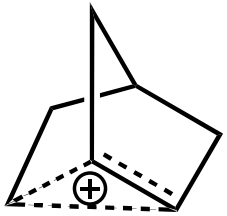
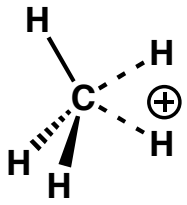
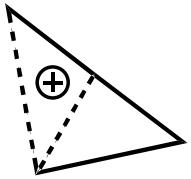


Nonclassical Carbocations

From Controversy to Convention

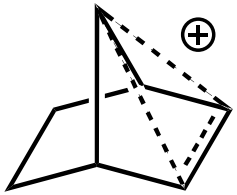


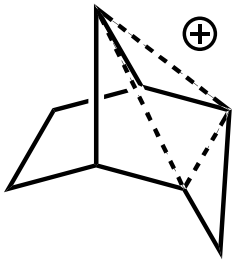


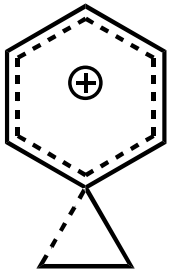
A Stoltz Group Literature Meeting
brought to you by

Chris Gilmore

June 26, 2006
8 PM
147 Noyes







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1. Introduction

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   - Winstein, Brown, and the Great Debate
   - George Olah and ending the discussion
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3. The Nature of the Nonclassical Carbocation
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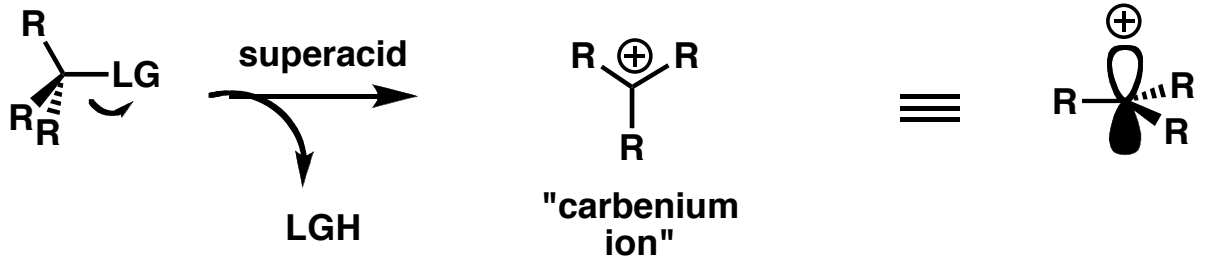
   - Interesting rearrangements
   - Overman and the Prins-Pinacol

Carbocations: An Introduction

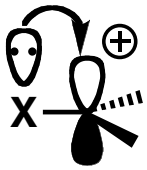
Traditional carbocation is a low-valent, trisubstituted electron-deficient carbon center:



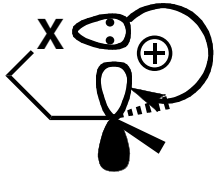
- 6 valence e^-
- planar structure
- empty *p* orbital

Modes of stabilization:

Heteroatomic Assistance

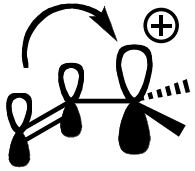


Lone Pair Resonance

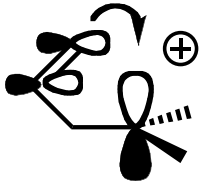


Anchimeric Assistance

π-bond Resonance

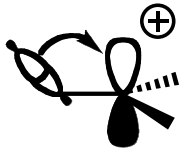


Allylic Stabilization

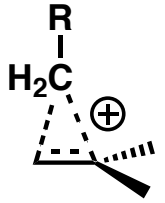


Homoconjugation

σ-bond Participation



Hyperconjugation



Non-Classical Interaction

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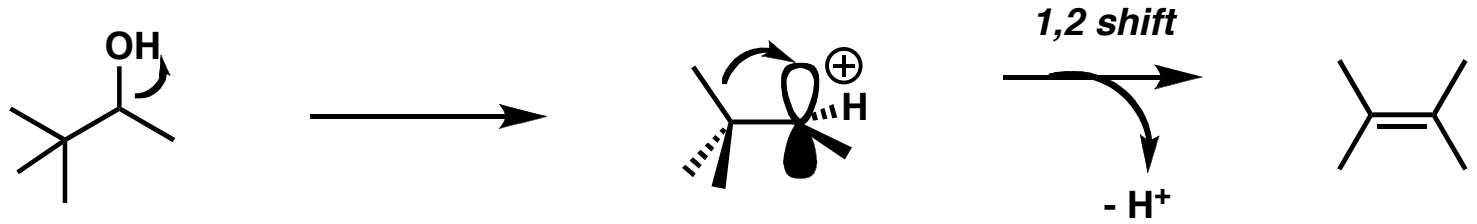
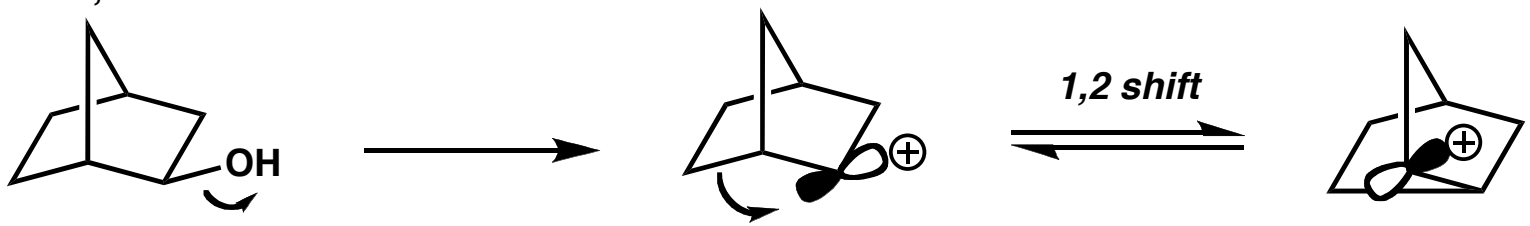
The Nonclassical Problem: Early Curiosities

Wagner, 1899:

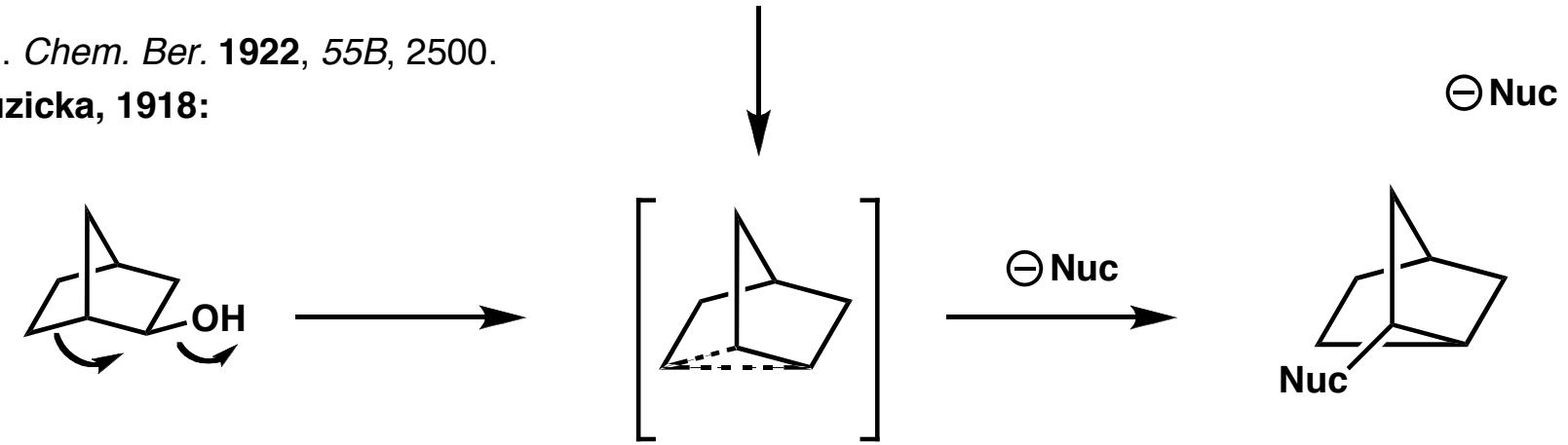


Meerwein, 1922:



Meerwin, H. *Chem. Ber.* **1922**, *55B*, 2500.

Ruzicka, 1918:

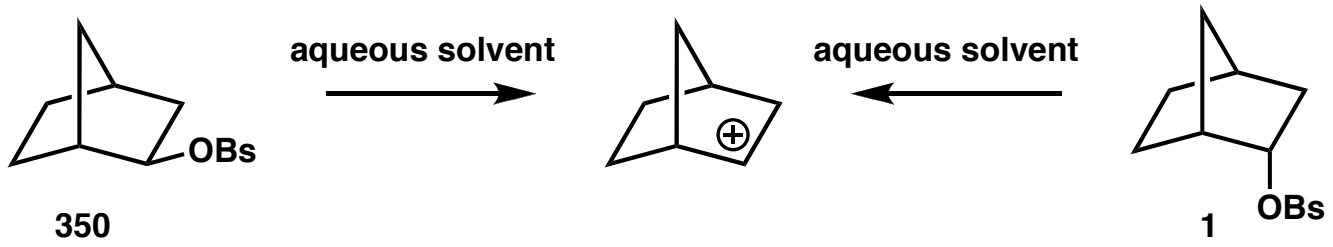


Ruzicka, L. *Helv. Chim. Acta,* **1918,** *1*, 110.

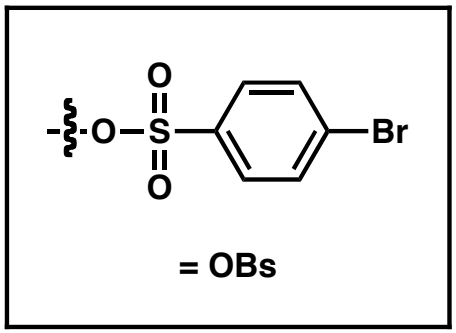
The Nonclassical Problem: An Indecent Proposal

Winstein and Trifan, 1949

Rates of solvolysis



350 **1**



Winstein, Trifan. *J. Am. Chem. Soc.,* **1949,** *71*, 2953.

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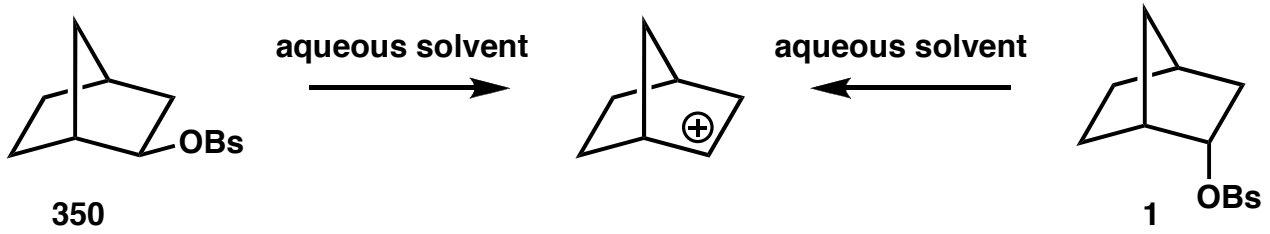
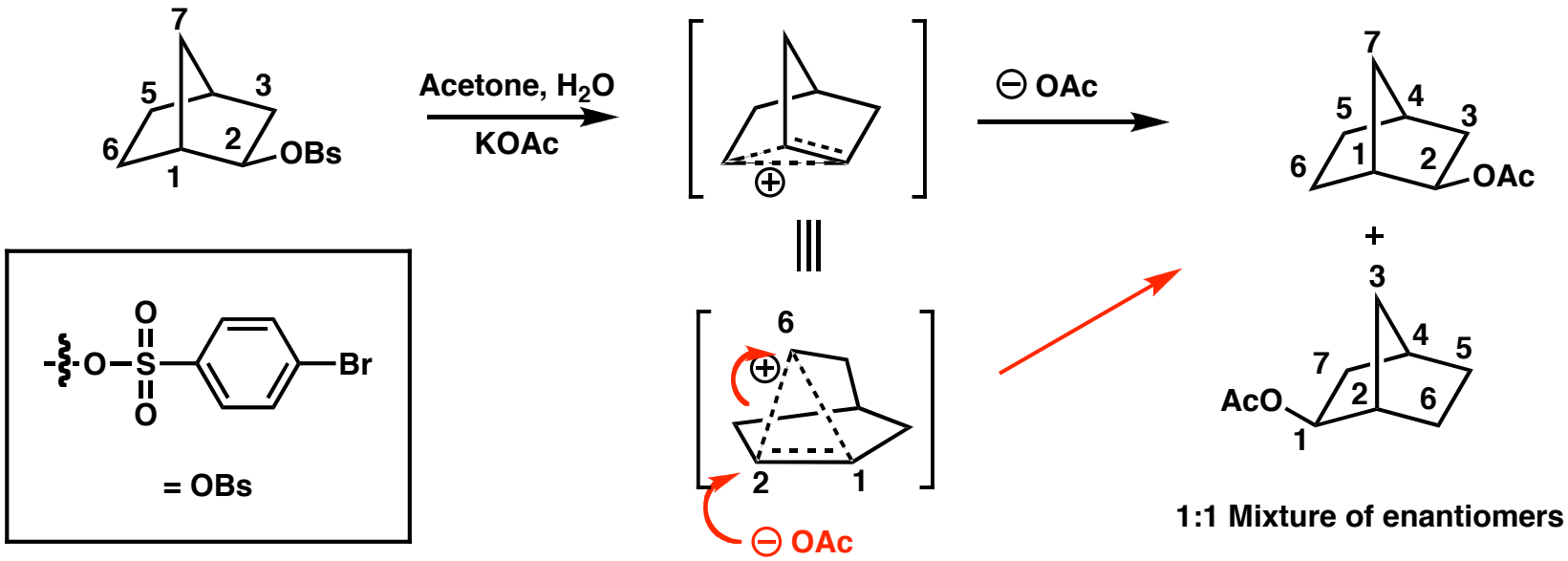


Enantiomerically pure starting material...



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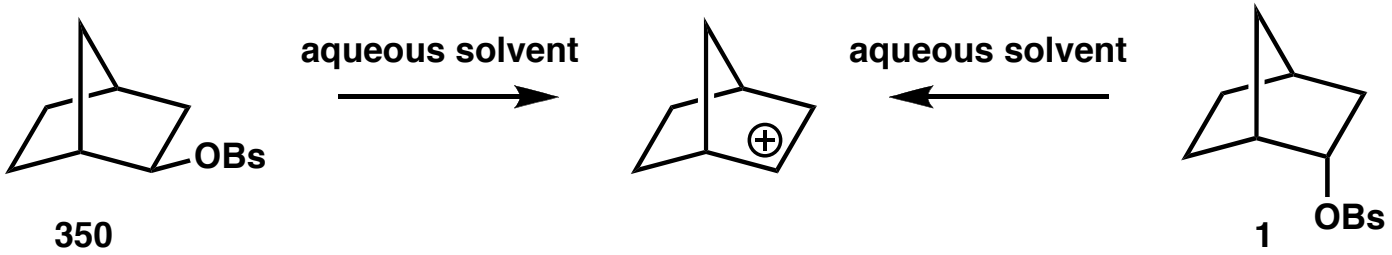

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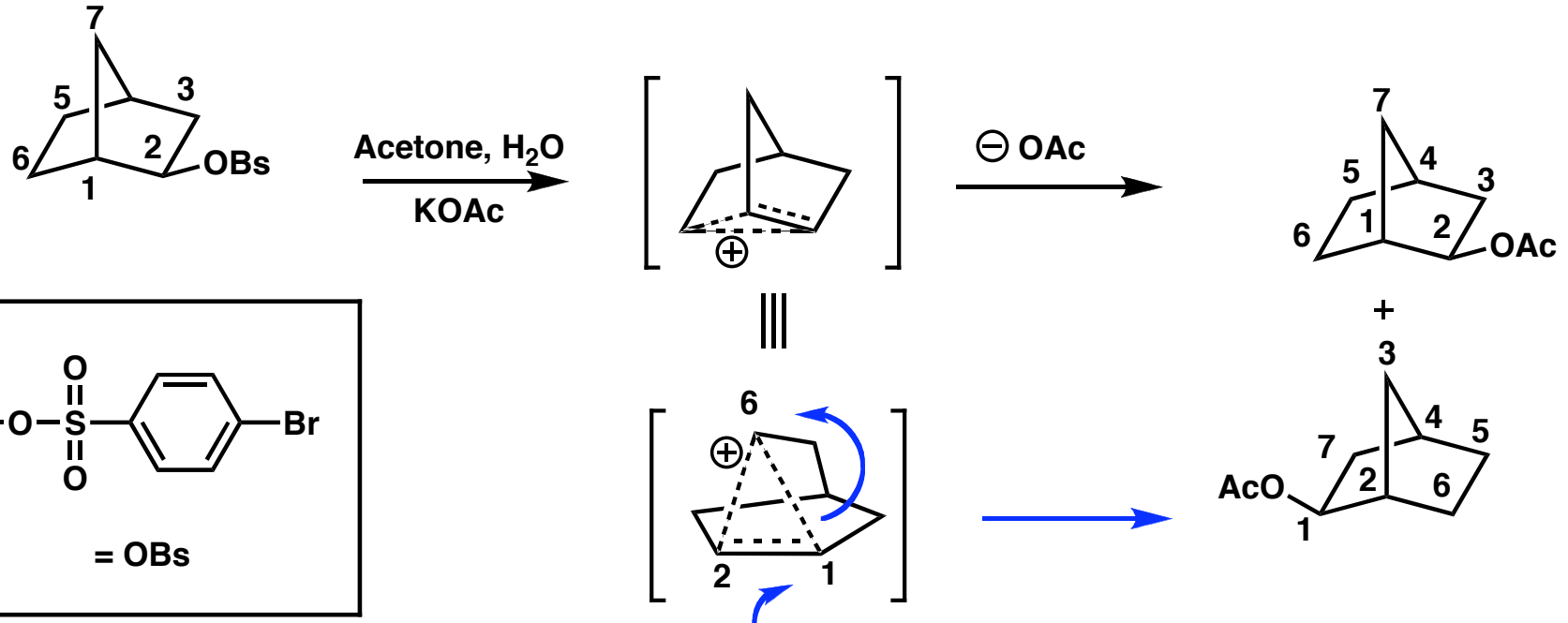
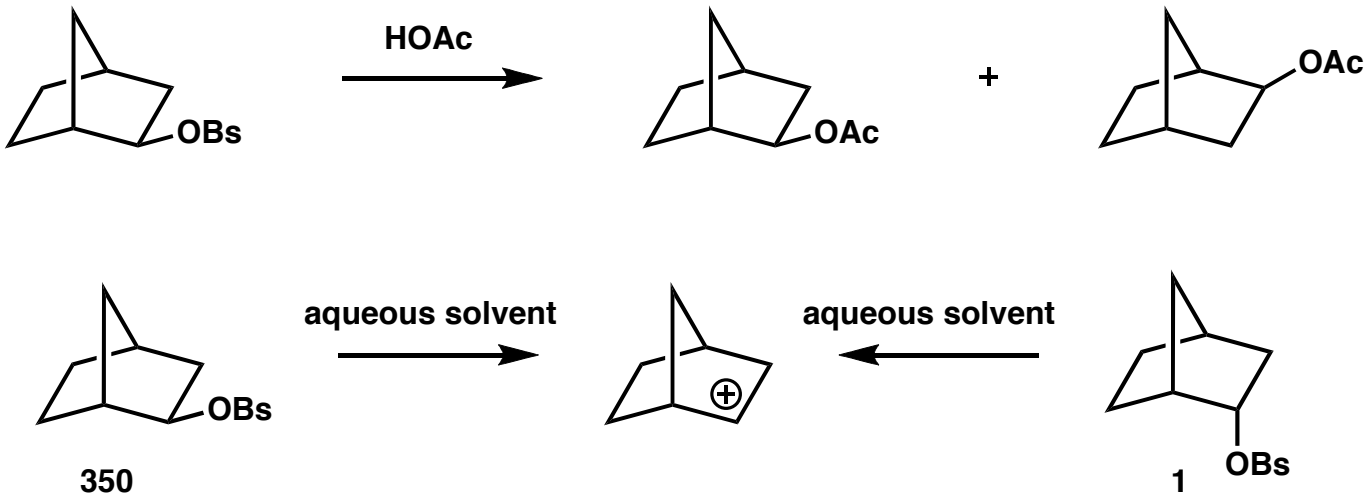


1:1 Mixture of enantiomers

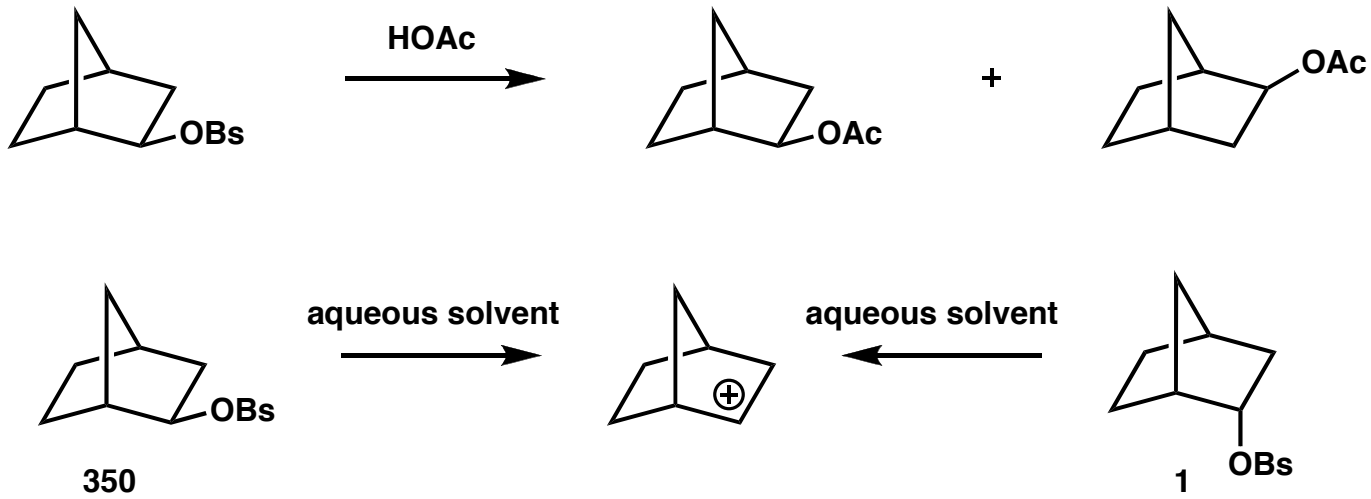
Winstein, Trifan. *J. Am. Chem. Soc.,* **1949,** *71*, 2953.

The Nonclassical Problem: An Indecent Proposal



"It is attractive to account for these results by way of the bridged (nonclassical) formulation for the norbornyl cation involving accelerated rate of formation from the exo precursor by anchimeric assistance." **-Saul Winstein**

The Nonclassical Problem: An Indecent Proposal



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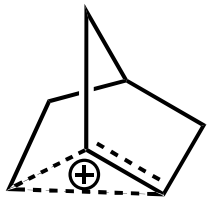
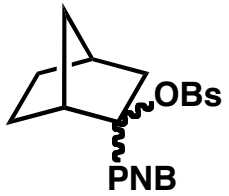


The Response of the Traditionalists- H. C. Brown

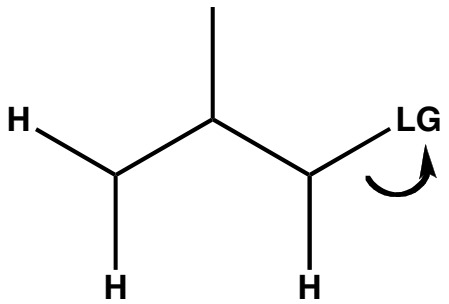
Strain release improves *exo* to *endo* ratio:



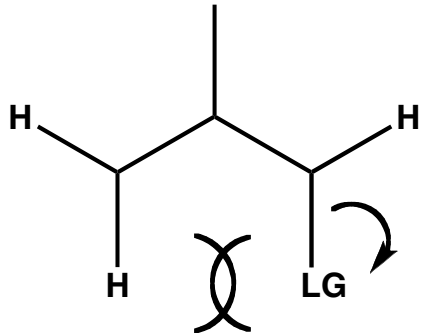
Exo/Endo	350	13	78

Not only must strain have some impact, but direct ionization hinders rate of solvolysis of *endo* norbornyl system.

exo



endo



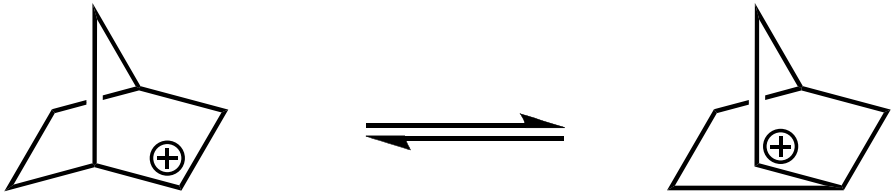
Solvolysis proceeds through unassisted ionization:

- **relief of strain accelerates *endo* ionization**
- **steric effects hinder ionization of *endo* isomer**
- ***exo* is not fast, *endo* is slow**

Brown, H.C. *J. Am. Chem. Soc.* **1964**, *86*, 1248-1250.

A Bonding Experience- Brown's Challenge

Brown insisted upon two stable, equilibrating classical carbocaitonic forms for the norbornyl cation:



"The norbornyl cation does not possess sufficient electrons to provide a pair for all of the bonds required by the proposed bridged structures. One must propose a new bonding concept, not yet established in carbon structures."

- H. C. Brown, 1965

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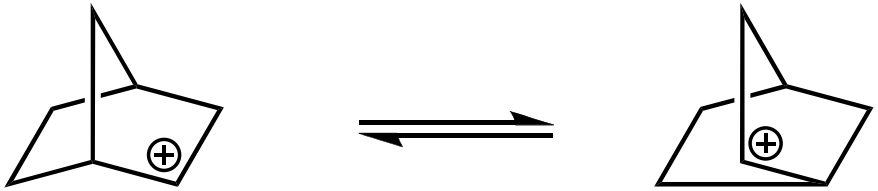

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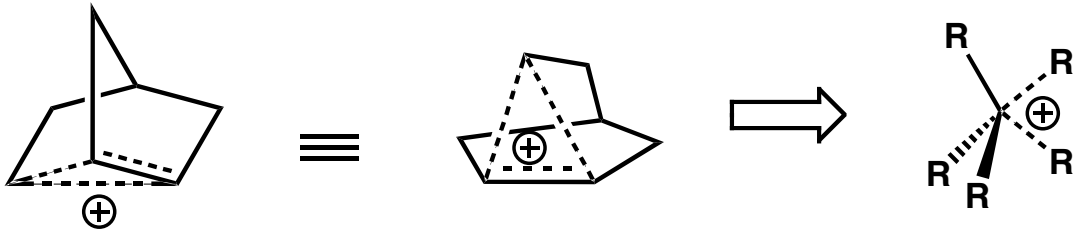
So, if not classical carbenium ions, what must nonclassical carbocations be?



"carbonium ion"

- a pentavalent carbon
- distinct 3-center, 2-electron bond
- 8 valence e^- between 6 atoms means electron-poor carbon

Brown, H. C. *J. Am. Chem. Soc.* **1965**, *87*, 2137-2153.
P.D. Bartlett, *Nonclassical Ions*, W.A. Benjamin, New York, 1965.

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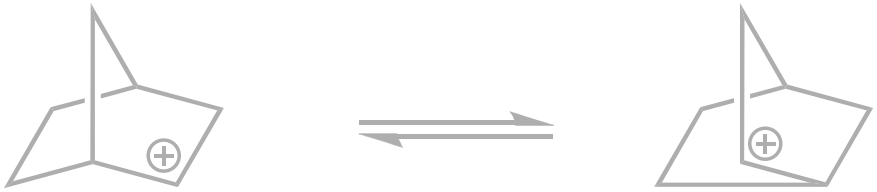

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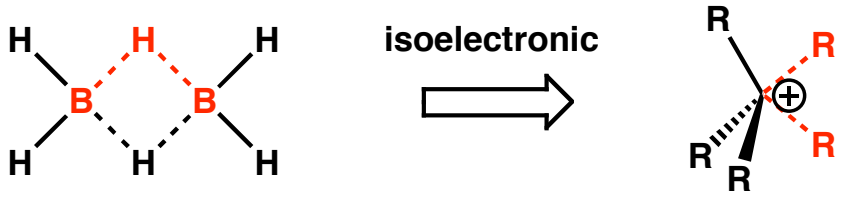


- a pentavalent carbon
- distinct 3-center, 2-electron bond
- 8 valence e^- between 6 atoms means electron-poor carbon

Contain too few electrons to allow a pair for each "bond"; must have delocalized σ electrons

P.D. Bartlett, *Nonclassical Ions*, W.A. Benjamin, New York, 1965.

Enter George Olah

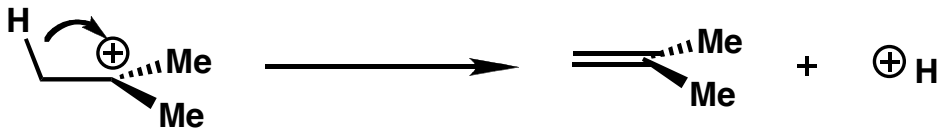
- Previous work with isolable carbocations possible because of superacids and stable ion media.

- Isolated the first stable carbocation in 1964 and was able to characterize with ^{13}C NMR

^{13}C shift was 300 ppm downfield from SM! (335.2 ppm)

J. Am Chem. Soc. **1964**, *86*, 1360

- Superacids designed to prevent proton elimination to quench carbocations



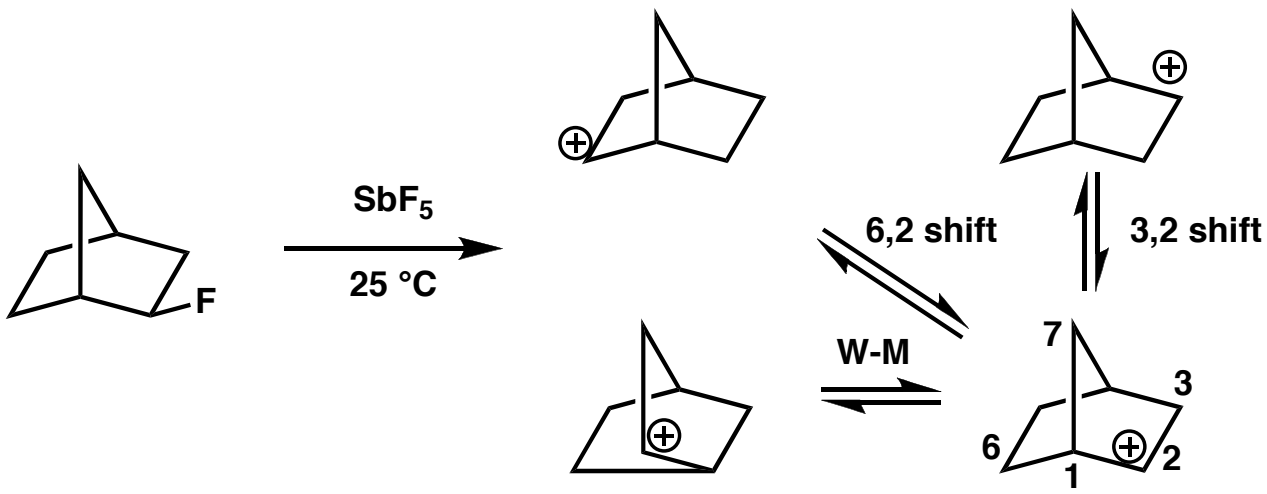
- pKa's are measured anhydrously by Hammet acidiy function H_o

	H_o
anhydrous sulfuric acid	-11.9
perchloric acid	-13.0
triflic acid	-14.1
magic acid ($FSO_3H \cdot SbF_5$)	-21.0

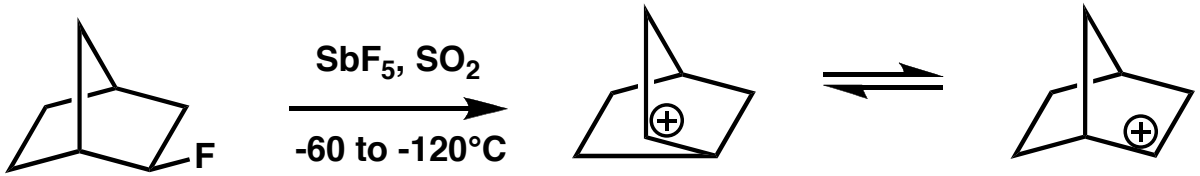
Superacids can reach acidities of H_o= -28, or 10^{16} times acidity of anhydrous sulfuric acid.

Proving the Existence of the Carbonium Ion

^{1}H NMR Studies of Olah, Saunders and Schleyer



Broad singlet corresponds to fast Wagner-Meerwein and hydride shifts, -3.75 — -3.1 ppm



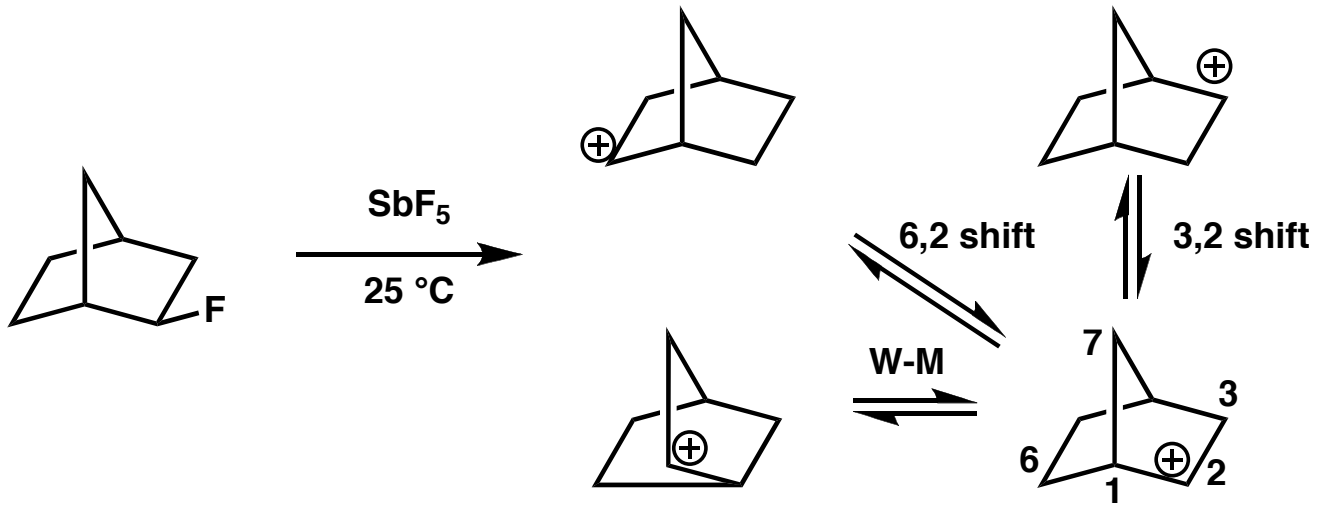
Resolves 3 singlets, 4:1:6 at -5.35, -3.15, -2.20 ppm

Shows 2-norbornyl ion stable in solution as equilibrating Wagner-Meerwein shifts OR mesomeric intermediate

Saunders, M.; Schleyer, P.; Olah, G. A. *J. Am. Chem. Soc.* **1964,** *86,* 5680.

Proving the Existence of the Carbonium Ion

^{1}H NMR Studies of Olah, Saunders and Schleyer



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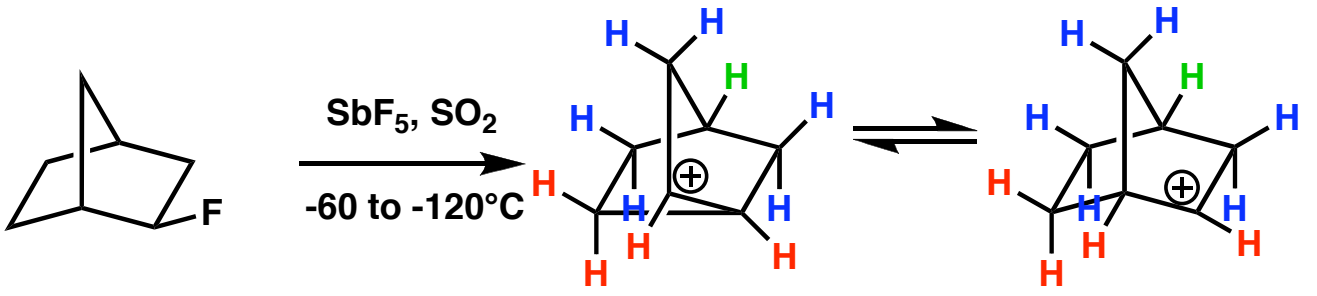


4 (-5.35 ppm)

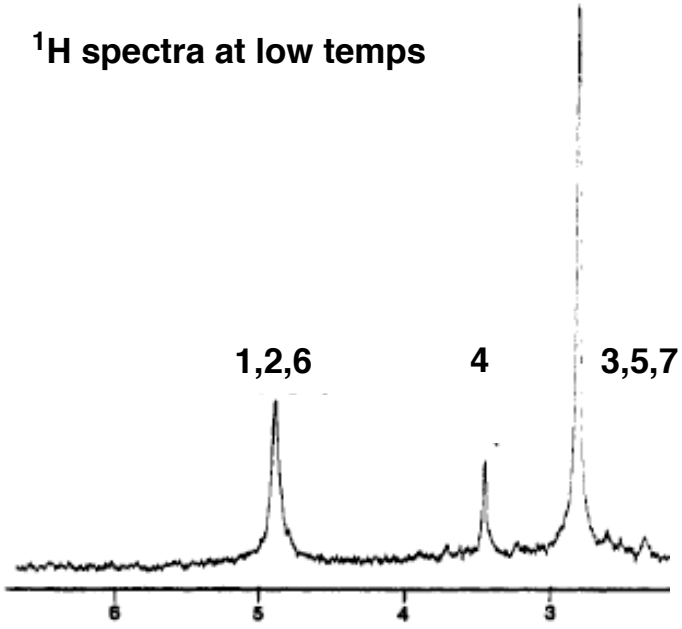
1 (-3.15 ppm)

6 (-2.20 ppm)

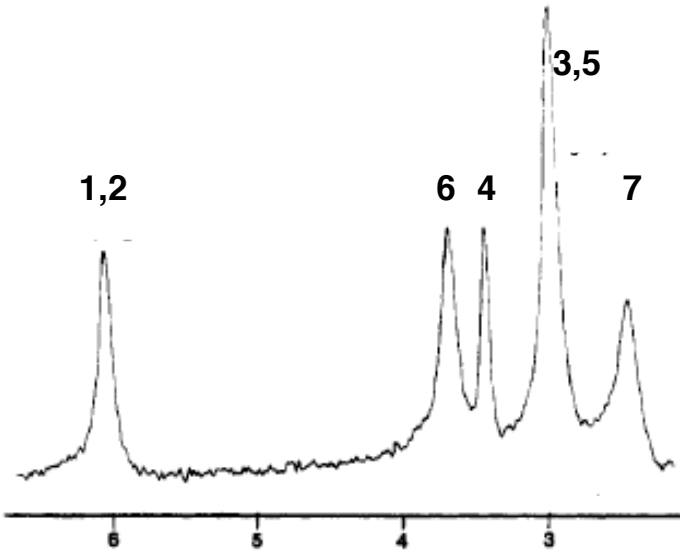
Saunders, M.; Schleyer, P.; Olah, G. A. *J. Am. Chem. Soc.* **1964,** *86,* 5680.

Proving the Existence of the Carbonium Ion

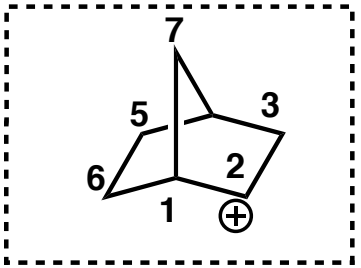
^{1}H spectra at low temps

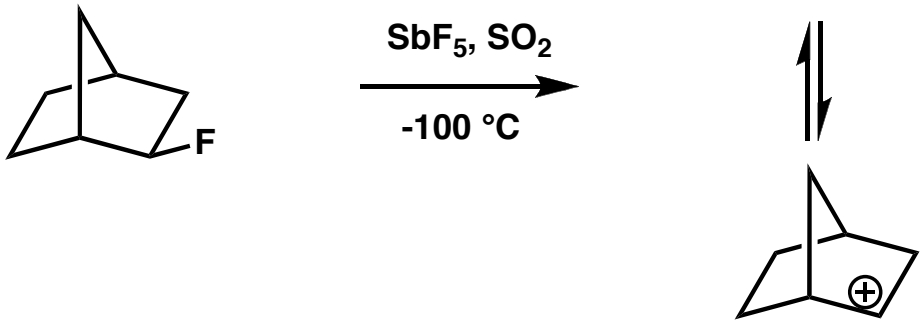


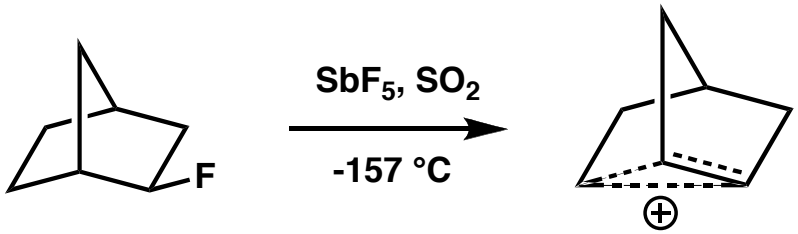
A



B

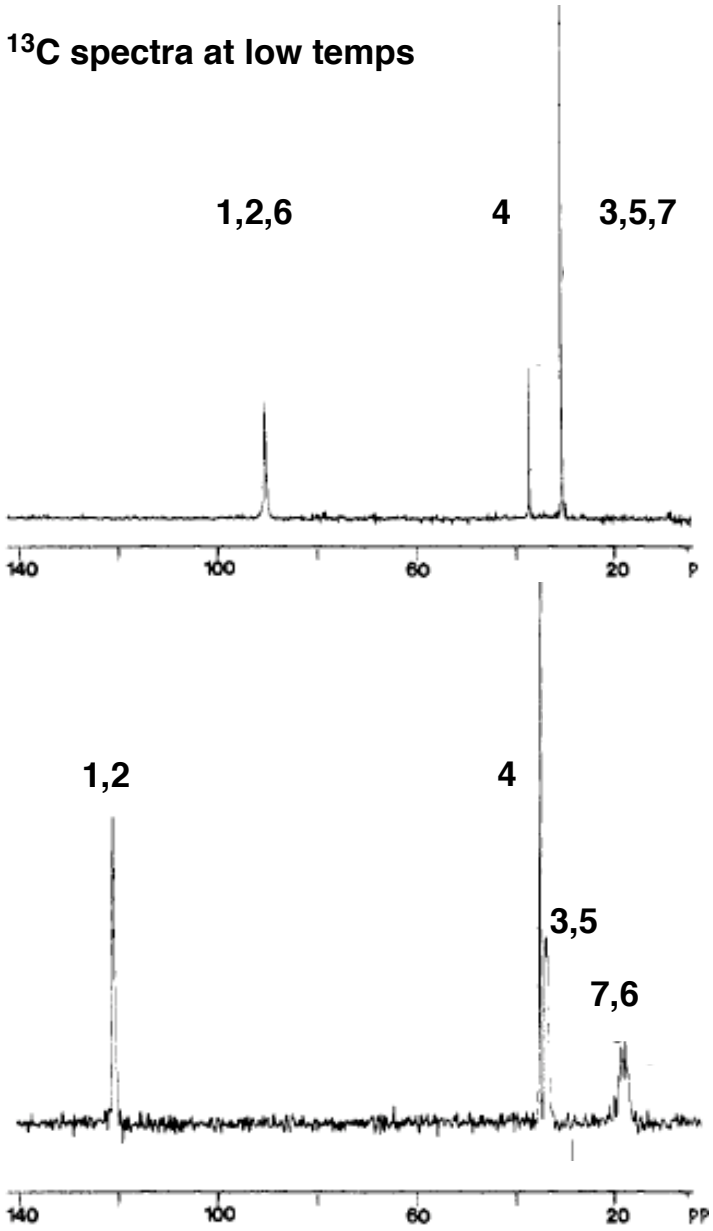




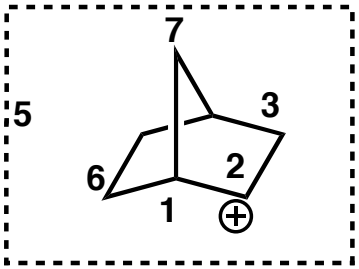


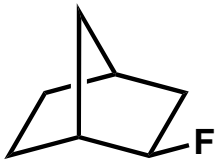
Olah, G. A. *J. Am. Chem. Soc.* **1982**, *104,* 7105.

Proving the Existence of the Carbonium Ion



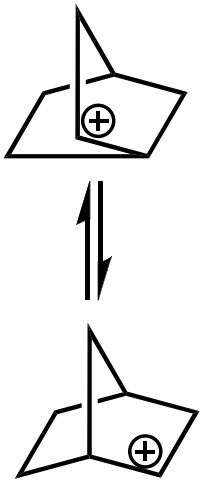
A



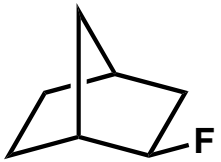


SbF_5, SO_2

-80 °C

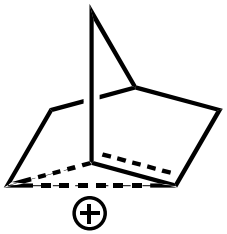


B



SbF_5, SO_2

-158 °C

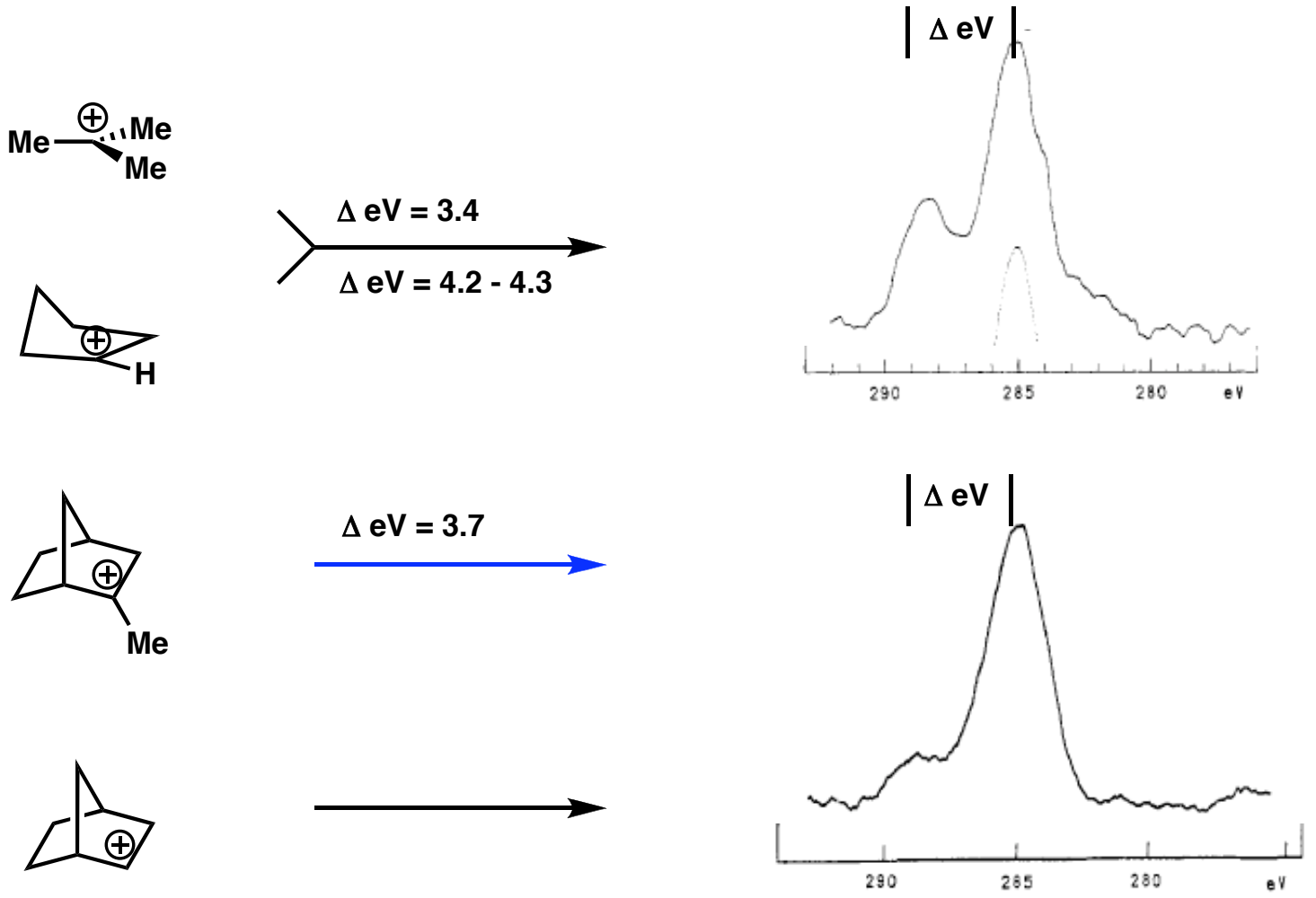


Olah, G. A. *J. Am. Chem. Soc.* **1982,** *104,* 7105.

Proving the Existence of the Carbonium Ion

Core Electron Spectroscopy for Chemical Analysis (ESCA)

- **Exploits photoelectric effect to measure ion affinity for electrons.**
- **Trivalent classical carbocation shows charge localization on 1 atom increases e^- binding energy by ~5eV**
- **Timescale is ~ 10^{18} Hz, much faster than NMR and Wagner-Meerwein shifts**



Olah, G. A.; Mateescu, L. A. *J. Am. Chem. Soc.* **1970**, *92*, 7231.
Olah, G. A.; Mateescu, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 2529.

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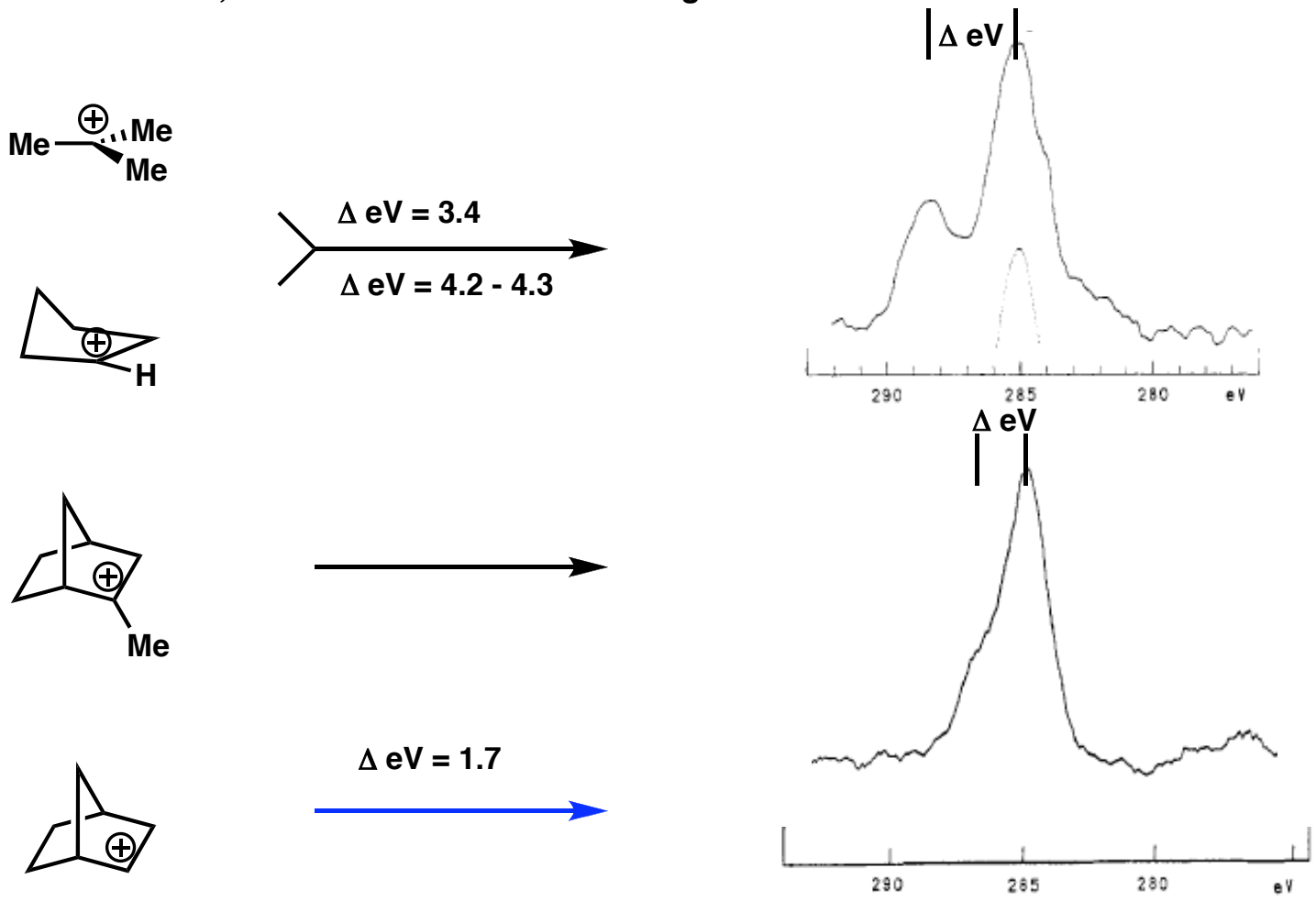
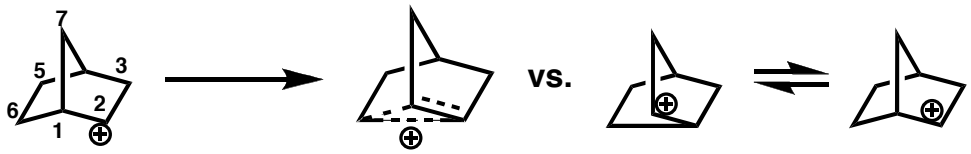
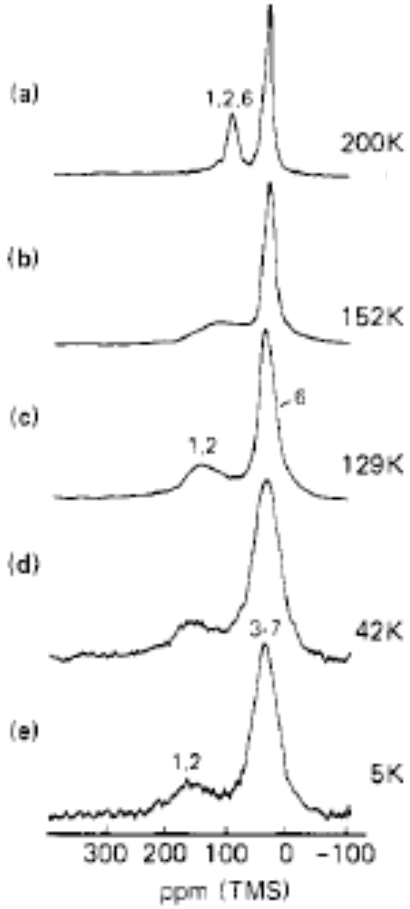


Olah, G. A.; Mateescu, L. A. *J. Am. Chem. Soc.* **1970**, *92*, 7231.
Olah, G. A.; Mateescu, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 2529.

Closing the Debate

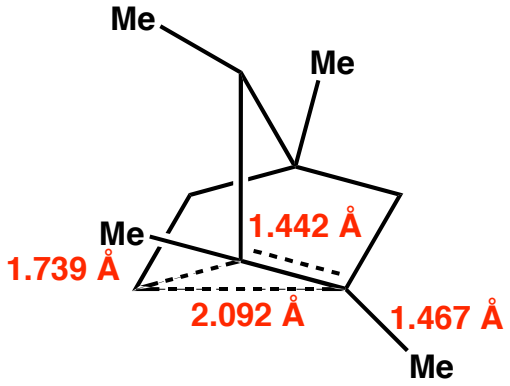


Solid-state ^{13}C NMR studies at 5 K



Calculations reveal that Wagner-Meerwein shifts would require a barrier of 0.2 kcal/mol and occur at 10^5 Hz to avoid resolution at 5 K, setting migration equal to a vibrational transition

Isolated crystals allowed x-ray determination of ion's structure:



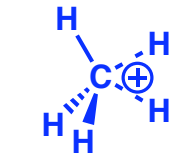
Laube, T. *Angew. Chem. Int. Ed. Engl.* **1987,** *26*, 560

For an excellent review of the nonclassical ion controversy:

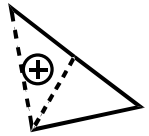
- Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440-449.
- Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1393-1405

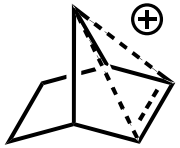
Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.* **1982,** *104*, 7381-7383

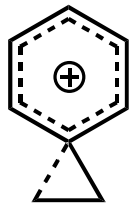
Other Important Nonclassical Carbocations

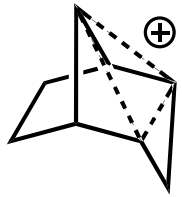


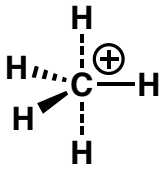
methonium



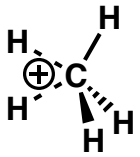




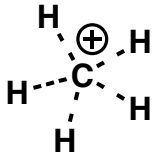




trigonal bipyramidal



C_s

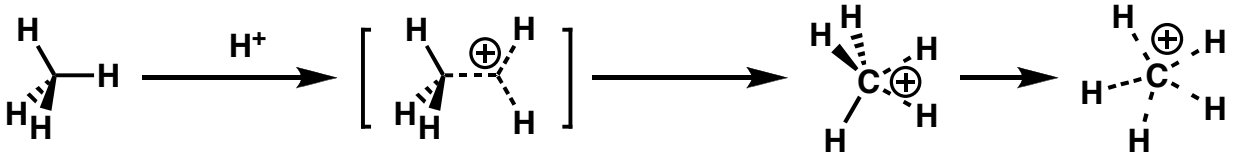


delocalized

- Parent for all nonclassical carbocations.
- 8 Valence electrons rendered deficient by electron pair sharing between 3 atoms

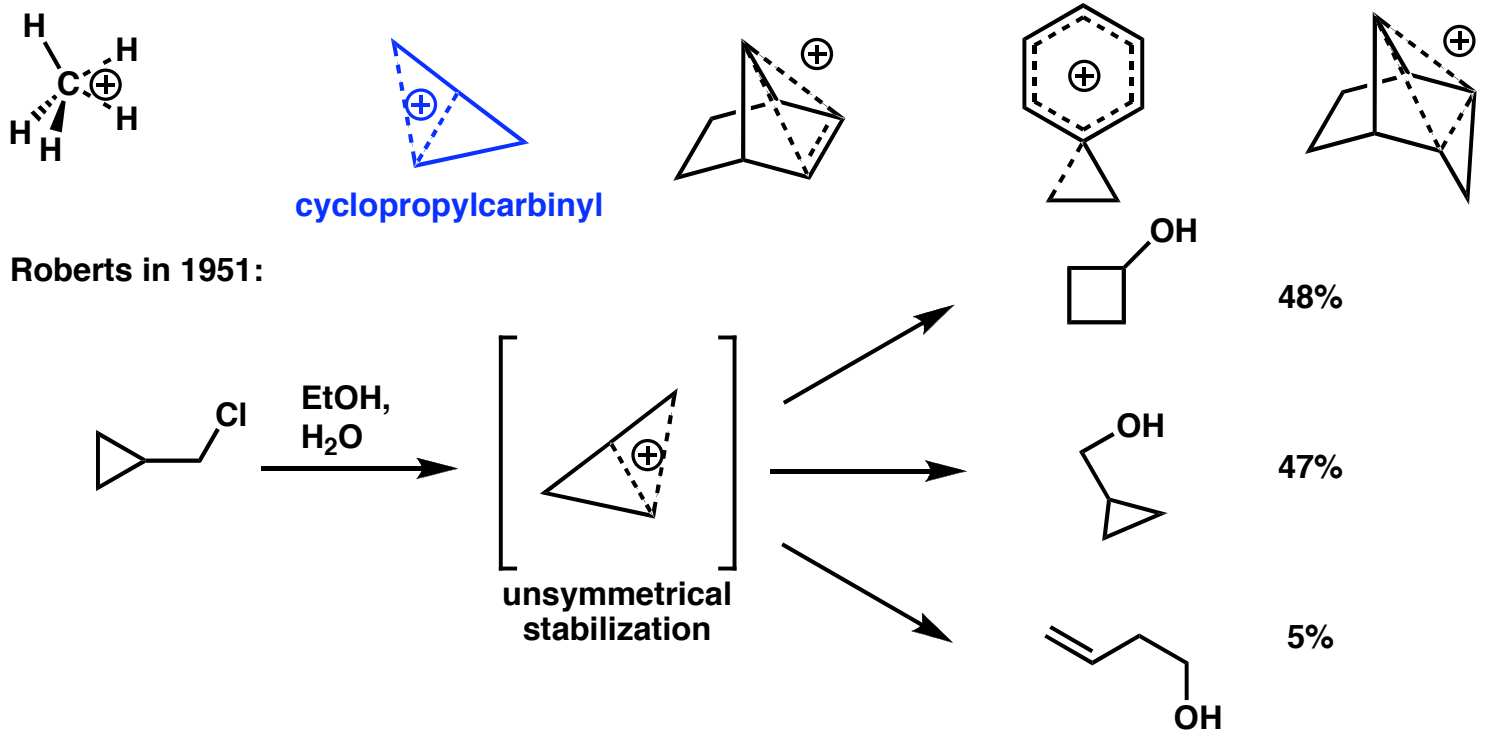
Geometry:

- initially suggested trigonal bipyramidal structure
- *Ab initio* calculations postulated C_s symmetry (as shown)
- Low bond-bond proton migration barriers lend to completely delocalized theory of bonding



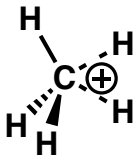
Olah, G. A.; Klopman, G. *J. Am. Chem. Soc.* **1969**, *91,* 3261

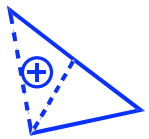
Other Important Nonclassical Carbocations



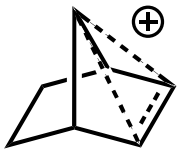
Roberts, J.D.; et. al. *J. Am. Che. Soc.* **1951,** *73*, 3542.

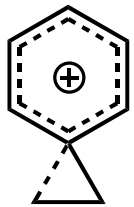
Other Important Nonclassical Carbocations

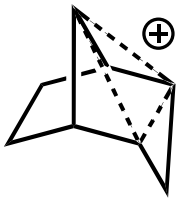




cyclopropylcarbinyl







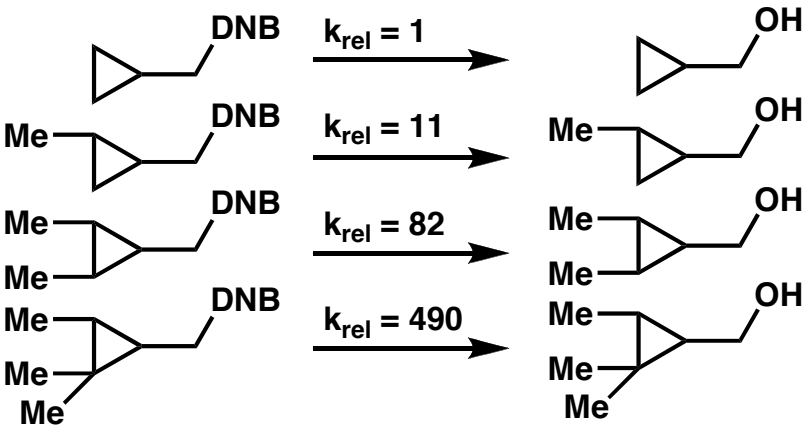
Studies by Roberts in 1951:

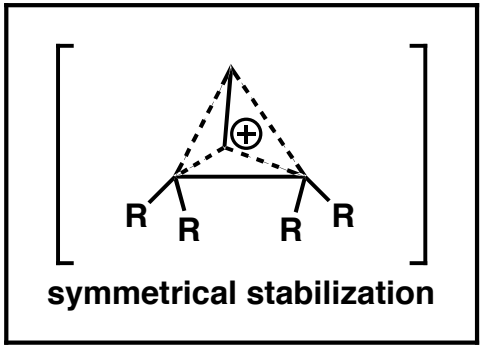
48%

47%

5%

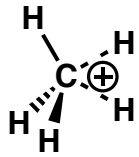
Schleyer's Solvolytic Studies and Structural Revision in 1966:

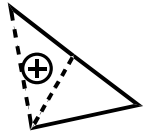


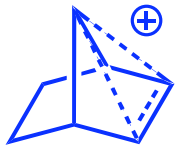


Schleyer, P. v. R. *J. Am. Chem. Soc.* **1966**, *88*, 2321.

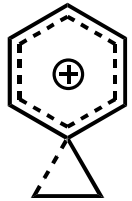
Other Important Nonclassical Carbocations

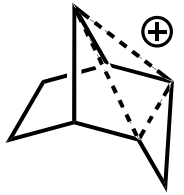




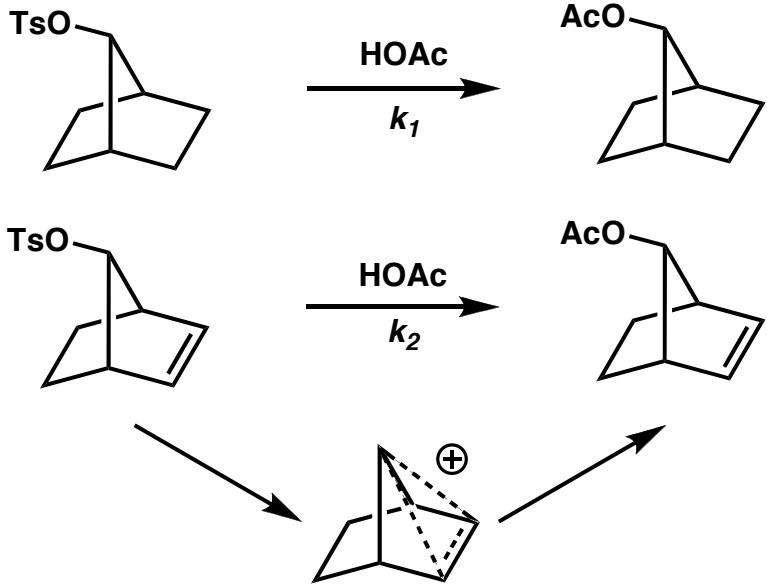


7-norbornenyl





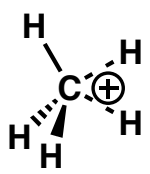
Solvolytic studies by Winstein (*JACS* **1956**, *78*, 592)

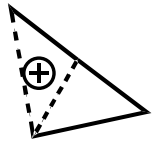


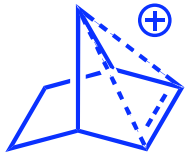
$k_2/k_1 = 10^{11}$

Norbornene Solvolysis occurs with complete retention of stereo-chemistry!

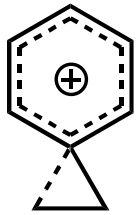
Other Important Nonclassical Carbocations

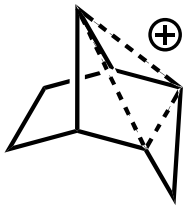






7-norbornenyl





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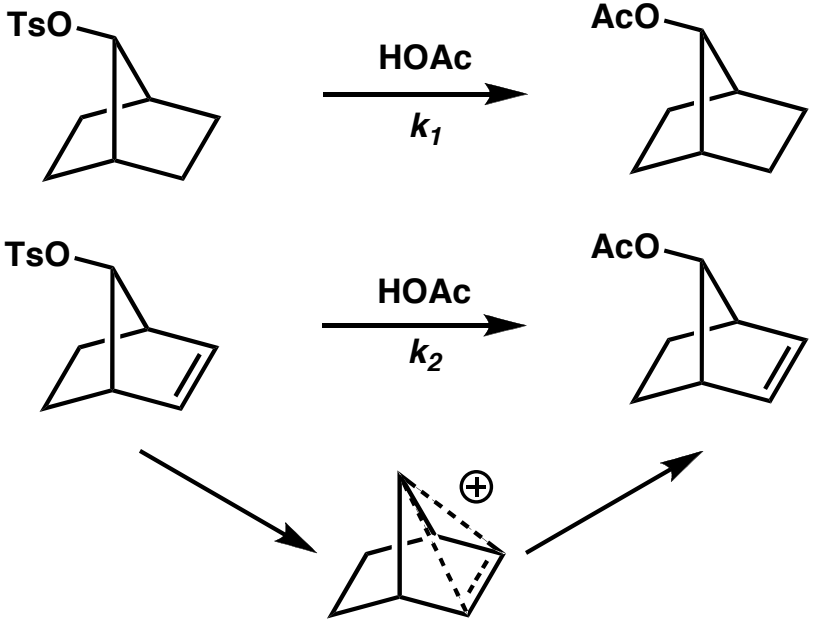
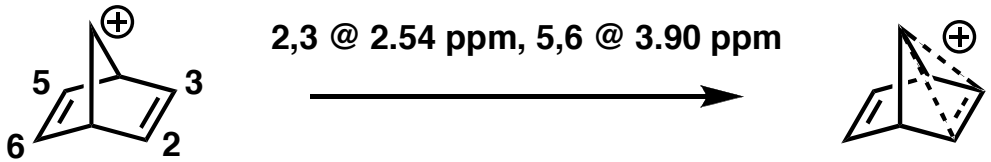


$k_2/k_1 = 10^{11}$

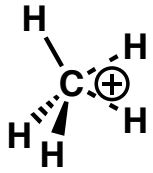
Norbornene Solvolysis occurs with complete retention of stereo-chemistry!

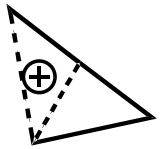
^{1}H NMR study of norbornadienyl model system proved nonequivalence of protons in norbornenyl cation

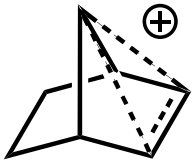


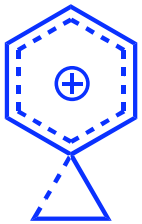
Winstein, S.; Brookhart, M. *J. Am. Chem. Soc.* **1972**, *94*, 2347.

Other Important Nonclassical Carbocations

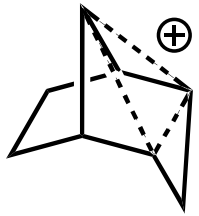






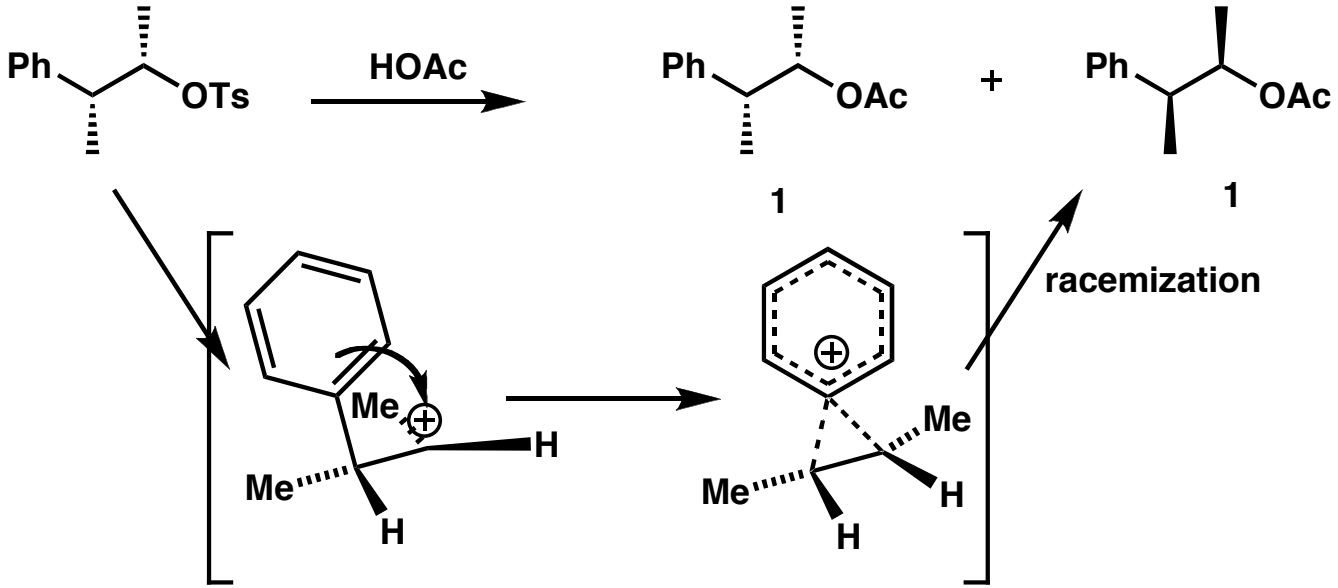


phenonium ion



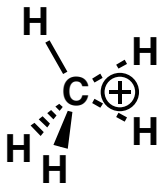
Aromatic group participation

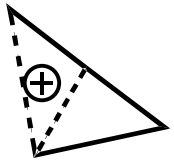
Walden Inversion:

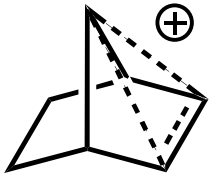


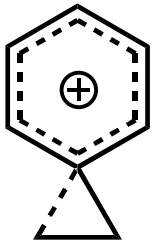
Cram, D. D. *J. Am. Chem. Soc.* **1949**, *71*, 3183

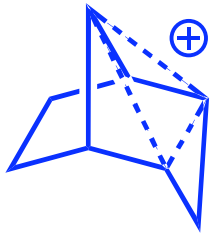
Other Important Nonclassical Carbocations





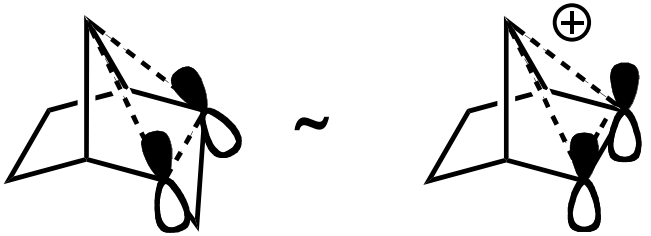


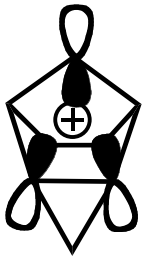




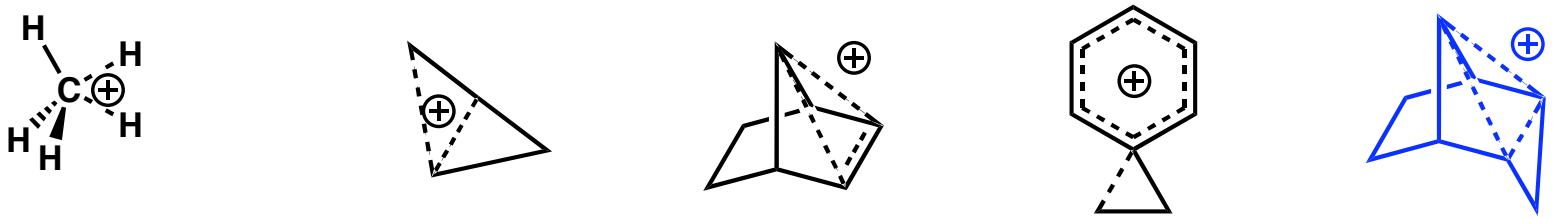
cyclopropyl assistance

Properties of Cyclopropane are similar to an olefin:



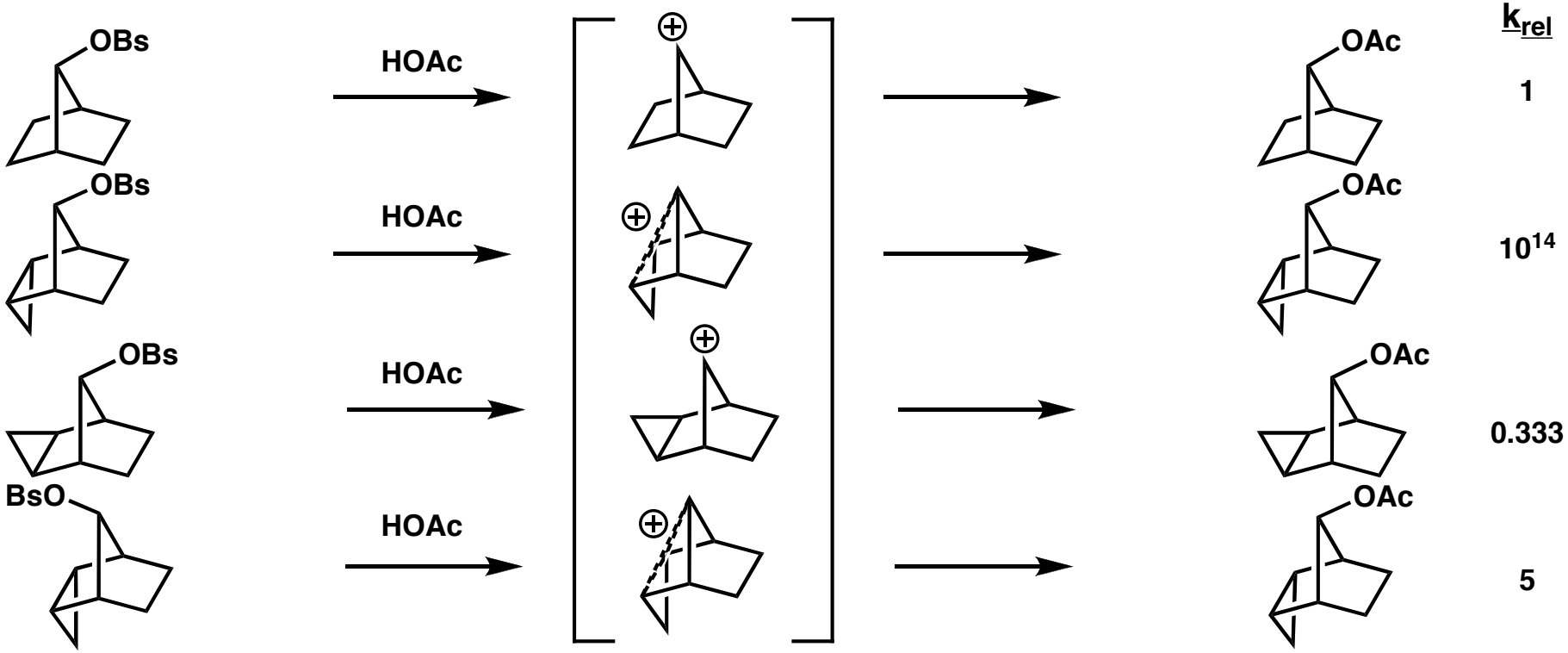


Other Important Nonclassical Carbocations



cyclopropyl assistance

Problem solved by solvolysis



Tsuji, et. al. *J. Am. Chem. Soc.* **1967**, *89,* 1953.; Wells, et. al. *Tetrahedron*, **1966**, *22,* 2007.

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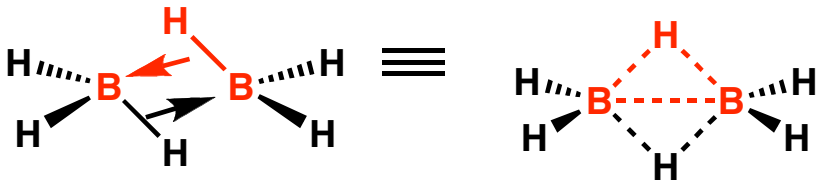
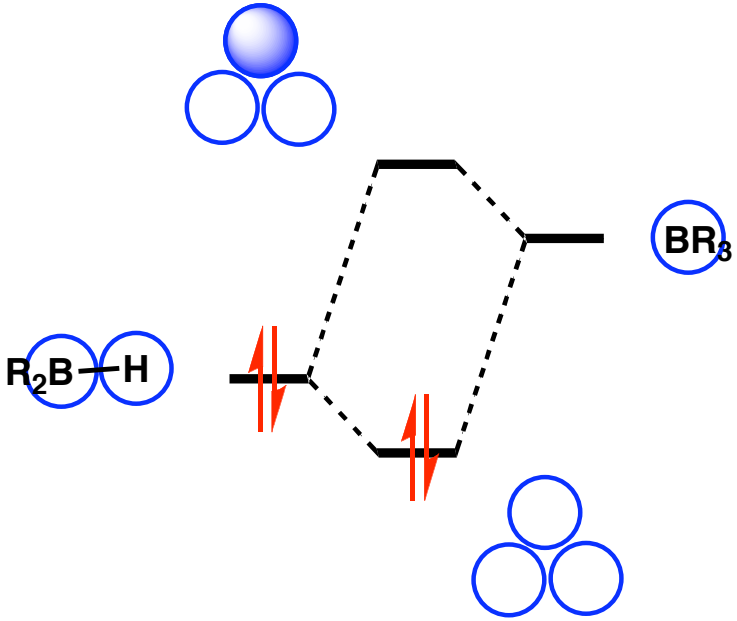
The 3-Center, 2-electron Bond

Diborane and the stable 3-center 2-electron bond.

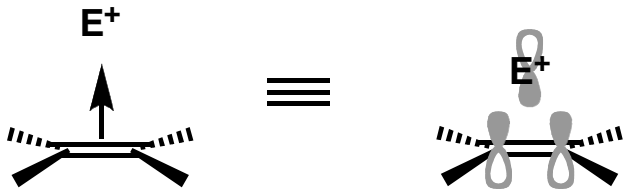




- Borane dimers consist of two 3-center 2-electron bonds
- Delocalized electron-poor region at center of dimer

Electon-poor carbon analogs: π-bond donors

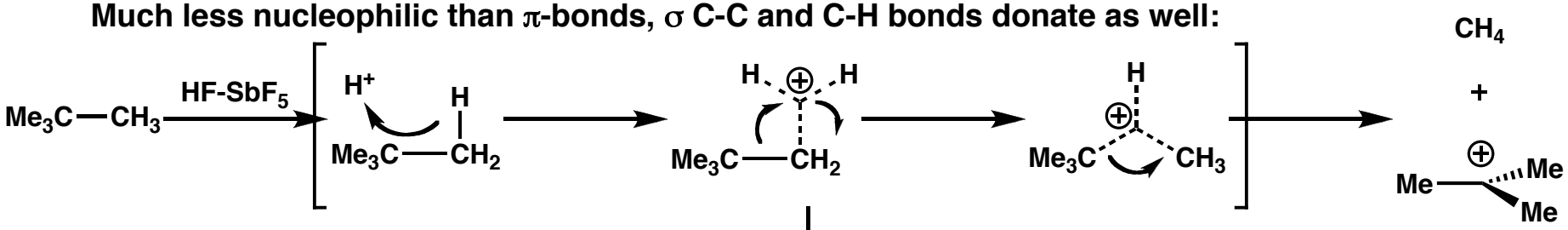
Postulated first by DeWar in 1945 as π-complex



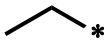
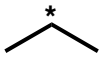
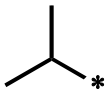
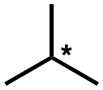
Cationic π–complexes and MO theory

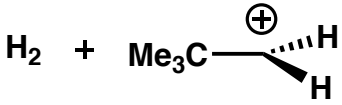
Protonating an Alkane

Much less nucleophilic than π-bonds, σ C-C and C-H bonds donate as well:

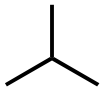


Calculated Protonolysis Activation Barriers ($Sb_2F_{11}{\cdot}HF_2$ @ 298K)

Alkane	ΔH^o (kcal/mol)
CH_4	21.0
C_2H_6	19.3
	19.3
	18.7
	19.9
	18.3



Calculated C-C Cracking Activation Barriers ($Sb_2F_{11}{\cdot}HF_2$ @ 298K)

Alkane	ΔH^o (kcal/mol)
C_2H_6	35.0
C_3H_8	30.0
	28.7

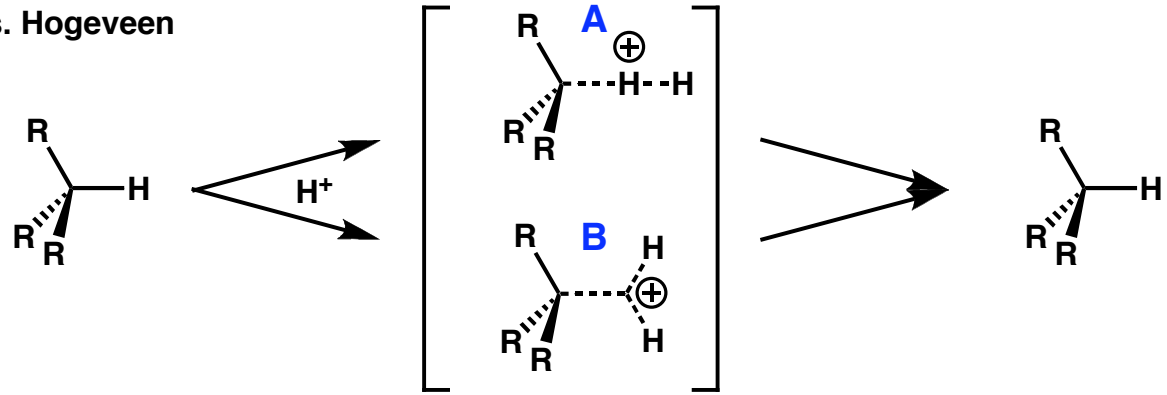
Mota, et. al. *J. Phys. Chem. B* **2001**, *105*, 4331.
Ramsden *Tetrahedron* **2004**, *60*, 3293.
Olah, et al. *Angew. Chem. Int. Ed. Eng.* **1973**, *12*, 173.

Protonating an Alkane

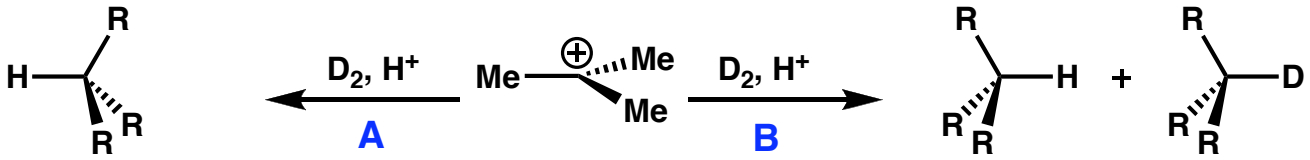
Much less nucleophilic than π-bonds, σ C-C and C-H bonds donate as well:

Linear or bridged transition state in σ protonation?

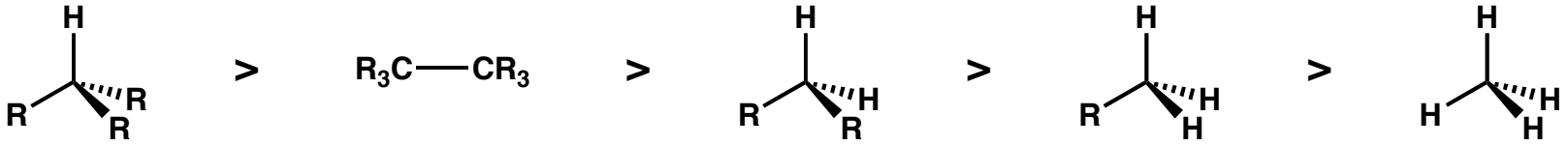
Olah vs. Hogeveen



Olah, 1971



Olah's general order of alkane σ–bond reactivity:

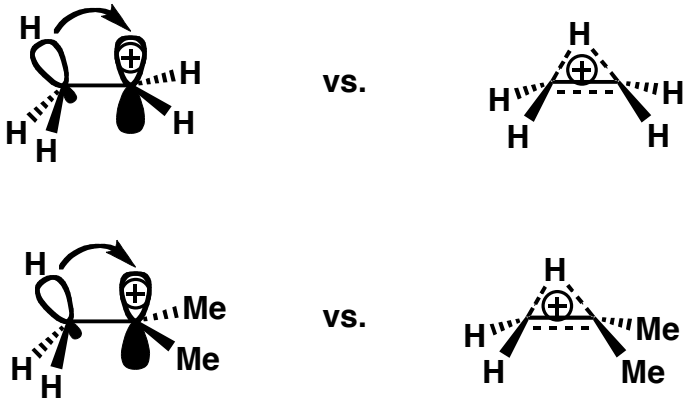


Olah, et al. *J. Am. Chem. Soc.* **1971**, *93*, 1251.
Hogeveen, et al. *Recl. Trav. Chim. Pays-Bas.* **1969**, *88*, 703.
Olah, et al. *Angew. Chem. Int. Ed. Eng.* **1973**, *12*, 173.

Leveling the Field

The 3-center, 2-electron bond changes how all carbocations are precieved

Ethyl cation: hyperconjugation or hypervalence?



- Carbenium ions are prone to rearrangement
- Rapid scrambling of 5 H's in ethyl cation indicative of some delocalized intermediate
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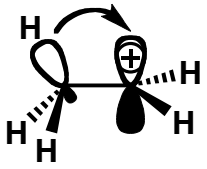
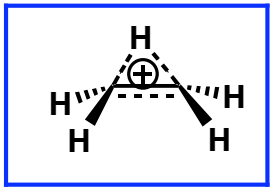
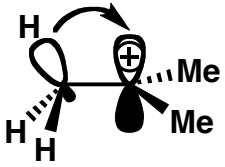


vs.





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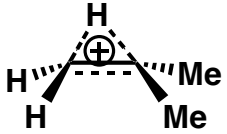

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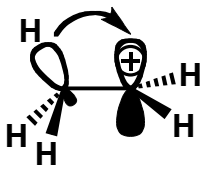

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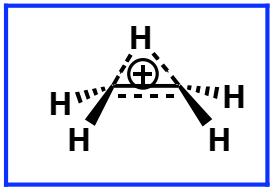
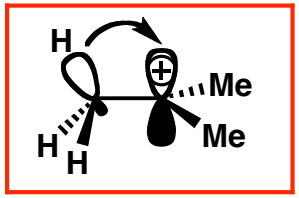
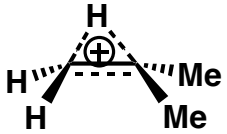




vs.



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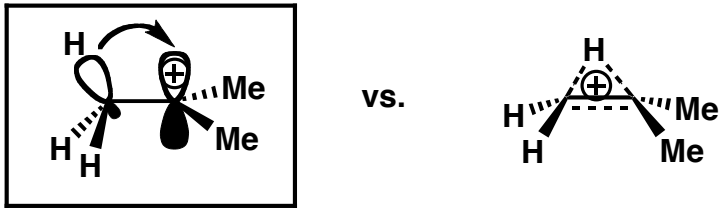

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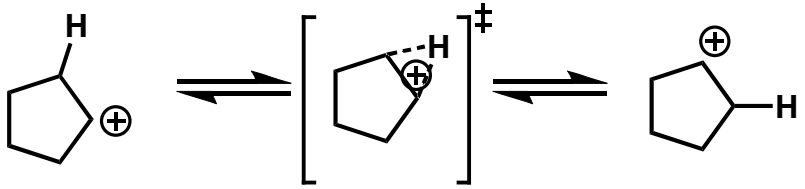
Wagner-Meerwein shifts and isomerization

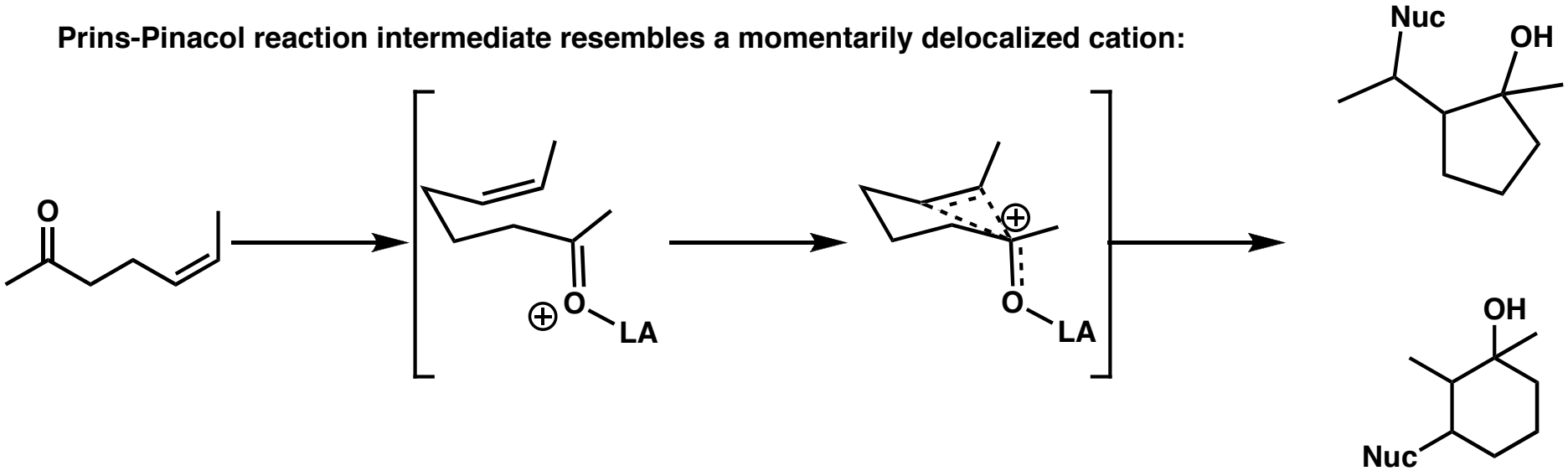


- **1 ^{13}C NMR Shift at -139 °C**
- **Rearrangements occur ~ 3.1 x 10^7 Hz**

A Whole New Ballgame...

Delocalized intermediates also participate in assisting leaving group departure

Prins-Pinacol reaction intermediate resembles a momentarily delocalized cation:



Many of the carbocationic rearrangements basic to organic chemistry can be associated with nonclassical carbocationic intermediates.

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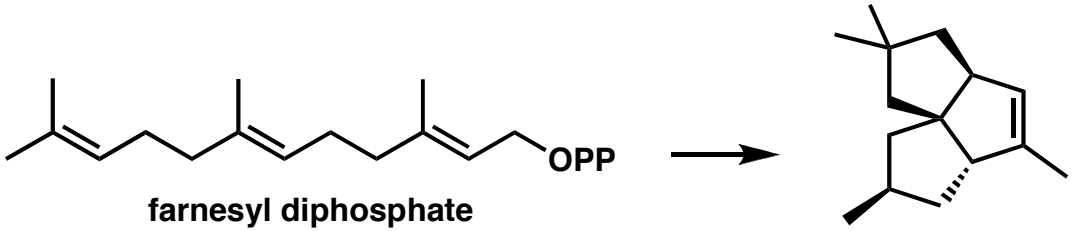
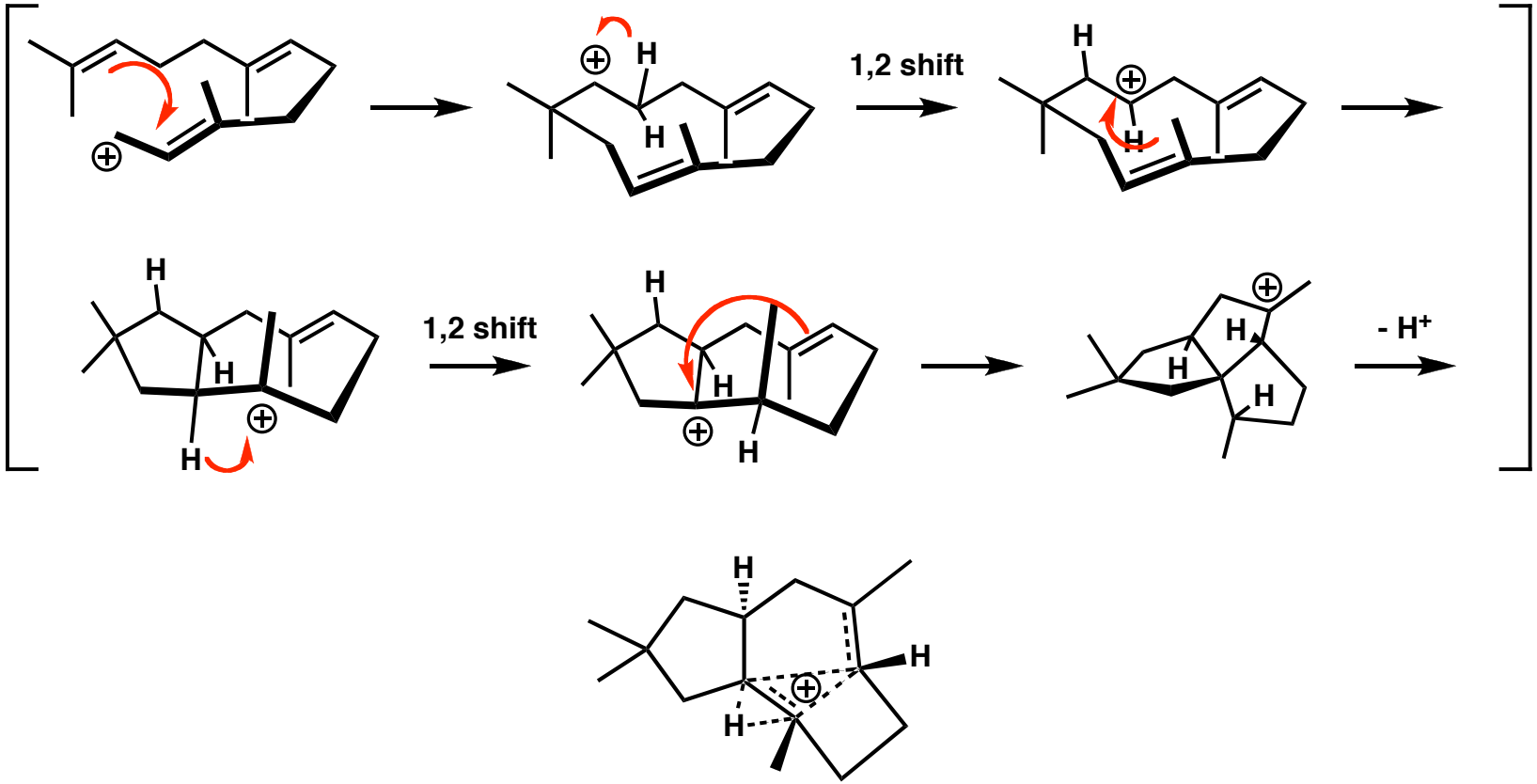
Carbocationic Cascades- Biosynthesis



farnesyl diphosphate

pentalenene

- isolated from *streptomyces*
- precursor to pentalenolactone antibiotics



Tantillo *J. Am. Chem. Soc.* **2006**, *128*, 6172.

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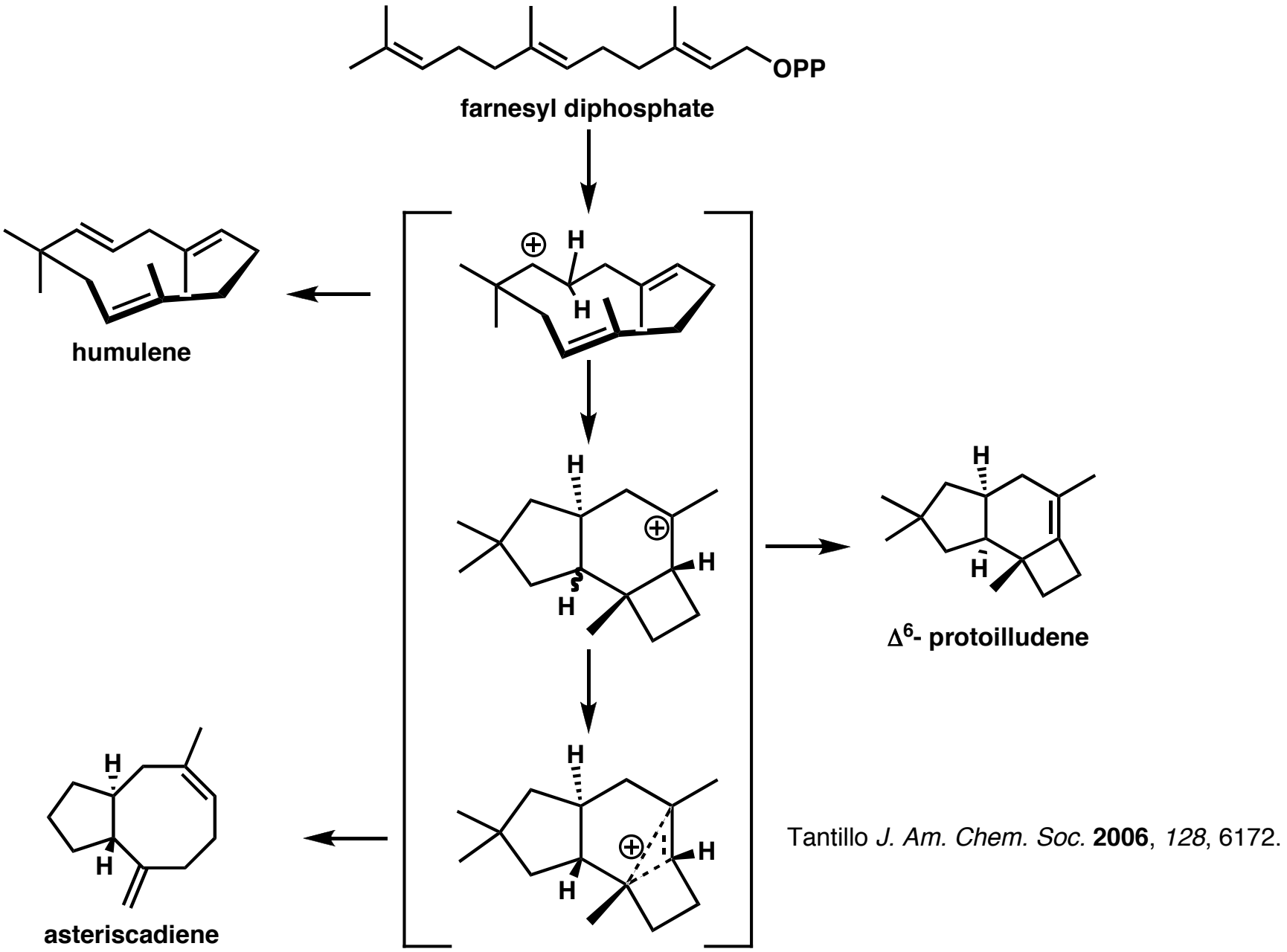
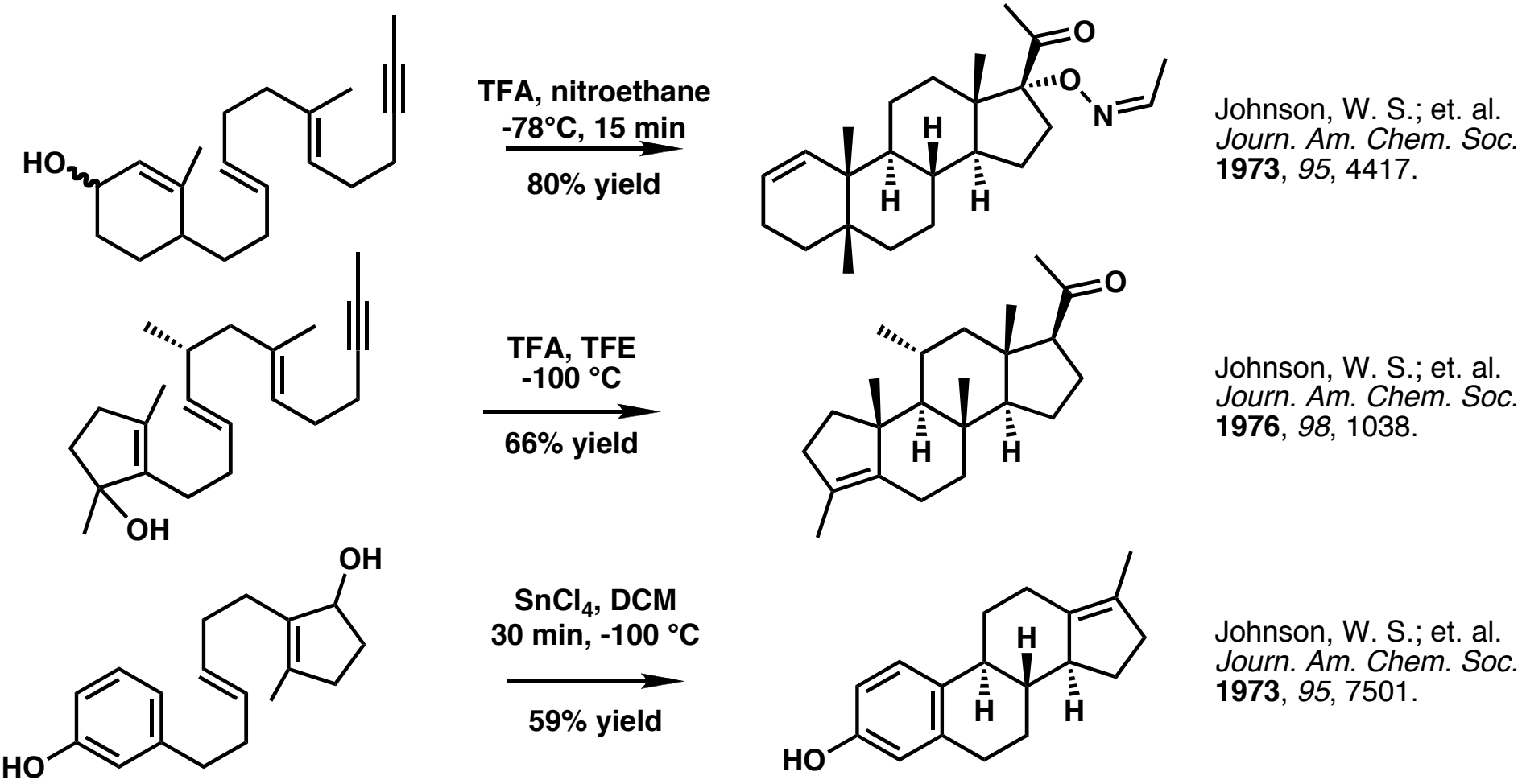


Tantillo *J. Am. Chem. Soc.* **2006**, *128*, 6172.

W.S. Johnson's Approach to Steroid Skeletons



Johnson, W. S.; et. al. *Journ. Am. Chem. Soc.* **1973**, *95*, 4417.

Johnson, W. S.; et. al. *Journ. Am. Chem. Soc.* **1976**, *98*, 1038.

Johnson, W. S.; et. al. *Journ. Am. Chem. Soc.* **1973**, *95*, 7501.

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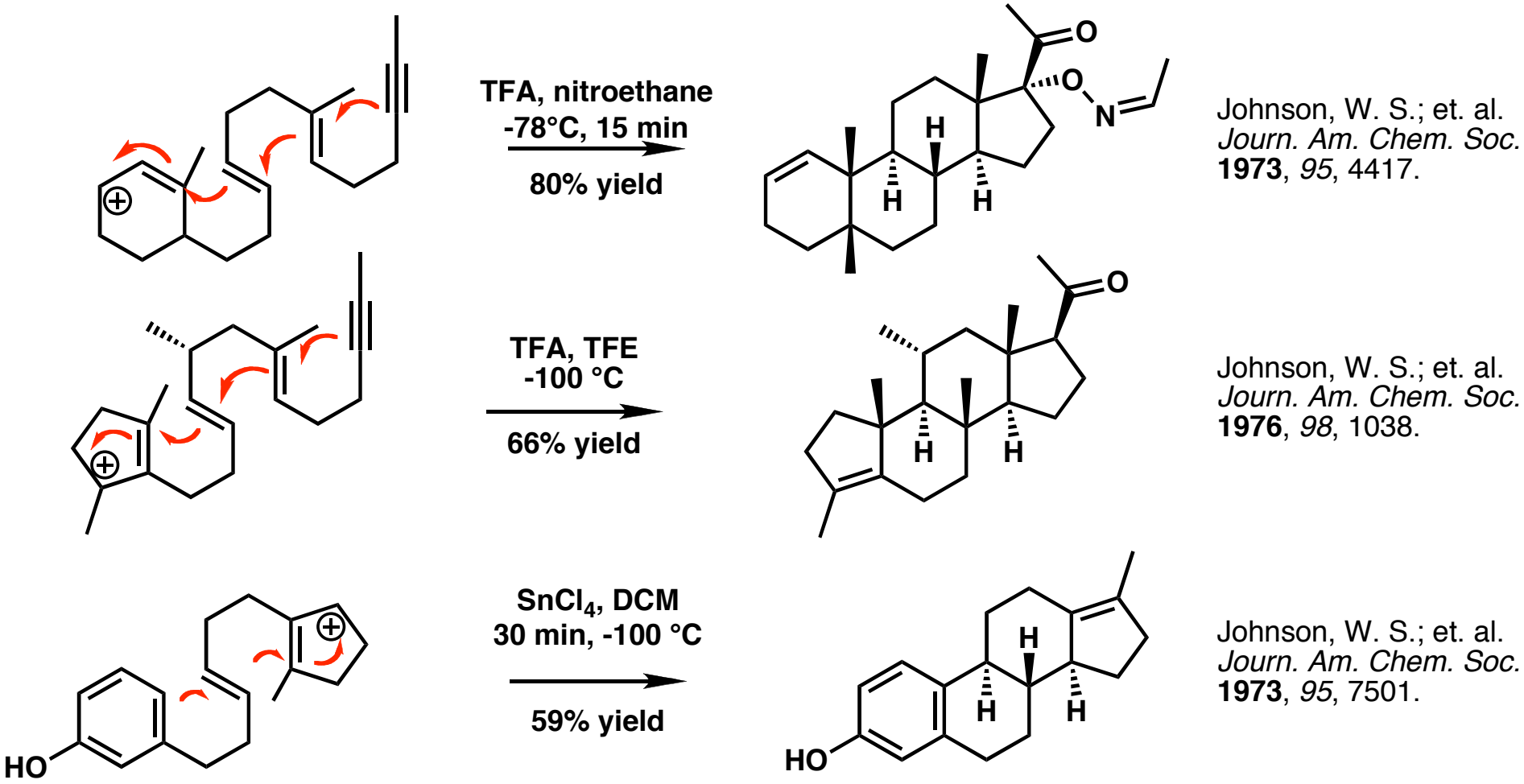

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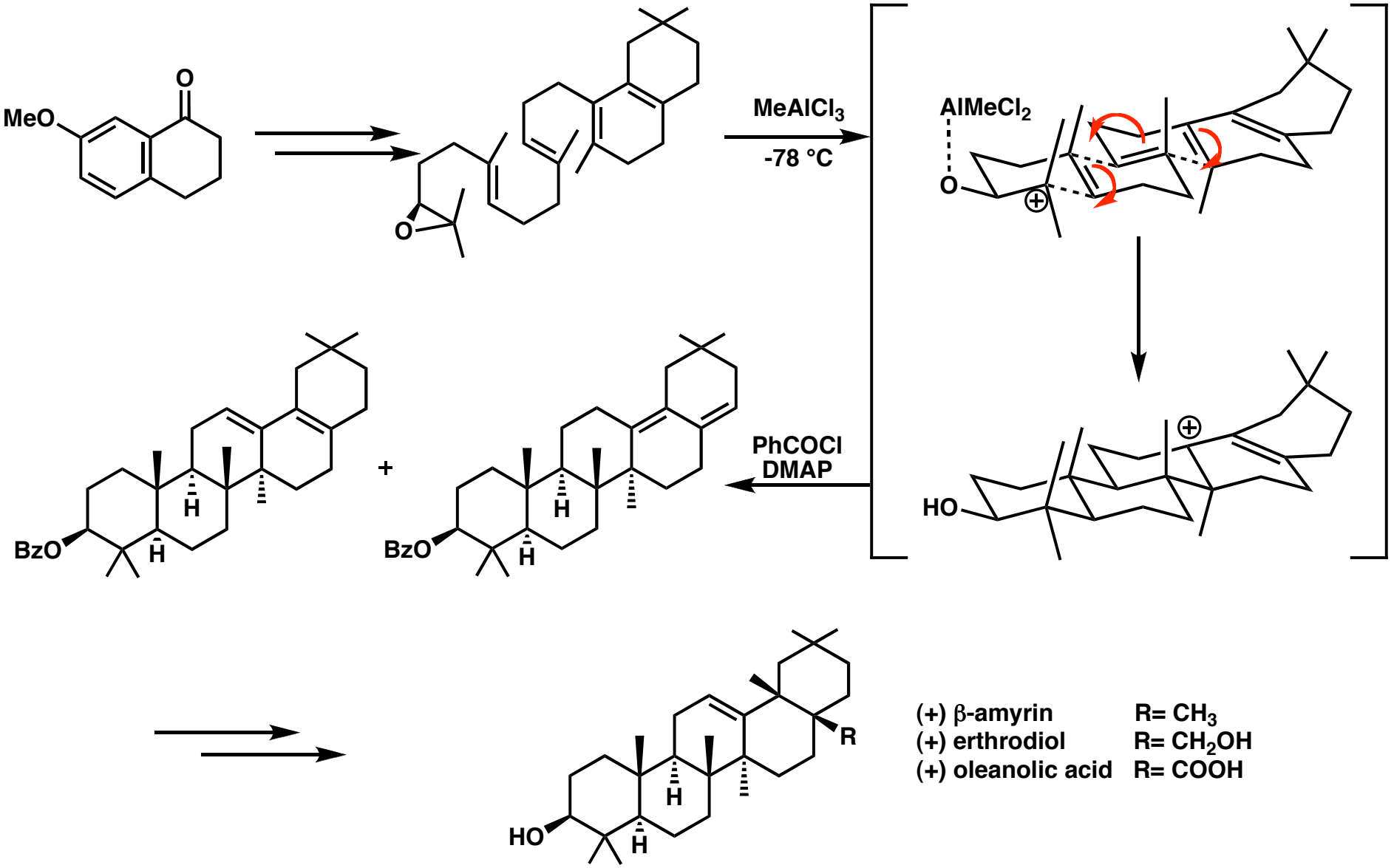
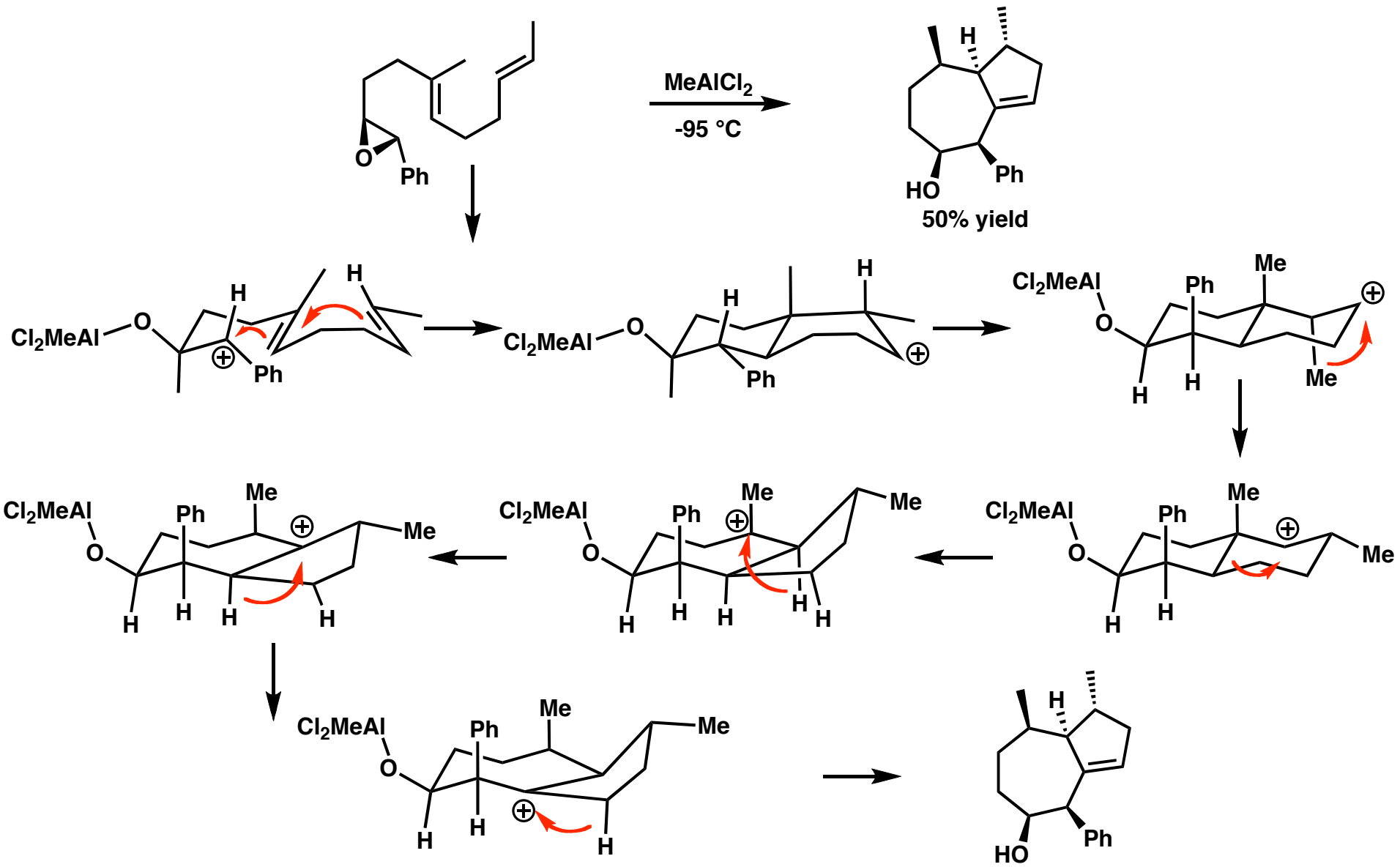
Johnson, W. S.; et. al. *Journ. Am. Chem. Soc.* **1973**, *95*, 7501.

Carbocationic Cascades- Corey and Oleananes



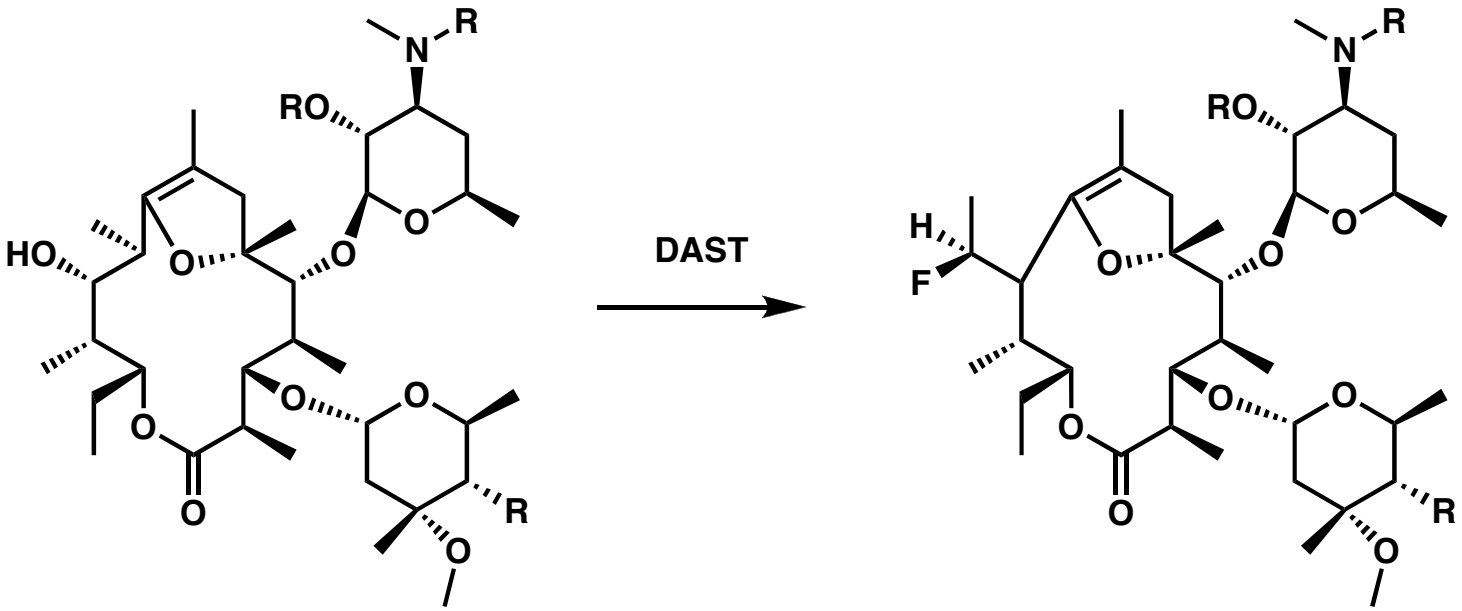
Corey, E.J *J. Am. Chem. Soc.* 1993, 115, 8873-8874

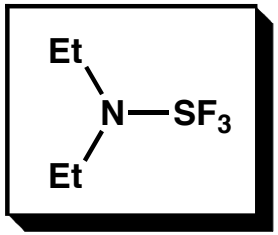
Some other unique rearrangements



Corey, E. J.; Roberts, B.E. *Tetrahedron Lett.* **1997,** *38*, 8921.

Some other unique rearrangements





Lartey, et. al. *J. Org. Chem.* **1996**, *61*, 5153.

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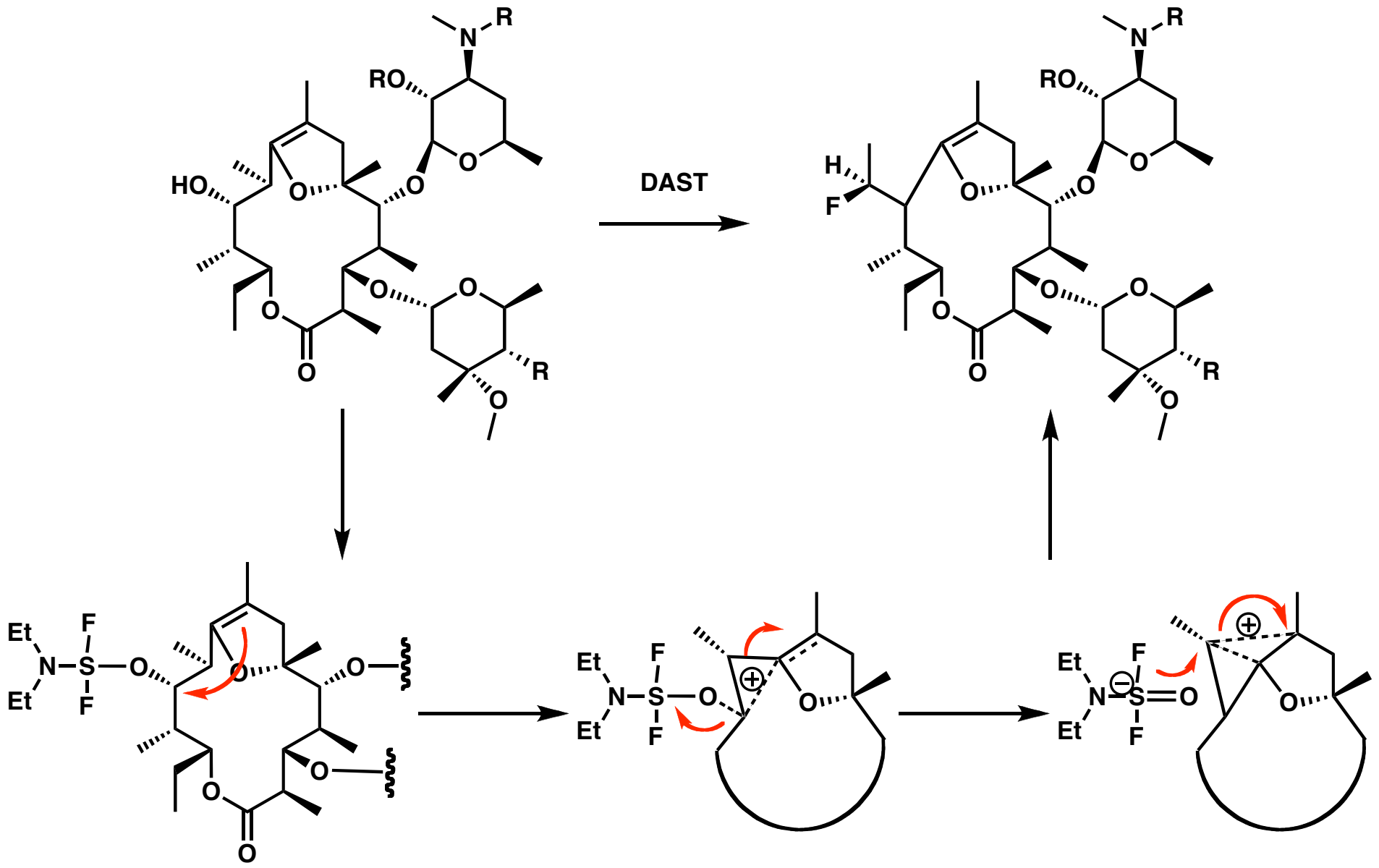

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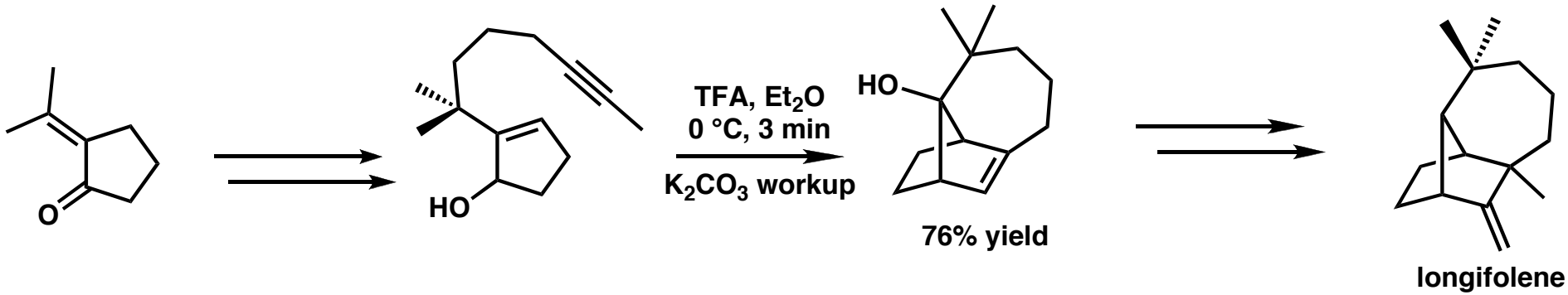
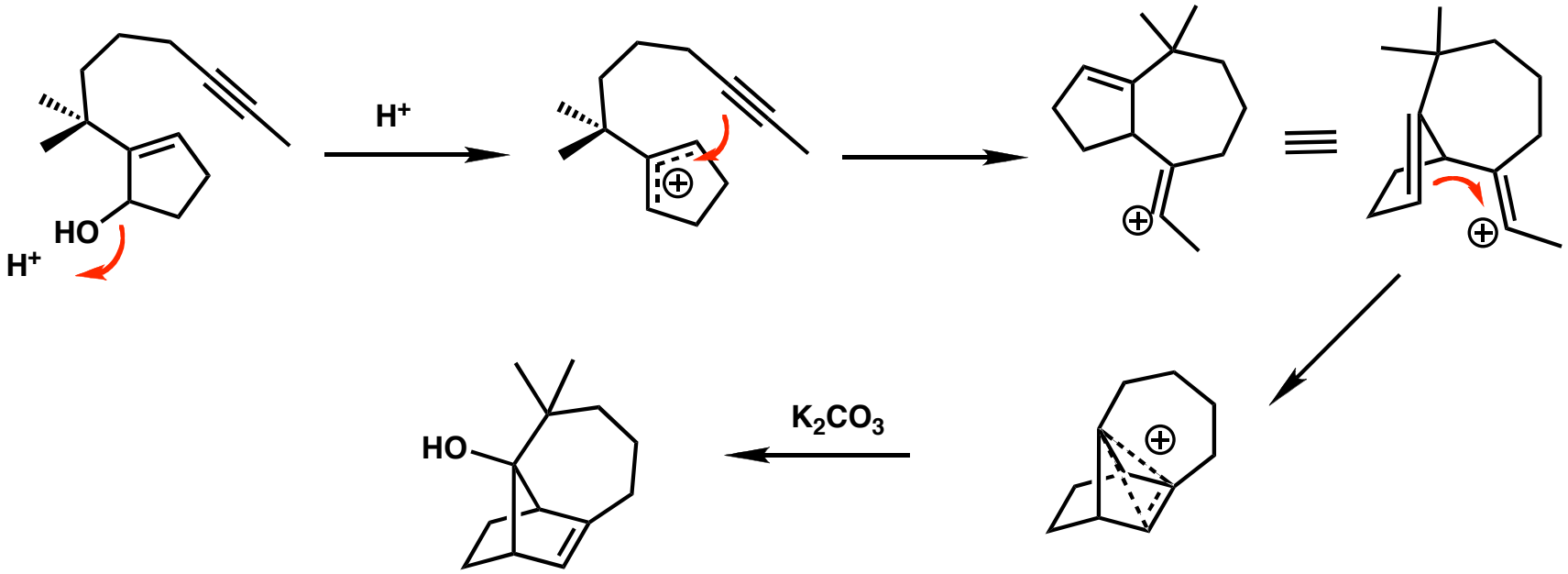
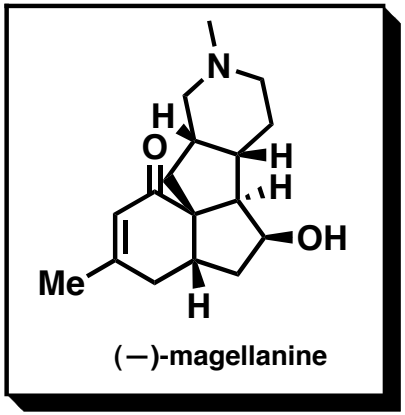
Cationic Cascade to Longifolene

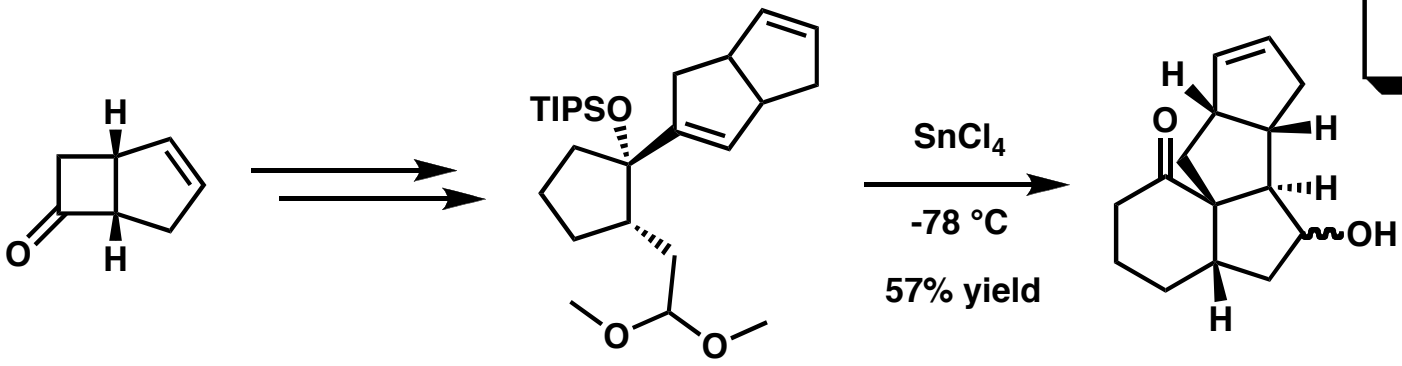




Johnson, W. S., et. al. *J. Am. Chem. Soc.* **1975**, *97*, 4777.
Tantillo, D. J., et al. *J. Org. Chem.* **2005,** *70,* 5139.

Larry Overman and the Prins-Pinacol





Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 2992.

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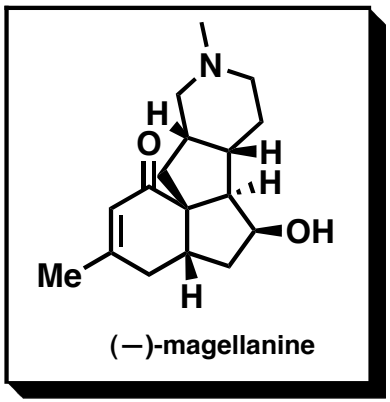
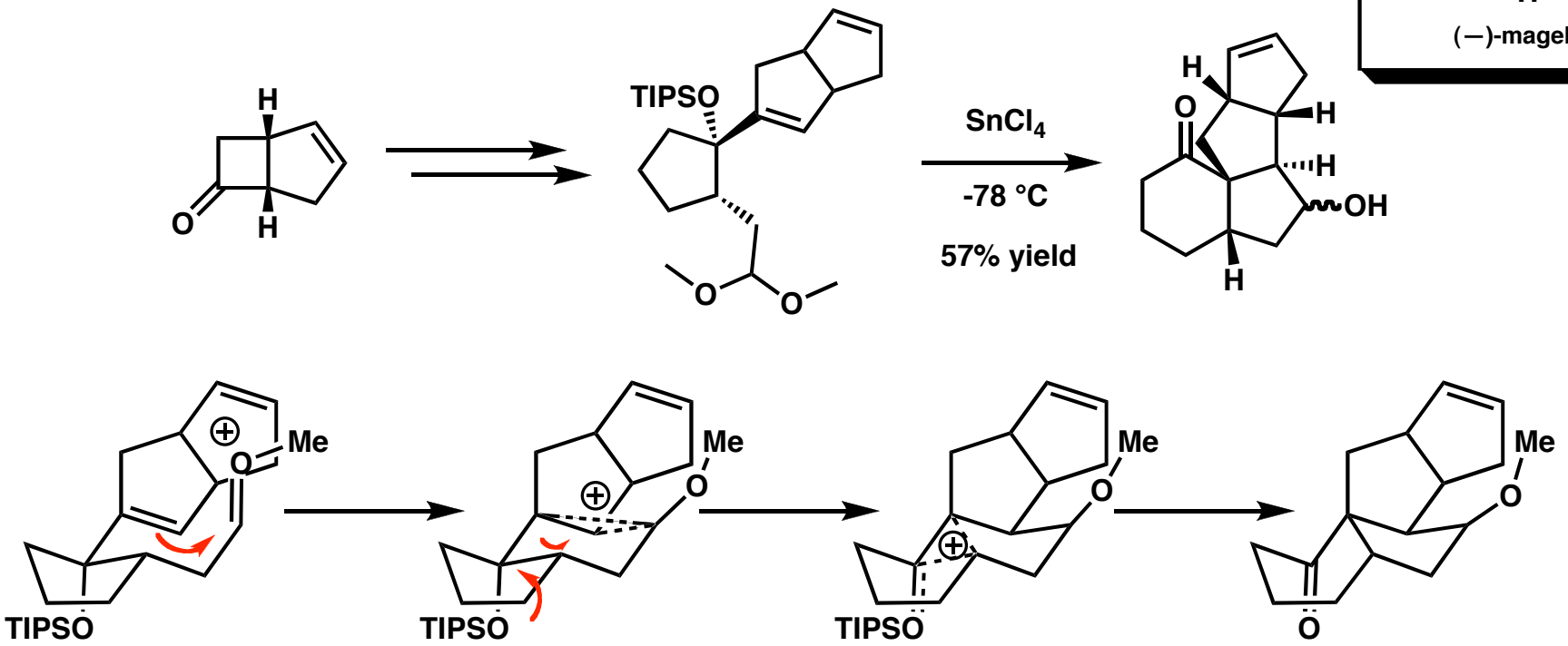


(−)-magellanine



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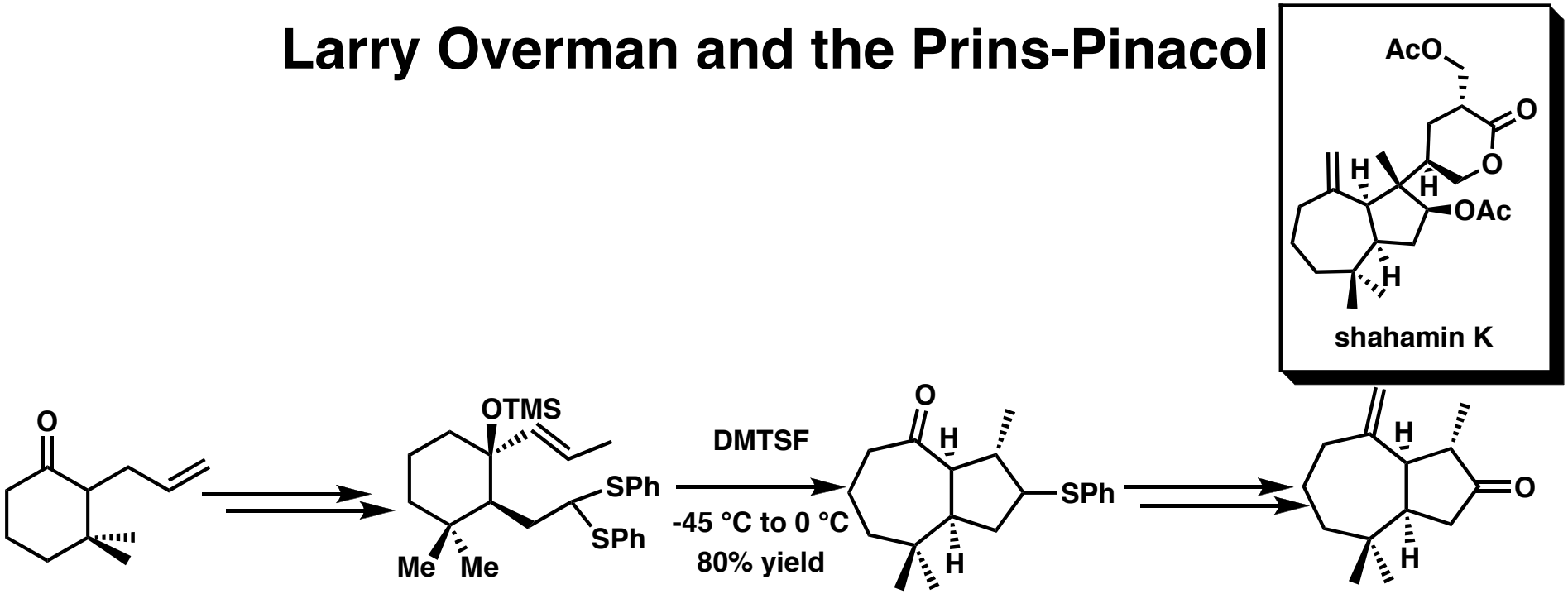
Larry Overman and the Prins-Pinacol



Overman, L.E. *J. Am. Chem. Soc.* **2001**, *123*, 4851

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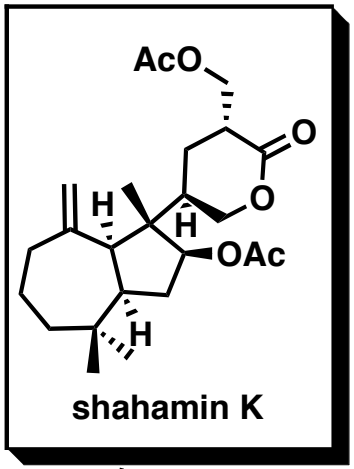

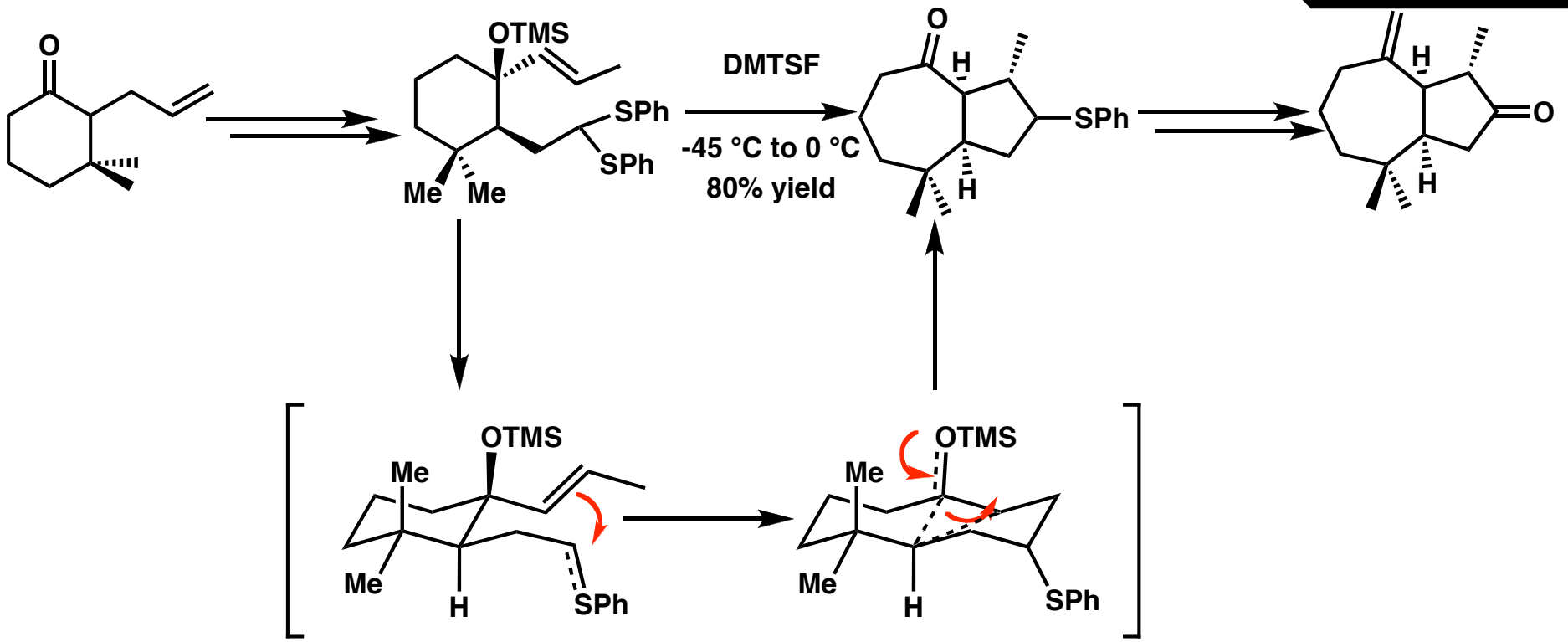

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Summary and Parting Thoughts

- The nonclassical carbocation controversy opened the realm of physical organic chemistry, established the idea of delocalized, electron-poor bonding in intermediates and transition states for organic reactions, and encouraged an intense debate that has led to the affirmation of many instrumental and experimental techniques used today

- The 3-center, 2-electron bond is prevalent in carbocation chemistry, often as a stable intermediate or transition state, and sometimes as a stable molecule itself

- Carbocation chemistry and its variants have found an effective place in synthesis, but there exists a large gap in controlled carbocationic methodology that has only recently been explored.

Thanks to JT for the Carbocation book and Meyer for helpful advice