



Crack Notes [Organic Chem 2] Hydrocarbons, Alcohols & Substitutions

ALKANES

Water-insoluble, low density C-C single bonds

Higher MW $\rightarrow$ higher BP, higher MP

Branching $\rightarrow$ lower BP, higher MP

Forms *cycloalkanes* which can have ring strain

Cyclohexane: chair vs. boat configuration (chair more stable b/c less ring strain)

$\rightarrow$ Chair: equatorial vs. axial hydrogens, can undergo a ring flip exchanging groups

$\rightarrow$ Axial substituents can interfere so larger substituents usually on equatorial position

Combustion: react with oxygen to form $\text{CO}_2 + \text{H}_2\text{O} + \text{heat}$

Combustion is a radical process and exothermic

Higher heat of combustion (enthalpy change) = less stable, more reactive

Halogenation: react with F, Cl, Br to form alkyl halides - radical process, exothermic

1) *Initiation*: halogen cleaved by heat/light to form free radical

2) *Propagation*: halogen radical reacts with alkane to form alkyl radical, alkyl radicals can react with other alkanes to form more radicals

3) *Termination*: two radicals combine to form a stable compound

F is most reactive, so will usually create primary radical + primary product

Br is most selective, so will usually create most stable product

$\rightarrow$ Radical stability: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

Can have multiple halogenations if there's lots of halogen



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ALKENES

Water insoluble, as $C=C$ double bond

Most substituted alkenes are most stable (b/c electrons have room to spread out)

Higher MW $\rightarrow$ higher BP, higher MP

Branching $\rightarrow$ lower BP, higher MP

Synthesis - E1/E2 reactions

E1: two step reaction, first step is slowest

(1) Leaving group leaves in presence of weak base, forms carbocation

(2) Carbocation rearrangement can occur ($3 > 2 > 1 > \text{methyl}$)

(3) Weak base extracts a hydrogen, creating double bond

Saytzeff rule: major product is most substituted alkene

Dehydration: alcohol + hot acid $\rightarrow$ alkene

Dehydrohalogenation: alkyl halide + weak base $\rightarrow$ most substituted alkene

E2: one step reaction

$\rightarrow$ Strong base extracts hydrogen at same time leaving group leaves, creating double bond

If base is too bulky then least substituted alkene will be created (violation of Saytzeff's rule)

Dehydrohalogenation: alkyl halide + strong/bulky base $\rightarrow$ least substituted alkene

Catalytic Hydrogenation - exothermic

Alkene + H_2 (with heterogeneous Ni, Pd or Pt catalyst) $\rightarrow$ alkane

Hydrogens added to same side of alkene (syn-addition)

Alkynes $\rightarrow$ alkenes by this process

Oxidation/Ozonolysis

Alkene + (1) O_2 , (2) Zn/H_2O $\rightarrow$ two carbonyls

Cleaves double bond, attaches a double bonded O to each side

Alkynes $\rightarrow$ carboxylic acids by this process



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Electrophilic Addition - b/c alkenes have a huge cloud of electrons

Alkene + hydrogen halide (HF/HCl/HBr/HI) $\rightarrow$ alkyl halide

Markovnikov's rule: hydrogen attaches to least substituted carbon

Carbocation rearrangement can occur

When there's peroxides (ROOR) with HBr the hydrogen will attach to the most substituted carbon (anti-Markovnikov addition)

Hydration

Alkene + H_2O $\rightarrow$ Alcohol (in cold dilute acid)

Oxymercuration/Demercuration

Alkene + $Hg(OAc)_2$ + H_2O $\rightarrow$ alcohol

Alkene + $Hg(OAc)_2$ + alcohol $\rightarrow$ ether

Markovnikov addition of OH and H (anti addition)

Carbocation rearrangement doesn't occur

Hydroboration

Alkene + BH_3 + H_2O_2 + OH^- $\rightarrow$ anti Markovnikov addition of OH and H (syn addition)

Halogenation

Alkene + Br_2 $\rightarrow$ vic-dihalide (anti addition of two Br's)

BENZENE

Generally undergoes substitution rather than addition

Ortho, meta, para positions

$\rightarrow$ Electron withdrawing groups direct to meta

Includes things containing double bonds with O, triple bonds, (+) charges

Halogens are EWG but direct to ortho/para

$\rightarrow$ Electron donating groups direct to ortho/para

Includes things with negative charges, things single bonded with O, alkyl groups



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SUBSTITUTION REACTIONS

SN1: 2 steps, rate depends on first step

1) Planar carbocation forms when leaving group leaves

2) Nucleophile attacks carbocation, attaches to carbon

Can form both enantiomers b/c carbocation is planar

Only tertiary carbons will undergo SN1

SN2: one step

-> Nucleophile attacks carbocation at same time as leaving group leaves

Opposite enantiomer will be created (inversion of configuration)

SN1 vs SN2:

Nucleophile: SN2 needs strong nucleophile (lots of electrons)

Substrate: SN2 needs non sterically hindered substrate

Solvent: SN2 needs less polar solvent, SN1 likes polar solvents

Speed: SN2 depends both substrate/nucleophile, SN1 depends on substrate

Stereochemistry: SN2 inverts configuration, SN1 creates both enantiomers

Skeleton: SN1 can have carbocation rearrangement

ALCOHOLS

Polar, slightly acidic

Organometallic Synthesis (Grignard reagents)

Carbonyl + R-MgX -> alcohol with R attached

Reduction Synthesis

Carbonyl + NaBH₄/LiAlH₄ -> alcohol with H attached

Ester + LiAlH₄ -> alcohol

Nucleophilic Addition/Substitution

Oxidation: (reacts with things with a lot of O's)

Primary alcohol -> aldehyde -> carboxylic acid

Secondary alcohol -> ketone



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Alkyl Halides

Alcohol + HCl $\rightarrow$ Alkyl halide

Mesylates/Tosylates

Alcohol + sulfur compound $\rightarrow$ alkyl tosylate/mesylate, which has a great leaving group

Pinacol Rearrangement

Vicinal diol + hot sulfuric acid $\rightarrow$ Pinacolone (ketone with tertiary alpha carbon)

ETHERS

Not very reactive, can react with HI/HBr to form alcohols

EPOXIDES

Reacts with water in acid to form diols