



Alkyl Halide

Organic Chemistry

Chemical Properties

Nucleophilic Substitution Reactions

1. Hydrolysis (Formation of Alcohol)- $R-OH$
2. Formation of Ether (Williamson's Synthesis)- $R-OR$
3. Formation of Alkane Nitrile- $R-CN$
4. Formation of Alkane Isonitrile- $R-NC$
5. Formation of Alkane Nitrite- $R-ONO$
6. Formation of Nitro Alkane- $R-NO_2$
7. Formation of Amine – $R-NH_2$

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Chemical Properties of Alkyl Halide



Chemical Reaction of Alkyl Halide

I. Nucleophilic Substitution Reactions ✓

II. Elimination Reaction

III. Reaction with Metal



I. Nucleophilic Substitution Reactions

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Reagent

H₂O, KOH

RO-Na

KCN

AgCN

KONO

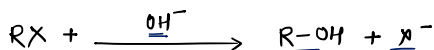
AgONO

NH₃

Chemical Properties of Alkyl Halide

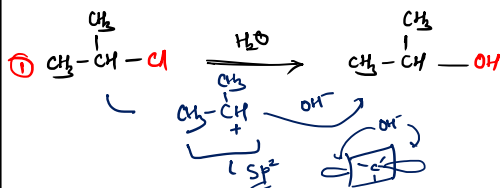


1. Hydrolysis (Formation of Alcohol)- R-OH



Reagent-

- ↳ H_2O - SN^1R , 3° Alkyl halide prefer
 - ↳ dry $NaOH$
 - ↳ dry KOH
 - ↳ moist $AgOH$
 - ↳ moist Ag_2O
- } - Strong Nu^- - SN^2R
 1° Alkyl halide



- ✓ SN^1 Reaction Mechanism - depends on C^+ stability
- C^+ Intermediate
- ✓ Weak nucleophile attack
- Retention (front attack) & Inversion (back attack) possible

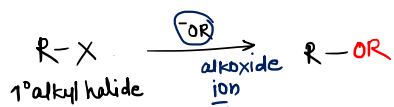


- ✓ SN^2 Reaction Mechanism
- stability $\propto 1/\text{steric hindrance}$
- Strong Nu^- attack
- ✓ Inversion (Back side) attack

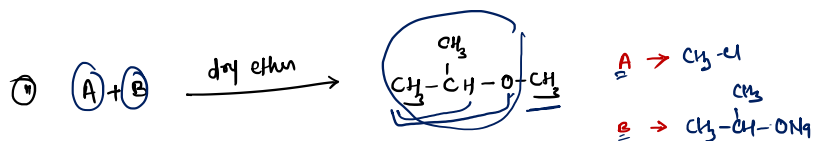
Chemical Properties of Alkyl Halide



2. Formation of Ether- R-OR (Williamson's Synthesis)



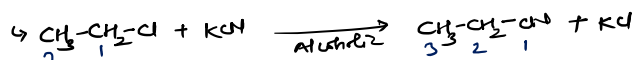
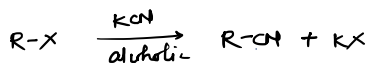
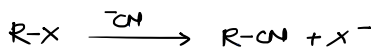
- ✓ SN^2 Reaction Mech.
- * Alkyl halide should be 1°



Chemical Properties of Alkyl Halide



3. Formation of Alkyl cyanide/Alkane Nitrile- R-CN



K-CN Mechanism -

↳ CN⁻ → Strong Nu⁻

↳ S_N² mechanism

↳ Ascent of chain - ⊖ ?

4. Formation of Alkyl Isocyanide/Alkane isonitrile- R-NC



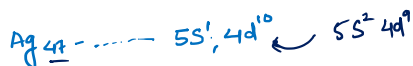
R-NC (R- $\overset{+}{N}\equiv C$)
 Ag-C≡N # Fazari's Rule → Covalent character in ionic bond

↳ Small ⊕ & Large ⊖

↳ Pseudo noble gas configuration of cation

K-CN → Ionic bond, attack from C-side

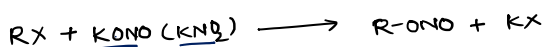
Ag-CN → Covalent bond character - attack from N-side



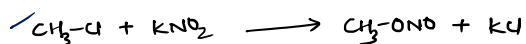
Chemical Properties of Alkyl Halide



5. Formation of Alkyl nitrite/Alkane Nitrite- R-ONO

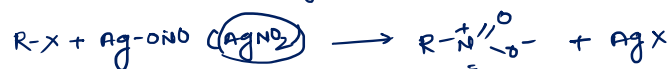


S_N²



6. Formation of Nitro Alkane R-NO₂

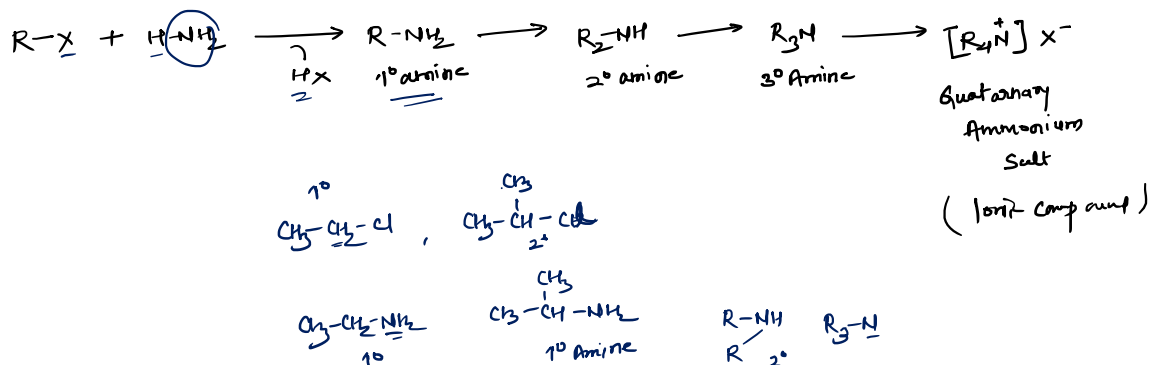
S_N²



Chemical Properties of Alkyl Halide



7. Formation of Amine, R-NH₂



Alkyl Halide



Organic Chemistry Chemical Properties

Elimination Reactions

E1 and E2

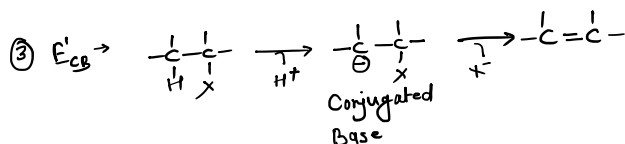
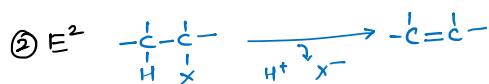
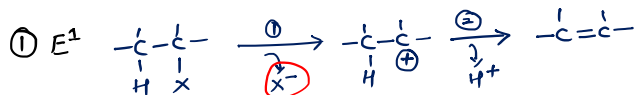
Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide



- ✓ Smaller Group/atom are eliminated
- ✓ Saturated to unsaturated
- ✓ Endothermic $\Delta H > 0$, High temp $50-80^\circ\text{C}$
- ✓ Spontaneous at high temp
- ✓ Alfa-Beta elimination
- ✓ Alfa-gama elimination

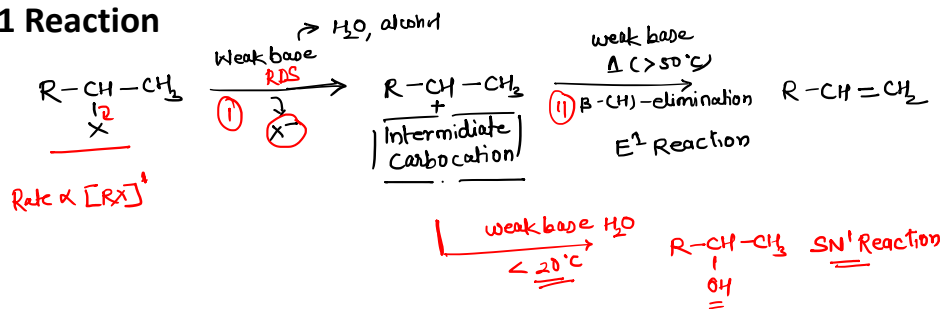


Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E1 Reaction

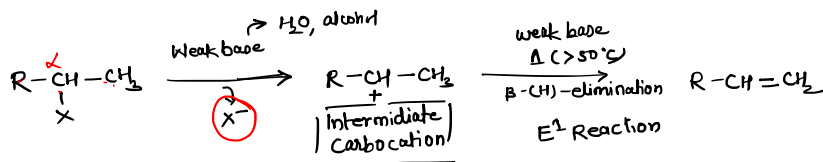


Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E1 Reaction



Imp Points: -

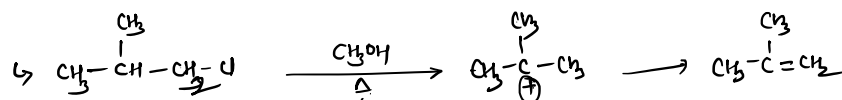
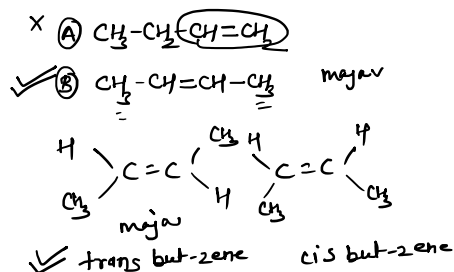
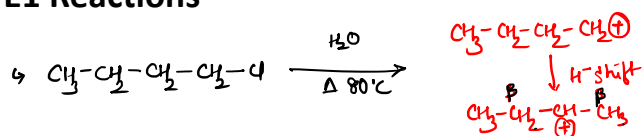
- 1) Occurs in +ve of weak base - H_2O , $\text{C}_2\text{H}_5\text{OH}$, also act as solvent
- 2) Nature of solvent \rightarrow Polar Protic \rightarrow solvation of X^-
 \rightarrow break the R-X bond
- 3) Rate \rightarrow α stability of C^+ \rightarrow $3^\circ >$ benzylic $>$ allylic $>$ $2^\circ >$ 1° , alkyl halide
 α tendency of leaving group - $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
- 4) β -H elimination \rightarrow Saytzeff Rule \rightarrow stable alkene
 \rightarrow eliminate from C-atom which contain lowest H atom
- 5) C^+ Intermediate, Rearrangement
 $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$, H shift $>$ PR^- shift $>$ CH_3^- shift

Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E1 Reactions

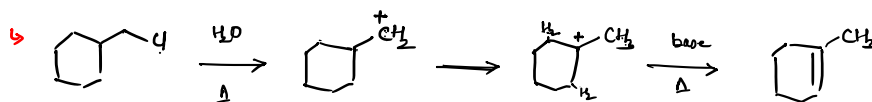


Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E1 Reactions

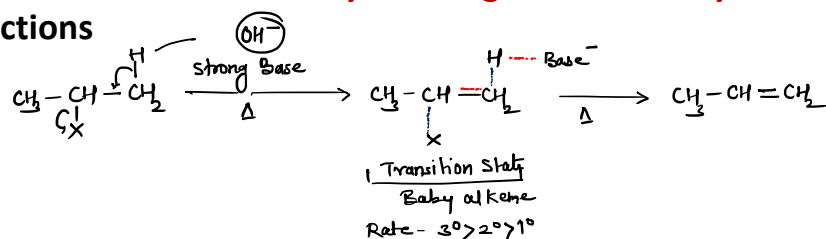


Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E2 Reactions

Imp. Point

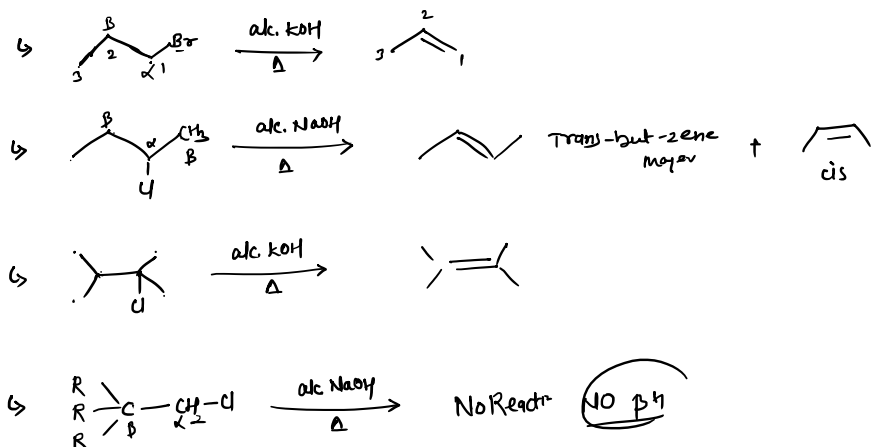
- (i) Occurs in tce of strong Base - alc NaOH, alc KOH, $\text{NaNH}_2/\text{NH}_3$
- (ii) Endothermic $\Delta H > 0$, at High temp.
- (iii) Single step reaction, Rate $\propto [\text{RX}][\text{KOH}]$, 2nd order kinetic
- (iv) No C^+ , transition state - bulky alkene, Saytzeff product-
- (v) solvent - Polar Aprotic
- (vi) Rate $\rightarrow 3^\circ > 2^\circ > 1^\circ$ Rx
Rx = $\text{R}_1 > \text{R}_2 > \text{R}_3 > \text{R}_4 > \text{R}_5$

Chemical Properties of Alkyl Halide



Elimination Reactions or Dehydrohalogenation of alkyl Halide

E2 Reactions



Alkyl Halide



Organic Chemistry Chemical Properties

Reaction with
Metals
(Na, Zn, Li, Mg)

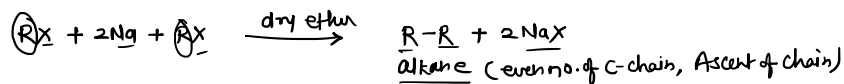
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Chemical Properties of Alkyl Halide



Reaction with Metal

1. Reaction with Sodium \Rightarrow Wurtz Reaction



2. Reaction with Zinc \Rightarrow Frankland Reaction



3. Reaction with Lithium



Dialkyl lithium-cuprate
Gilman's Reagent
 Used in Corey House Synthesis
 (odd C-chain Alkane)

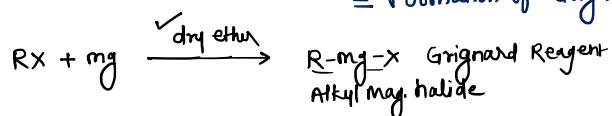
Chemical Properties of Alkyl Halide



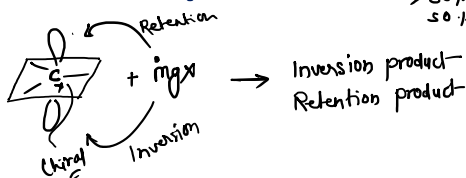
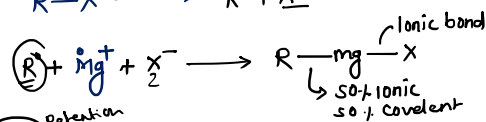
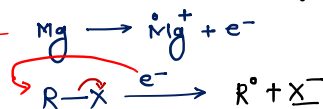
Reaction with Metal

2. Reaction with Magnesium

= Formation of Grignard's Reagent



Mechanism

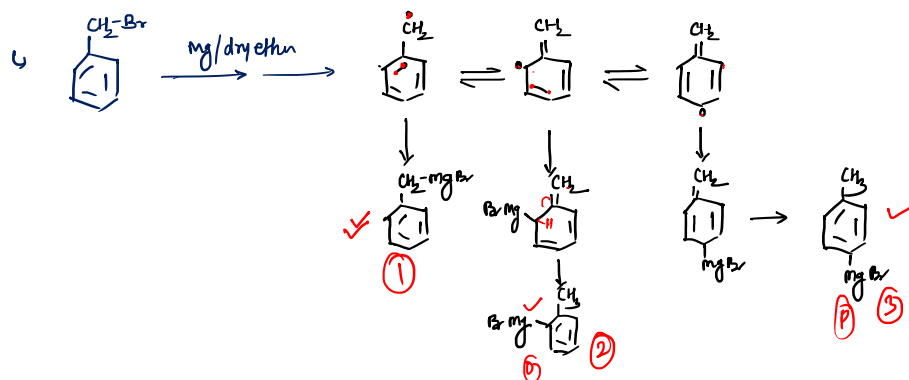
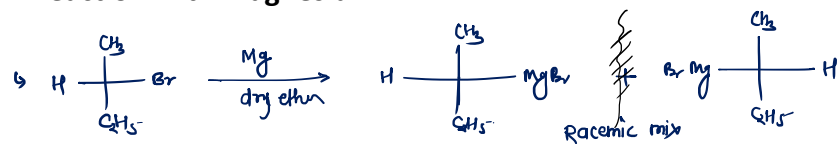


Chemical Properties of Alkyl Halide



Reaction with Metal

4. Reaction with Magnesium

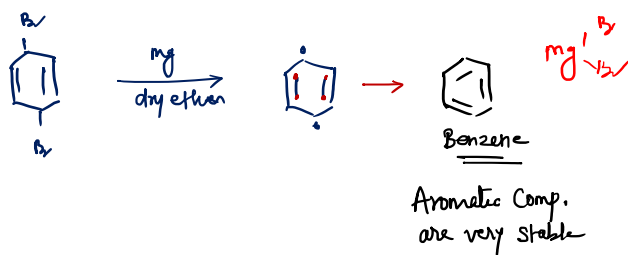


Chemical Properties of Alkyl Halide



Reaction with Metal

4. Reaction with Magnesium





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