



Organic Chemistry Lecture 2 - Hydrocarbons, Alcohols, Substitutions

Examkrackers MCAT Comprehensive Course, Charles Feng

fenguin@gmail.com / (224) 532-0039

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: $3 > 2 > 1 > \text{methyl}$

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 -> higher BP, higher MP

Branching -> 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 > methyl)

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

Saytzeff rule: major product is most substituted alkene

Dehydration: alcohol + hot acid -(E1)-> alkene

Dehydrohalogenation: alkyl halide + weak base -(E1)-> most substituted alkene

E2: one step reaction

-> 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 -(E2)-> least substituted alkene

Catalytic Hydrogenation - exothermic

Alkene + H₂ (with heterogeneous Ni, Pd or Pt catalyst) -> alkane

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

Alkynes -> alkenes by this process

Oxidation/Ozonolysis

Alkene + (1) O₂, (2) Zn/H₂O -> two carbonyls

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

Alkynes -> 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 + H₂O \rightarrow Alcohol (in cold dilute acid)

Oxymercuration/Demercuration

Alkene + Hg(OAc)₂ + H₂O \rightarrow alcohol

Alkene + Hg(OAc)₂ + alcohol \rightarrow ether

Markovnikov addition of OH and H (anti addition)

Carbocation rearrangement doesn't occur

Hydroboration

Alkene + BH₃ + H₂O₂ + OH⁻ \rightarrow anti Markovnikov addition of OH and H (syn addition)

Halogenation

Alkene + Br₂ \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