



Crack the DAT

Crack Notes [Organic Chem 5] Organic Chemistry Crash Course

ELECTROPHILE: ATTRACTS ELECTRONS (a.k.a. Lewis acid)

Generally a cation or has an incomplete octet

- Acids (H-X), alkyl halides (R-X)
- Halogens (F_2 , Cl_2 , Br_2 , I_2)
- Carbonyls (C=O), acyl halides (R-C=O-X)
- Organometallic compounds ($\text{Hg}(\text{OAc})_2$)
- Carbonyl carbons of carbonyls

NUCLEOPHILE: DONATES ELECTRONS (a.k.a. Lewis base)

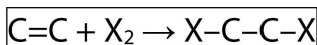
Generally an anion or has a free pair of electrons

- Water (H_2O), alcohols (R-OH), thiols (R-SH)
- Ammonia (NH_3), amines (NH_2R , NHR_2 , NR_3)
- Compounds with pi bonds (alkenes, alkynes)
- Halogen anions (Br^- , Cl^- , etc)
- Alpha carbons of carbonyls (b/c keto-enol tautomerism)
- Grignard reagents (R-MgX)
- Ylides (P-C^-)

ELECTROPHILIC ADDITION

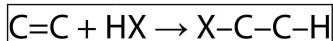
- Pi bond attacked by electrophile

Halogenation



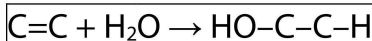
- Generally attacks opposite sides due to formation of bromonium/chloronium "triangle"

Hydrohalogenation



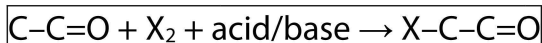
- Generally follows Markovnikov (H attaches to C w/ most H's)
- With HBr & peroxide: anti-Markovnikov

Hydration



- Generally follows Markovnikov w/ carbocation rearrangement
- With $\text{Hg}(\text{OAc})_2$, NaBH_4 : Markovnikov, no carbocation rearrangement
- With BH_3 , H_2O_2 : anti-Markovnikov

Carbonyl Halogenation



- HCX_3 is called a haloform



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ELECTROPHILIC SUBSTITUTION

- Electrophile replaces group (usually hydrogen)

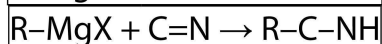
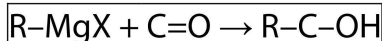
Aromatic substitution

- Aromatic system binds to electrophile

NUCLEOPHILIC ADDITION

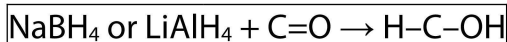
- Nucleophile attacks one side of pi bond, pi bond breaks

Grignard Reaction



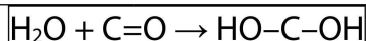
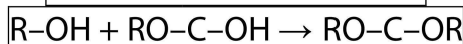
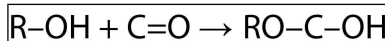
- Basically you can treat R-MgX as R:⁻
- Also works with C≡N, S=O, N=O

Carbonyl Reduction



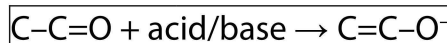
- LiAlH₄ is the stronger reducing agent

Acetalization/Ketalization



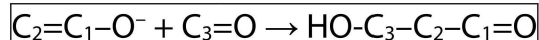
- RO-C-OH is a hemiketal/hemiacetal (depending on whether original C=O was an ketone or aldehyde)
- RO-C-OR is a ketal/acetal
- Can use a diol (HO-R-OH) to protect carbonyls, forming a ring which can then be changed back to carbonyl by acid

Keto-Enol Tautomerization



- Left is keto, right is enol

Aldol Addition

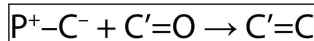


Aldol Condensation



- Creates an enal

Wittig Reaction



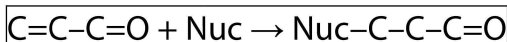
- Ylide: something with adjacent positive and negative charges



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Conjugate Addition



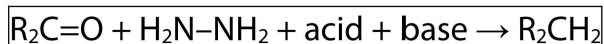
- Can have 1,4 and 1,2 additions for an alpha/beta-unsaturated carbonyl

Enamine/Imine Formation



- Double bond between carbons = enamine; double bond between C and N = imine

Wolf-Kishner Reduction



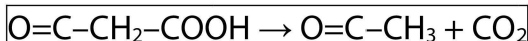
NUCLEOPHILIC SUBSTITUTION

- Nucleophile attacks carbon bonded to leaving group, replaces it

SN1 vs. SN2

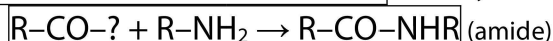
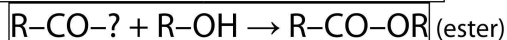
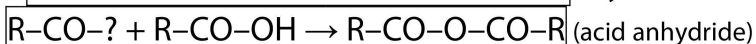
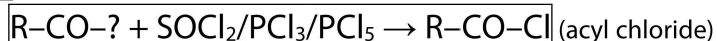
- *Nucleophile*: weak nucleophile = SN1, strong = SN2
- *Substrate*: sterically hindered substrate = SN1, unhindered = SN2
- *Solvent*: polar solvent = SN1, nonpolar = SN2
- *Speed*: SN1 depends on substrate, SN2 depends on substrate and nucleophile
- *Stereochemistry*: SN1 creates racemic, SN2 has inversion of configuration
- *Skeleton*: SN1 has rearrangement, SN2 doesn't

Decarboxylation

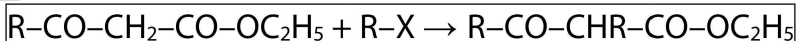


- Reactant needs to be a beta-keto acid

Nucleophilic Acyl Substitution



Acetoacetic Ester Synthesis

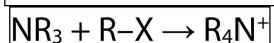
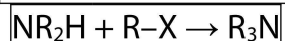
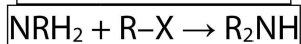
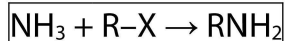




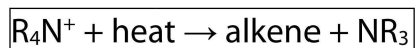
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Alkylation



Hofmann Elimination



- Creates the least substituted alkene (Hofmann product)

Hofmann Degradation

