

Roadmap Reaction Legend

Reaction 20.1

HX

- Gives 1,2 addition at lower temperatures under kinetic control in which most rapidly formed product predominates
- Gives 1,4 addition at higher temperature under thermodynamic control in which the reaction is at equilibrium and most stable product predominates

Reaction 21.3

1. CO₂, H₂O 2. HCl, H₂O

- The Kolbe synthesis
- The phenoxide anion adds to carbon dioxide followed by keto-enol tautomerism
- Makes a new C-C bond

Reaction 21.5

H₂CrO₄

- A benzylic carbon bonded to at least one hydrogen atom is oxidized all the way to a carboxylic acid

Reaction 20.2

A dienophile such as an electron deficient alkene

- The Diels-Alder reaction
- Concerted 1 step mechanism
- The configuration of the diene and dienophile (cis vs. trans) are conserved
- Endo product predominates
- Makes two new C-C bonds

Reaction 21.4

H₂CrO₄

- Gives 1,2 quinones or 1,4 quinones depending on the phenol

Reaction 21.6

NBS

- Halogenation is specific for the benzylic position
- Occurs by a radical chain mechanism

Reaction 22.1

X_2, FeX_3

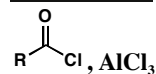
- The X_2 reacts with the Lewis acid FeX_3 to give the electrophile X^+

Reaction 22.3

SO_3

- The electrophile is either SO_3 or HSO_3^+ depending on conditions

Reaction 22.5



- Friedel-Crafts acylation
- The acid chloride reacts with $AlCl_3$ to give the acylium ion electrophile
- Makes a new C-C bond

Reaction 22.7

Alcohol, Brønsted or Lewis acid

- The alcohol reacts with the Brønsted or Lewis acid to give a carbocation electrophile
- Makes a new C-C bond

Reaction 22.10

H_2, Ni or other transition metal

- This converts a nitro group into a primary aryl amine making it a very useful reaction
- These conditions also reduce alkenes or other susceptible groups using a strong base treatment in the second step

Reaction 23.5

RNH_2 or NH_3

- This method is seldom used because of overalkylation

Reaction 23.10

HNO_2

- Treating a cyclic vicinal amino alcohol with HNO_2 gives ring expansion and a ketone

Reaction 23.12

H_2O , heat

- Important method for creating phenols

Reaction 23.14

$CuCN, KCN$

- The Sandmeyer reaction
- Also works with $CuCl$ and $CuBr$ to give aryl halides

Reaction 23.16

H_3PO_2

- Important method for removing nitrogen from an aryl ring

Reaction 22.2

HNO_3, H_2SO_4

- The electrophile is NO_2^+ formed by the reaction of HNO_3 with H_2SO_4

Reaction 22.4

$R-X, AlCl_3$

- Friedel-Crafts alkylation
- The haloalkane reacts with the Lewis acid $AlCl_3$ to give the carbocation electrophile
- Rearrangements can be a problem
- Makes a new C-C bond

Reaction 22.6

Alkene, Brønsted or Lewis acid

- The alkene reacts with the Brønsted or Lewis acid to give a carbocation electrophile
- Makes a new C-C bond

Reaction 22.8

$NaNH_2, NH_3(l)$

- The strong base causes an elimination reaction to give a benzyne intermediate followed by addition of NH_2^-

Reaction 22.11

1. $HCl, FeCl_3$, 2. $NaOH$

- This converts a nitro group into a primary aryl amine making it a very useful reaction
- The initially formed salt is converted to the amine

Reaction 23.6

1. KN_3 2. H_2O 3. $LiAlH_4$ 4. H_2O

- The azide anion reacts with an epoxide to give a vicinal azido alcohol with anti stereochemistry, that is reduced by the $LiAlH_4$ to give a vicinal amino alcohol

Reaction 23.11

HNO_2, HCl

- Important method because it converts an aniline to the highly reactive arenediazonium
- The key reactive intermediate is $HONO$

Reaction 23.13

HBF_4

- The Schiemann reaction
- Important method for creating aryl fluorides

Reaction 23.15

KI

- Important method for creating aryl iodides

Reaction 23.17

Conversion to ammonium hydroxide, heat

- The Hoffman elimination
- Anti stereoselective elimination of quaternary ammonium hydroxides occurs preferentially to form the least substituted carbon-carbon double bond (Hofmann's rule)

Reaction 23.18

Conversion to amine oxide, heat

- *The Cope elimination*

- *Elimination is syn stereoselective and involves a cyclic flow of six electrons in a planar transition state*