Crack the DAT

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

ALKANES

Water-insoluble, low density C-C single bonds
Higher MW -> higher BP, higher MP
Branching -> lower BP, higher MP
Forms *cycloalkanes* which can have ring strain
Cyclohexane: chair vs. boat configuration (chair more stable b/c less ring strain)
-> Chair: equatorial vs. axial hydrogens, can undergo a ring flip exchanging groups
-> Axial substituents can interfere so larger substituents usually on equatorial position

Combustion: react with oxygen to form CO_2 + H_2O + 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
-> Radical stability: 3 > 2 > 1 > 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) -> 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 -> Alcohol (in cold dilute acid)

Oxymercuration/Demercuration
Alkene + Hg(OAc)2 + H2O -> alcohol
Alkene + Hg(OAc)2 + alcohol -> ether
Markovnikov addition of OH and H (anti addition)
Carbocation rearrangement doesn't occur

Hydroboration
Alkene + BH3 + H2O2 + OH- -> anti Markovnikov addition of OH and H (syn addition)

Halogenation
Alkene + Br2 -> vic-dihalide (anti addition of two Br's)

BENZENE

Generally undergoes substitution rather than addition
Ortho, meta, para positions
-> Electron withdrawing groups direct to meta
    Includes things containing double bonds with O, triple bonds, (+) charges
    Halogens are EWG but direct to ortho/para
-> 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 + $NaBH_4$/$LiAlH_4$ -> alcohol with H attached
Ester + $LiAlH_4$ -> 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-> Alkyl halide

Mesylates/Tosylates
Alcohol + sulfur compound -> alkyl tosylate/mesylate, which has a great leaving group

Pinacol Rearrangement
Vicinal diol + hot sulfuric acid -> 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