**Organic Chemistry**

**Organic Acid and Base**

**Acid:**
- Electron-pair acceptor (Lewis acid)
- Proton donor (Bronsted-Lowry acid);
  example: carboxylic acid

**Base:**
- Electron-pair donor (Lewis base)
- Proton acceptor (Bronsted-Lowry base);
  example: amine

**Factors enhancing acid strength (HA):**
- Weaker H-A bond
- Greater electron negativity of “A”
- Inductive effect of substituent on “A” (electron withdrawal enhances transfer).
- More “s” character in hybrid orbital (s-orbital is lower in energy than p-orbital)
- Resonance stabilized conjugate base (A-)

**Factors enhancing base strength:**
- Reverse of acid-strength guidelines

A base is a nucleophile; Electronic effects which shift electron density to the atom with the lone-pair increases base-strength.

**Alkene >C=C<**

**Properties:** Similar to alkane; non-polar, flammable

**Nomenclature:**
- Add -one to prefix; Use # to denote C=C position
- Isolated C=C-C=C-C; cumulative -C=C-C-C
- Polyunsaturated fatty acid: 2 or more C=C
- Alkene: adjacent C=C
- Vinyl group: H=CH-
- Methylene group: H2C=
- Allyl group: H3C-CH=CH2-
- Vinyl halide: halide replaces -H on >C=C<
- Conjugated: alternate C-C and C=C (resonance)
- Alkadiene, 2 conjugated C=C; example: butadiene;
  s-cis and s-trans (rotate about C-C bond)
- Alkatriene, 3 conjugated C=C
- Annulene: conjugated monocyclic compound;
  example: [6] annulene = benzene
- Aromatic cyclic ions: cyclopentadiene anion, cycloheptatriene cation (6 electrons)

**Isomers:** No free rotation of C=C

**Alkane >-C<**

**Properties:**
- Hydrocarbon
- Weak intermolecular forces
- Non-cyclic: general formula CnH2n+2
- Tetrahedral C-C-C (109˚)
- Non-cyclic: general formula CnH2n+2
- Hydrocarbon
- Properties:
  - Haloalkane: substitute halide for -H
  - Halogenate (Br2/Cl2), vic dihaloalkane (X2,CCl4; anti)
  - Hydrohalogenate (HX) (Markovnikof)
  - Oxymercurate-demercurate to alcohol
  - Hydrogenate to alkane (Pt, H2; syn-addition)
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**Synthesis:**
- Dehydrate alcohol (H+; heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate vic dihalide (Zn, acetic acid)
- Hydrogenate alkene:
  - syn, Z/cis-isomer (H2,P-2 catalyst)
  - anti, E/trans-isomer (Li, NH3, -78˚C)
  - Wittig, aldehyde/ketone to alkene

**Reaction:**
- Combustion (O2)
  - Hydrate to 2/3 alcohol (H+ H2O); 1˚ from ethene; can rearrange (Markovnikof)
  - Hydrate to alcohol; hydroborate/oxidize (THF/B2H6,H2O2/OH-) (syn, anti-Markovnikof)
  - Oxymerycurate-demercurate to alcohol
  - Hydrohalogenate (HX) (Markovnikof)
  - Halogenate (Br2/Cl2), vic dihaloalkane (X2,CCL4; anti)
  - Halohydrin (X2,H2O; anti-addition)
  - Hydroxylation to form a 1,2-diol (KMnO4, cold OH-; 1˚ from ethene)

**Organic Reactions**

**Reaction:**
- Combustion: alkane + O2 => CO2 + H2O
- Halogenation to haloalkane (Cl2/Br2, light or heat)

**Kinetics and Reaction Mechanism**

**Reaction:**
- Combustion: alkane + O2 => CO2 + H2O
- Halogenation to haloalkane (Cl2/Br2, light or heat)

**Kinetic vs. thermodynamic control:**
- ΔG and ΔH describe Thermodynamic Stability.
  - If ΔG is large and negative (exergonic), the product formation is likely controlled by “thermodynamics.”
  - Large Keq corresponds to a large amount of product, relative to reactant.
  - A large Ea may give rise to “kinetic” control; the energy of the TS controls the reaction, instead of the product-reactant thermodynamics.

**Solvent effects:** A solvent may stabilize an intermediate, decreasing Ea and increasing the rate of the reaction. Charged-complexes are stabilized by polar solvents.

**Hammond-Leffler postulate:** The TS is more like the reactant or product that is closer in energy; endothermic TS is like the product, exothermic TS is like the reactant.

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**Solvent effects:** A solvent may stabilize an intermediate, decreasing Ea and increasing the rate of the reaction. Charged-complexes are stabilized by polar solvents.
Properties: insoluble in water, miscible with non-polar organic solvents.

Nomenclature:
- Aromatic (or arene): Denote substituent using group name and ring position; ortho (1,2), meta (1,3), para (1,4).

- Examples: benzene C₆H₆; phenol, Ar-OH (carboxylic acid, hydroxybenzene, benzenol); aniline Ar-NH₂; toluene, Ar-Me (methyl benzene); xylene, dimethyl benzene.
- Fused rings: naphthalene, C₁₀H₈ (2 edge-sharing rings).
- Aryl or Phenyl group: Ar- (remove H from benzene).
- Aryl halide: halogen replaces an H atom; Ar-X.
- Alkeny: +H₂O => alkene; Zaitsev’ s rule; rate 3°>2°>1°.

General Reaction:
- Combustion (similar to alkane).
- Birch reduction (C₆H₆ to benzoic acid: CO + H₂O).
- Chlorination -Me of Toluene.
- Sulfonation: Ar-SO₂H.
- Halogenation: Ar-X (Cl, Br, I).

Electrophilic substitution:
- Allylation: Ar-R (Friedel-Crafts, RCI, AlCl₃).
- Nitration: Ar-NO₂ (HNO₃, H₂SO₄).
- Halogenation: Ar-Br (Br₂, FeBr₃).
- Acylation: Ar-CR=O (RCOCl, AlCl₃).
- Sulfonation: Ar-SO₂H (SO₃, H₂SO₄).

Reactivity of substituted benzene:
- A substituent alters the ring electronic structure.
- Activating group: More reactive than benzene; add electrons to the ring, stabilize the arenum cation.
- Deactivating group: Less reactive; pull electrons from the ring, destabilize the arenum cation.

- Ortho/para-director: 
  - Substituent tends to activate the ring (except for -X); electron density donated to ring creates “+” center on ortho/po sites.
  - Preferred reaction site.
  - Examples: -NO₂, -OH, -OR, -O', -X (halogen).

- Meta-director: 
  - Substituent tends to deactivate the ring; electron density withdrawn from the ring creating “-” center on meta site.
  - Preferred reaction site.
  - Examples: -NO₂, -CN, -COOH, -SO₂H, -COOR, -CHO, -CRO.

Reactivity of di-substituted benzene:
- Directing effects may be cooperative; e.g. “o”/“p” plus “m” at 1,4 positions.
- Otherwise: consider steric effects; activating group tends to dominate deactivating group.

- Reaction of alkyl substituent benzene:
  - Toluene to benzoic acid (KMnO₄, OH-, heat, H⁺).
  - Chlorinate –M of Toluene (Cl₂).
- Alkyne

Properties: -C≡C-

- Linear R’-C≡C-R".

Nomenclature:
- Add -yne to prefix.

Synthesis:
- CaC₂ + H₂O => Ca(OH)₂ + CH₂;
-
- Dehydrate halogenate vic-halokalene (NaNH₂, liq NH₃).
-
- Alkylate terminal alkylene (NaNH₂, liq NH₃, R-X).
-
- Oxidize to carboxylic acid (O₂, H₂O).
-
- Oxidize to carboxylic acid (KMnO₄, OH-, H⁺).

Alcohol

Properties: 
- Low molecular weight are water-soluble.
- H-bonding, polar.
- ROH acidic proton.
- Resonance stabilized ArO⁻ or RO⁻.

Nomenclature:
- Prefix “-anol”;
- Example: methanol Me-OH (methyl alcohol).
- Cyanohydrin: -OH and –CN.
- Hydrolyze –OH and halogen.
- Diol or glycol (two -OH); gem-diol: 1,1 diol; vic-diol: 1,2 diol.

Synthesis:
- Hydrate alkylene (H₂O, H⁺).
- Hydrobromate/oxidize alkylene (THF-BH₃, H₂O₂, OH⁻).
- Hydrogenate aldehyde (Hy/Ni or Pt catalyst).
- Hydrolyze 1 alkyl halide (water, OH⁻).
- Reduce aldehyde, ester, ketone or carboxylic acid.
- Ethanol: Ferment sugar or starch.
- Methanol: CO + H₂.
- Reduction (H₂, Pt).
- Pyrolyze cellulose.
- Hydrolyze water (water, acid).
- Dehydrate ether (H₂SO₄, heat).
- Grignard (RMgX): formaldehyde => 1° alcohol; aldehyde => 2° alcohol; ketone => 3° alcohol.
- Glycosylation from Ketone/aldehyde (H⁺ or Pb(OAc)₄).
- Hydrolyze epoxide (H₂O, H₂SO₄).

Reaction:
- Oxidize 1° to aldehyde (CuO, heat)
- or 2° to ketone (KmO₄, H⁺).
- Oxidize 1° to carboxylic acid (KmO₄, H⁺).
- Dehydrate to alkylene; Zaitsev’s rule; rate 3°>2°>1°.
- Dehydrate to ether (H₂SO₄, lower temperature).
- Dehydrate to ketone (2° alcohol) (H₂CrO₄).
- Form halokalene (HX; substitution).

Ether

Properties:
- Polar, hydrogen bonding.
- Oxygen lone-pair is a nucleophile.
- Flammable liquid.

Nomenclature:
- R'-O-R".
- Examples: diethyl ether, common solvent: Et-O-Et.

Synthesis:
- Williamson synthesis (R'I + NaOR).
- Epoxide or oxirane: 3-member ring.
- Dioxane: cyclic double ether.

Synthesis:
- Williamson synthesis (R'I + NaOR).
- Dehydrate 1° alcohol (H₂SO₄, heat).
- Epoxidation: alkylene + peroxide.
- Halohydrin + ROH => hydroxy ether.
- Alkylation: R-OH + Alkyl halide => R-O-R'.

Reactions:
- Hydrolyze to alcohol (H₂O) (H₂SO₄).
- Autoxidize to peroxide (oxygen in air).
- Dehydrate ortho to ketone (KMnO₄).
- Oxidize ether to epoxide.
- Autoxidize to peroxide in air.

EXPLOSIVE HAZARD!
**ALDEHYDE & KETONE °C=O**

**Properties:**
- Polar °C=O; low molecular weight are water-soluble
- Main chemical difference: ketone is harder to oxidize than aldehyde.

**Aldehyde nomenclature (RCHO):**
- Prefix “-anal”, also “R”.R’ ketone;’
- Example: HCHO, methanal (formaldehyde);
MeCHO, ethanol (acetaldelyde); Ar-CHO, benzaldehyde

**Ketone nomenclature (RR’CO):**
- Prefix “-ac”, also “R”.R’ ketone;’
- Example: 2-propanone (acetone or dimethyl ketone);

**Keto-enol tautomerism:**
- Enol form
- Keto form
- Nucleophile attacks °C=O of enol-form
- Acidic α-H, -CH2-CHO can form resonance stabilized carbanion (especially for diketone).
- Racemization via keto-enol: chiral ketone => achiral enol => achiral ketone

**Synthesis:**
- Oxidize alcohol: aldehyde from 1º (Cu, heat); ketone from 2º (H2, CrO3).
- Grignard: nitrile (RCN) + R’MgX => R-CO-NR
- Reduce RCO-Cl (LiAlH4)
- Reduce RCN (Zn-Hg, HCl)
- Hemiacetal: RCH(OH)-CH2-R
- Diketone: R-C(=O)-CH2-CO-R

**General Reaction:**
- Wittig, form alkene (phosphorus ylide)
- Form Oxime (C=O-NOH) (hydroxyl amine)
- Reduce to alcohol (Metal hydride, LiAlH4)
- Wolff-Kishner: RR’CO => RR’H
- Clemmenson reduction: RR’CO => RR’H (Zn/NaH, HCl)
- Hydrogenate to ROH
- Oxidize to RCOOH (peroxyacetic)
- Form cyanohydrin (RCOCH2-CHO)
- Reduce to ketone (Ba(OH)2)
- Decarbonylate keton to ketone (heat)
- α-halo acid: (X2, P, H2O)
- α hydroxy acid from halo acid (OH’/H+)
- α amino acid from halo acid (NH3 or amine)

**Carbonic acid and derivatives:**
- Carbonic acid: H2CO3 or HO-CO-OH
- Carbonyl dichloride (phosgene, CI-CO-CI; toxic gas)
- Phosgene + EtOH => diethylecarbonate, EtO-CO-OEt
- Phosgene + NH3 => HN-CO-NH3 (urea)
- Phosgene + ROH => RO-CO-Cl (alkyl chloroformate)
- RO-CO-Cl + NH3 => RO-CO-NH3 (urethane, carbamates)

**Ester continued**

**Properties:**
- Organic acid, resonance stabilizes dissociation
- Soluble in water, H-bonding, acid strength given by pKa

**Nomenclature:**
- Prefix “-oic acid”;
- Examples: HCOOH, methanoic acid (formic acid)
Me-COOH, ethanoic acid (acetic acid), Ar-COOH, benzoic acid (benzenecarboxylic acid)
- Oxalic acid (dicarboxylic acid, HOOC-COOH)
- Malonic acid (HOOC-CH2-COOH)

**Fatty acid:** °C long hydrocarbon (aliphatic) chain

**Derivatives:**
- Ester
- Acid anhydride: RCO-O-CO-R
- Peroxyacid: R-CO2H

**Synthesis:**
- Oxidize 1º alcohol (KMO4, H+): Oxidize aldehyde (Ag, H+):
- Hydrolyze nitrile or acyl chloride (H2O2, H2O)
- Acid anhydride + water
- Grignard and carbonation (RMgX + CO2, H+):
- Benzoic acid: oxidize 1º/2ºalkylbenzene (KMO4, H+, heat): From methyl ketone (Ar-CO-CH3) (X2, O2H, H+):

**Reaction:**
- Form acyl chloride (SOCl2, PCl3 or PCl5)
- Reduce to alcohol (LiAlH4)
- Neutralize with a base, form a salt
- Esterification: (ROH, H+):
- Reduce to ketone (BarOH2, heat)
- Decarbonylate keton to ketone (heat)
- α-halo acid: (X2, P, H2O): H2V2 (Hell-Volhard-Zelinski)
- α hydroxy acid from halo acid (OH’/H+):
- α amino acid from halo acid (NH3 or amine)

**Carbonic acid and derivatives:**
- Carbonic acid: H2CO3 or HO-CO-OH
- Carbonyl dichloride (phosgene, CI-CO-CI; toxic gas)
- Phosgene + EtOH => diethylecarbonate, EtO-CO-OEt
- Phosgene + NH3 => HN-CO-NH3 (urea)
- Phosgene + ROH => RO-CO-Cl (alkyl chloroformate)
- RO-CO-Cl + NH3 => RO-CO-NH3 (urethane, carbamates)

**AMINE RR’RN**

**Properties:**
- Substituted ammonia; polar, water soluble; °N-H forms H-bonds
- Organic base: strength denoted by pKb
- Structure: distorted pyramid (AX3E)

**Nomenclature:**
- °R1 R2 R3 amine”
- Example: Me-NH2, methyl amine;
Ar-NH2, phenylamine (aniline, amino benzene)

**Types of amines:**
- Primary (1º) amine
- Secondary (2º) amine
- Tertiary (3º) amine
- Quaternary ammonium salt (4º)

**Synthesis:**
- 1º: aminate haloalkane: RCH2-X + NH3
- reduce nitrite, RCoCl (LiAlH4 or H2, Ni)
- reduce nitroalkane, RN02 (LiAlH4)
- reduce oxime (Na, EIOH)
- from aldehyde/ketone (NH2, H+): H2
- 2º: haloalkane + 1º amine
- aldehyde/ketone + R’NH2 (H+): H2
- 3º: haloalkane + 2º amine
- reduce amide (LiAlH4, H2O)
- aldehyde/ketone + R’NH2 (H+): H2
- Aromatic Amine: Ar-N02 => Ar-NH2 (H2, catalyst; Fe, HCl, OH)

**Reaction of amine:**
- React as a base: amine + H+ => R3NH
- Nucleophilic N lone-pair
- Amine + sulfonyl chloride => sulfonamide
- amide formation: 1º + R’CCl => R’CO-NHR
- 1º + CH2-COOH => R-NO2
- amide formation: 2º + RCOCl
- Copper Elimination: oxidize 3º amine to tertiary ammonium oxide (RN’-O, H+), heat produces RHC=CH2
- Ar-NH2, o-p director, electrophilic aromatic substitution
- Ar-NH2: nucleophilic aromatic substitution: Step 1: Ar-NH2 + cold nitric acid => Ar-N2+ (diazonium salt, unstable)
Step 2: Depends on substitution: + CuO, Cu2, H2O => Ar- OH
+ CuCl => Ar-Cl
+ CuCN => Ar-CN
+ H3PO2 => Ar-H

**Hofmann elimination:**
- Quaternary ammonium hydroxide => amine (heat)
**AMINO ACID**

**Nomenclature:**
- Example: Me-CO-NH₂, acetamide
- Cyclic amide (lactam): N of amide forms ring with β, γ or δ carbon;
- β forms 4 membered ring; γ forms a 5 membered ring, δ forms a 6 membered ring.
- Observed in amino acids

**Synthesis:**
- Nitrile hydrolysis (R-CN + H₂O, conc. H₂SO₄)
- Acyl chloride + 1°/2° amine or ammonia
- Pyrolysis of ammonium salt + RCOOH
- Ammonolysis of ester: 1° or 2° amine + ester
- Polymide => polypeptide => protein

**Reaction:**
- Reduce to amine (LiAlH₄)
- Hydrolyze to acid (H₂O₂ or OH⁻)
- Dehydrate to nitrile, RCN (P₂O₅; heat)
- Hofmann Reaction: Form 1° amine (NaOBr)
- Grignard (RMgX) to ketone, R-CO-R'°
- Form aldehyde and 2° amine (LiAlH₄)

**Properties:**
- Basic (-NH₂) and acidic (-COOH) functionality
- Chiral isomers
- Zwitterion: self-ionization of amino acid to produce COO⁻ and NH₃⁺
- Isoelectric point, pH which produces equal + and - charges

**OTHER NITROGEN-COMPOUNDS**

**Nitrile:**
example: H₂C-CN; methane nitrile

**Synthesis:**
- Halokalane + NaCN
- Aldehyde/ketone => cyano hydrin (CN⁻ + H⁺)
- Dehydrate amide (P₂O₅, heat)

**Reaction:**
- Hydrolyze to carboxylic acid (acid, heat)
- Hydrolyze to carboxylate (base, heat)
- Reduce to 1° amine (Raney Ni, LiAlH₄)
- Form aldehyde (DIBAL-H + (i-Bu)₂AlH₂, H₂O)
- Form ketone (Grignard reagent or R-Li, H⁺)

**Imine:**
- >C=N-R

**Synthesis:**
- Aldehyde/ketone + 1° amine (H⁻)

**Reaction:**
- Intermediate in amimation of aldehyde/ketone

**ORGANIC POLYMER**

-M - M - M - M -
Monomers (M) bond to form a high molecular weight compound.

**Properties which influence properties:**
- Chain length, branching vs. linear, nature of the monomer, density, interchain bonds, hydrophobic and hydrophilic interactions.
- Examples:
  - PE (polyethylene)
  - PS (polystyrene)
  - HDPE (high density polyethylene)
  - LDPE (low density polyethylene)
  - PET (polyethylene terephthalate)

**Organic compounds:**

**SULFUR CHEMISTRY**

**Thiol Compounds**
- R-SH
- Disulfide: R-S-S-R'
- Thiol ester: R-S-SR'
- Thiocysteine: R-S-SR'
- Thiophenol: Ar-SH
- Thiol: R-SH
- Thiocysteine: R-S-SR'
- Thiophenol: Ar-SH
- Sulfonic acid: R-SO₂H
- Sulfonic acid: R-SO₂H
- Hydrogen sulfate: R-OSO₃H

**Synthesis:**
- Thiol: From alkyl bromide/iodide (KOH, H₂S)
- Thiol: RCH₂X + NaSH => RCH₂SH (EtOH, heat)
- Thiol ester: Acyl chloride + thiol
- Alkyl hydrogen sulfate (Alkene + cold conc. H₂SO₄)
- Thiol: Alkene + H₂S (H₂SO₄, heat)
  - (Markownikoff addition)
  - Thiol: Alkene+H₂S (peroxide or UV)
  - (Anti-Markownikoff addition)

**Reaction:**
- Form sulfide from thiol (NaOH, R’CH₂X)
- Form disulfide from thiol (I₂ or H₂O₂)
- Oxidize thiol to form sulfonic acid, RSO₃H (HNO₃)
- Dehydration of thiol to alkane (H₂, Ni)
- Sulfonate benzene (SO₃, conc. H₂SO₄)

**METAL REACTION**

**Organometallic:**
- Carbon atom bonded to a metal atom
- Types of bonding:
  - Ionic bond, Na,K: R-M⁻
  - Partial covalent, Mg, Li: R electrophilic character
  - Covalent, Pb, Sn, Hg: R-M

**Grignard reagent:**
- Strong base gives R electrophilic character:
  - Li + Br₂ => R-Li
  - RX + Mg => RMgX
  - ArX + Mg => ArMgX

**Organoborane:**
- Boron hydride, B₄H₁₀ example: diborane, B₂H₆

**Organolithium:**
- R-Li

**Synthesis:**
- Hydroboration: Alkene + Boron hydride

**Reaction:**
- Organoborane => alcohol (H₂O₂)
  - R-B⁺ => R-H (acetic acid, addition of H)

**Organocopper:**
- R-Cu
  - Add R₂ Cu to C-O of unsaturated carbonyl

**Organolead/mercury:**
- Stable compound, VOLATILE AND TOXIC
  - Tetraethyl lead (anti-knock agent in gasoline)

**CYCLIZATION: SYNTHESIS OF A CYCLIC COMPOUND**

**Synthesis:**
- Diels-Alder: diene + dienophile + heat => adduct
  - Diene
  - Dienophile
  - Adduct

**Reaction of cyclic compound:**
- Retro-Diels-Alder: thermally decompose cycloalkene
- Reduce aromatic to symmetric 1,4 cycloalkylene (Li or Na, EtOH, Liq NH₃)

**Systematic name:**
- Retro-Diels-Alder: monoalkene tautomerization
- Alkene + cold conc. H₂O; heat

**Cyclic compound:**
- [2.2] cycloaddition of alkenes giving cyclobutane adduct (two alkenes, photochemical reaction)

**Factors: chain length, branching vs. linear, nature of the monomer, density, interchain bonds, hydrophobic, and hydrophilic interactions.**

**Factors which influence properties:**
- Chain length, branching vs. linear, nature of the monomer, density, interchain bonds, hydrophobic, and hydrophilic interactions.

**SULFUR CHEMISTRY**

**Thiophene, Heterocyclic**

**Thiophene: R-SH**

**Sulfide or Thioether: R-S-R’°**

**Reaction:**
- Epoxide ring opening reaction
- Small ring is strained, may decompose to linear chain
- Epoxide ring opening reaction

**Sulfonic acid: R-SO₂H**

**Thiophenol: Ar-SH**

**Thiol: R-SH**

**Disulfide: R-S-S-R’°**

**Sulfuric acid: R-SO₃H**

**Hydrogen sulfate: R-OSO₃H**

**Sulfonic acid: R-SO₂H**

**Chloroform: R-Cl**

**Fluorohydride: R-F**

**Bromohydride: R-Br**

**Iodohydride: R-I**

**Hydrogen sulfide: R-H₂S**

**Thiol: R-SH**

**Sulfide or Thioether: R-S-R’°**

**Organic compounds:**

**Sulfur Chemistry**

**Thiol Compounds**
- R-SH
- Disulfide: R-S-S-R’°
- Thiol ester: R-S-SR’°
- Thiocysteine: R-S-SR’°
- Thiophenol: Ar-SH
- Thiol: R-SH
- Thiocysteine: R-S-SR’°
- Thiophenol: Ar-SH
- Sulfonic acid: R-SO₂H
- Sulfonic acid: R-SO₂H
- Hydrogen sulfate: R-OSO₃H

**Synthesis:**
- Thiol: From alkyl bromide/iodide (KOH, H₂S)
- Thiol: RCH₂X + NaSH => RCH₂SH (EtOH, heat)
- Thiol ester: Acyl chloride + thiol
- Alkyl hydrogen sulfate (Alkene + cold conc. H₂SO₄)
- Thiol: Alkene + H₂S (H₂SO₄, heat)
  - (Markownikoff addition)
  - Thiol: Alkene+H₂S (peroxide or UV)
  - (Anti-Markownikoff addition)

**Reaction:**
- Form sulfide from thiol (NaOH, R’CH₂X)
- Form disulfide from thiol (I₂ or H₂O₂)
- Oxidize thiol to form sulfonic acid, RSO₃H (HNO₃)
- Dehydration of thiol to alkane (H₂, Ni)
- Sulfonate benzene (SO₃, conc. H₂SO₄)