*CHEM 342 – Lecture 10 03/03/2015*

Overheads: - Today’s Outline

So far: Have focussed on pericyclic reactions: rearrangement of neutral molecules by moving of electrons in ring.

Carbocation Rearrangements:



Why does it happen?

* To make more stable C+!

- 2° → 3°

- localized → delocalized (resonance)

- strained ring → less strained ring

Can C+ ever go from 3° → 2° or 2° → 1° ?

- very unlikely to make product of less stable C+, BUT less stable C+ may be formed along reaction pathway.



→ 1° C+ may not “actually” be formed as a distinct species; next step happens to fast

→ “superacids” stabilize C+, so 1° might last longer than usual

C+ rearrangements can be “assisted” by groups that can donate electrons:

e.g. Pinacol Rearrangement

Unsymmetrical cases

* Two questions:

1. Which OH gets protonated/leaves?



1. Which R group moves?



Migratory Aptitude:

Generally: H > aryl > alkyl (3° > 2° > 1°)

Phenyl moves more easily than CH3



Related Reaction: “semi-pinacol”





Favorskii Rearrangement



→ can be used to make smaller ring (ring contraction)

- opposite of diazomethane reaction!

