#### Generation and Rearrangements of Electron Deficient Centers

1. Carbon cation formation by ionization
   1. Loss of leaving group
   2. Examples of “stable cations”
   3. Assisted by polar solvents and Lewis acids





ROH + SO2 R+ + HSO3- mechanism?







* 1. Combination of antimony pentafluoride and fluorosulfonic acid make magic acid (pKa < -20) protonates even aliphatic CH, behave as a “base” hydride



* + 1. Many cations can be observed in superacid medium by NMR
    2. SO2 and SO2ClF are unreactive solvents, why?
  1. primary carbon cation is never detected in solution, only secondary and tertiary
  2. simple hydrocarbons form t-butyl cation in superacid media
     1. hydride “abstraction” may be concerted or stepwise



* + 1. methane, ethane, propane
  1. protonation of CH bond -detect CH5+ in gas phase



* 1. Sommer & Bukal*a Acc. Chem. Res* **1993**, *26*, 370

1. Carbon cations by addition of cation to double bond
   1. Protonation of olefin



* 1. Protonation of lone pair: carbonyl



* 1. Protonation of lone pair: alcohol, reverse of 2.1
  2. Lewis acid addition to carbonyls



* 1. Ion addition to phenyl ring



* 1. Hydride abstraction



Keq = 1011

1. Stability of carbon cations
   1. 3o > 2o >1o >methyl
      1. *t*-Bu+, (CH3)3C+ stable at 170 ºC in SbF5/FSO3H for 4 weeks
      2. other cations rearrange to *t*-Bu+
   2. Planar structure important (10-14?)



* 1. Delocalized cations
     1. : benzyl and allyl



* + 1. cycloheptatrienyl (2.6) and cyclopropenyl 103 more stable

 

* + 1. hydroxyl methyl (see above, 1.3)

 

* 1. Phenonium ions, charge balance



1. Reactions of carbon cations
   1. 4 principle reactions
      1. addition of nucleophile
      2. elimination of proton
      3. addition to  bond
      4. rearrangement
   2. Messy if primary leaving group is involved
   3. Primary cations normally do not form in solution
      1. example: diazonium/diazotization
      2. avoid high energy primary cation, text out of date



1. Rerrangements of carbon cations
   1. Given an opportunity cations will rearrange to more stable ions
   2. Non-skelatal rearrangement
      1. Rearragement with primary leaving group probably concerted



* + 1. Why does this tertiary carbon cation rearrange to secondary?



* + 1. Allylic rearrangement with poor nucleophile (SN1 conditions): Explain



* + 1. High concentrations of good nucleophile: explain



* 1. Skelatal rearrangement
     1. Neopentyl rearrangements
     2. Types of rearrangements known as Wagner-Meerwein rearrangements



* 1. Rearrangement of alkenes



1. Pinacol rearrangement
   1. 1,2-diols rearrange to ketone in acid



* 1. Works with alcohols that have  leaving group



* 1. Migration is a [1,2] sigmatropic shift (concerted)
     1. supra,supra topology
     2. Retention of configuration, migrating group not free to invert (bridging? Common transition state)



* 1. Migration preference Ph > 3o > 2 o >1 o > Me (Ph not concerted)
  2. examination of product not clear indication of preference for migration since cation formation is often RDS



* 1. Use symmetrical diol: Ar = *p*-MeOC6H4 (500) > *p*-MeC6H4 (15.7) > C6H5 (1)> *p*-ClC6H4 (0.7) (consider 2,3,diphenyl-23-butandiol)



* 1. Stereochemistry of 1,2 rearrangement
     1. Migrating group, migrating target, migrating origin
     2. Migrating group is not free, no crossover, no inversion when chiral center used
     3. Bridging favors Inversion of target and origin, but does not always occur



1. Wolf rearrangement: try stepwise mechanism for last step. What is wrong? Arrow



1. Diazonium formation from primary amines? See below: overall change? Loss of O
   1. Amine is oxidized by moving electrons to oxygen
   2. Protons migrate N to O
   3. Nitrite N looses O, activated by protonation
   4. Amine nitrogen is oxidized, oxygen is reduced





* 1. Aliphatic alkyldiazonium cations are unstable, good method of forming carbon cations
  2. Phenyl diazonium cations are stable at room temperature, why?

1. Migration to electron deficient nitrogen
   1. Hoffman rearrangement
      1. Convert nitrogen to nucleophile, then electrophile with leaving group
      2. Retention of configuration of R



* 1. Lossen rearrangement: try a non-concerted migration-dissociation.
     1. What does it mean that electron donating R accelerates the reaction and electron withdrawing R’ slow it down (RDS?)



* 1. Curtius rearrangement: write resonance forms of triazo compound and preserve octets.



* 1. Schmidt Rearrangement



* 1. Beckman rearrangement
     1. Hydroxylimine rearrangement to amide, only trans to OH group migrates



* + 1. Converts cyclohexane hydroxylimine to lactam: precursor toNylon-6



1. Migration to electron deficient oxygen
   1. Bayer-Villager Oxidation of ketones
      1. Hydrogen peroxide or acid peroxide adds to ketone or aldehyde
      2. Acid catalyzes reaction



* 1. Alkyl peroxides
     1. Catalyzed by acid: makes oxygen more electron deficient
     2. Migration and water loss is concerted: evidence?



* 1. Product of following reaction? Add water



1. Norbornyl cations



???

