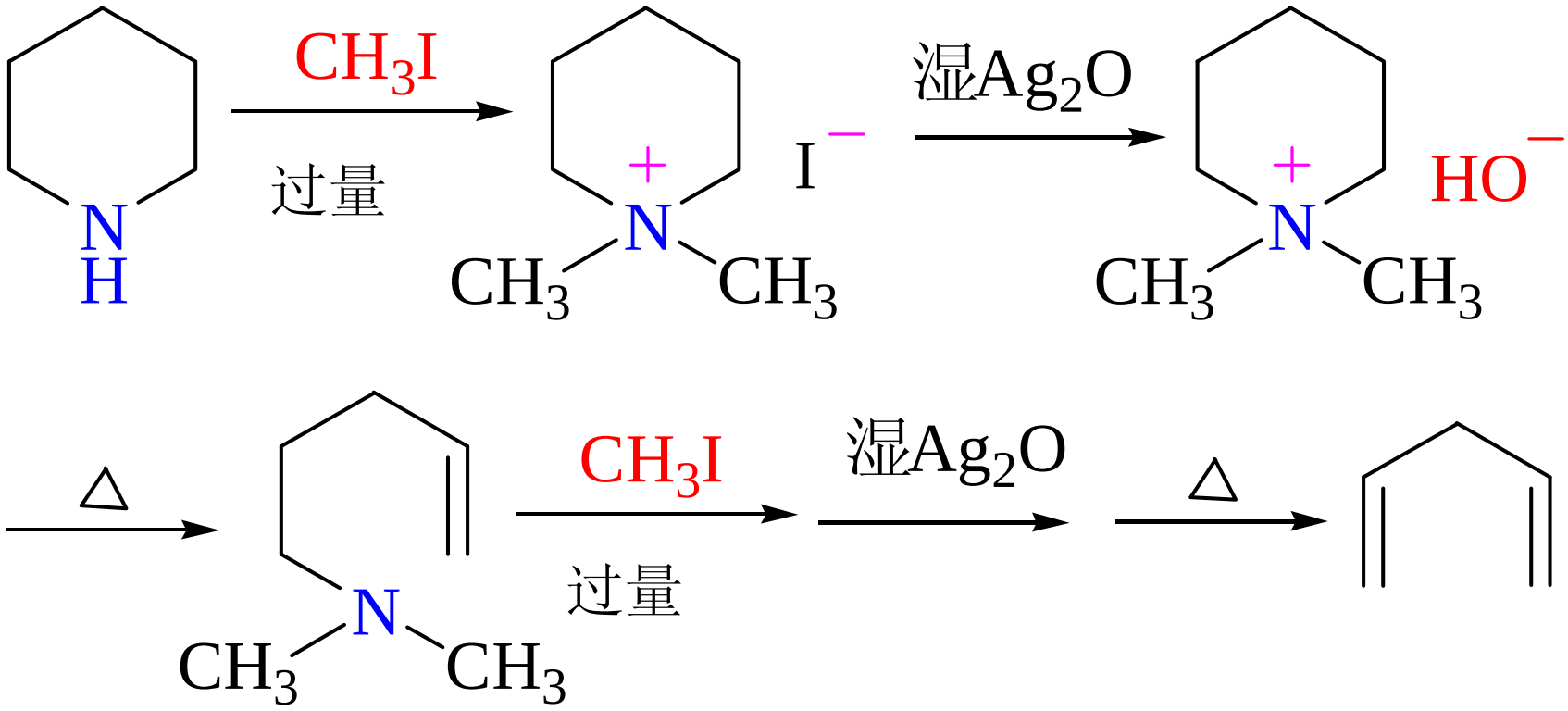
当四级铵碱分子中有两个以上不同的氢原子可被消除时，反应主要从含氢较多的碳原子上消去氢原子，即主要生成双键碳原子上烷基取代较少的烯烃。

特例：



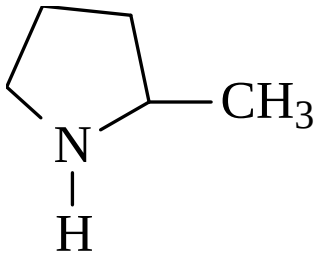


应用：推测胺的结构



$C_5H_{11}N$ (A) —彻底甲基化→ —湿Ag_2O→ —加热→ $C_7H_{15}N$ (B) —彻底甲基化→ —湿Ag_2O→ —加热→ 三甲胺 + 1，4-戊二烯

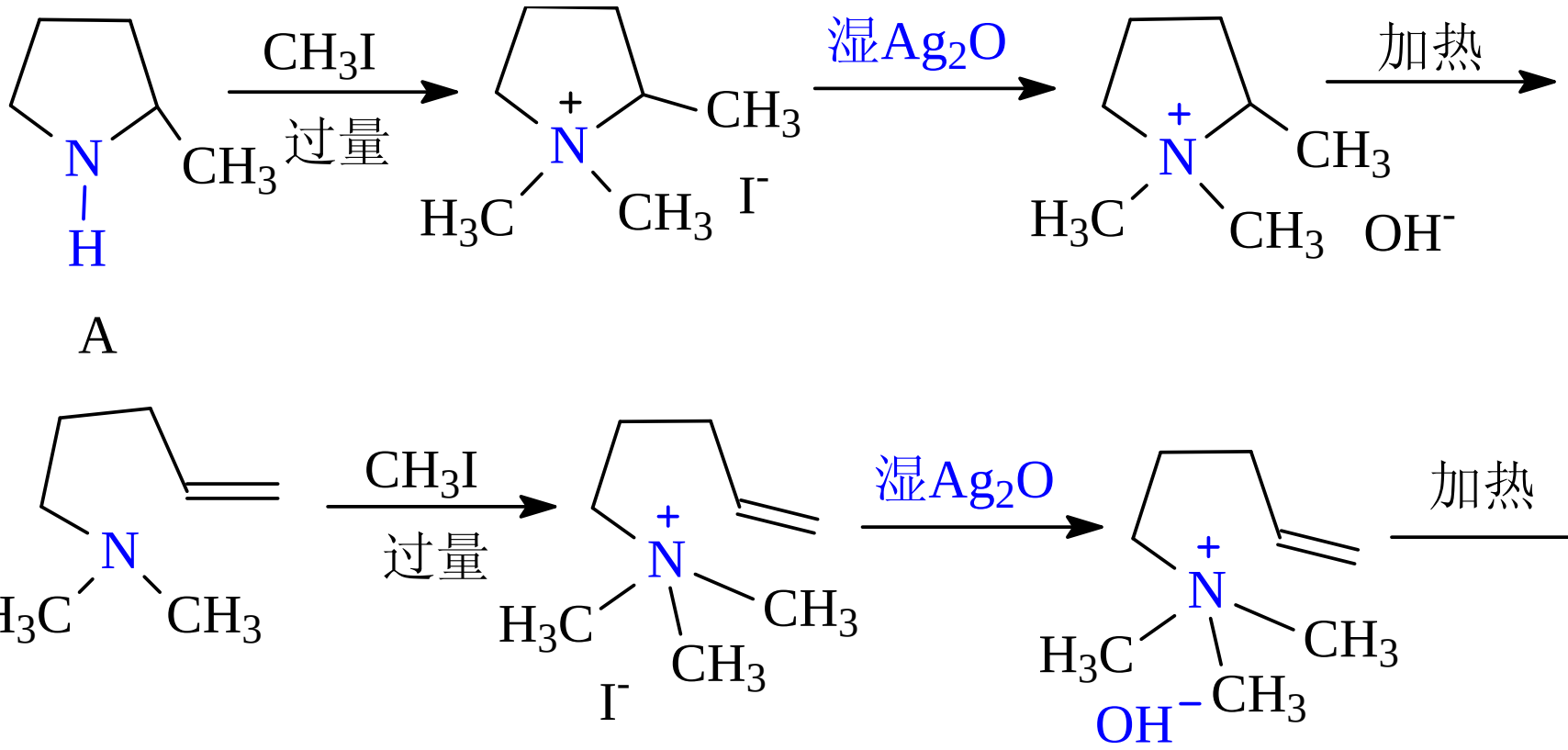
请写出A和B的结构式



A

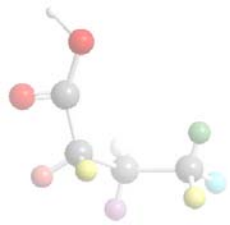
$CH_2=CHCH_2CH_2CH_2\text{-}N(CH_3)_2$

B

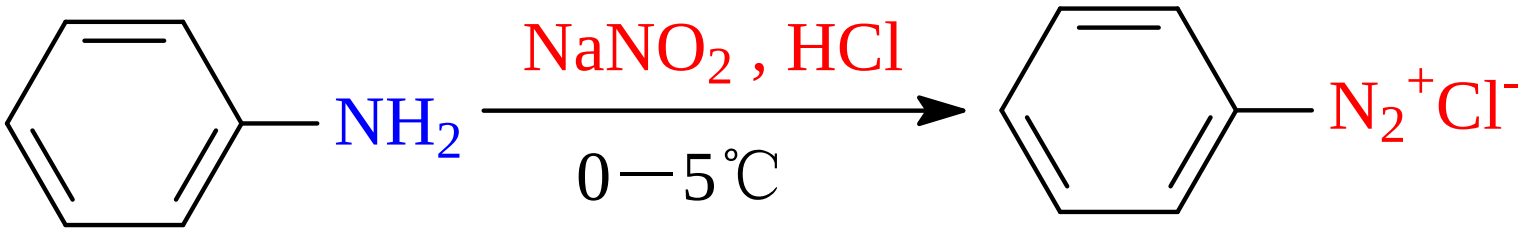


三甲胺 + 1,4-戊二烯

14.6 重氮与偶氮化合物



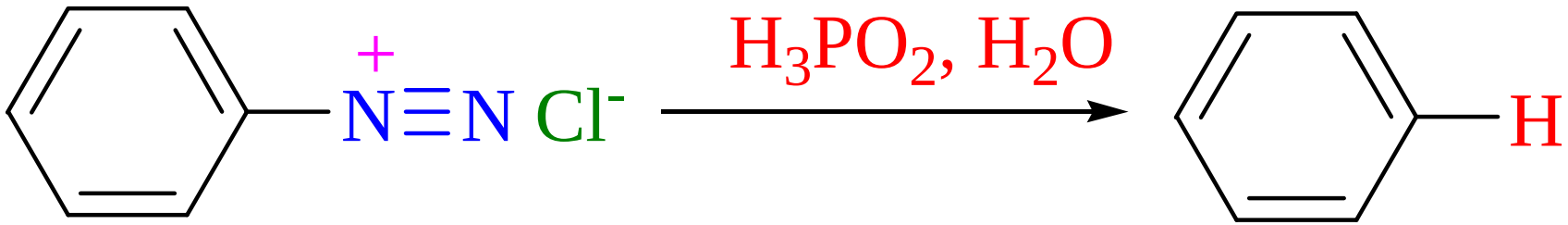
14.6.1 重氮盐的制备——重氮化反应



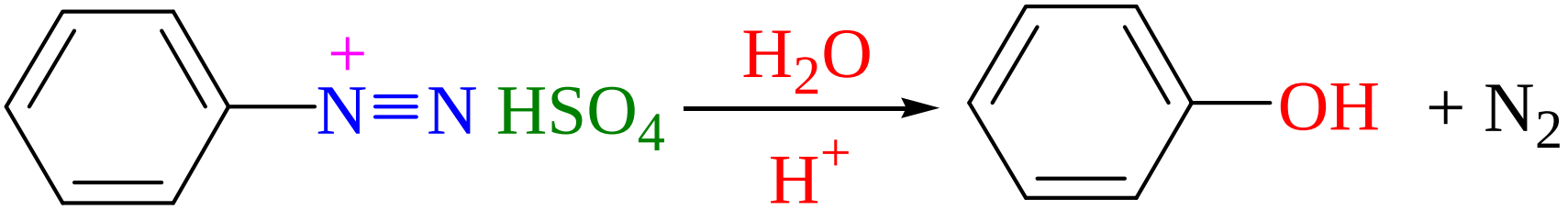
14.6.2 芳香重氮盐在合成上的应用

1. 失去氮的反应

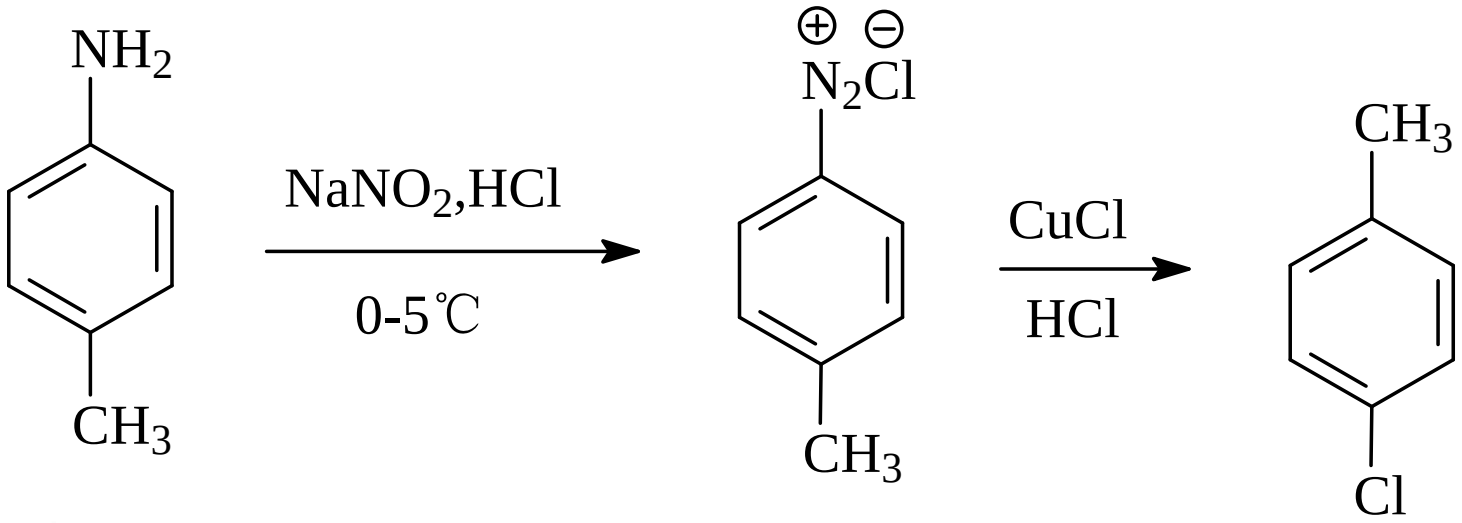
(1) 重氮基团被氢所取代（去氨基还原）

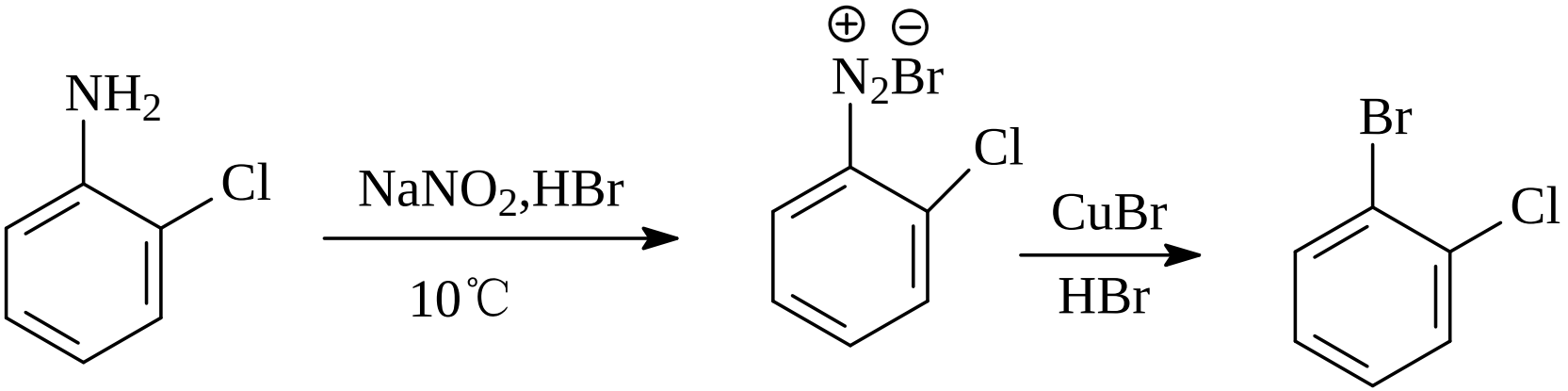


(2) 被羟基所取代

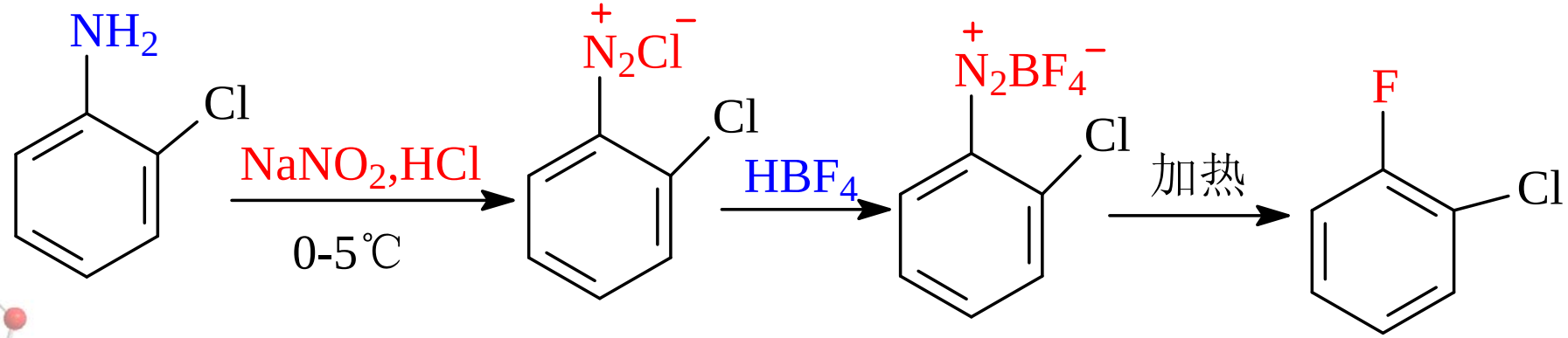


(3) 重氮盐被卤素取代

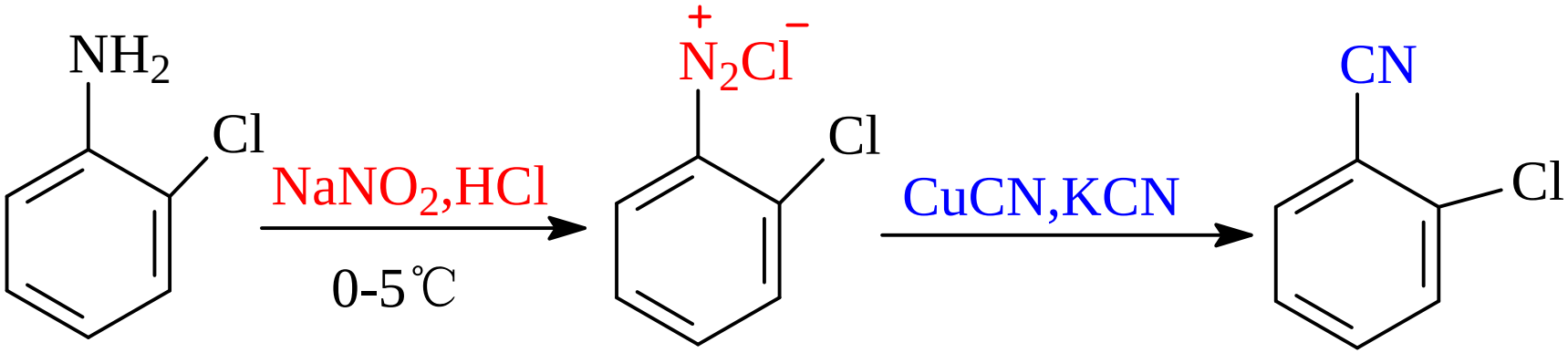



NH2
Cl
NaNO2,HBr
10℃
N2Br
Cl
CuBr
HBr
Br
Cl


N≡N Cl-
+ NaI
I

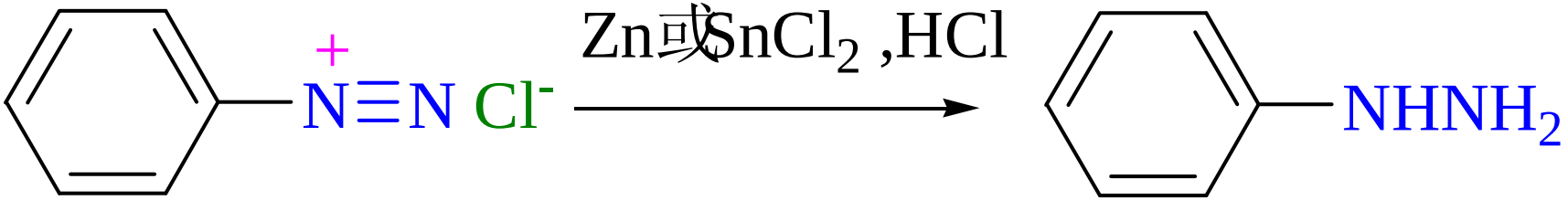

NH2
Cl
NaNO2,HCl
0-5℃
N2Cl
Cl
HBF4
N2BF4
Cl
加热
F
Cl

(4) 被氰基取代



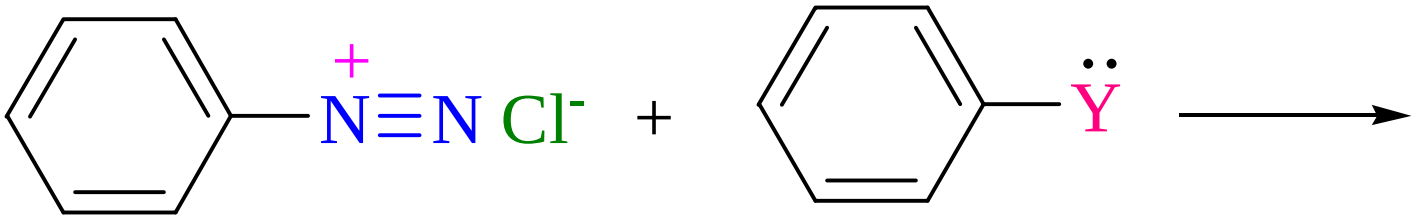
2. 保留氮的反应

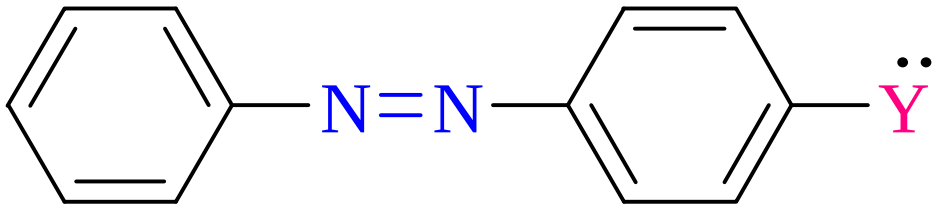
(1) 还原反应



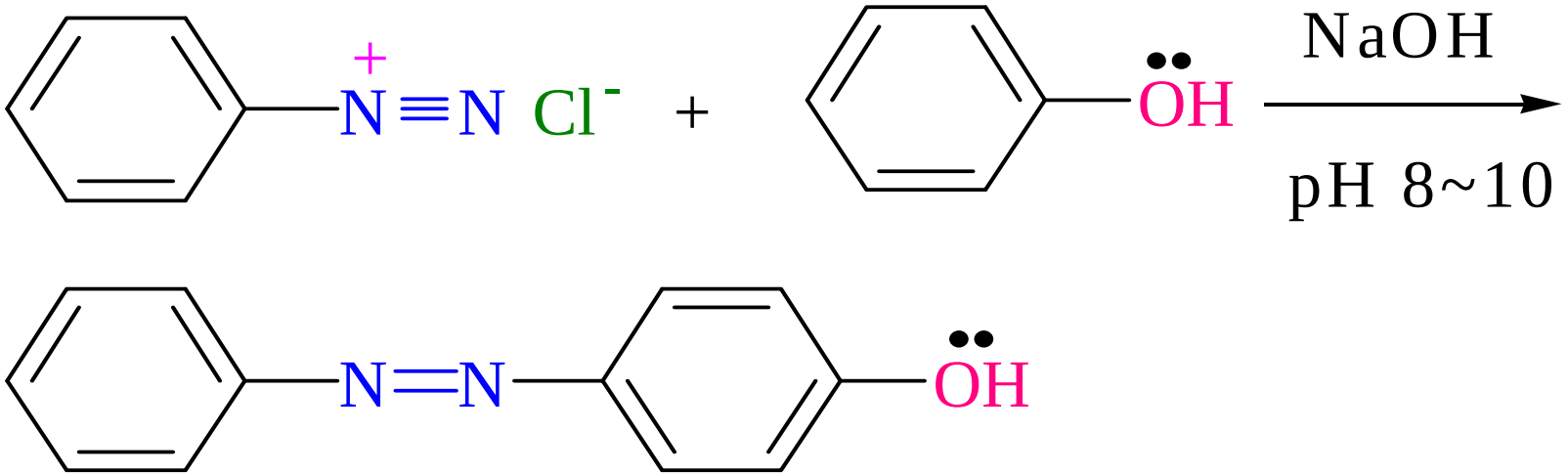
(2) 偶联反应

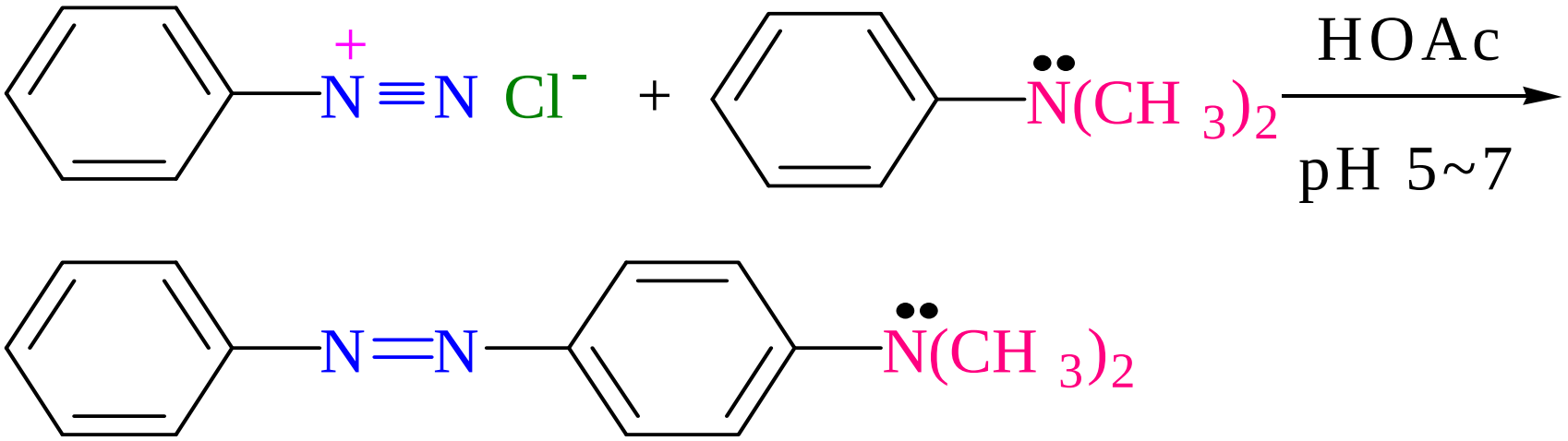
在微酸性中性或微碱性溶液中，重氮盐正离子作为亲电试剂可与连有强供电基的芳香族化合物，如酚芳胺等发生亲电取代反应生成偶氮化合物.

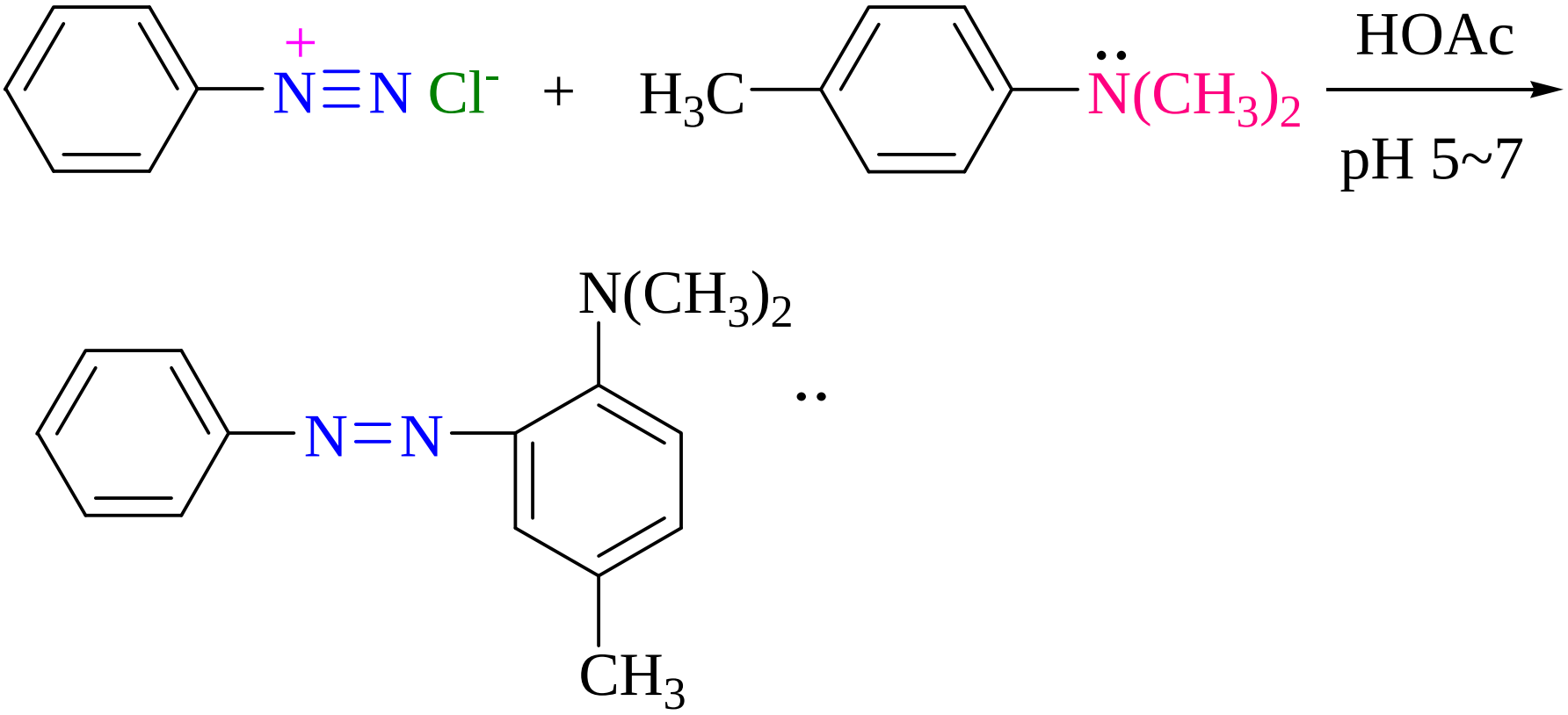




偶氮化合物


+
N≡N Cl-
+
OH
NaOH
pH 8~10
N=N
OH


+
N≡N Cl-
+
N(CH 3)2
HOAc
pH 5~7
N=N
N(CH 3)2


+
N≡N Cl-
+
H3C
N(CH3)2
HOAc
pH 5~7
N(CH3)2
N=N
CH3