

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.

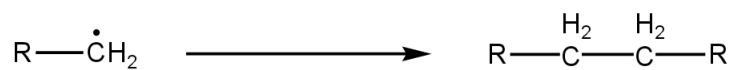
ii. **Disproportionation**

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

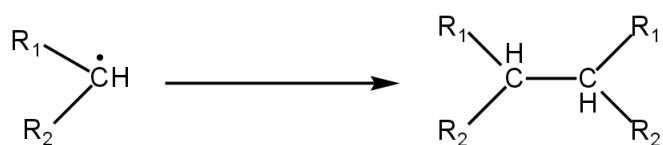
1.2 Important facts about Free Radicals

- 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.

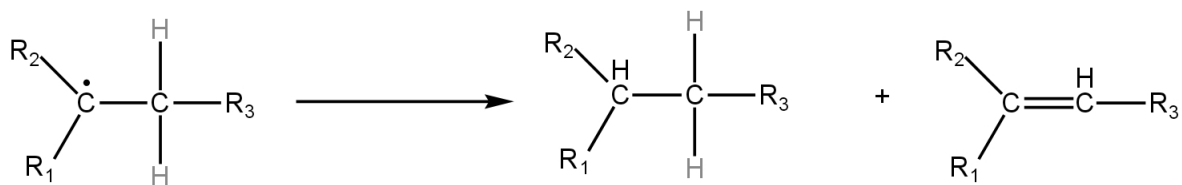
1° Radical Combination



2° Radical Combination



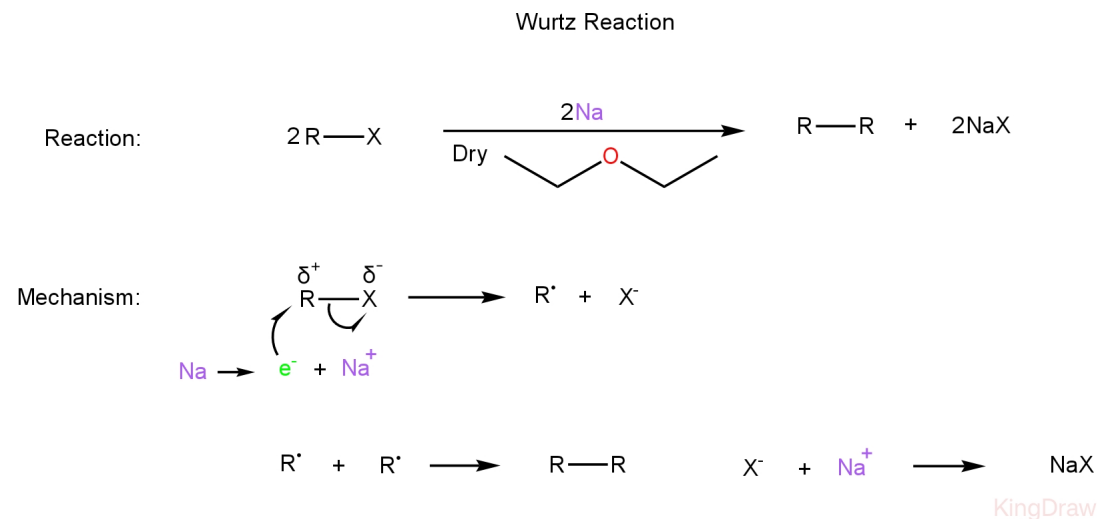
3° Radical Disproportionation



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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 (+).

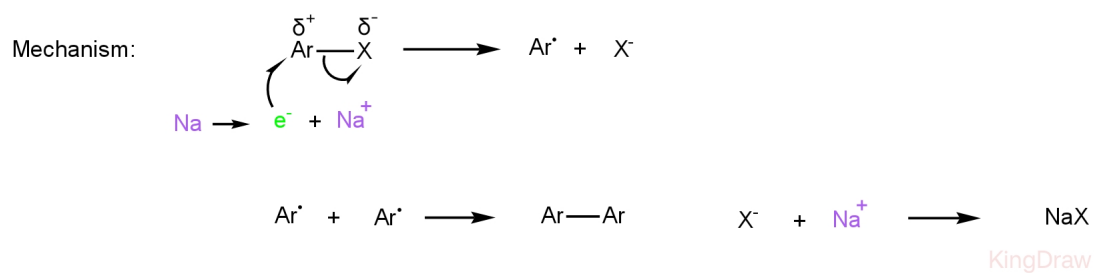
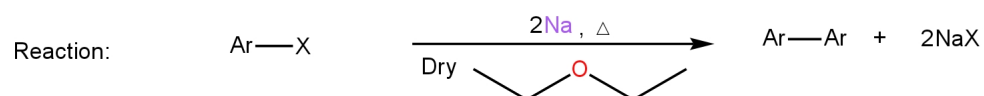
2.4 Reaction Observations

- i. Free radical or C^\cdot obtained as intermediate.
- ii. Breaking of RX bond is RDS.
- iii. ROR for RX , $RI > RBr > RCl$
- iv. $Stability \text{ of } R^\cdot \propto ROR$
- v. RF doesn't react.
- vi. CH_4 can never be obtained.
- vii. Only symmetrical even number of $^{12}_6C$ obtained in very good yield.
- viii. Unsymmetrical compound obtained in very poor yield.

3 Fittig Reaction

3.1 Reaction and Mechanism

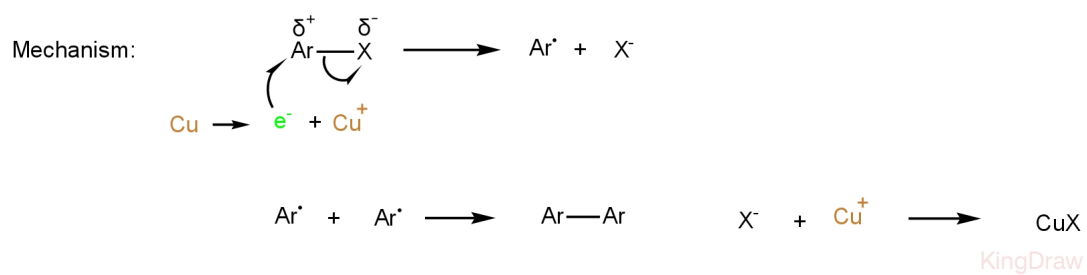
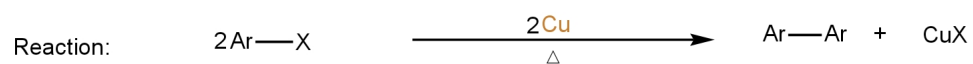
Fittig Reaction



4 Ulmann Reaction

4.1 Reaction and Mechanism

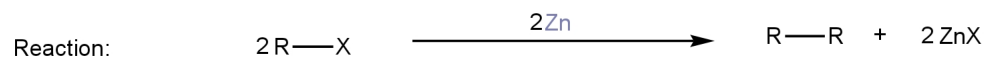
Ulmann Reaction



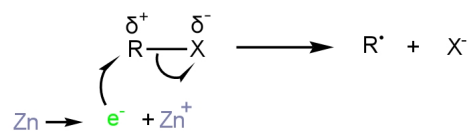
5 Frankland Reaction

5.1 Reaction and Mechanism

Frankland Reaction



Mechanism:

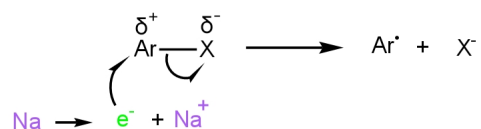
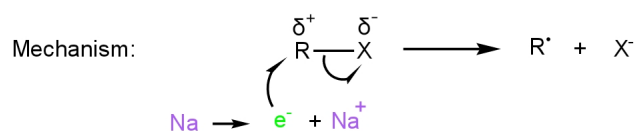
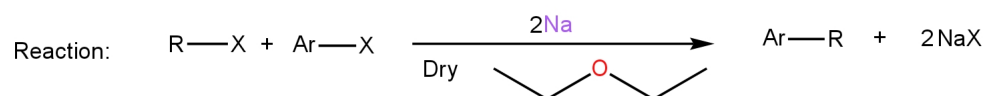


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6 Wurtz-Fittig Reaction

6.1 Reaction and Mechanism

Wurtz-Fittig Reaction

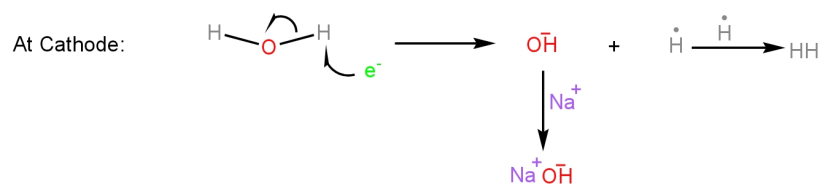
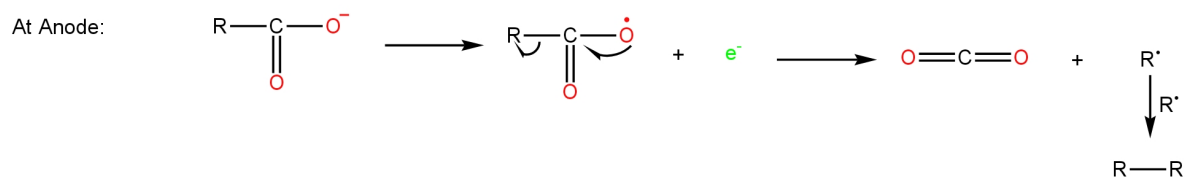
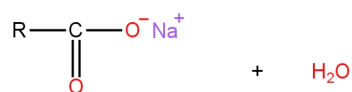


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7 Kolbe's Electrolysis

7.1 Reaction and Mechanism

Kolbe's Electrolysis



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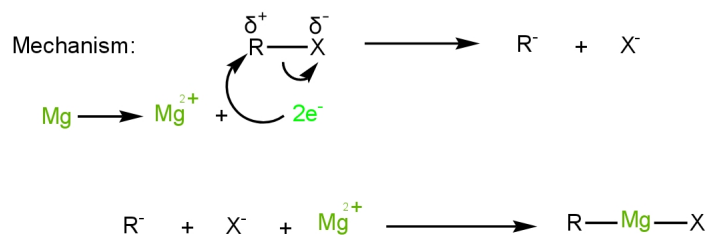
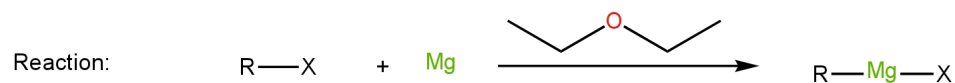
7.2 Reaction Observations

- C^\bullet obtained as intermediate.
- pH of medium increases due to formation of NaOH .
- CO_2 obtained at anode and H_2 at cathode.
- CH_4 can never be obtained.

8 Formation of Grignard's Reagent

8.1 Reaction and Mechanism

Formation of Grignard's Reagent



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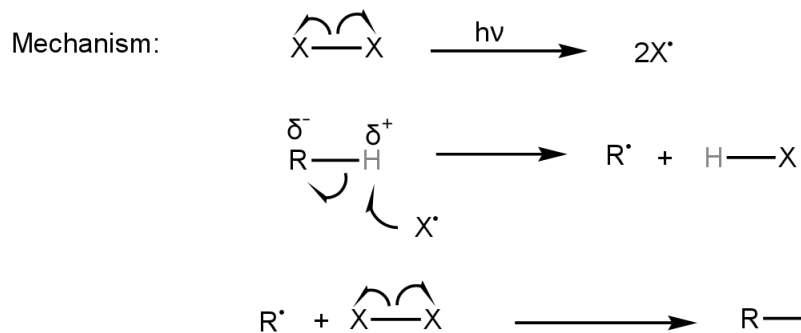
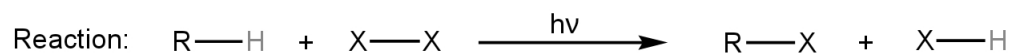
8.2 Reaction Observations

- C^- and C^\bullet obtained as intermediate.
- RMgX is also known as Organometallic Compound due to $^{12}_6\text{C}$ metal bond.
- ROR for RX , $\text{RI} > \text{RBr} > \text{RCl}$
- Reaction doesn't occur in RF
- Dry Et_2O or THF is used as solvent.

9 Photo Halogenation

9.1 Reaction and Mechanism

Photo Halogenation



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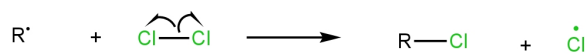
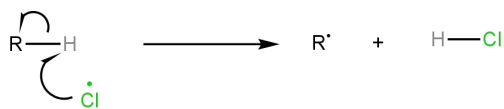
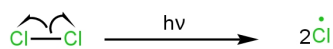
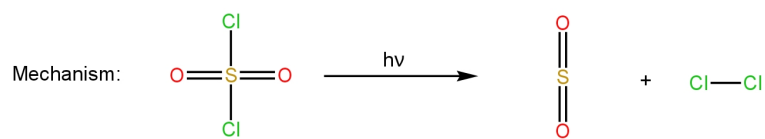
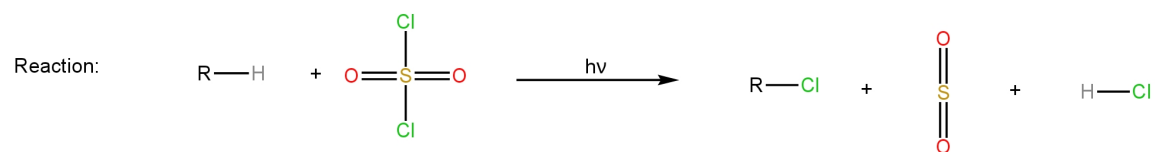
9.2 Reaction Observations

- 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. $\text{ROR} \propto \text{Stability of } \text{C}^\bullet$
- vii. ROR for X_2 , $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

10 Reed's Reaction

10.1 Reaction and Mechanism

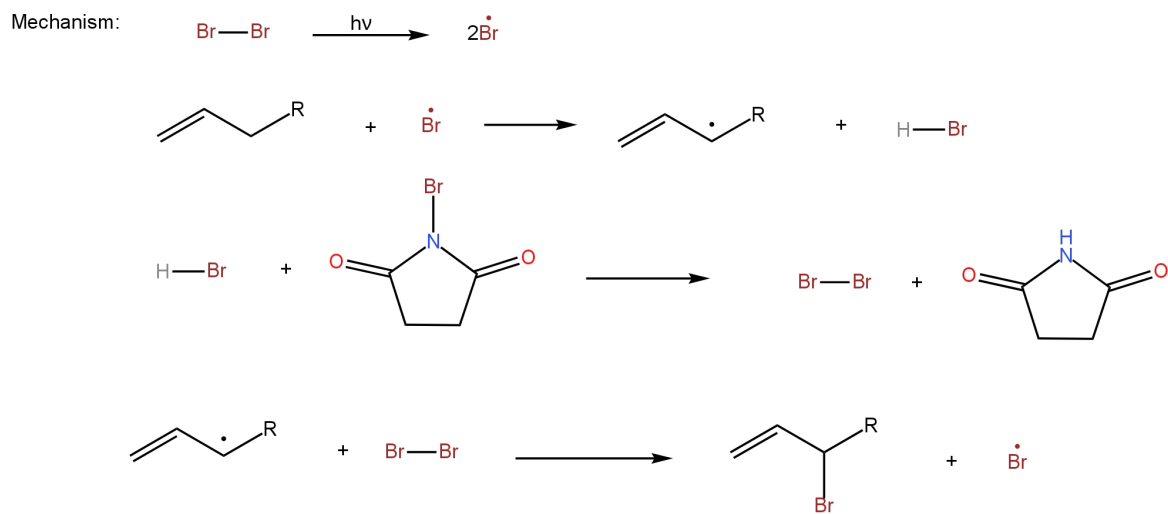
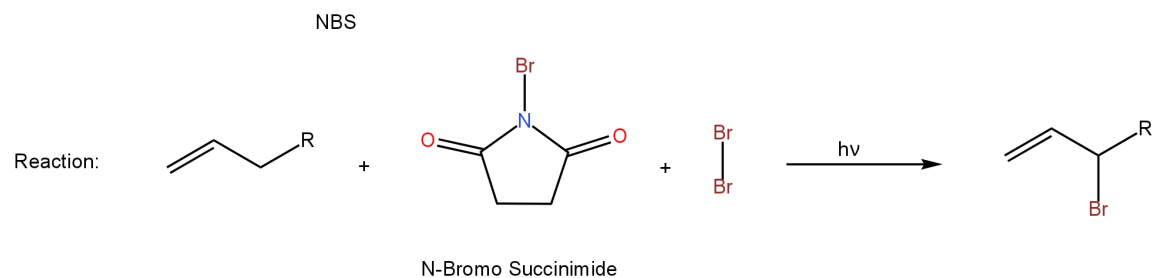
Reed's Reaction



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11 NBS

11.1 Reaction and Mechanism



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11.2 Reaction Observations

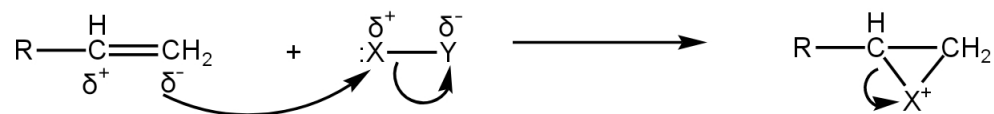
- i. Reacts only with Allylic and Benzylic positions.
- ii. C^\bullet obtained as intermediate.
- iii. Example of Substitution Reaction.
- iv. Pure NBS is inert, hence, impurity of HBr or Br_2 is added.
- v. Example of Oxidation Reaction.

12 Electrophilic Addition Reaction

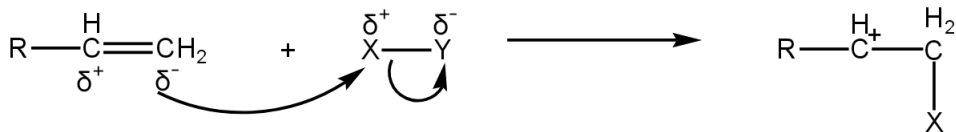
12.1 Reaction and Mechanism

Electrophilic Addition Reaction

X has lone pair



X does not have lone pair



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12.2 Reaction Observations

12.3 X doesn't have lone pair

- C^+ obtained as intermediate.
- Rearrangement can occur.

12.4 X has lone pair

- Non Classical Carbocation (NCC or Cyclohalonium ion) obtained as intermediate.
- 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
$H^+/H_2O, H_3O^+, \text{dil. } H_2SO_4$	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

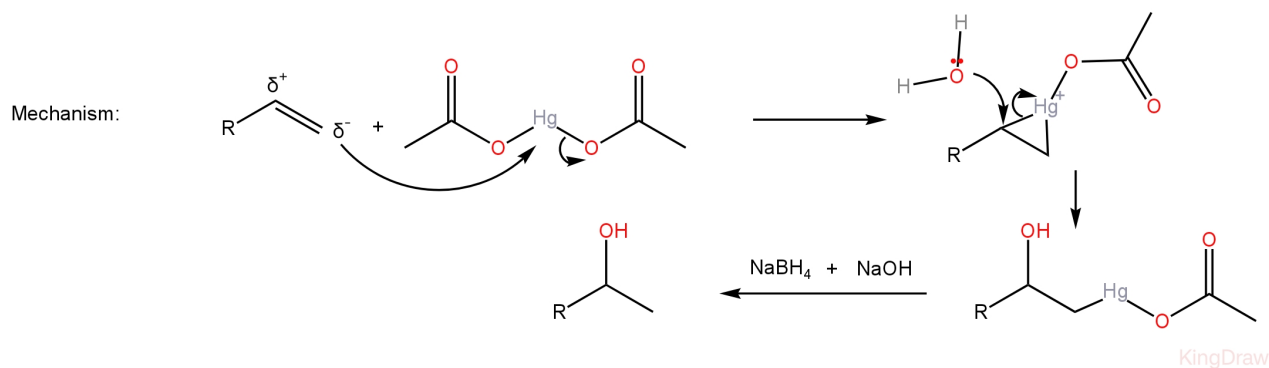
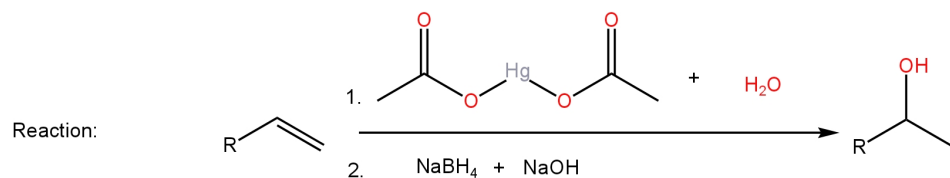
12.6 KCP and TCP

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 ($-80, -40, 0^\circ C$)	Favors high temperature

13 Oxymercuration Demercuration

13.1 Reaction and Mechanism

Oxymercuration Demercuration Reaction



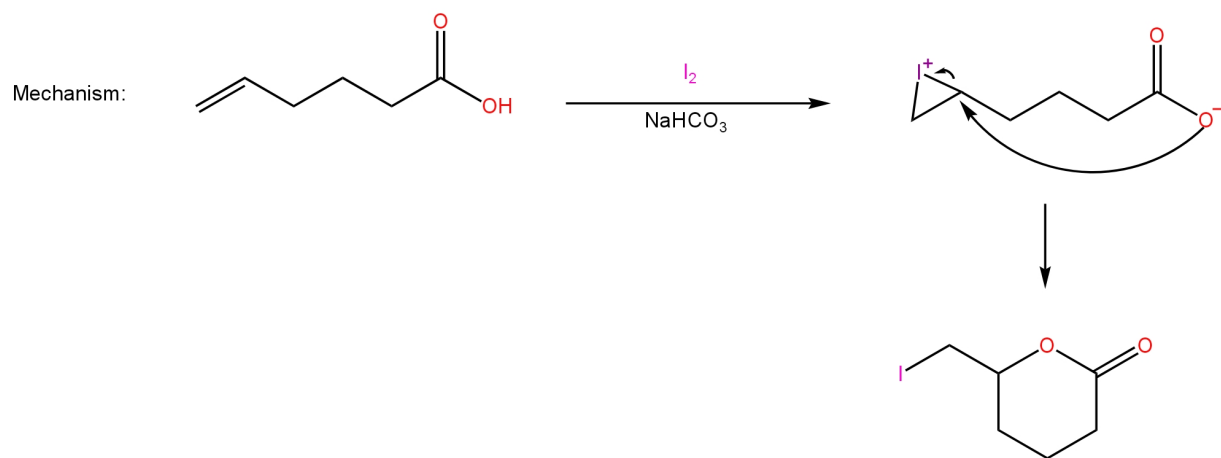
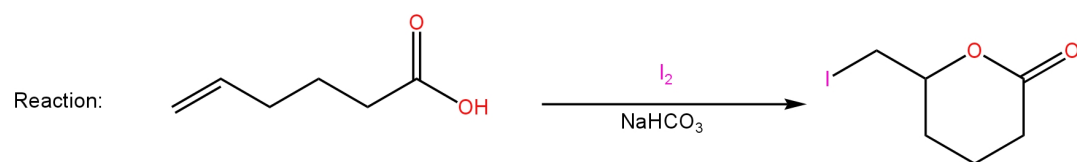
13.2 Reaction Observations

- Markonikov addition.
- No rearrangement.
- Both Syn and anti addition.
- OM is anti addition, DM involves C^\bullet , hence both syn and anti addition.
- Metal Hg^\bullet is obtained.

14 Iodolactonization

14.1 Reaction and Mechanism

Iodolactonization

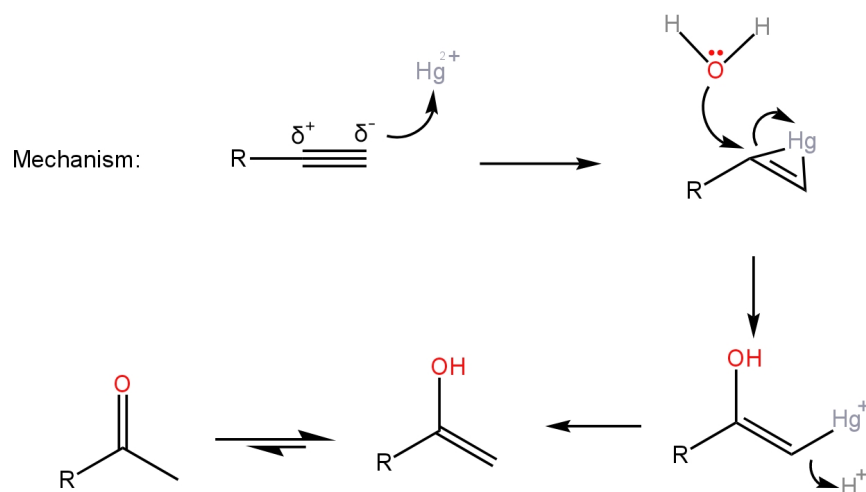


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15 Kuchrov's Reaction

15.1 Reaction and Mechanism

Kuchrov's Reaction



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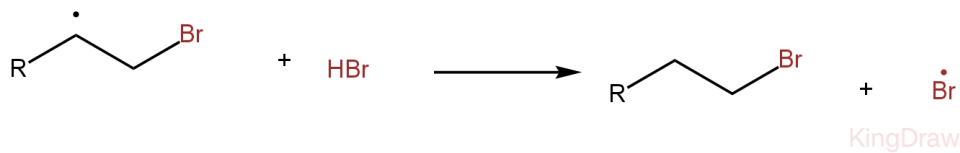
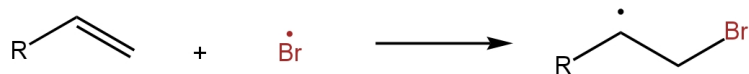
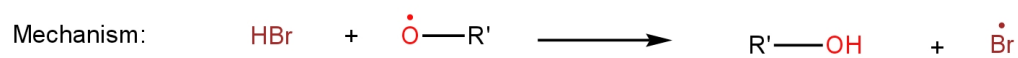
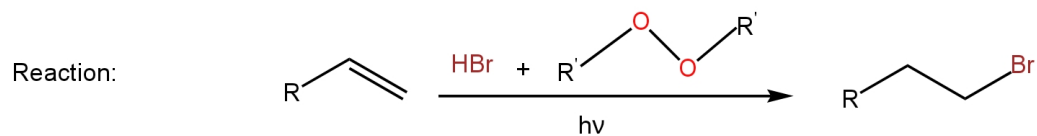
15.2 Reaction Observations

- Example of Electrophilic Addition Reaction.
- NCC type intermediate is obtained.
- Involves tautomerism.
- Mixed carbonyl are obtained.

16 Kharasch Effect

16.1 Reaction and Mechanism

Kharash Effect



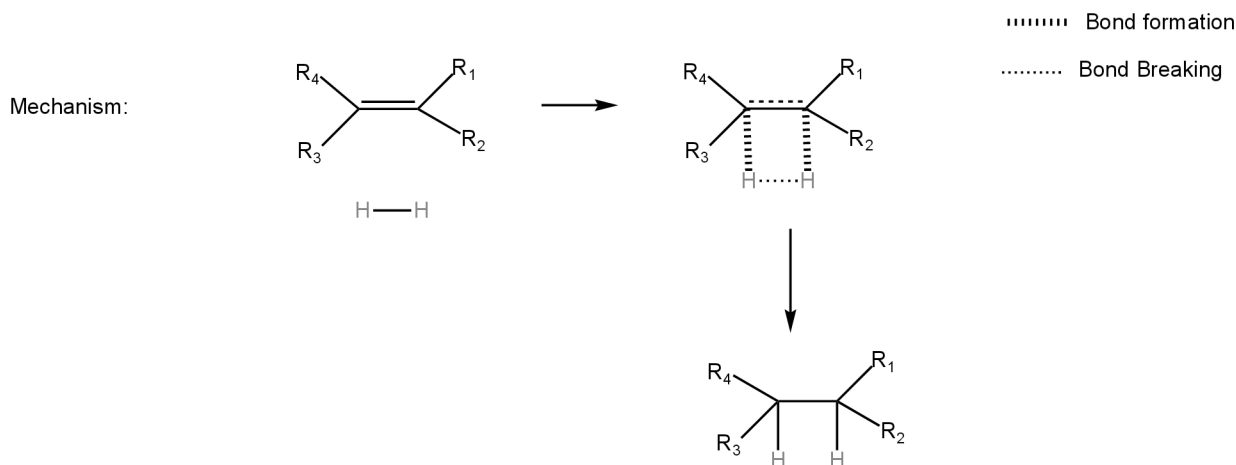
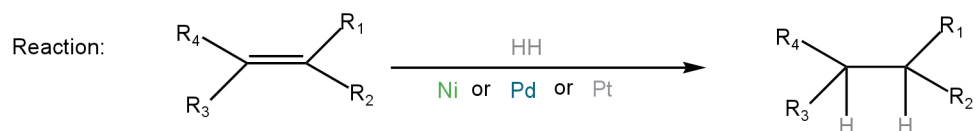
16.2 Reaction Observations

- C^\bullet obtained as intermediate.
- Example of C^\bullet addition Reaction.
- Anti-markonikov addition
- Only HBr shows peroxide effect (Kharasch Effect).

17 Catalytic Hydrogenation

17.1 Reaction and Mechanism

Catalytic Hydrogenation



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17.2 Reaction Observations

- i. Example of addition and Redox reaction.
- ii. syn addition
- iii. Example of surface phenomenon and involves 4 MCTS.
- iv. Pd/BaSO_4 a.k.a Lindlar's Catalyst and Quinoline is added as poison.
- v. In case of conjugated diene, 1,4 addition takes place due to 6 MCTS.
- vi. Reactivity,
 $C-S \text{ bond} > \text{Alkyne} > Ar-NO_2 > R-COCl > \text{Alkene} > RCHO > RCOR > \text{Benzene}^* > RCOOH^* < \text{acid derivative}^*$
 $\propto \frac{1}{\text{Steric Hindrance}}$

* require heat

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

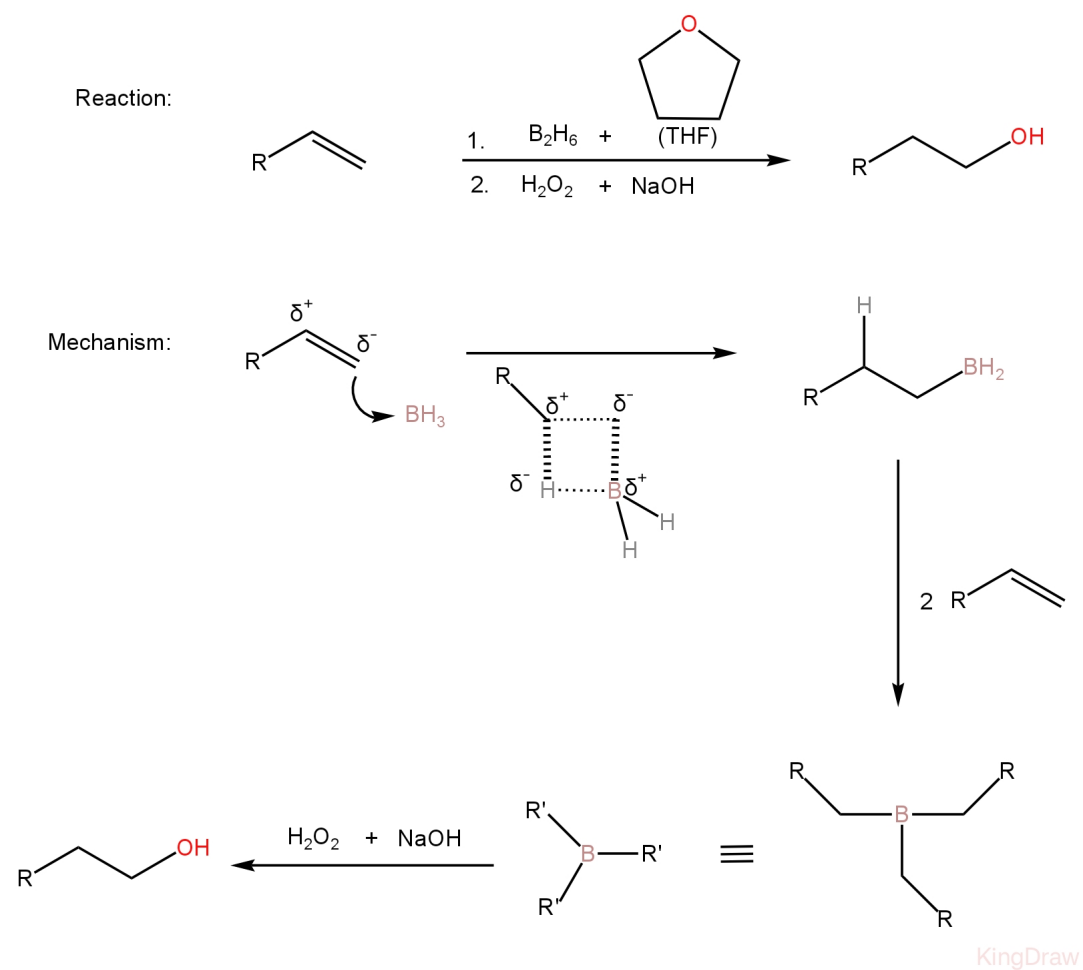
18 Rosenmund Reaction

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19 Hydroboration Oxidation

19.1 Reaction and Mechanism

Hydroboration Oxidation



19.2 Reagent Table

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

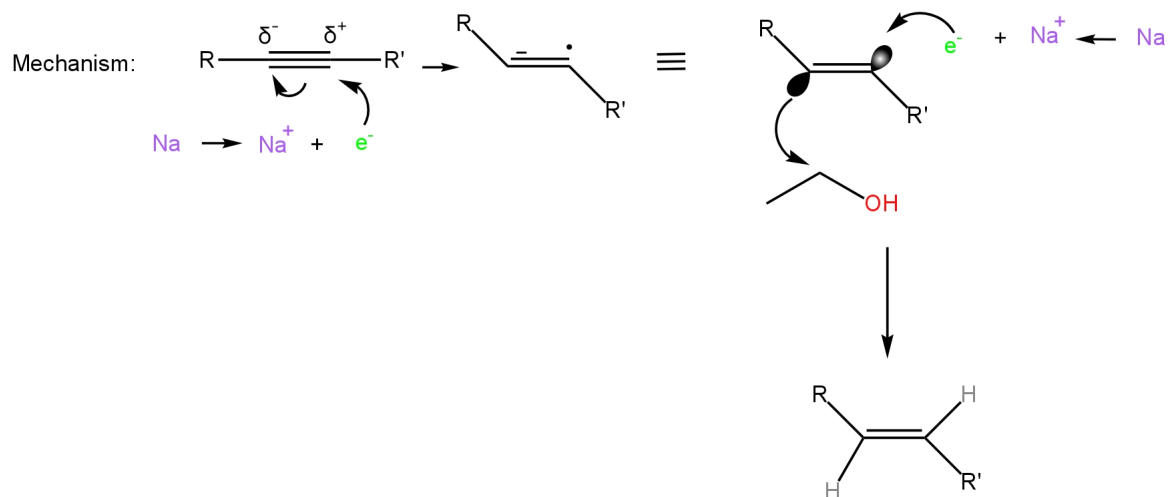
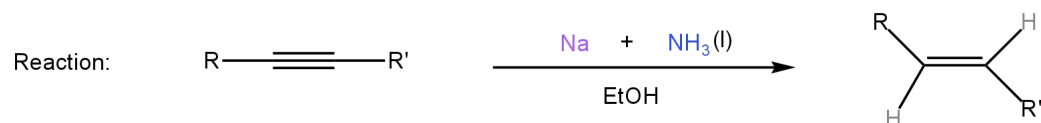
19.3 Reaction Observations

- Syn addition.
- Anti-markonikov addition.
- Involves 4MCTS.
- In case of acid or water, reduction occurs.
- Generally, 3 *mol.* alkene is required for 1 *mol.* BH_3
- 9 – BBN, Sia_2BH is used for selective addition on less crowded terminal alkene.

20 Birch Reduction

20.1 Reaction and Mechanism

Birch Reduction



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20.2 Reaction Observations

- $\text{Na}/\text{NH}_3(l)$ is a blue color solution.
- Both C^{\bullet} and C^- obtained as intermediate.
- ROH is used as proton source.
- Terminal Alkyne will not give alkene, acid base reaction will occur.
- In case of substituted benzene, more stable alkene is major product.