

Chemistry 3A Reaction Summaries Outline – Major Products

IS THE REACTANT AN...

1. ALCOHOL

a. Metal Hydride

- i. Metal Alkoxide and Hydrogen gas forms

b. PBr_3

- i. $\text{S}_{\text{N}}2$: Br splits off and PBr_2^+ attaches to the $-\text{OH}$; Br^- undergoes $\text{S}_{\text{N}}2$ with HOPBr_2^+

c. SOCl_2

- i. $\text{S}_{\text{N}}2$: Cl splits off and SOCl^+ attaches to the $-\text{OH}$; Cl replaces the $-\text{OH}$

d. Strong Nucleophilic Acid (HBr , HI , HCl)

- i. Primary; $\text{S}_{\text{N}}2$: The anionic nucleophile replaces the $-\text{OH}$
- ii. Secondary; $\text{S}_{\text{N}}1$: The anionic nucleophile replaces the $-\text{OH}$

e. Strong Non-Nucleophilic Acid (H_2SO_4 , H_3PO_4)

- i. Primary; High Temperature
 1. $\text{S}_{\text{N}}2$: Identical Alcohol replaces the $-\text{OH}$ group
- ii. Primary; Very High Temperature
 1. E2: Alcohol dehydrated and double bond forms
- iii. Secondary/Tertiary; E1: The H^+ protonates the $-\text{OH}$ group
 1. Is there a more stable carbocation location?
 - a. Shift (alkyl or hydride) before double bond
 2. Else...
 - a. Double bond forms with adjacent carbon(s)

f. Tertiary Alcohol ($(\text{CH}_3)_3\text{COH}$)

- i. The tertiary alcohol loses its $-\text{OH}$ group and replaces the hydroxyl $-\text{H}$ on the other alcohol, forming an ether

2. ETHER

a. Oxacyclopropane?

i. Anionic Reagent/Strong Base (LiAlH_4 , NaOH , RO^-)

1. $\text{S}_{\text{N}}2$: Nucleophilic "Back-Attack" at a less substituted carbon, opens the ring at the $\text{C}-\text{O}$ bond of the attacked carbon forming an alcohol

ii. Nucleophilic Strong Acid (HBr , H_2O)

1. $\text{S}_{\text{N}}2$: H^+ attaches to the $-\text{O}-$, creating more positive charges at the carbons; Nucleophilic "Back-Attack" at the more substituted carbon, opening the ring at the $\text{C}-\text{O}$ bond of the attacked carbon, forming an alcohol; if the nucleophile is $-\text{OH}$, a vicinal diol is formed

iii. Grignard Reagents (RMgX)

1. $\text{S}_{\text{N}}2$: The R of the Grignard reagent combines with an opened oxacyclopropane (e.g. from H^+ in THF)

b. Else...

i. O_2

1. Ether reacts with O_2 to form 2 Hydroperoxide ethers which then react to form an ether peroxide

ii. Strong Nucleophilic Acid (HBr , HI , HCl)

1. $\text{S}_{\text{N}}2$: $-\text{O}-$ is protonated and $-\text{X}$ replaces the $-\text{OR}$ substituent

iii. H_2O

3. ALKANE

a. Reactive Haloalkane (Br, Cl, I)

i. Primary?

1. H₂O

a. S_N2: -OH replaces -X, forms alcohol

2. Alkoxide (RO⁻)

a. S_N2: Williamson Ether Synthesis: -OR replaces -X, forms ether

3. Organometallic (Grignard, RMgX, LiAlH₄)

a. Aldehyde and chain attached to it replaces -X, forms alcohol

ii. Else...

1. Strong Base (-OH, -OR, -NR)

a. E2 or E1: Forms a double bond between the carbon that had the Halogen and an adjacent carbon if E2; forms a double bond between a carbon with a stable carbocation configuration and an adjacent carbon if E1

b. Else...

i. Haloalcohol

1. Strong Base (-OH)

a. S_N2: Intramolecular Williamson Ether Synthesis: base accepts proton from alcohol, -O⁻ replaces -X in S_N2.

4. ALKENE

a. H₂O and Strong Non-Nucleophilic Acid (H₂SO₄)

i. Cold, Markovnikov: Less-substituted side is protonated, -OH group attaches to the more substituted side; Reversible

b. Halogen (Cl₂, Br₂, I₂)

i. Cold, no H₂O

1. Anti-Addition: Both ends of the double bond are halogenated, with X⁺ forming a 3-member ring with the two double-bond carbons and the X back-attacking the more substituted carbon

ii. H₂O solvent

1. Anti-Addition: Forms a haloalcohol with the same mechanism as 3.b.i.1 (above)

c. Strong Hydrohalide (HBr, HCl, HI)

i. ROOR Reagent, Heat

1. Radical Halogenation, Anti-Markovnikov: Adds a hydrogen to the more substituted side and the X radical to the less substituted side

ii. Concentrated acid

1. Markovnikov: Addition with the halogen attaching to the more substituted carbon

d. Oxymercuration (Hg(OAc)₂ + NaBH₄ + H₂O/ROH)

i. Markovnikov: Forms a C-C-HgR ring until -OH back-attacks the more substituted carbon. S_N2 reaction between an H from NaBH₄ and HgR

e. Hydroboration (BH₃ + THF + H₂O₂ + NaOH)

i. Anti-Markovnikov: 3 alkenes that accept a proton from and bond with BH₃. Reaction with peroxide forms 3 alcohols and NaBO₃

f. Carbene (CN₂H₂, ICH₂ZnI)

i. Forms a cyclopropane where the double bond used to be

g. Halogenated Carbene (CCl₃H)

- i. Forms a halogenated cyclopropane where the double bond used to be
- h. Peroxycarboxylic acid ($R(CO)OOH$)**
 - i. Forms an oxacyclopropane at the double bond site along with a carboxylic acid; can be hydrolyzed
- i. $KMnO_4 / OsO_4 + H_2S$**
 - i. Forms a *syn* diol at the double bond site
- j. Ozonolysis ($O_3 + Zn / CH_3COOH$)**
 - i. Undergoes a two-step mechanism to split an alkene in the middle of a double bond, placing $-O$ at the ends (forming ketones).
- k. Strong Non-Nucleophilic Acid ($NO H_2O$)**
 - i. Markovnikov: Undergoes a polymerization that breaks at the formation of a double bond in the polymer
- l. $ROOR + Heat$**
 - i. Undergoes a polymerization that breaks at the formation of a double bond in the polymer that breaks after a number of possible termination step possibilities ($\bullet OR, \bullet R$)

5. ALKYNE

- a. $Pt / Pd + H_2$**
 - i. Full reduction to alkane
- b. Lindlar Catalyst ($H_2 + Pd + Pt + \text{"poisoned chemicals"}$)**
 - i. *-cis* reduction to alkene
- c. $NaNH_3$**
 - i. *-trans* reduction to alkene
- d. Strong Nucleophilic Acid (HBr, HI)**
 - i. Anti-Addition; Markovnikov: forms a geminal Haloalkane – two halogens attached to one carbon; anti and *syn*
- e. Halogenation ($Br_2 + CH_3COOH + LiBr / Br_2 CCl_4$)**
 - i. Anti-Addition: forms an anti halogen addition, forming a dihaloalkane; if reacted again with another halogen, the alkene becomes a tetrahaloalkane
- f. Mercuric Hydration ($H_2O + HgSO_4$)**
 - i. Markovnikov: reduces the double bond by protonating the less-substituted side and forming a ketone on the more substituted carbon through tautomerization
- g. $HBr + ROOR$**
 - i. Anti-Markovnikov: similar mechanism to 3.c.i.1.
- h. Hydroboration ($R_2BH + H_2O_2 + THF$)**
 - i. Anti-Markovnikov: R_2BH bonds with alkyne before reacting with a peroxide to obtain an alkenol; only way to obtain aldehydes (through tautomerization)

6. SULFUR-CONTAINING

- a. Thioester (RSR)**
 - i. Strong Base ($-OH$)**
 1. An alcohol and sulfur-containing organic compound forms
- b. Thiol**
 - i. I_2**
 1. Oxidation of thiol yielding disulfides – a peroxide analog ($R-SS-R$)