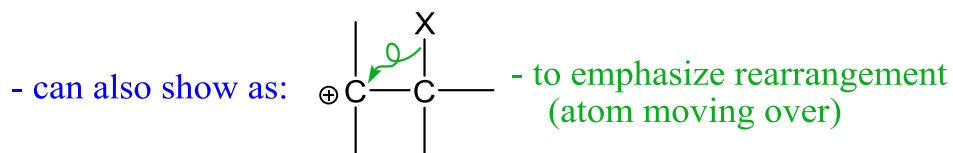
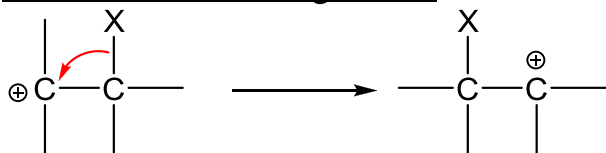


Overheads: - Today's Outline

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

Carbocation Rearrangements:

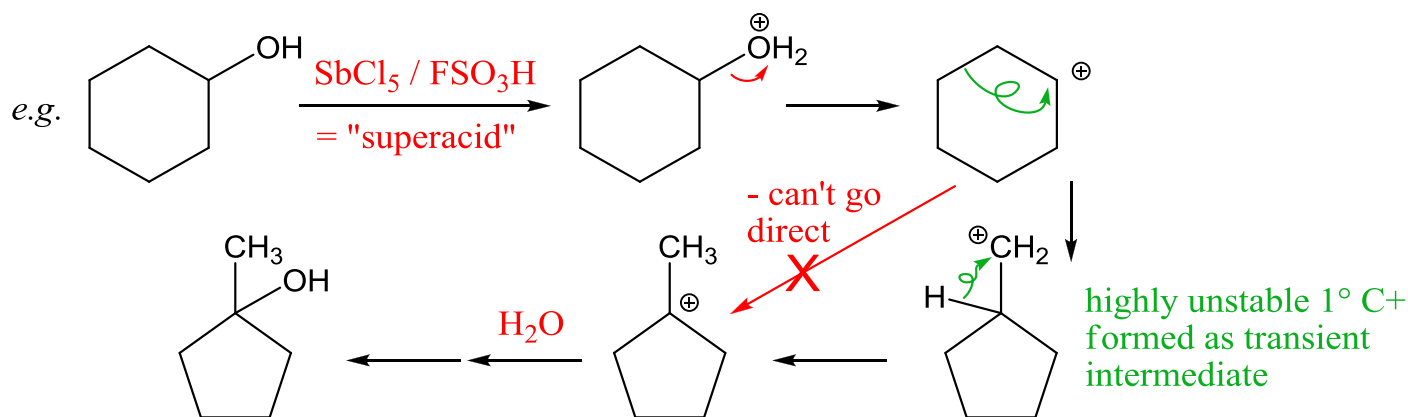


Why does it happen?

- To make more stable C+!
 - $2^\circ \rightarrow 3^\circ$
 - localized \rightarrow delocalized (resonance)
 - strained ring \rightarrow less strained ring

Can C+ ever go from $3^\circ \rightarrow 2^\circ$ or $2^\circ \rightarrow 1^\circ$?

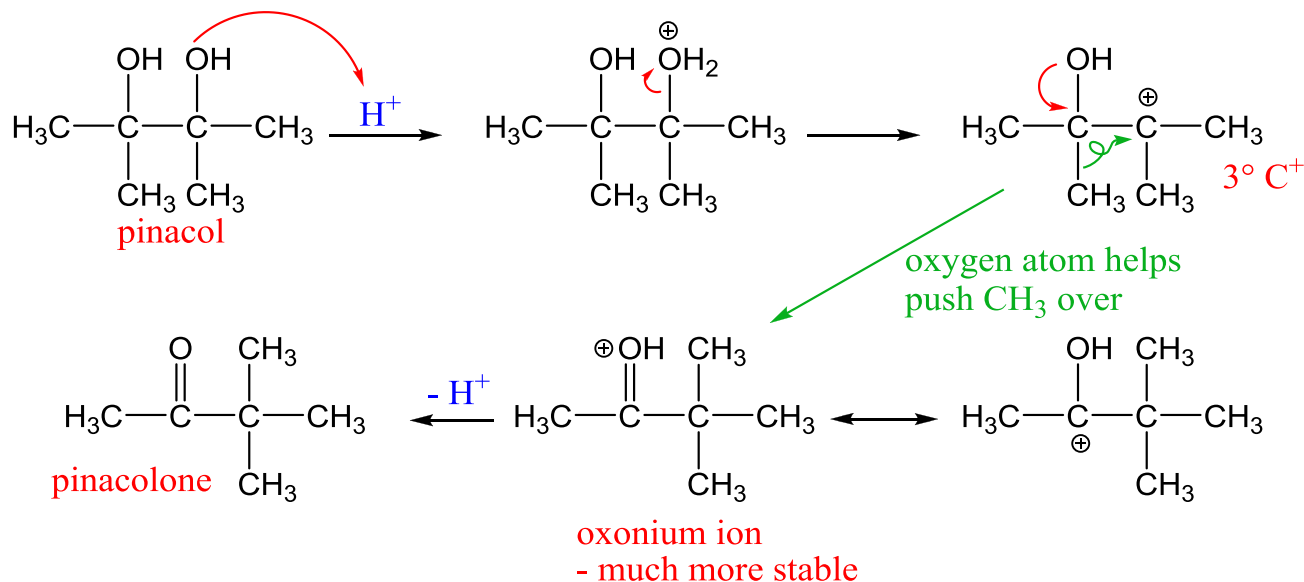
- very unlikely to make product of less stable C+, BUT less stable C+ may be formed along reaction pathway.



\rightarrow 1° C+ may not “actually” be formed as a distinct species; next step happens too fast
 \rightarrow “superacids” stabilize C+, so 1° might last longer than usual

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

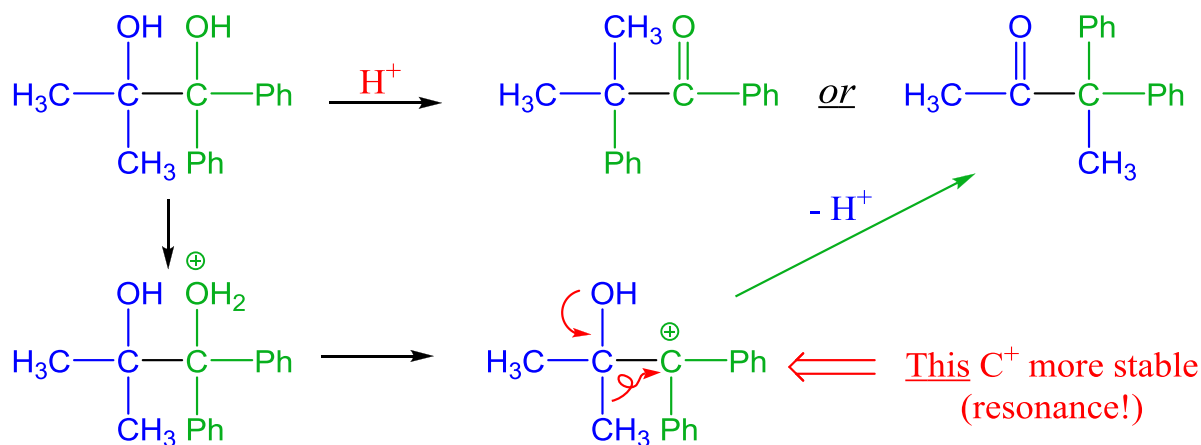
e.g. Pinacol Rearrangement



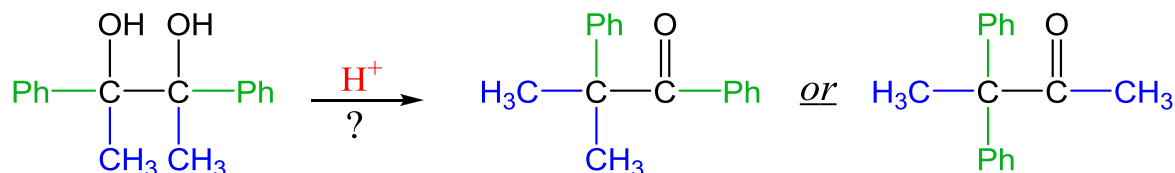
Unsymmetrical cases

- Two questions:

1) Which OH gets protonated/leaves?



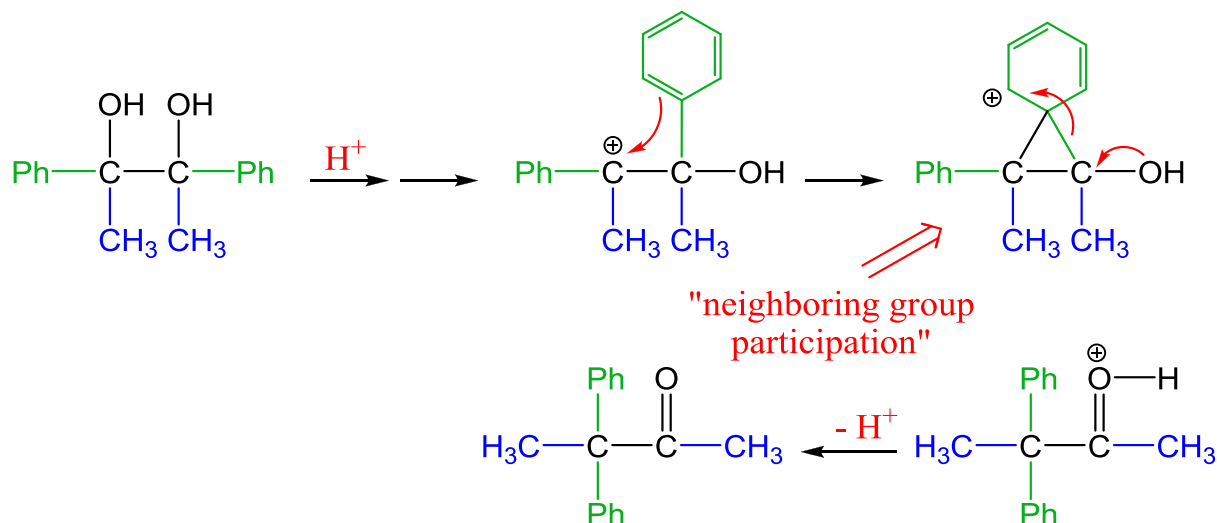
2) Which R group moves?



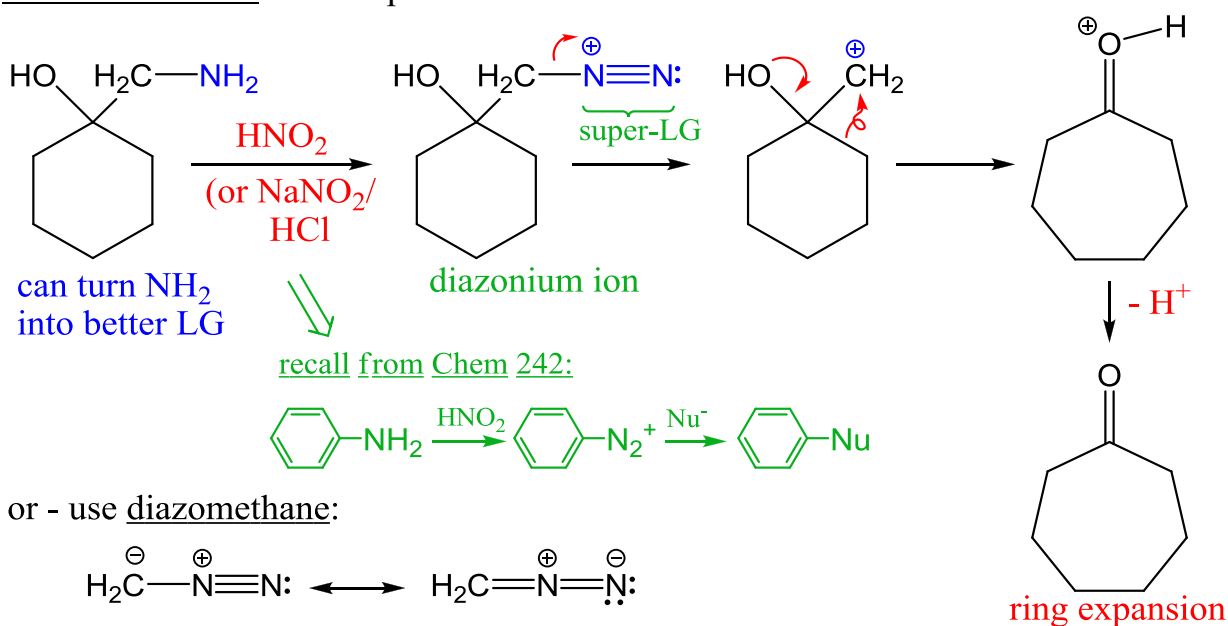
Migratory Aptitude:

Generally: $H > \text{aryl} > \text{alkyl} \Rightarrow (3^\circ > 2^\circ > 1^\circ)$

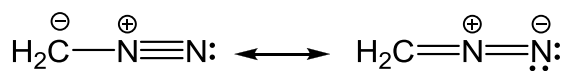
Phenyl moves more easily than CH_3



Related Reaction: "semi-pinacol"



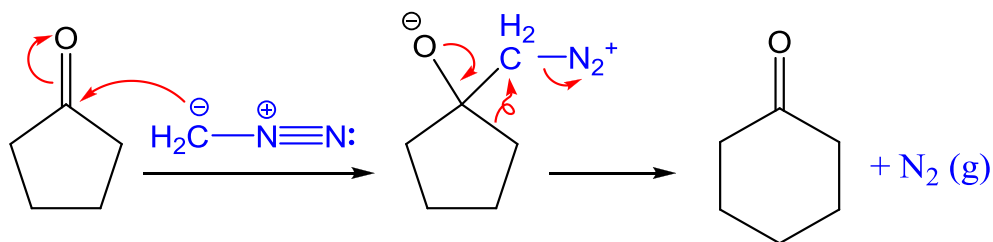
or - use diazomethane:



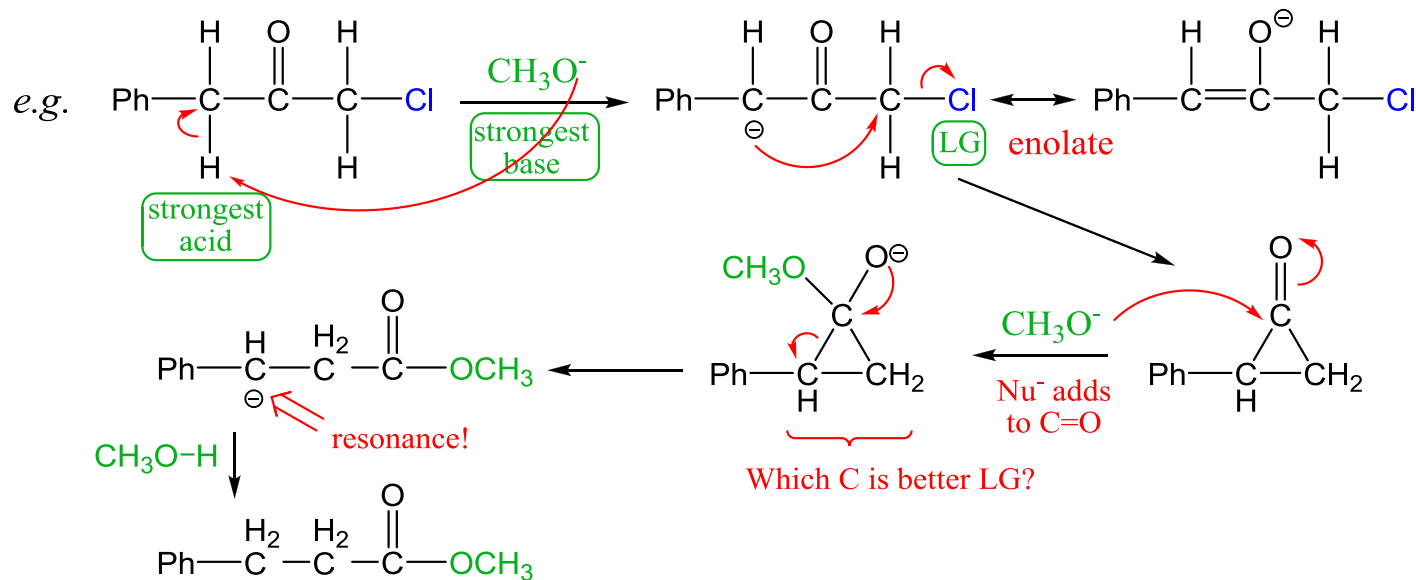
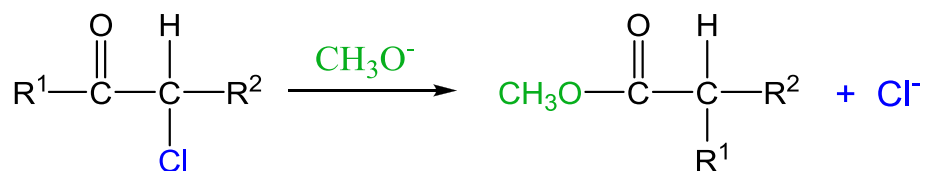
- bright yellow liquid
- highly shock sensitive! (BOOM!)
- made from "diazald", but must use only polished glassware (no ground glass joints / sharp edges)

Aldrich Chemical Company:

- first product was diazald - made in a garage
- now largest fine chemical company



Favorskii Rearrangement



→ can be used to make smaller ring (ring contraction)
- opposite of diazomethane reaction!

