

# 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.

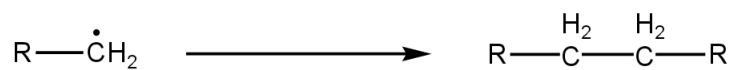
ii. **Disproportionation**

In case of  $3^\circ$  radical combination is not possible, hence disproportionation occurs.

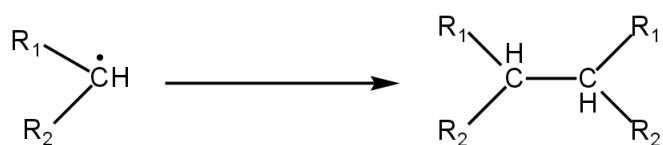
### 1.2 Important facts about Free Radicals

- 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.

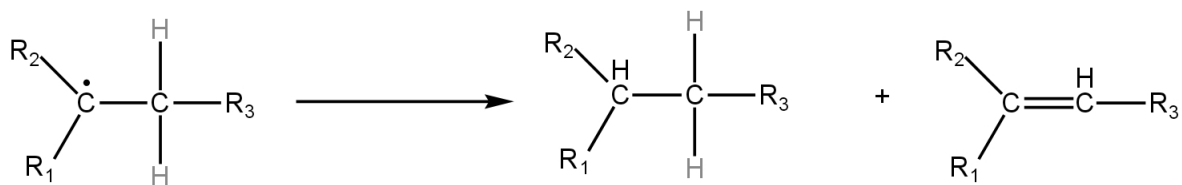
1° Radical Combination



2° Radical Combination



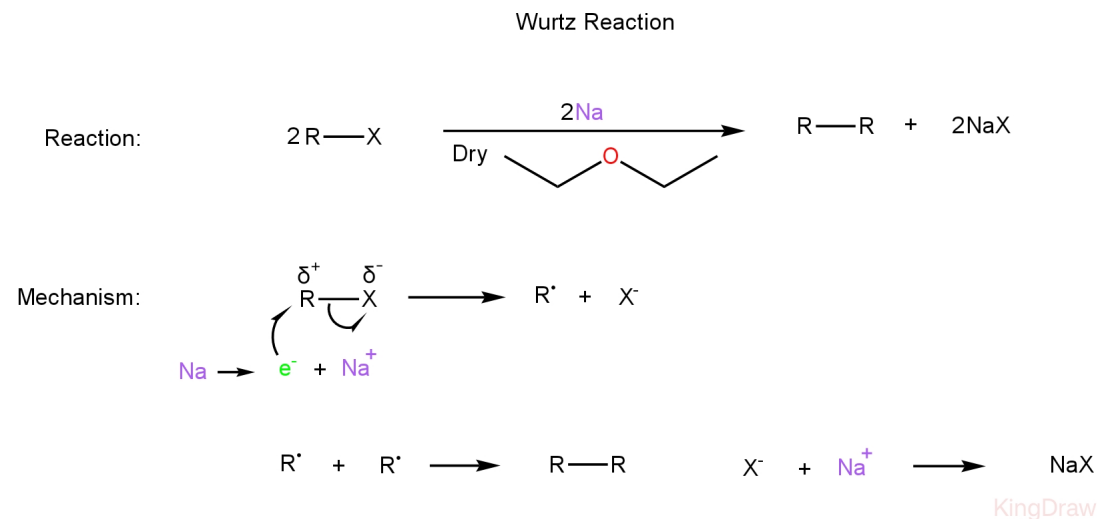
3° Radical Disproportionation



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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 (+).

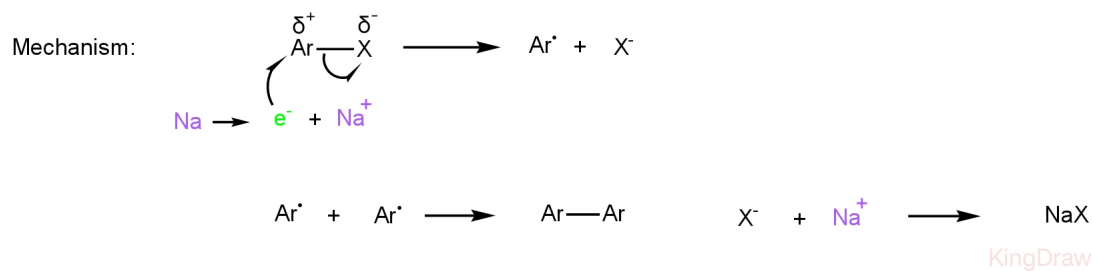
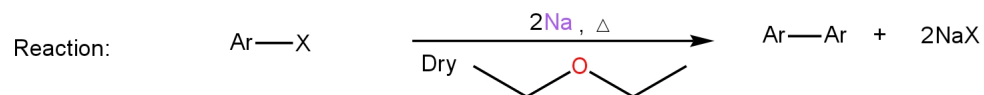
### 2.4 Reaction Observations

- i. Free radical or  $C^\cdot$  obtained as intermediate.
- ii. Breaking of  $RX$  bond is RDS.
- iii.  $ROR$  for  $RX$ ,  $RI > RBr > RCl$
- iv.  $Stability\ of\ R^\cdot \propto ROR$
- 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

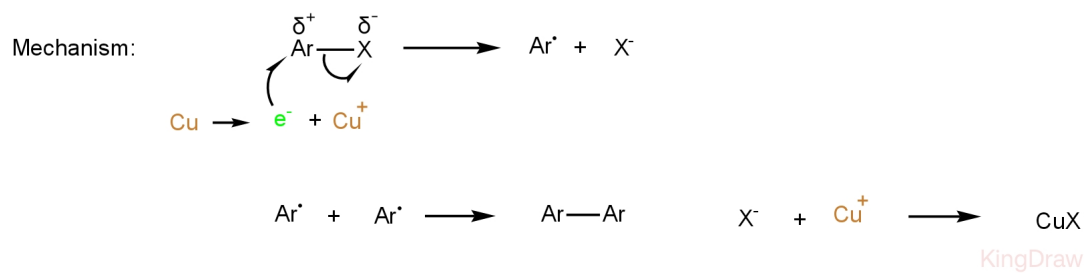
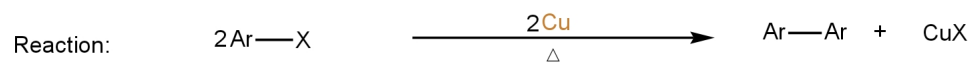
##### Fittig Reaction



### 4 Ulmann Reaction

#### 4.1 Reaction and Mechanism

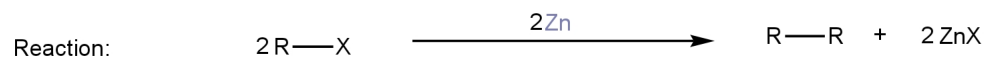
##### Ulmann Reaction



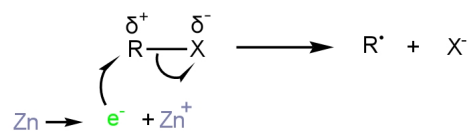
## 5 Frankland Reaction

### 5.1 Reaction and Mechanism

#### Frankland Reaction



Mechanism:

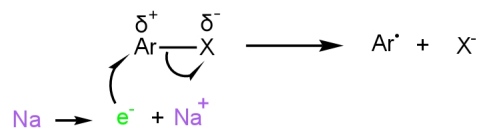
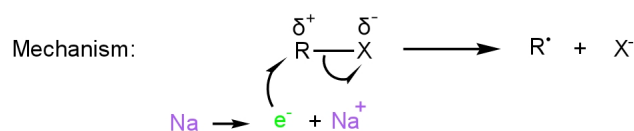
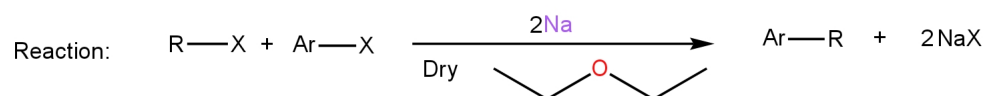


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## 6 Wurtz-Fittig Reaction

### 6.1 Reaction and Mechanism

Wurtz-Fittig Reaction

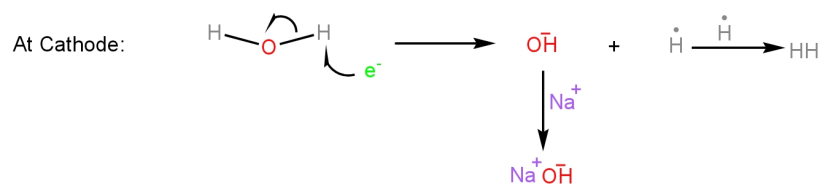
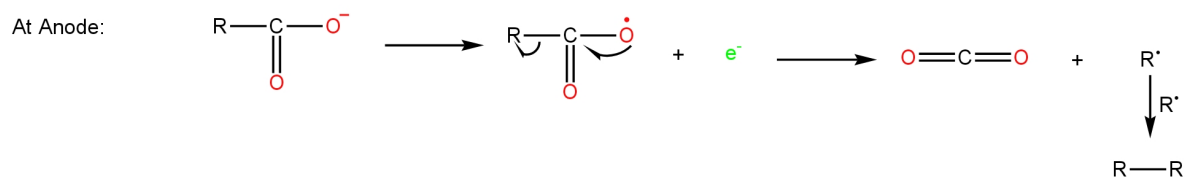
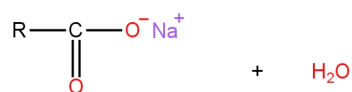


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## 7 Kolbe's Electrolysis

### 7.1 Reaction and Mechanism

Kolbe's Electrolysis



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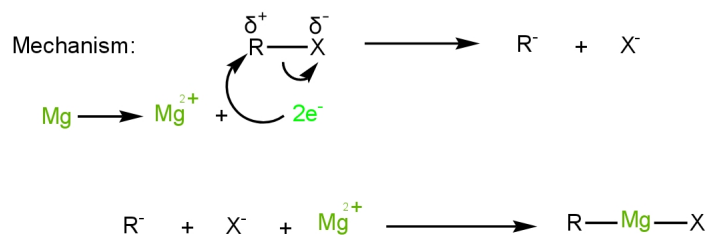
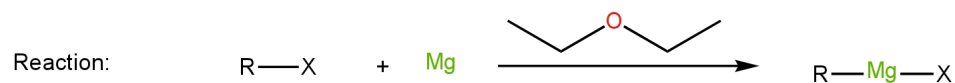
### 7.2 Reaction Observations

- i.  $\text{C}^\bullet$  obtained as intermediate.
- ii.  $pH$  of medium increases due to formation of  $\text{NaOH}$ .
- iii.  $\text{CO}_2$  obtained at anode and  $\text{H}_2$  at cathode.
- iv.  $\text{CH}_4$  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

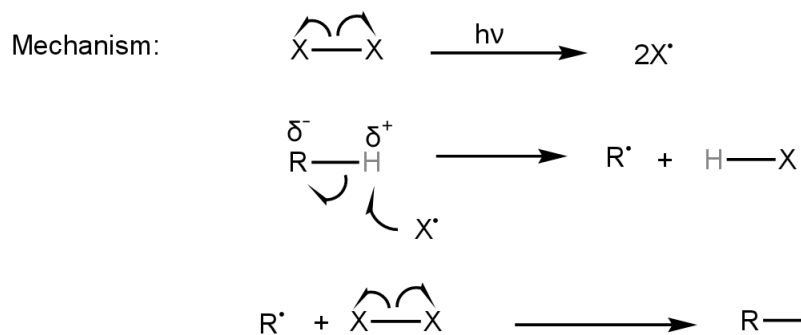
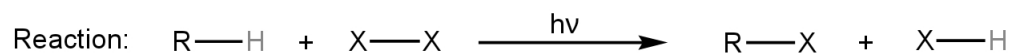
- $\text{C}^-$  and  $\text{C}^\bullet$  obtained as intermediate.
- $\text{RMgX}$  is also known as Organometallic Compound due to  $^{12}_6\text{C}$  metal bond.
- $\text{ROR}$  for  $\text{RX}$ ,  $\text{RI} > \text{RBr} > \text{RCl}$
- Reaction doesn't occur in  $\text{RF}$
- Dry  $\text{Et}_2\text{O}$  or  $\text{THF}$  is used as solvent.



## 9 Photo Halogenation

### 9.1 Reaction and Mechanism

#### Photo Halogenation



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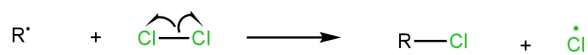
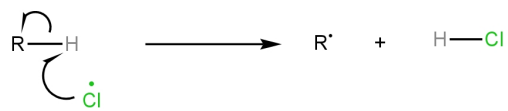
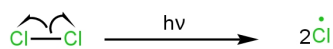
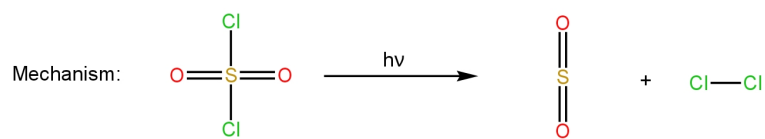
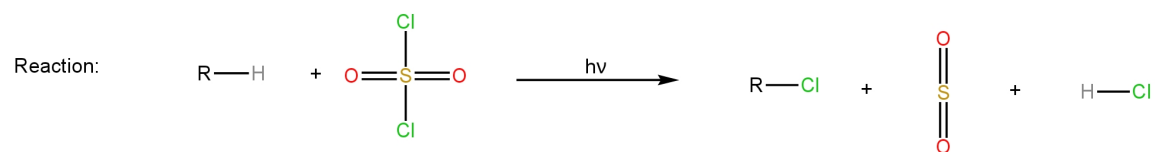
### 9.2 Reaction Observations

- $\text{C}^\bullet$  obtained as intermediate.
- Example of  $\text{C}^\bullet$  substitution reaction.
- Kinetic isotopic effect is observed.
- Example of Oxidation reaction.
- Formation of  $\text{C}^\bullet$  is RDS.
- $\text{ROR} \propto \text{Stability of } \text{C}^\bullet$
- $\text{ROR}$  for  $\text{X}_2$ ,  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

## 10 Reed's Reaction

### 10.1 Reaction and Mechanism

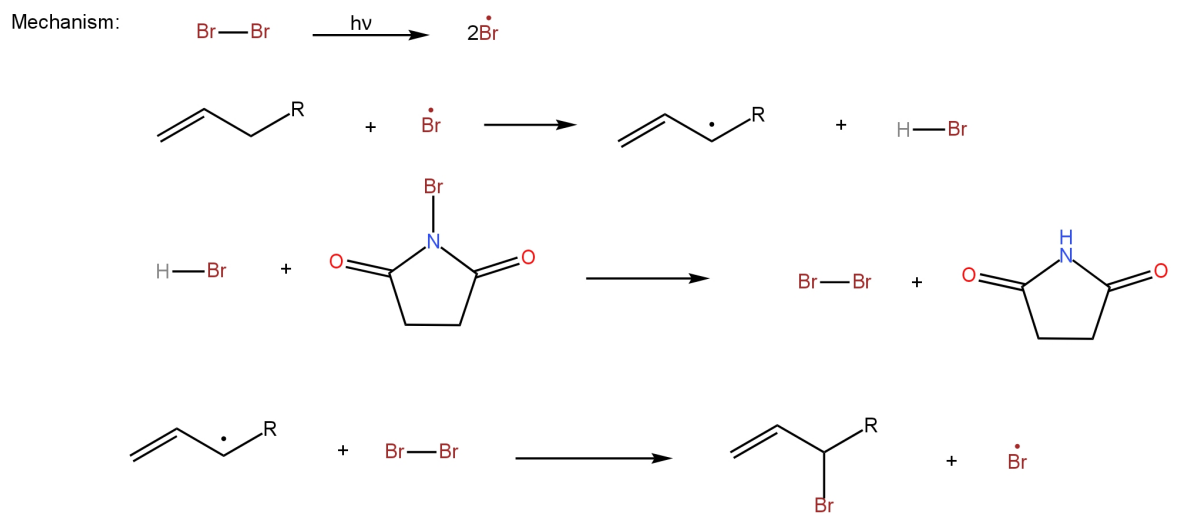
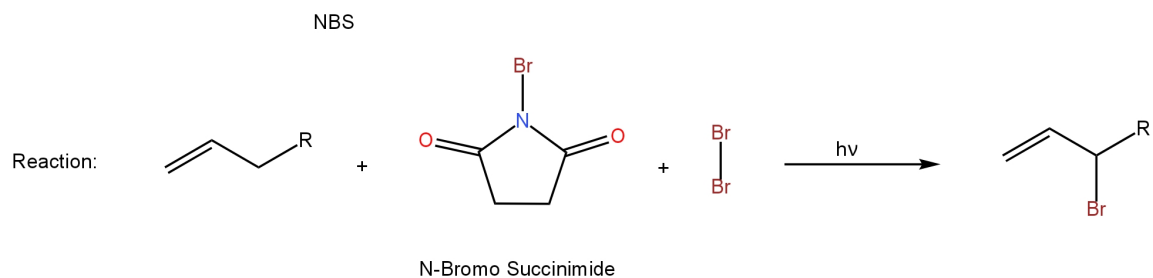
#### Reed's Reaction



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## 11 NBS

### 11.1 Reaction and Mechanism



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### 11.2 Reaction Observations

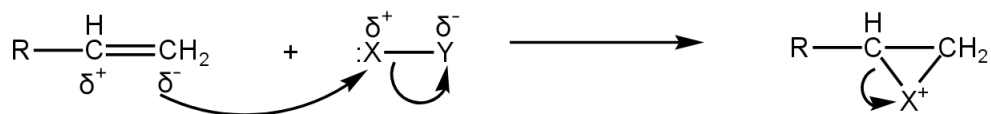
- Reacts only with Allylic and Benzylic positions.
- $\text{C}^\bullet$  obtained as intermediate.
- Example of Substitution Reaction.
- Pure NBS is inert, hence, impurity of  $\text{HBr}$  or  $\text{Br}_2$  is added.
- Example of Oxidation Reaction.

## 12 Electrophilic Addition Reaction

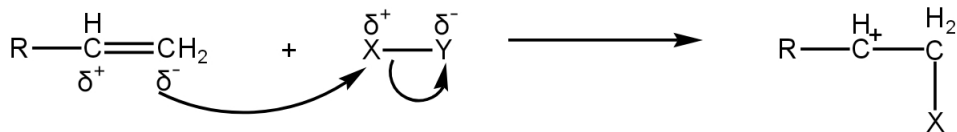
### 12.1 Reaction and Mechanism

#### 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

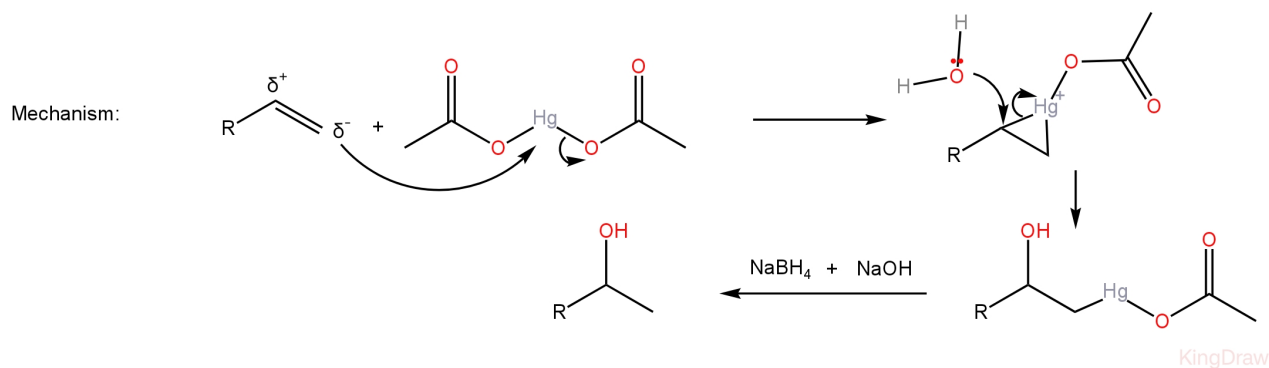
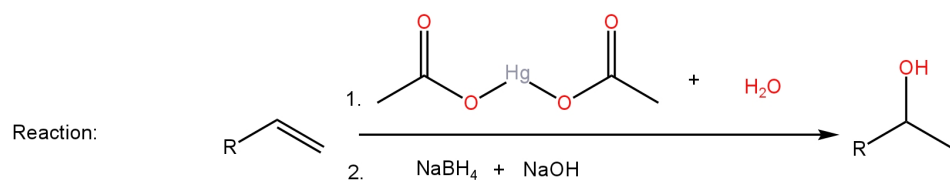
## 12.6 KCP and TCP

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



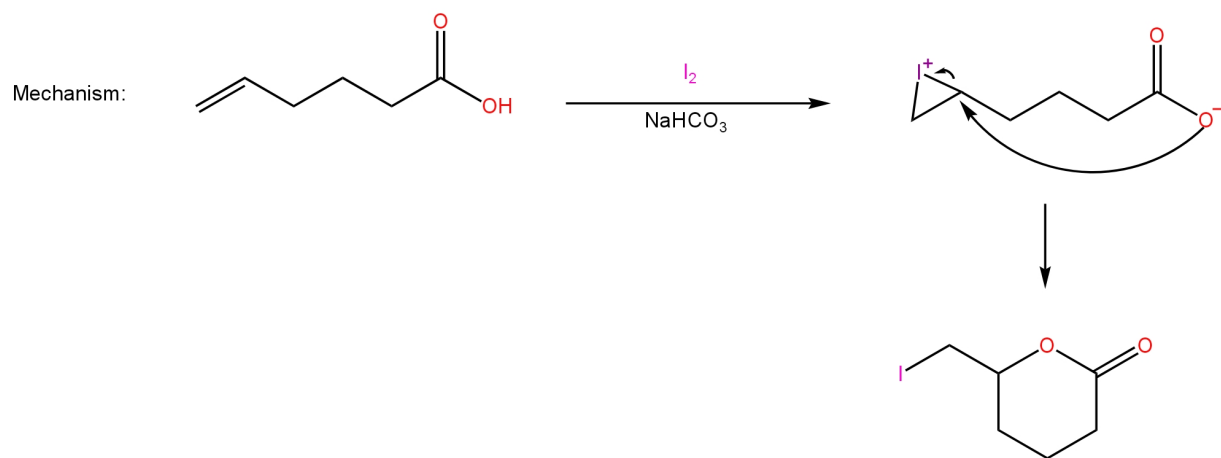
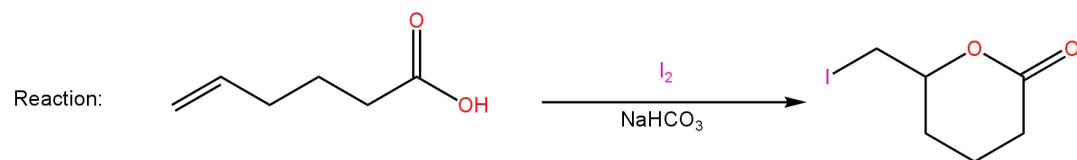
### 13.2 Reaction Observations

- i. Markonikov addition.
- ii. No rearrangement.
- iii. Both Syn and anti addition.
- iv. OM is anti additon, DM involves  $\text{C}^\bullet$ , hence both syn and anti addition.
- v. Metal  $\text{Hg}^\bullet$  is obtained.

## 14 Iodolactonization

### 14.1 Reaction and Mechanism

Iodolactonization

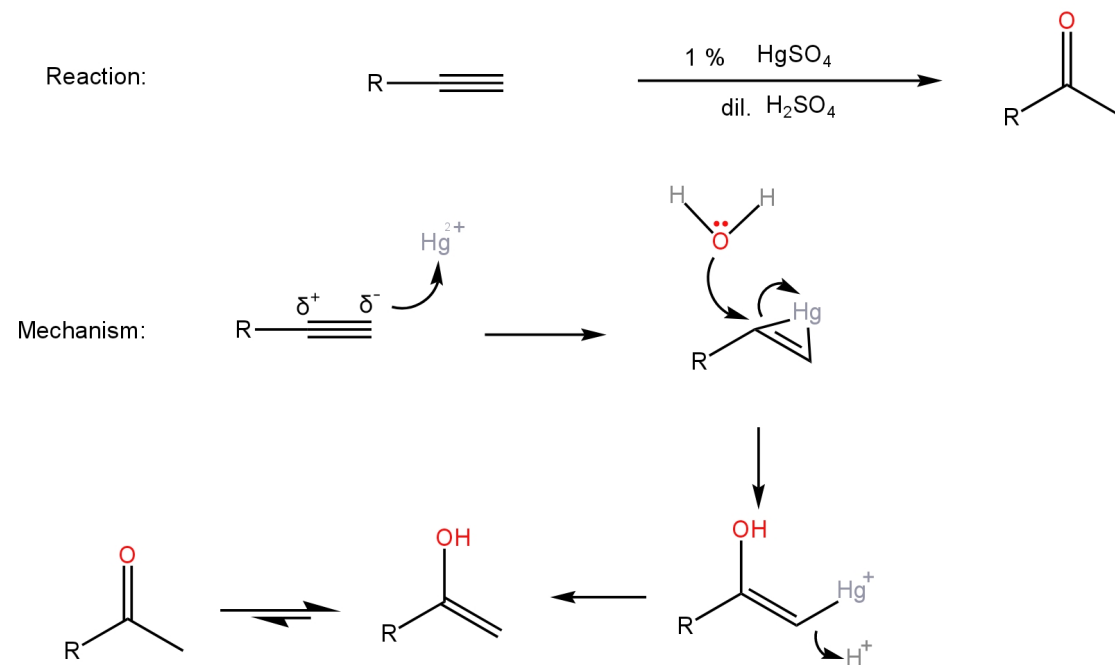


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## 15 Kuchrov's Reaction

### 15.1 Reaction and Mechanism

Kuchrov's Reaction



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### 15.2 Reaction Observations

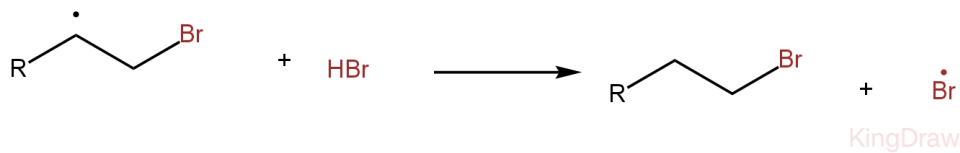
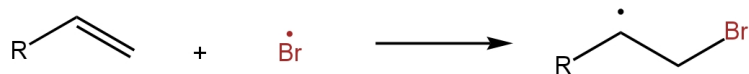
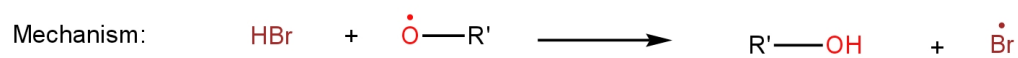
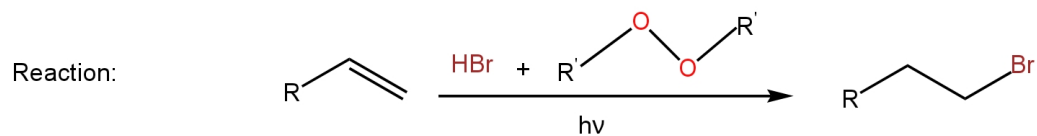
- Example of Electrophilic Addition Reaction.
- NCC type intermediate is obtained.
- Involves tautomerism.
- Mixed carbonyl compounds are obtained.



## 16 Kharasch Effect

### 16.1 Reaction and Mechanism

Kharasch Effect



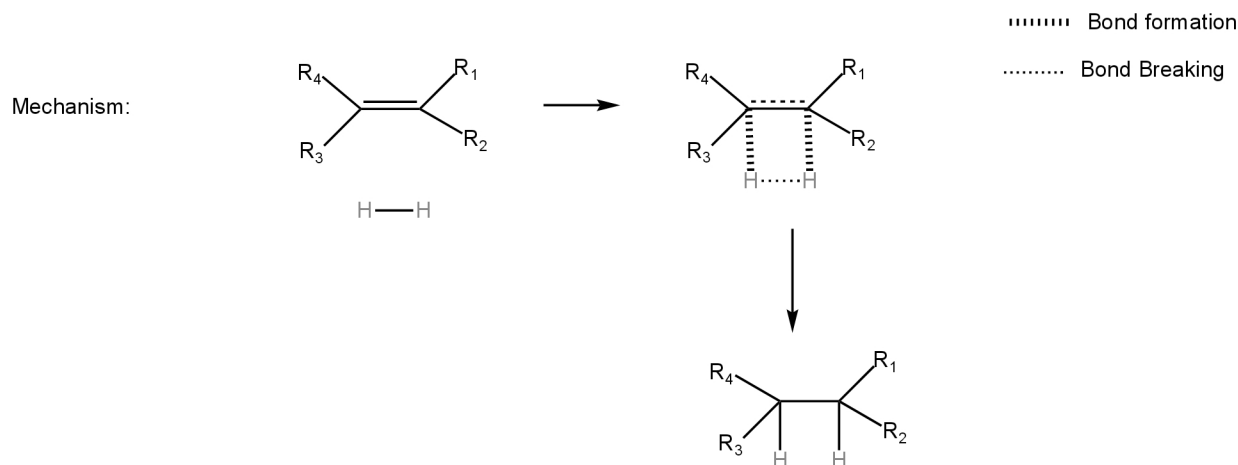
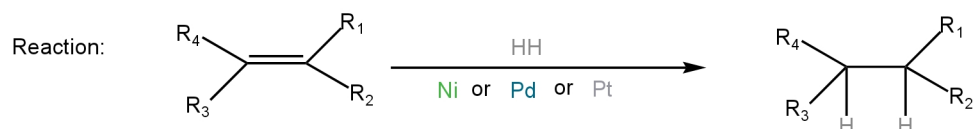
### 16.2 Reaction Observations

- $\text{C}\cdot$  obtained as intermediate.
- Example of  $\text{C}\cdot$  addition Reaction.
- Anti-markonikov addition
- Only  $\text{HBr}$  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.  $\text{Pd}/\text{BaSO}_4$  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,  
 $C-S \text{ bond} > \text{Alkyne} > \text{Ar}-\text{NO}_2 > \text{R}-\text{COCl} > \text{Alkene} > \text{RCHO} > \text{RCOR} > \text{Benzene}^* > \text{RCOOH}^* < \text{acid derivative}^*$  \* require heat  
 $\propto \frac{1}{\text{Steric Hindrance}}$

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

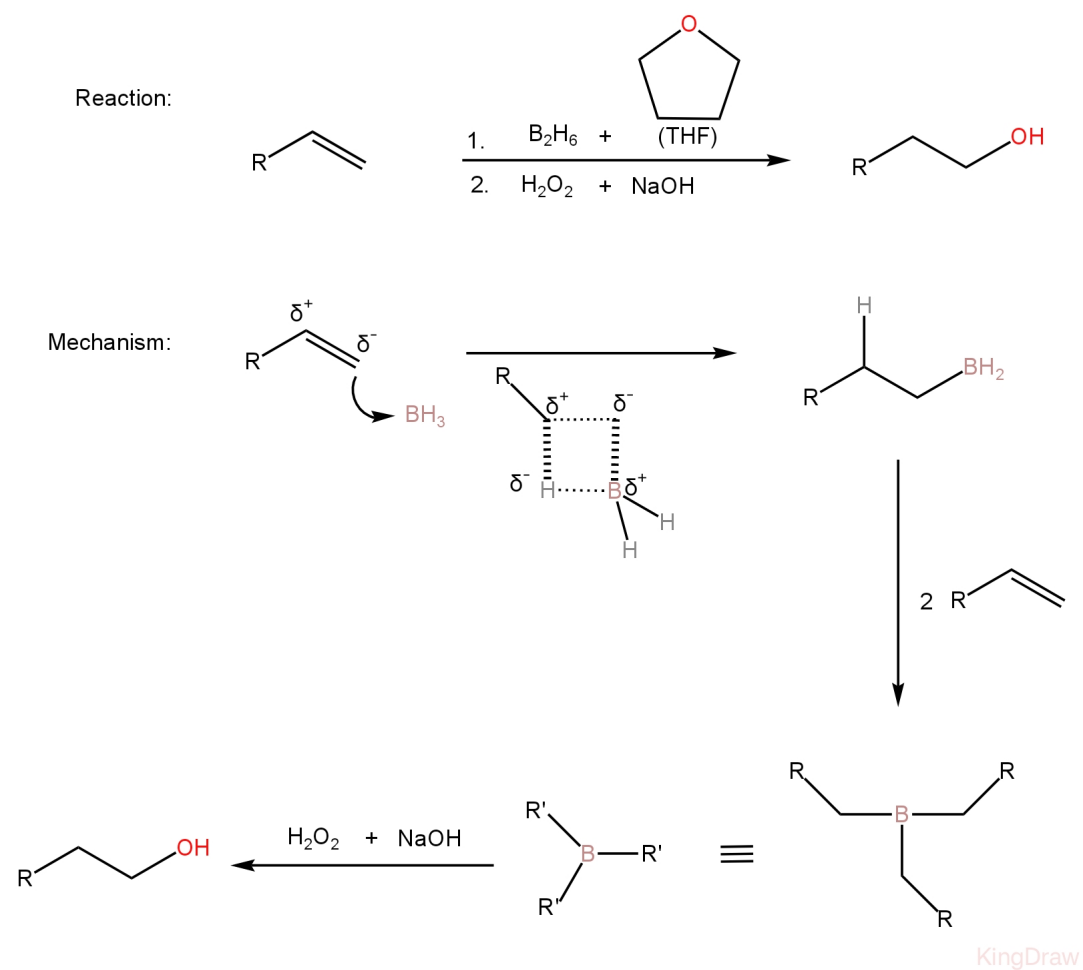
## 18 Rosenmund Reaction

*onhold*

## 19 Hydroboration Oxidation

### 19.1 Reaction and Mechanism

Hydroboration Oxidation



## 19.2 Reagent Table

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

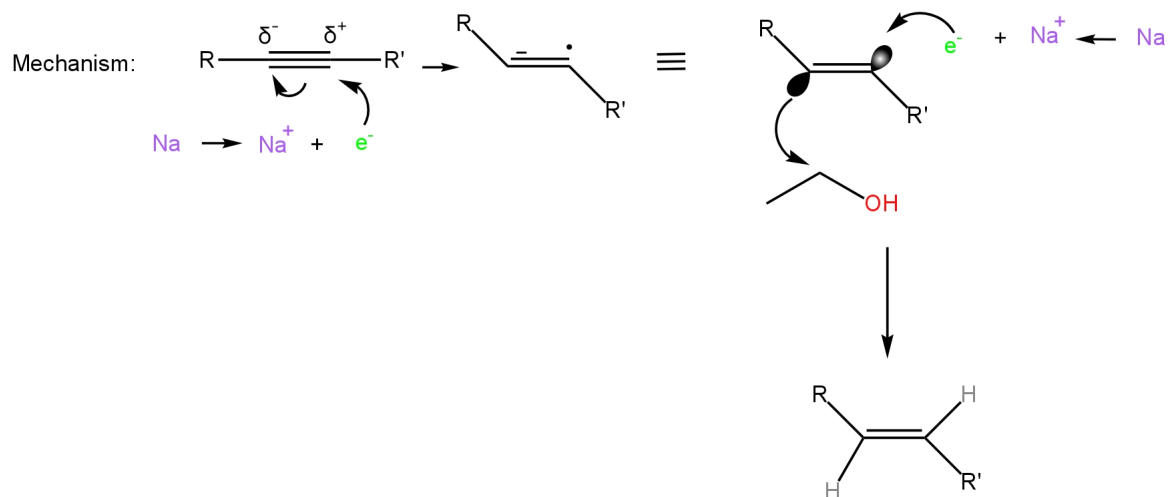
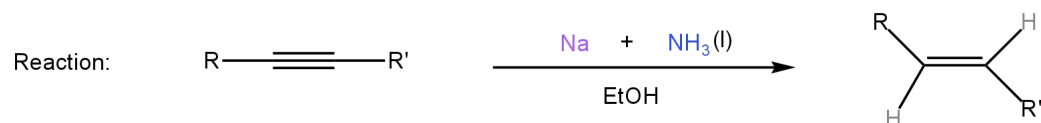
## 19.3 Reaction Observations

- 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  $\text{C}^\bullet$  and  $\text{C}^-$  obtained as intermediate.
- $\text{ROH}$  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.