Hydrocarbon

1 Free Radical Reactions

1.1 Reactions Shown by Free Radical

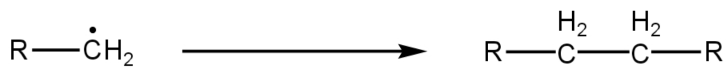
i. **Combination**
Joining of two radicals, $2^\circ, 1^\circ$ majorly show combination.

ii. **Disproportionation**
In case of 3° radical combination is not possible, hence disproportionation occurs.

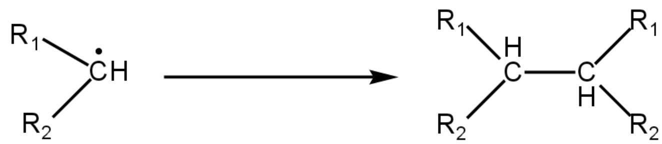
1.2 Important facts about Free Radicals

- Incomplete octet, 1 unpaired e^-
- Highly unstable
- Paramagnetic
- Can be stabilized by both EDG and EWG.
- Neither a Lewis base nor a Lewis acid.
- sp^2 hybridized.
- Trigonal Planer Geometry.

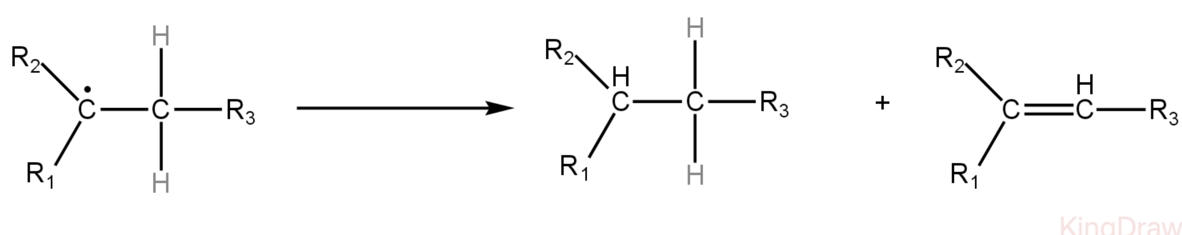
1° Radical Combination



2° Radical Combination

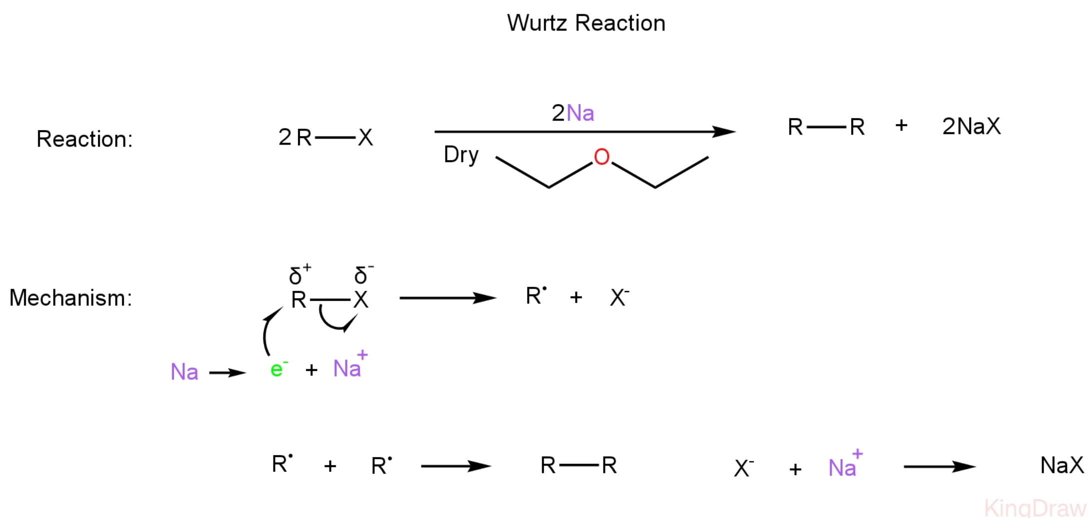


3° Radical Disproportionation



2 Wurtz Reaction

2.1 Reaction and Mechanism



2.2 Why dry Et_2O is used instead of moisture?

Water and Sodium metal react vigorously to form Sodium Hydroxide and evolve hydrogen gas, to avoid this reaction taking place dry environment is preferred.

2.3 Why Et_2O is used?

Et_2O is a PAS, hence it solvates only the cationic part (+).

2.4 Reaction Observations

i. Free radical or C^- obtained as intermediate.

ii. Breaking of RX bond is RDS.

iii. ROR for RX, $RI > RBr > RCl$

iv. $Stability\ of\ R^{\cdot} \propto ROR$

v. RF doesn't react.

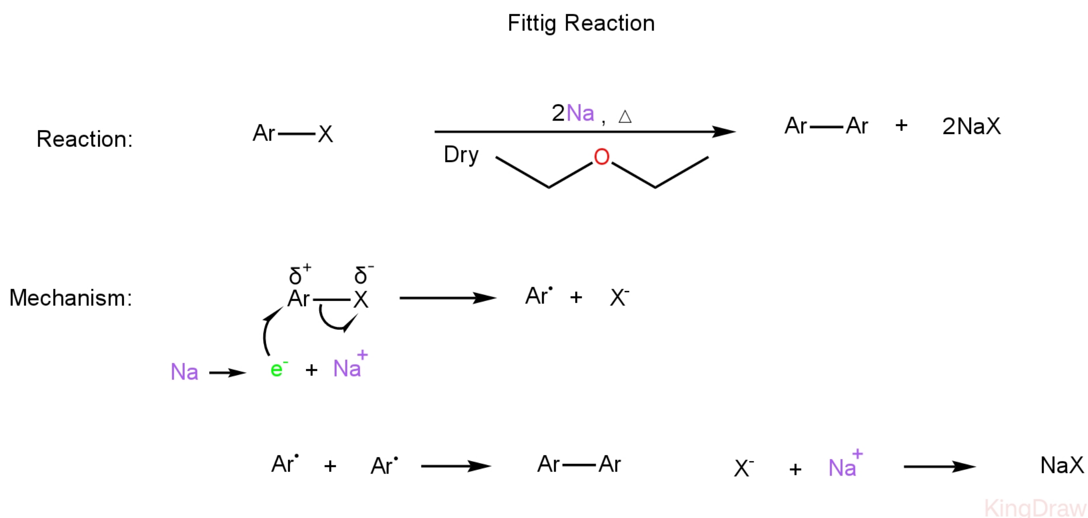
vi. CH_4 can never be obtained.

vii. Only symmetrical even number of ${}^{12}_{6}C$ obtained in very good yield.

viii. Unsymmetrical compound obtained in very poor yield.

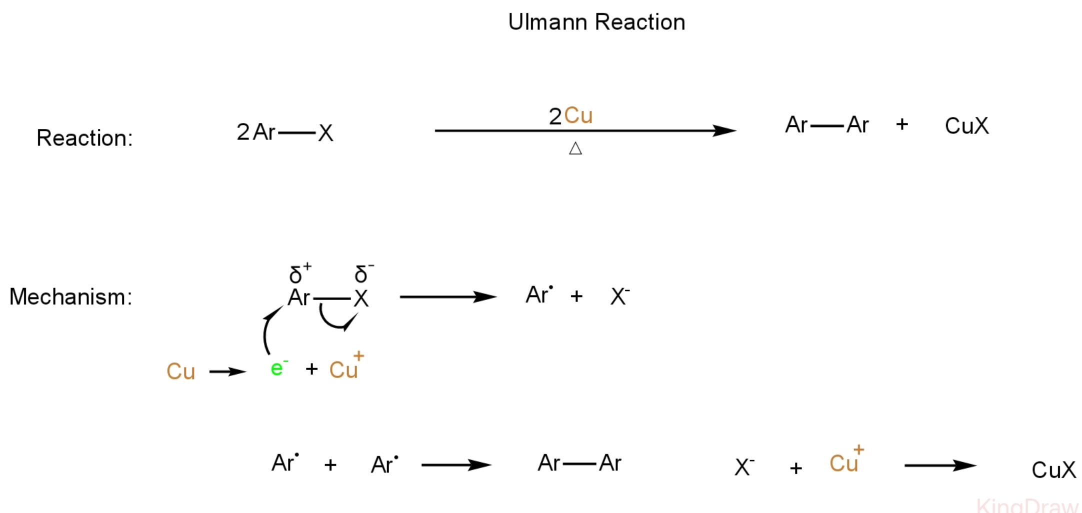
3 Fittig Reaction

3.1 Reaction and Mechanism



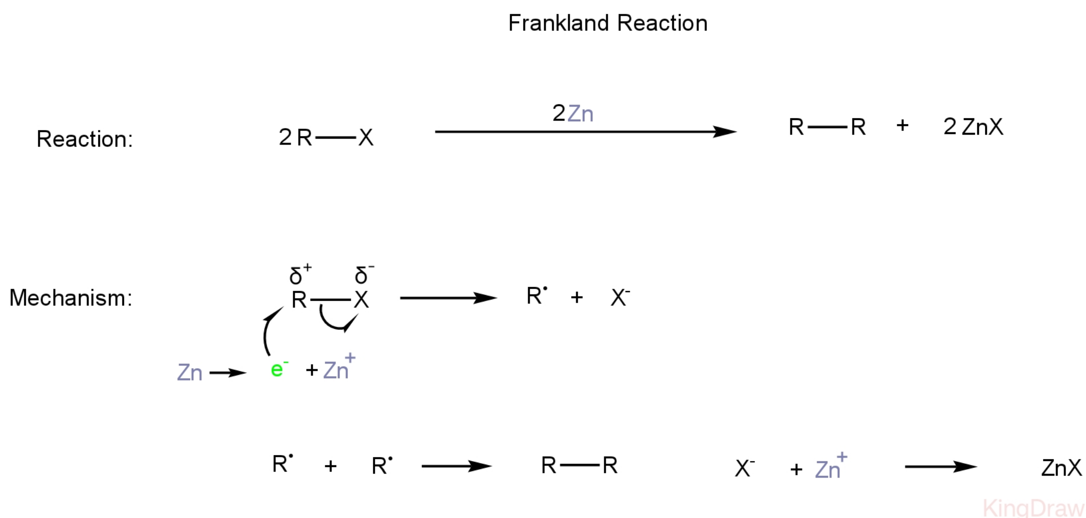
4 Ulmann Reaction

4.1 Reaction and Mechanism



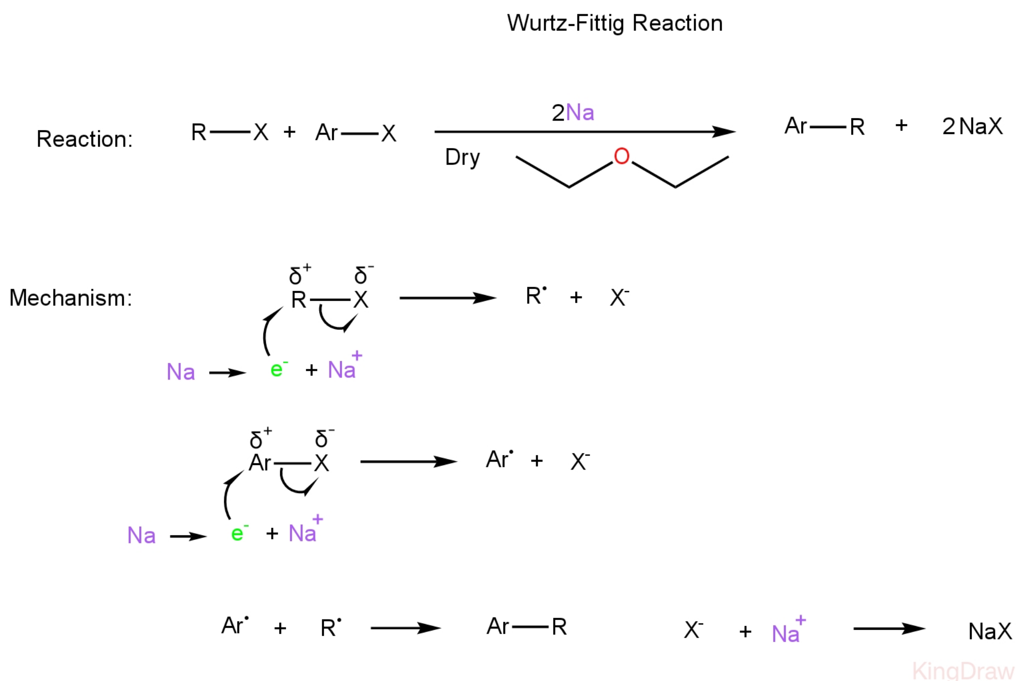
5 Frankland Reaction

5.1 Reaction and Mechanism



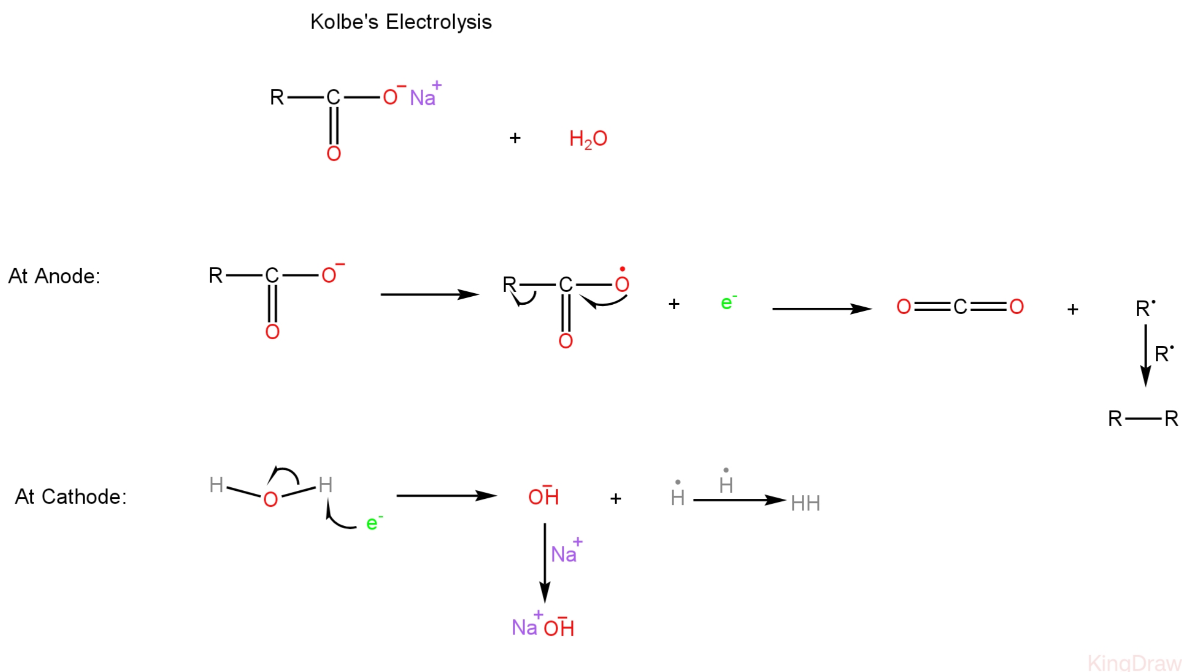
6 Wurtz-Fittig Reaction

6.1 Reaction and Mechanism



7 Kolbe's Electrolysis

7.1 Reaction and Mechanism



7.2 Reaction Observations

i. $C^{\bullet}$ obtained as intermediate.

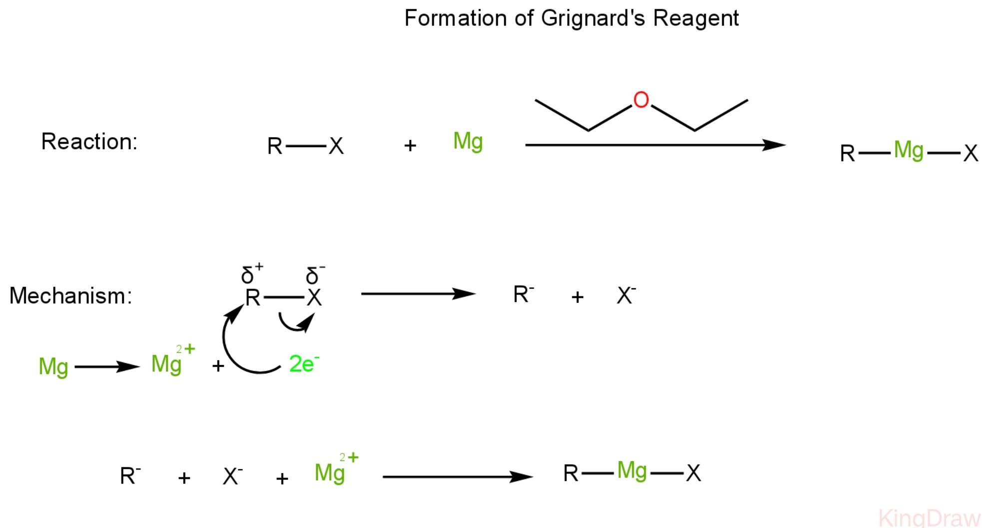
ii. pH of medium increases due to formation of $NaOH$.

iii. CO_2 obtained at anode and H_2 at cathode.

iv. CH_4 can never be obtained.

8 Formation of Grignard's Reagent

8.1 Reaction and Mechanism



8.2 Reaction Observations

i. C^- and $C^\bullet$ obtained as intermediate.

ii. $RMgX$ is also known as Organometallic Compound due to ${}^{12}_{6}C$ metal bond.

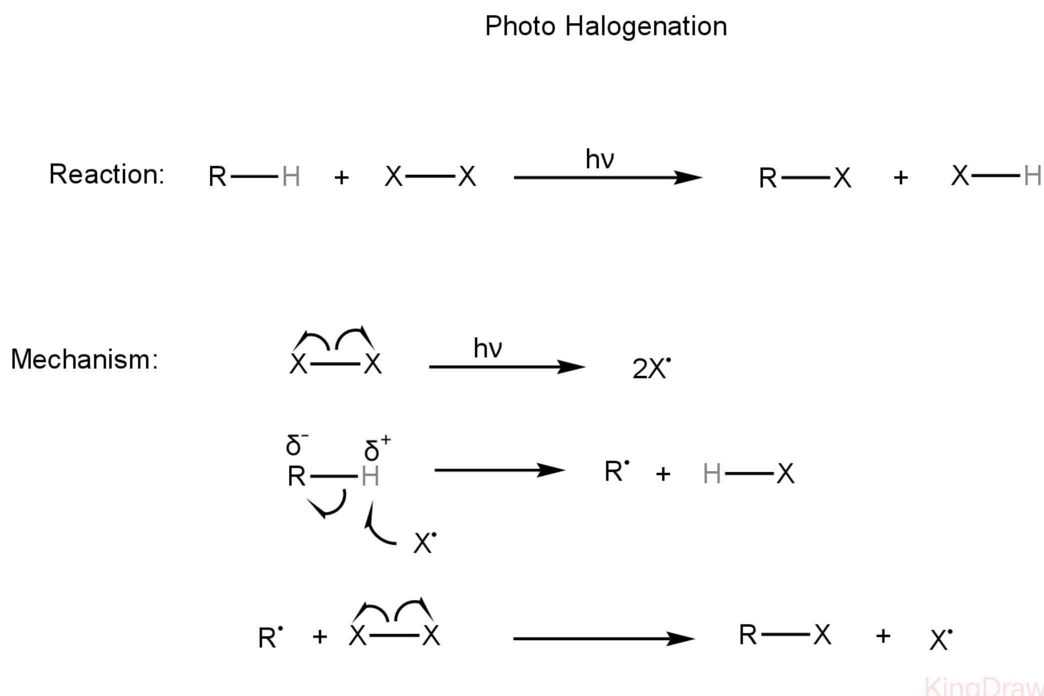
iii. ROR for RX, $RI > RBr > RCl$

iv. Reaction doesn't occur in RF

v. Dry Et_2O or THF is used as solvent.

9 Photo Halogenation

9.1 Reaction and Mechanism



9.2 Reaction Observations

i. $C^\bullet$ obtained as intermediate.

ii. Example of $C^\bullet$ substitution reaction.

iii. Kinetic isotopic effect is observed.

iv. Example of Oxidation reaction.

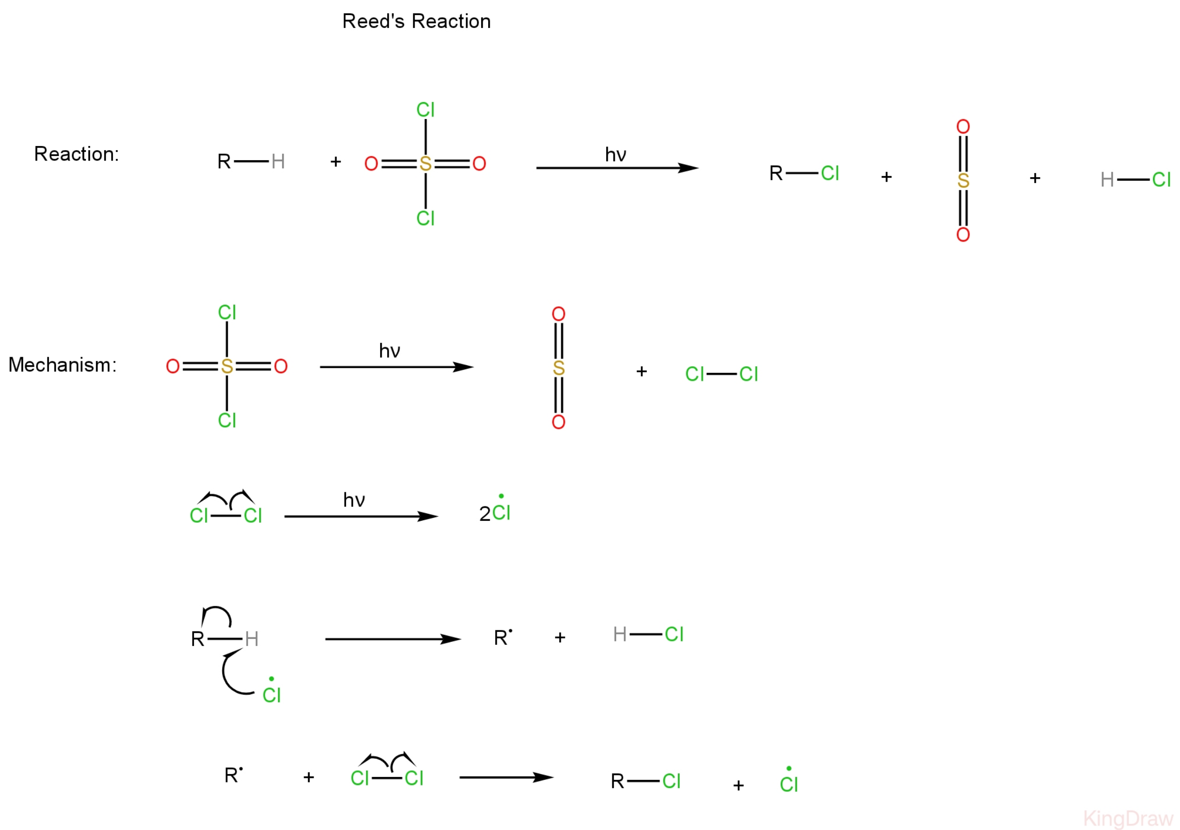
v. Formation of $C^\bullet$ is RDS.

vi. $ROR \propto$ *Stability of* $C^\bullet$

vii. ROR for X_2, $F_2 > Cl_2 > Br_2 > I_2$

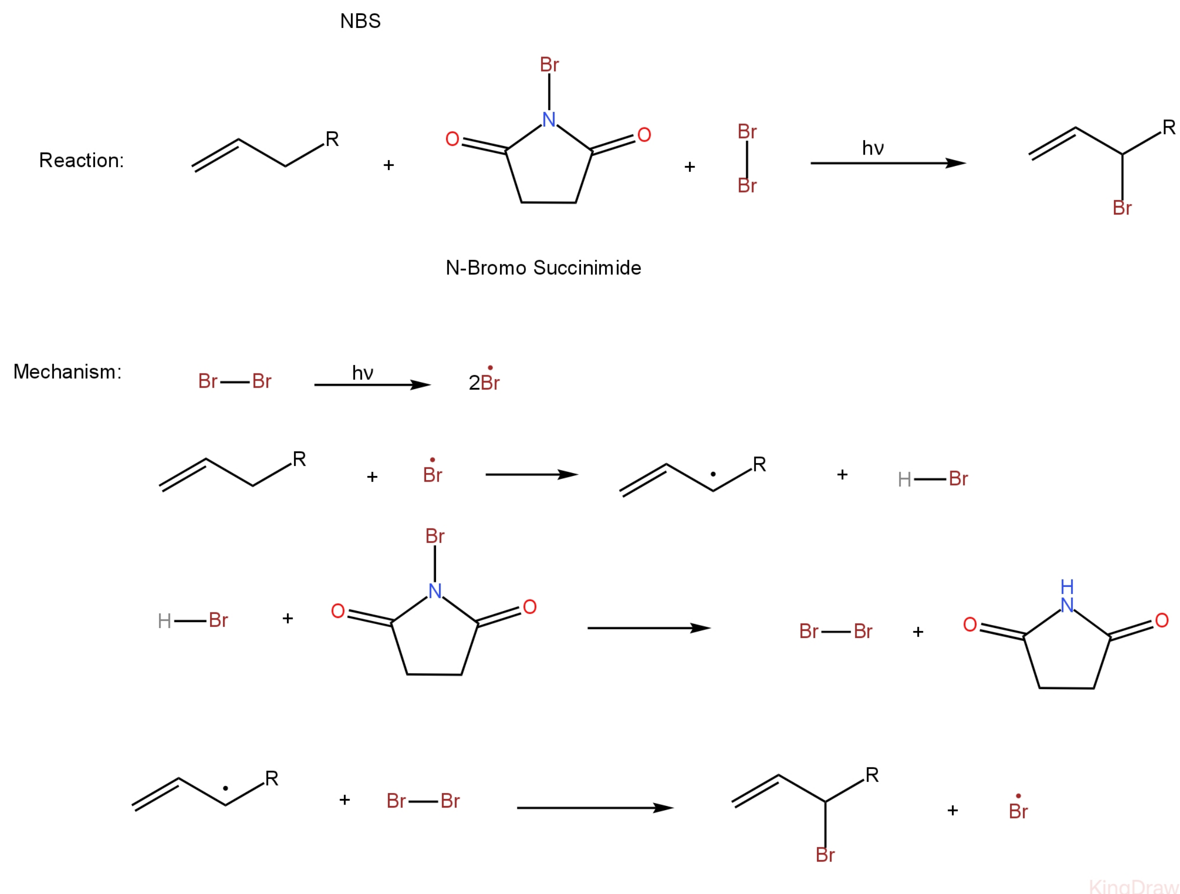
10 Reed's Reaction

10.1 Reaction and Mechanism



11 NBS

11.1 Reaction and Mechanism



11.2 Reaction Observations

i. Reacts only with Allylic and Benzylic positions.

ii. $C^{\bullet}$ obtained as intermediate.

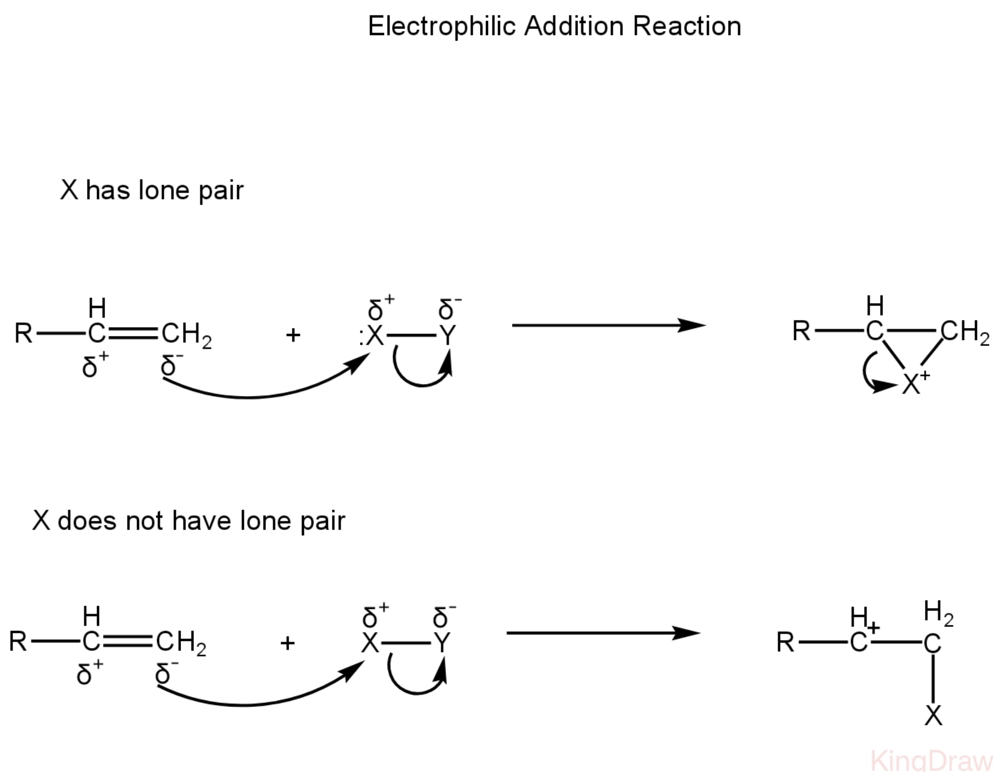
iii. Example of Substitution Reaction.

iv. Pure NBS is inert, hence, impurity of HBr or Br_2 is added.

v. Example of Oxidation Reaction.

12 Electrophilic Addition Reaction

12.1 Reaction and Mechanism



12.2 Reaction Observations

12.3 X doesn't have lone pair

i. C^+ obtained as intermediate.

ii. Rearrangement can occur.

12.4 X has lone pair

i. Non Classical Carbocation (NCC or Cyclohalonium ion) obtained as intermediate.

ii. No Rearrangement.

12.5 Reagent Table

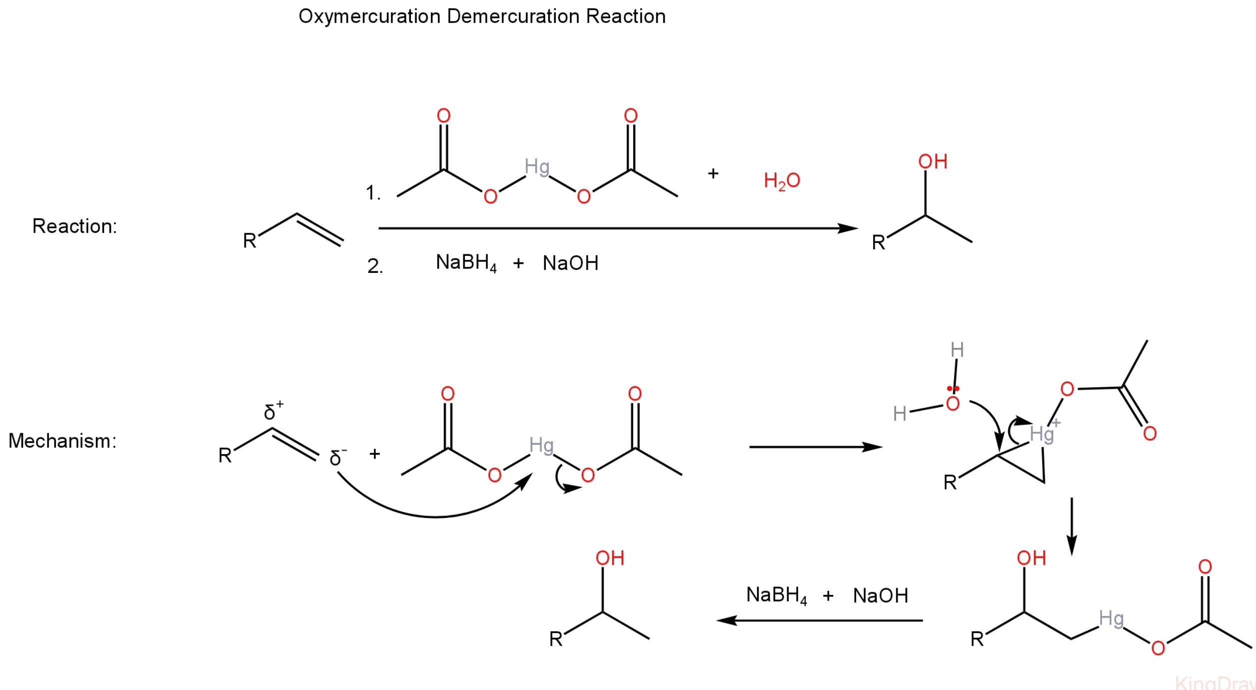
Reagent	E^+	Nu^-	Path
HCl, HBr, HI	H^+	Cl^-, Br^-, I^-	X does not lone pair
DCl	D^+	Cl^-	X does not lone pair
$H^+/H_2O, H_3O^+$, dil.H_2SO_4	H^+	OH^-	X does not lone pair
ROH/H^+	H^+	OR^-	X does not lone pair
$RCOOH/H^+$	H^+	$RCOO^-$	X does not lone pair
X_2/CCl_4	X^+	X^-	X has lone pair
Br_2/H_2O or $HOBr$	Br^+	Br^-, OH^-	X has lone pair
Br_2/H_2O in Brine	Br^+	Br^-, OH^-, Cl^-	X has lone pair
$NOCl$ (Tilden Reagent)	NO^+	Cl^-	X has lone pair
IN_3	I^+	N_3^-	X has lone pair

12.6 KCP and TCP

KCP	TCP
Kinetically Controlled Product	Thermodynamically Controlled Product
$1, 2-$ Product is assumed to be KCP	Can be $1, 2$ and $1, 4$
Fast Rate	Stable Product
Favors at low temperature $(-80, -40, 0°C)$	Favors high temperature

13 Oxymercuration Demercuration

13.1 Reaction and Mechanism



13.2 Reaction Observations

i. Markonikov addition.

ii. No rearrangment.

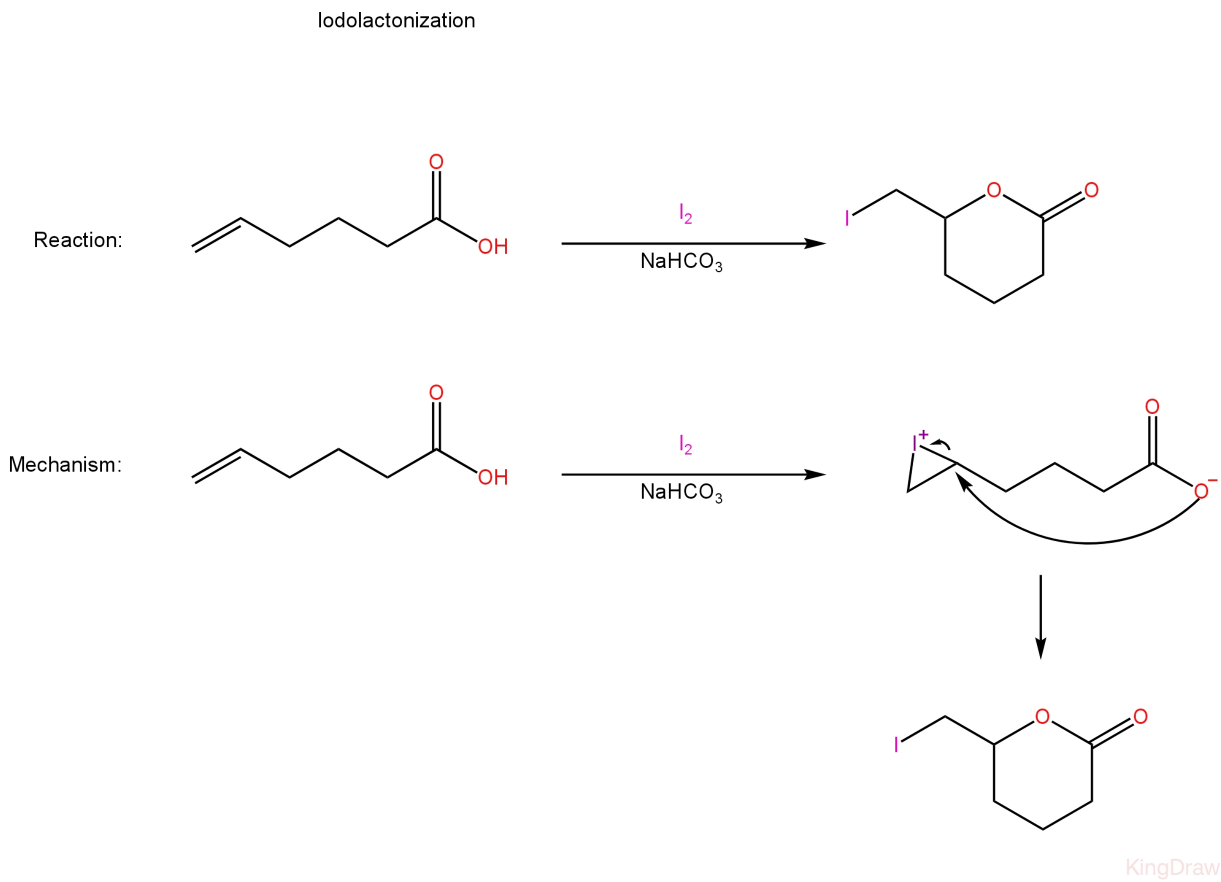
iii. Both Syn and anti addition.

iv. OM is anti additon, DM involves $C^{\bullet}$, hence both syn and anti addition.

v. Metal $Hg^{\bullet}$ is obtained.

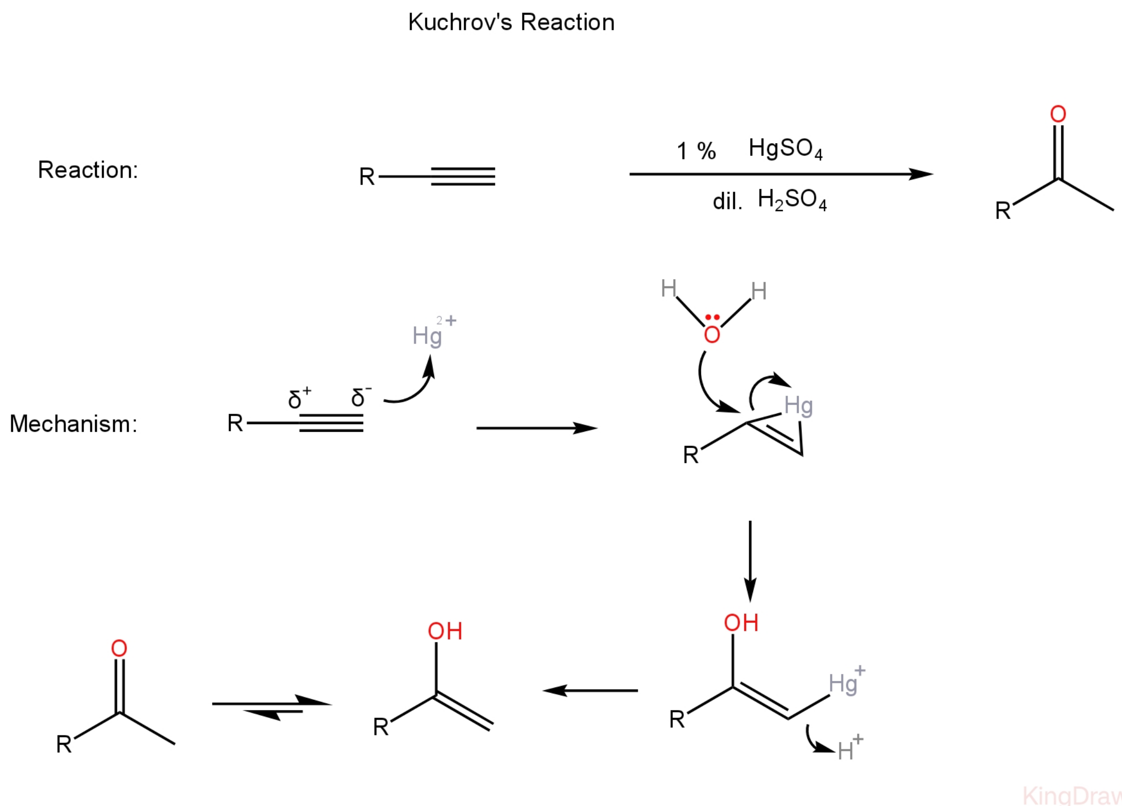
14 Iodolactonization

14.1 Reaction and Mechanism



15 Kuchrov's Reaction

15.1 Reaction and Mechanism



15.2 Reaction Observations

i. Example of Electrophilic Additon Reaction.

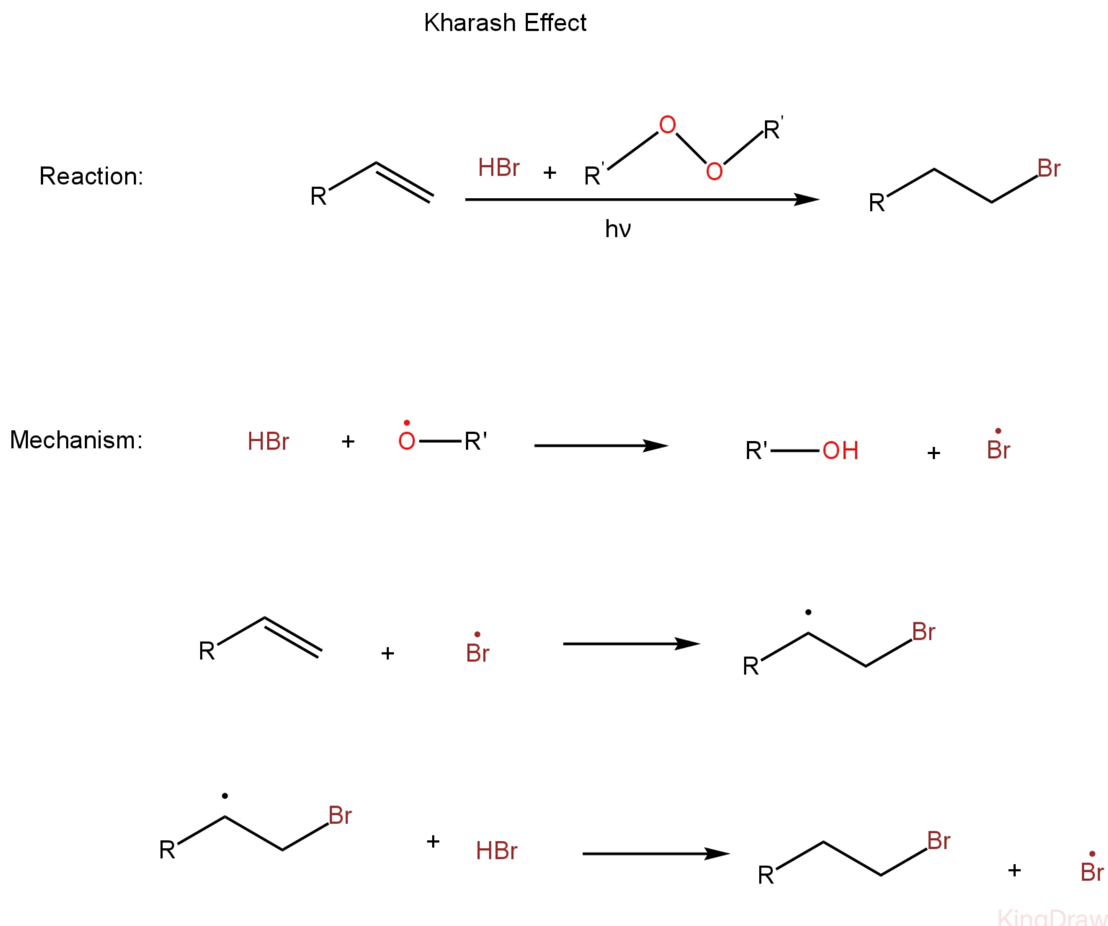
ii. NCC type intermediate is obtaied.

iii. Involves tautomerism.

iv. Mixed carbony are obtaied.

16 Kharasch Effect

16.1 Reaction and Mechanism



16.2 Reaction Observations

i. $C^{\bullet}$ obtained as intermediate.

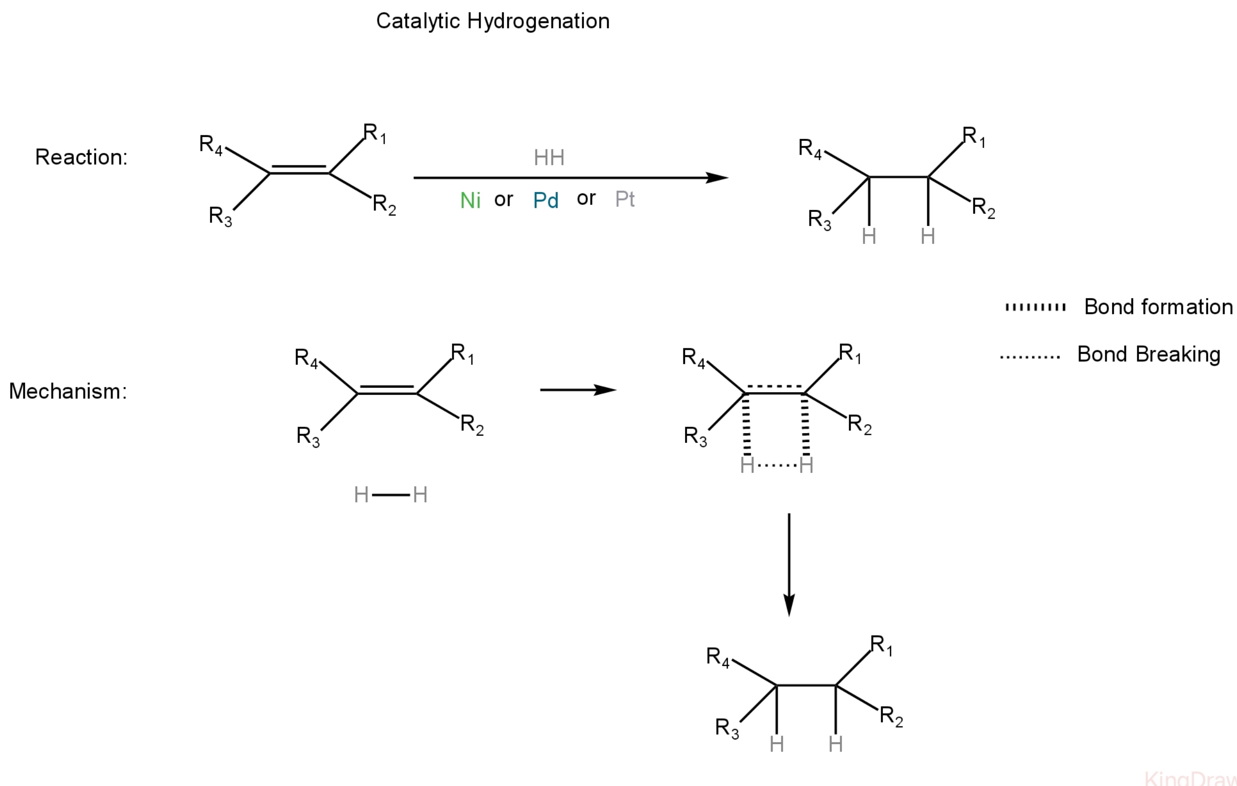
ii. Example of $C^{\bullet}$ addition Reaction.

iii. Anti-markonikov addition

iv. Only HBr shows peroxide effect (Kharasch Effect).

17 Catalytic Hydrogenation

17.1 Reaction and Mechanism



17.2 Reaction Observations

i. Example of additon and Redox reaction.

ii. syn additon

iii. Example of surface phenomenon and involvs 4 MCTS.

iv. $Pd/BaSO_4$ a.k.a Lindlar's Catalyst and Quinoline is added as poison.

v. In case of conjugated diene, 1,4addition takes place due to 6 MCTS.

vi. Reactivity,
$C - S$ bond $>$ Alkyne $> Ar - NO_2 > R - COCl >$ Alkene $> RCHO >$ $RCOR > Benzene^* > RCOOH^* < acid\ derivative^*$ $\quad *$ require heat
$\propto \dfrac{1}{\text{Steric Hindrance}}$

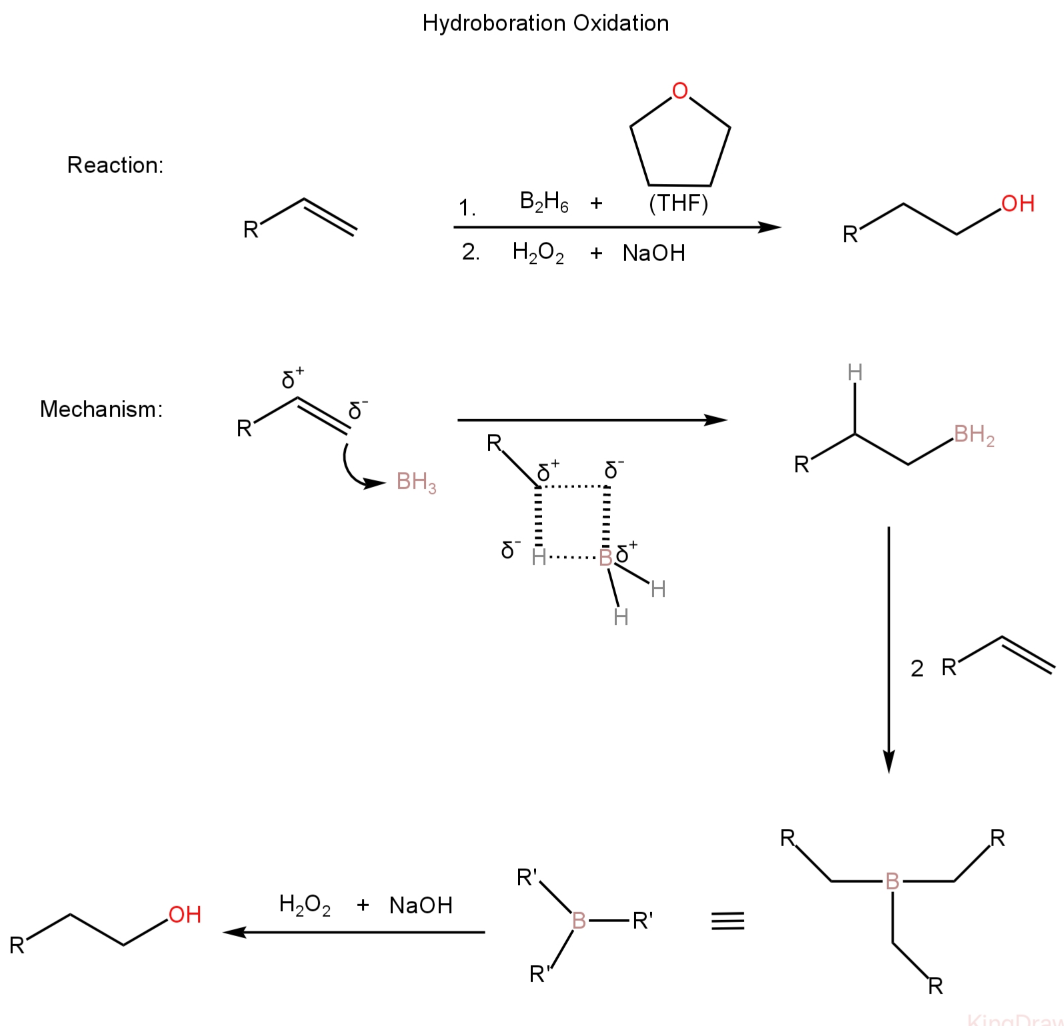
$$\propto \frac{1}{\text{Stability of Alkene}}$$

18 Rosenmund Reaction

onhold

19 Hydroboration Oxidation

19.1 Reaction and Mechanism



19.2 Reagent Table

Reactant	Reagent	Product
R'_3B	$H_2O_2/NaOH$	$3R'OH$
	H_2O	$3R'H$
	$RCOOH$	$3R'H$
	Cl_2	$3R'Cl$

19.3 Reaction Observations

i. Sys addition.

ii. Anti-markonikov addition.

iii. Involvs 4MCTS.

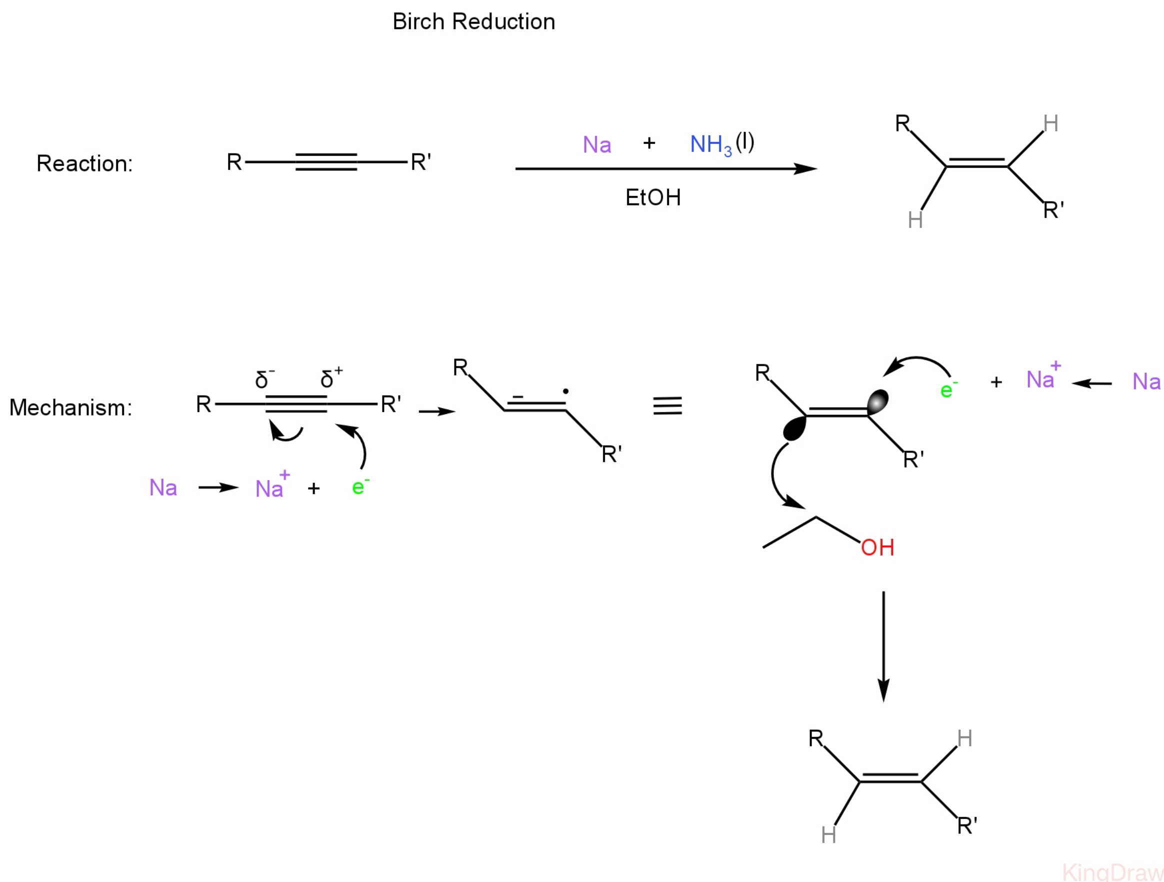
iv. In case of acid or water, reduction occurs.

v. Generally, 3 $mol.$ alkene is required for 1 $mol.$ BH_3

vi. $9 - BBN$, Sia_2BH is used for selective addition on less crowded terminal alkene.

20 Birch Reduction

20.1 Reaction and Mechanism



20.2 Reaction Observations

i. $Na/NH_3(l)$ is a blue color solution.

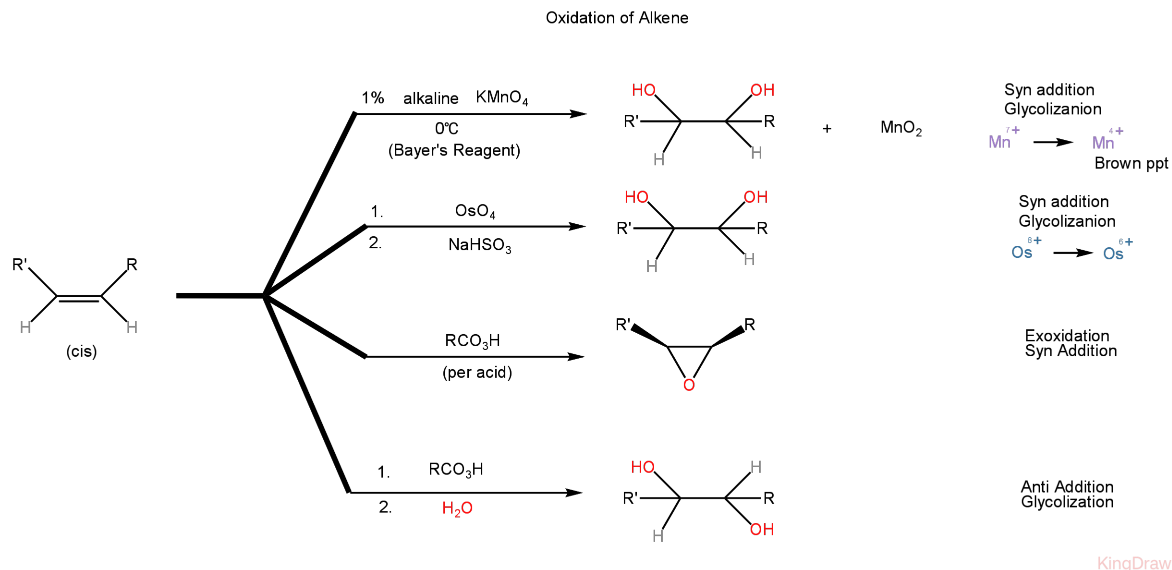
ii. Both $C^{\bullet}$ and C^{-} obtained as intermediate.

iii. ROH is used as proton source.

iv. Terminal Alkyne will not give alkene, acid base reaction will occur.

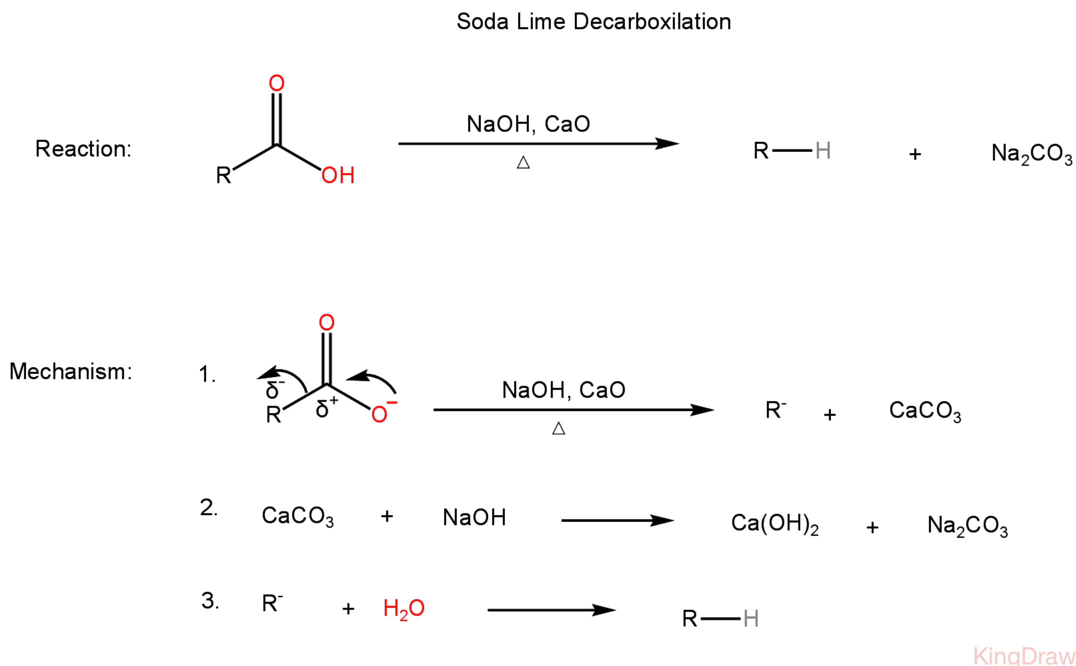
v. In case of substituted benzene, more stable alkene is major product.

21 Oxidation of Alkene



22 Soda Lime Decarboxylation

22.1 Reaction and Mechanism



22.2 Reaction Observations

i. 3 : 1 of $NaOH$ and CaO taken respectively.

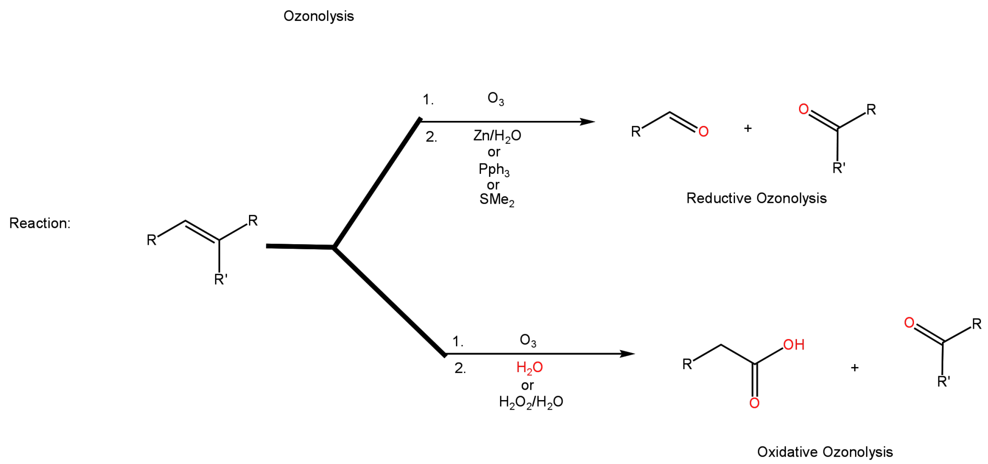
ii. C^- obtaied as intermediate.

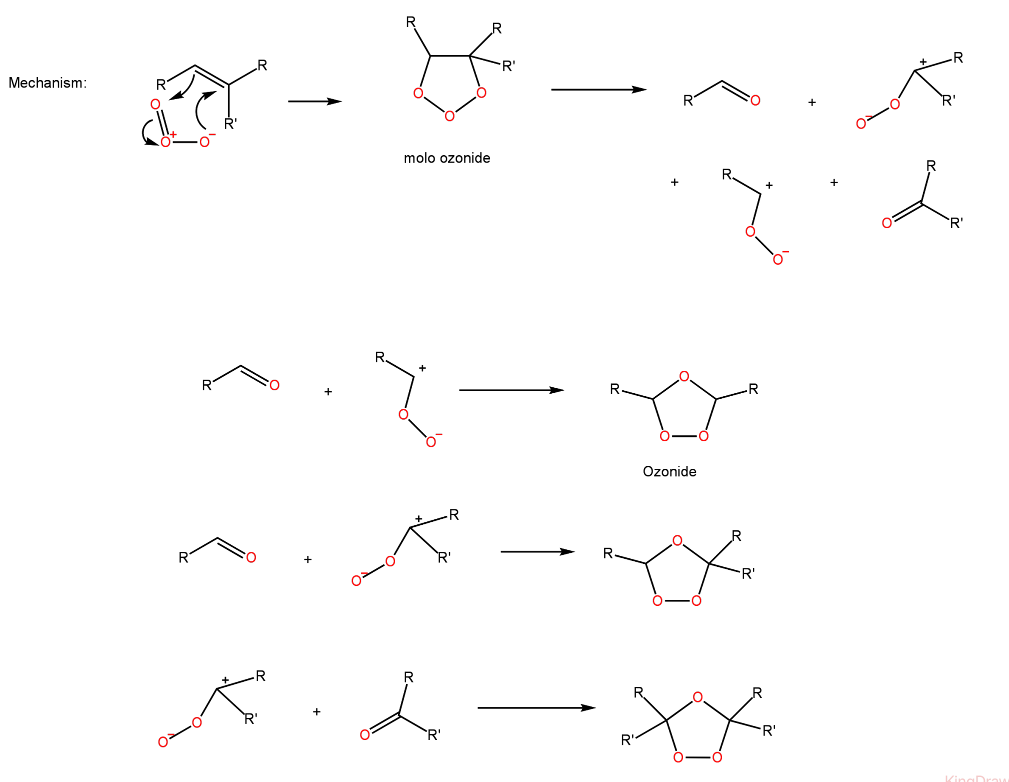
iii. $ROR \propto$ *Stability of* C^-

iv. a.k.a Oakwood Degradation

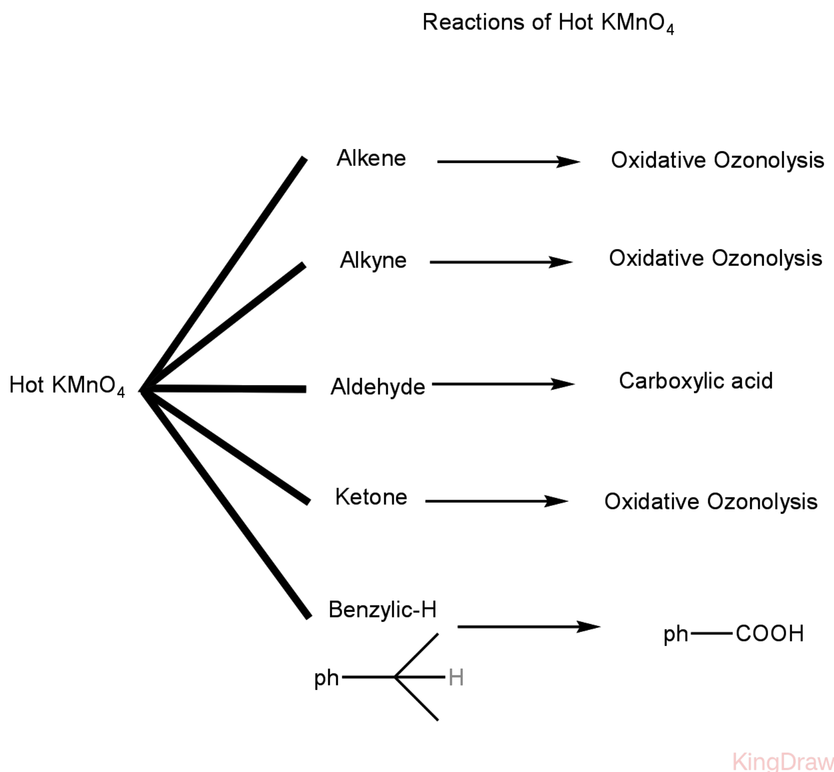
23 Ozonolysis

23.1 Reaction and Mechanism





24 Reactions of Hot $KMnO_4$



i. If Benzylic ${}^{12}_{6}C$ has any $-H, =, \equiv$ present then it will convert to benzoic acid.

ii. If there are multiple rings present in a compound, then the ring with more electron density will oxidize first.

25 Hydrolysis of Carbides

i. Hydrolysis of a Carbide results in formation of a Hydrocarbon and Hydroxide.

ii. Hydrolysis is a non redox reaction,
Hence,

$$oxidation\ state\ of\ {}^{12}_{6}C\ in\ carbide = oxidation\ state\ of\ {}^{12}_{6}C\ in\ hydrocarbon.$$

$$Oxidation\ state\ of\ Metal\ in\ Carbide = Oxidation\ of\ metal\ in\ Hydroxide$$

iii. The suffix $-ide$ in Carbide indicates that oxidation state of ${}^{12}_{6}C < 0$ i.e. it is an anion.

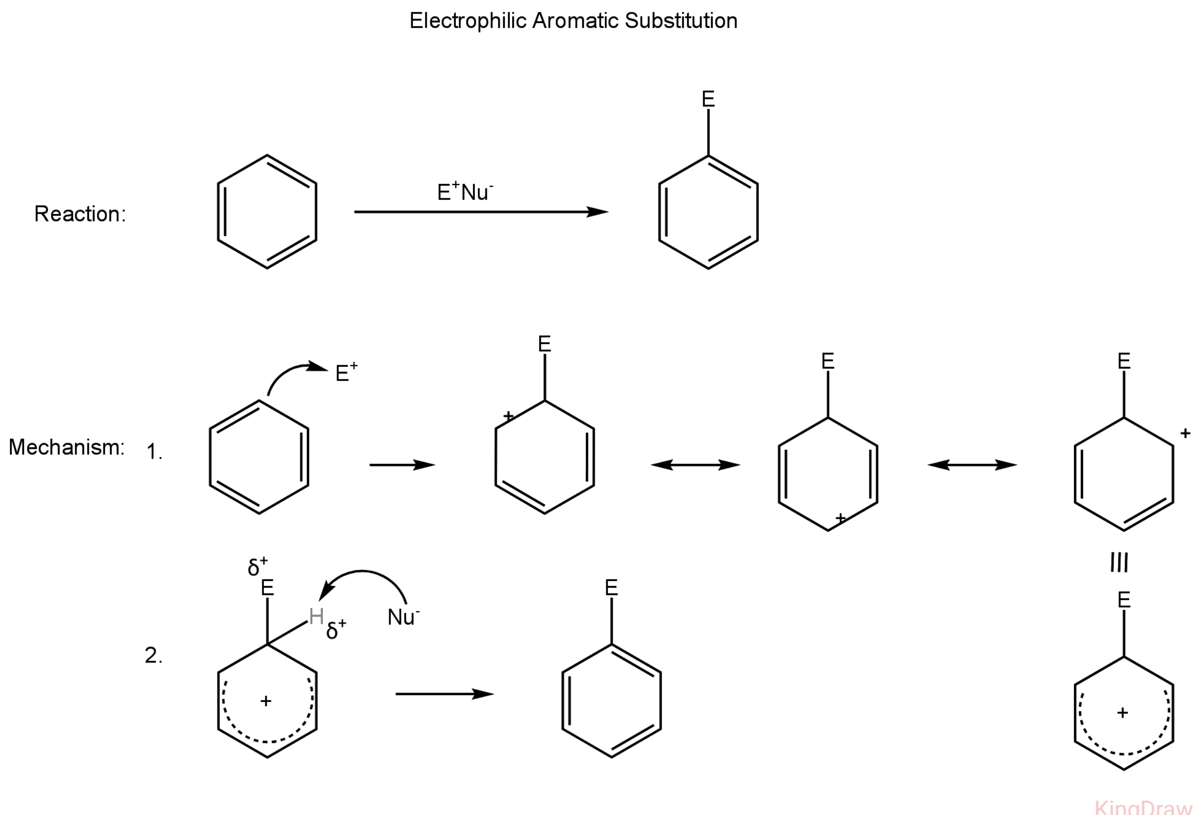
26 Aromatization Reactions

26.1 Reaction of Alkyne inside Red Hot Fe Tube

onhold

27 Electrophilic Aromatic Substitution

27.1 Reaction and Mechanism



27.2 Reaction Observations

i. σ complex obtaied as intermediate.

ii. Formation of arenium ion is RDS.

iii. Rate law, $ROR = k[Ar - H][E^{+}]$

iv. Bimolecular Reaction

v. $ROR \propto$ *Stability of* C^+

vi. EDG will increase the rate.

vii. Reaction can be reversible and irreversible.

27.3 Reversiblity of EAS

EAS can be Reversible if,

- E^+ is very stable [Alkylation (tert-Butyl cation), Iodination (I^+)]
- E is gasous [Sulphonation (SO_3), Carboxylation (CO_2), Azotization (N_2), etc.]

27.4 Reativity and Orientation

- Reacitvity is decided by net effect of E.
- Orientation is decided by stability of σ complex.
- Reactivity, $EDG > Robinhood > EWG$
- EDG are o, p directing.
- EWG are m directing.
- Robinhood are o, p directing.