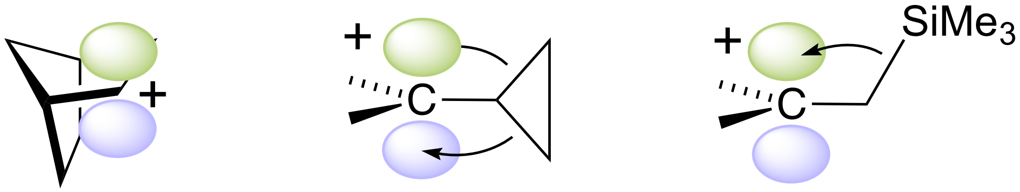
Professor David L. Van Vranken
Chemistry 201: Organic Reaction Mechanisms I

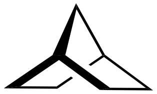
Topic 6: Stabilization of Carbocations by Vicinal Sigma Bonds



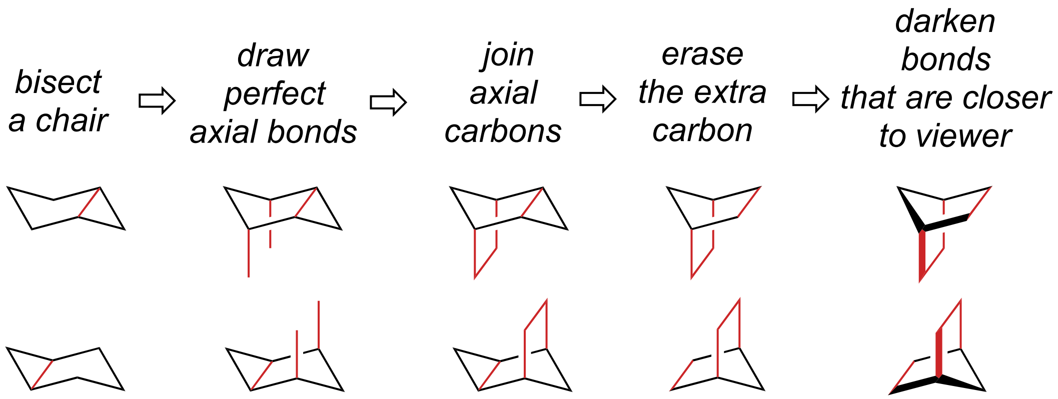
Reading: I. Fleming *Molecular Orbitals and Organic Chemical Reactions*, **2.2.1, 2.2.2**

Drawing Norbornyl Ring Systems

- Don’t draw norbornane like a coat hanger

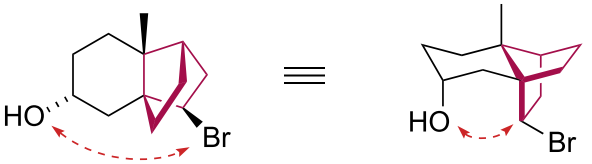


- Instead, **draw norbornane by starting with a chair conformation**



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 <u>essential</u> for predicting chemistry.

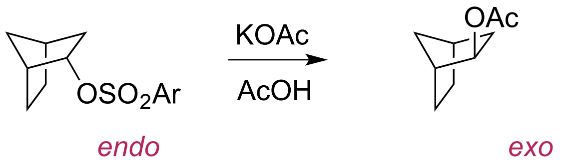


close?

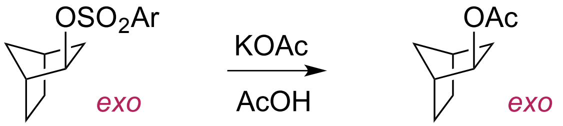
obviously close

Solvolysis of 2-Norbornyl Derivatives

■ Observations

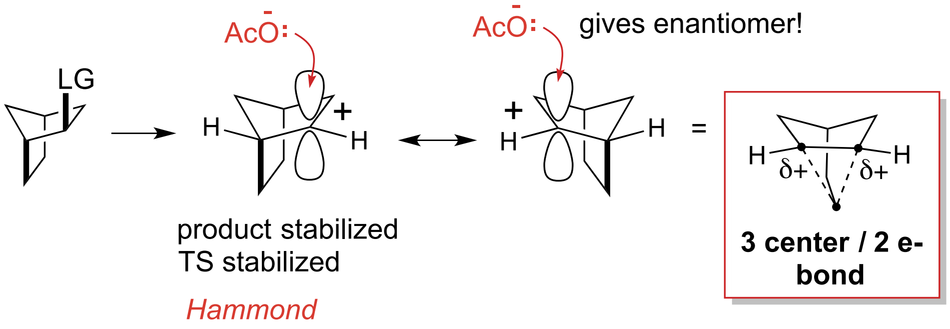


- Not S$_N$2
- Racemic product

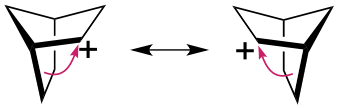


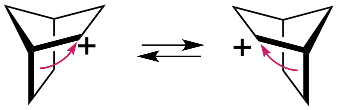
- 350x faster

■ **Perfect bond alignment** leads to stabilization of the 2-norbornyl cation and weakens the exo bond.



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

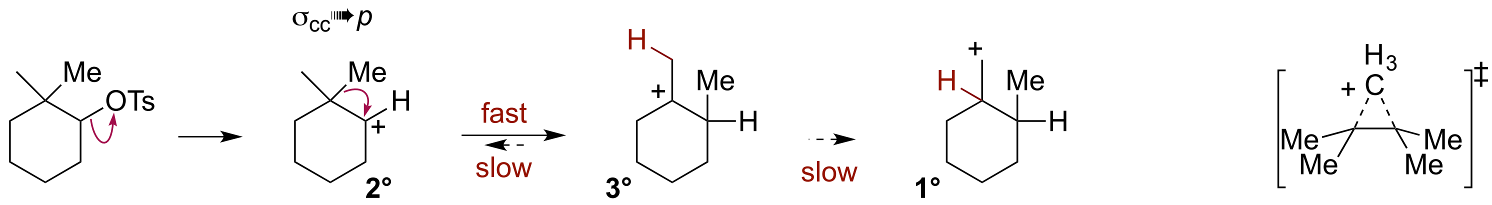




Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III; "Why the Classical and Nonclassical Norbornyl Cations Do Not Resemble the 2-endo- and 2-exo-Norbornyl Solvolysis Transition States" *J. Org. Chem.* **1997**, *62*, 4216-4228.

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

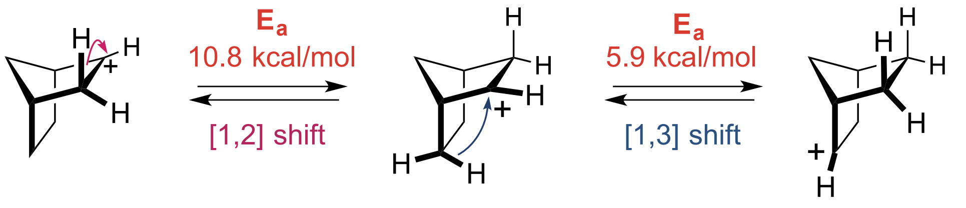
■ Unstable carbocations (e.g., 2° alkyl) undergo rapid alkyl migrations, referred to as [1,2] shifts, as long as they are not going uphill in energy.



$\Delta G^{\ddagger} < 5$ kcal/mol

$t_{1/2} < 10$ 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.



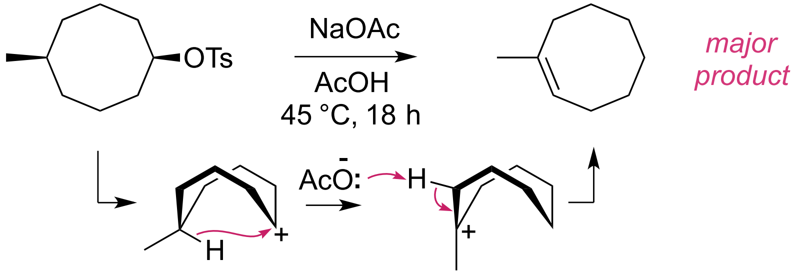
Arrhenius Eq.

$$k = A\,e^{\left(\frac{E_a}{RT}\right)}$$

E_a is similar to $\Delta H^{\ddagger}$

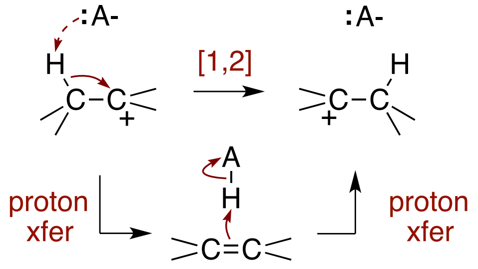
Olah, G. A, et al..
J. Am. Chem. Soc.
1970, *92*, 4627-4640.

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



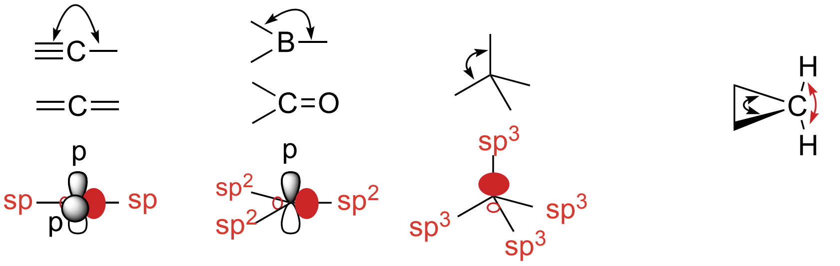
J. Am. Chem. Soc. **1963**, *85*, 3743

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



Bonding in Cyclopropanes

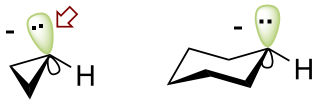
- Bonds: Smaller angle = more p character = more nucleophilic.



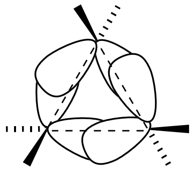
				CCC	HCH
angle	180°	120°	109.5	≠ 60°	~ 120°
%p	**50%**	**66%**	**75%**	**83%**	**66%**

10^5 less basic

(b/c less 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)

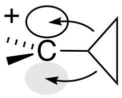


bent bonds in cyclopropane called "banana bonds"

- Conclusion: strained rings should be able to stabilize adjacent carbocations

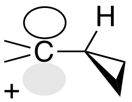
conformational requirements

GOOD



both strained C-C bonds donate into empty p orbital

BAD

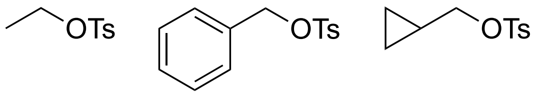


neither strained C-C bond donates into empty p orbital

Cyclopropylcarbinyl Cations

■ Cyclopropyl groups lead to surprising stabilization

S_N1 in AcOH



k_{rel}	1	1,400	120,000

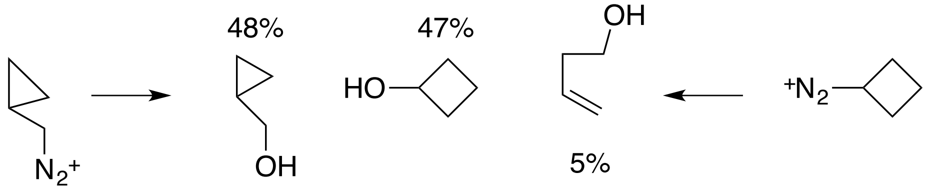
■ Cyclopropylcarbinyl cations are **more stable than Ph_3C+**

Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. “Long-Lived Cyclopropylcarbinyl Cations” *Chem. Rev.* **1992**, *92*, 69-95.

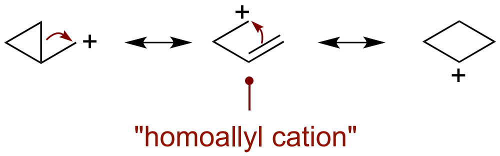
■ Conformational requirement: strained bonds overlap with empty p or σ*

acetolysis at 25 °C

■ Cyclopropylcarbinyl cations lead to various products



■ Resonance picture



Beta Metal Carbocations

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

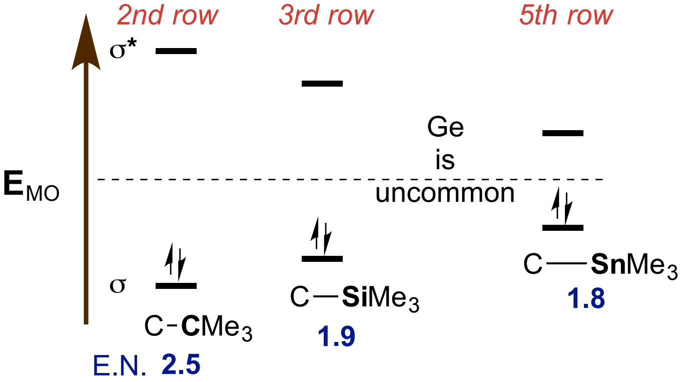
38 kcal/mol more stable!

Lambert, J. B.; et al.
Acc. Chem. Res. **1999**, *32*, 183.

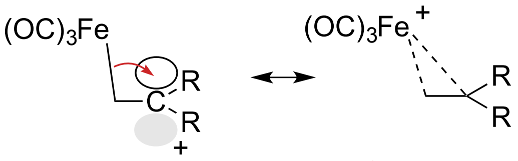
- **Longer bonds are more nucleophilic**

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

(this isn't due to electronegativity)



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



more correct,
but useless for arrow-pushing