Topic 6: Stabilization of Carbocations by Vicinal Sigma Bonds

Reading: I. Fleming Molecular Orbitals and Organic Chemical Reactions, 2.2.1, 2.2.2
Drawing Norbornyl Ring Systems

■ Don’t draw norbornane like a coat hanger

■ Instead, **draw norbornane by starting with a chair conformation**

- bisect a chair
- draw perfect axial bonds
- join axial carbons
- erase the extra carbon
- darken bonds that are closer to viewer

■ Why base your depiction on a chair? So you can fuse other chairs using staggered bonds, visualize antiperiplanar relationships, and estimate atom-atom distances. Correct angles and distances are **essential** for predicting chemistry.

![Examples of norbornane structures]

- close? (not obviously close)
Solvolysis of 2-Norbornyl Derivatives

- Observations
  - Perfect bond alignment leads to stabilization of the 2-norbornyl cation and weakens the exo bond.
  - Not S_N2
  - Racemic product

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- Racemic product

- 350x faster

- In complex mechanisms, I will allow you to connect 2-norbornyl structures with resonance arrows or reaction arrows.

[1,2] Alkyl and [1,2] Hydride Shifts

- Unstable carbocations (e.g., 2° alkyl) undergo rapid alkyl migrations, referred to as [1,2] shifts, as long as they are not going uphill in energy.

  ![Chemical Structure](image)

  $\Delta G^+ < 5 \text{ kcal/mol}$
  $t_{1/2} < 10 \text{ msec}$

- [1,2] Hydride shifts can also be fast too. Longer range hydride transfers are rare. 2-Norbornyl cations undergo a fast [1,3] hydride shift but that is atypical.

  ![Chemical Structure](image)

  $E_a = 10.8 \text{ kcal/mol}$
  $E_a = 5.9 \text{ kcal/mol}$

  Arrhenius Eq. $k = A e^{(-E_a/RT)}$

  $E_a$ is similar to $\Delta H^+$


- Be cautious about invoking longer range hydride transfers. They are rare.

  ![Chemical Structure](image)

  $NaOAc$ AcOH $45^\circ C, 18 \text{ h}$

  major product

- It will often be difficult to know whether 1,2-hydride shifts or proton transfers were involved.

  ![Chemical Structure](image)

  proton xfer

  $J. Am. Chem. Soc. 1963, 85, 3743$
**Bonding in Cyclopropanes**

- **Bonds:** Smaller angle = more p character = more nucleophilic.

  - C-H = acidic (lots of s character)
  - C-C = nucleophilic (lots of p character)

- Regions of maximum electron density are not on the C-C axis
- C-C = nucleophilic (lots of p character)
- C-H = acidic (lots of s character)

- **Conclusion:** Strained rings should be able to stabilize adjacent carbocations

  - Bent bonds in cyclopropane called "banana bonds"

  - Conformational requirements:
    - **GOOD** both strained C-C bonds donate into empty p orbital
    - **BAD** neither strained C-C bond donates into empty p orbital
Cyclopropylcarbinyl Cations

- Cyclopropyl groups lead to surprising stabilization
  
  \[
  \text{SN1 in AcOH} \quad \begin{array}{c}
  \text{OTs} \\
  \text{Ph} \text{OTs} \\
  \text{OTs}
  \end{array}
  \]
  
  \[k_{\text{rel}} \quad 1 \quad 1,400 \quad 120,000\]

- Cyclopropylcarbinyl cations are more stable than Ph\(_3\)C+
  

- Conformational requirement: strained bonds overlap with empty p or σ*
  
  acetolysis at 25 °C

- Cyclopropylcarbinyl cations lead to various products

- Resonance picture

  "homoallyl cation"
Beta Metal Carbocations

- Beta silyl carbocations are super stabilized by the adjacent nucleophilic C-Si bond

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me} \quad \text{R} \quad \text{C} \quad \text{R} \\
\text{H} & \quad \text{Me} \quad \text{R} \quad \text{C} \quad \text{R}
\end{align*}
\]

38 kcal/mol more stable!


- Longer bonds are more nucleophilic

Nucleophilicity: \( \sigma_{\text{C-C}} < \sigma_{\text{C-Si}} < \sigma_{\text{C-Ge}} < \sigma_{\text{C-Sn}} \)

(this isn’t due to electronegativity)

- All beta metals stabilize carbocations. They have long, nucleophilic metal-carbon bonds.

\[
\begin{align*}
\text{(OC)}_3\text{Fe} & \quad \text{Me} \quad \text{R} \quad \text{C} \quad \text{R} \\
\text{(OC)}_3\text{Fe}^+ & \quad \text{Me} \quad \text{R} \quad \text{C} \quad \text{R}
\end{align*}
\]

more correct, but useless for arrow-pushing