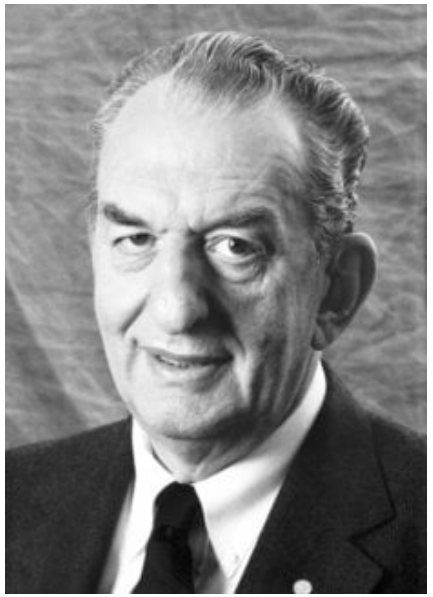
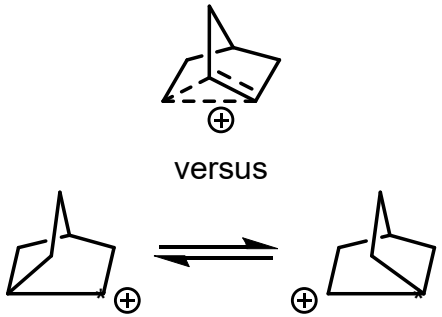
Non-Classical Cation Debate:
Structure and Reactivity of the 2-Norbornyl Cation



G. A. Olah



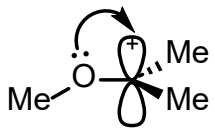
H. C. Brown

Nick Wade

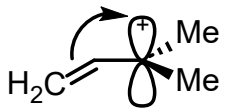
Denmark Group Meeting

February 18th, 2025

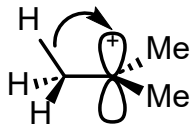
Many Ways to Stabilize A Carbocation

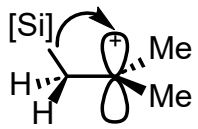


n → p

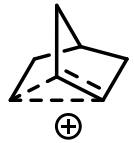


π-bond stabilization (resonance)



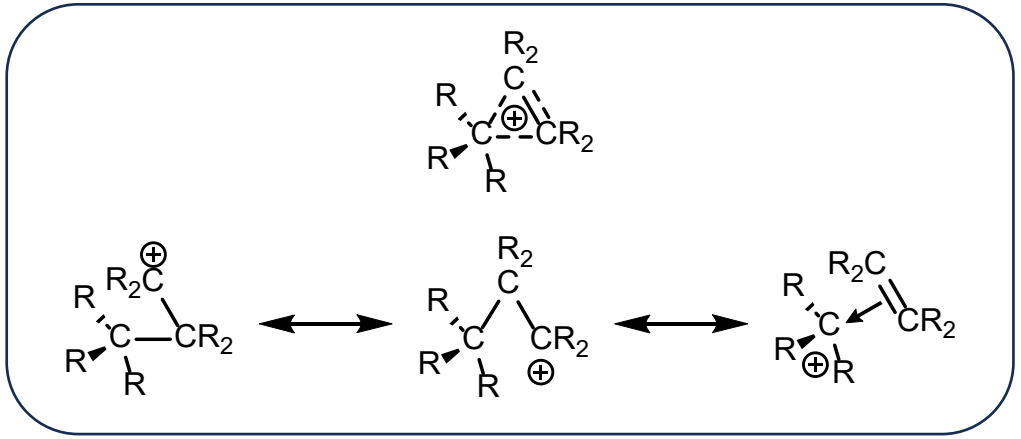


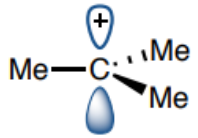
σ-bond stabilization (hyperconjugation, β-Si effect)



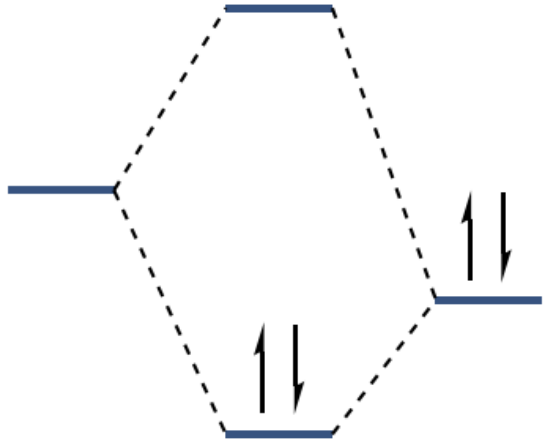
Non-classical stabilization

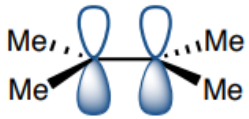
3-center, 2-electron bond:





LUMO (p)



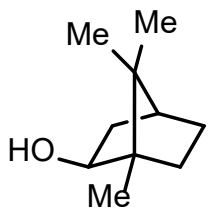


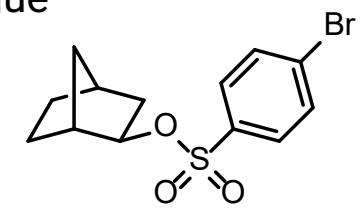
HOMO (π)

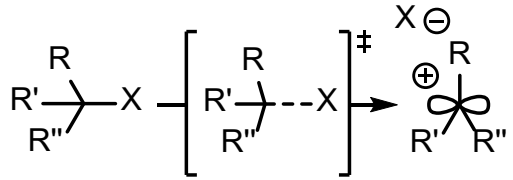
P. D. Bartlett. Nonclassical Ions, W.A. Benjamin, New York, 1965

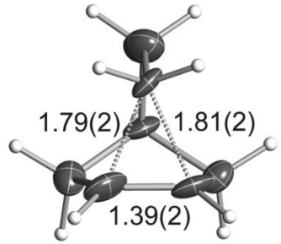
Presentation Overview

Early Intrigue





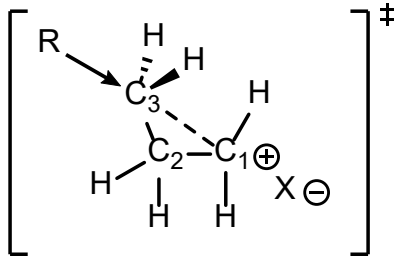


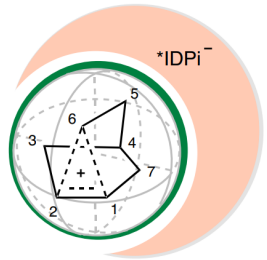


Modern Perspective

1900

2020

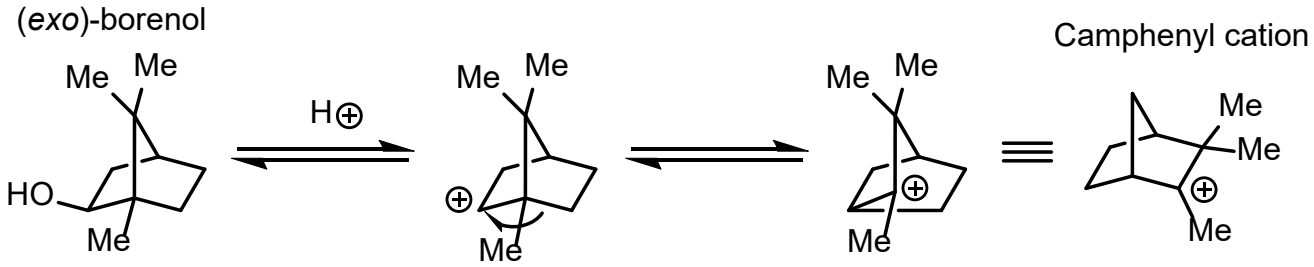


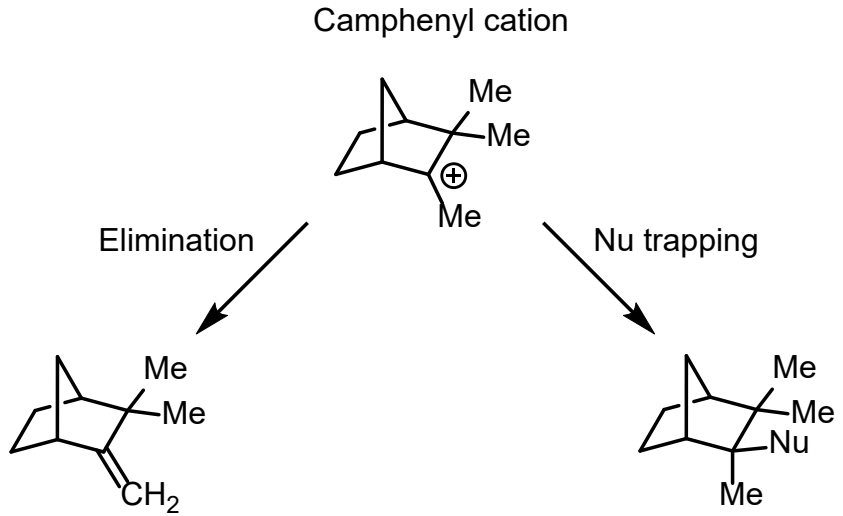


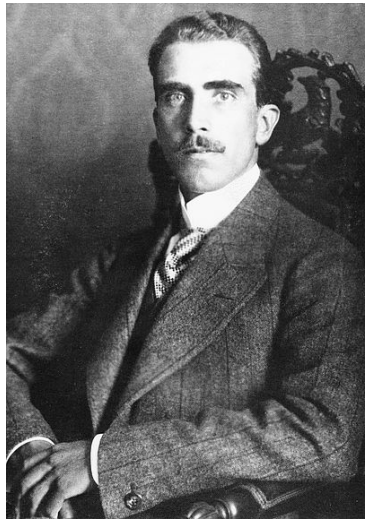
Both Sides' Evidence

Wagner-Meerwein Borenol-Camphene Rearrangement

Yegor Wagner
(1849-1903)







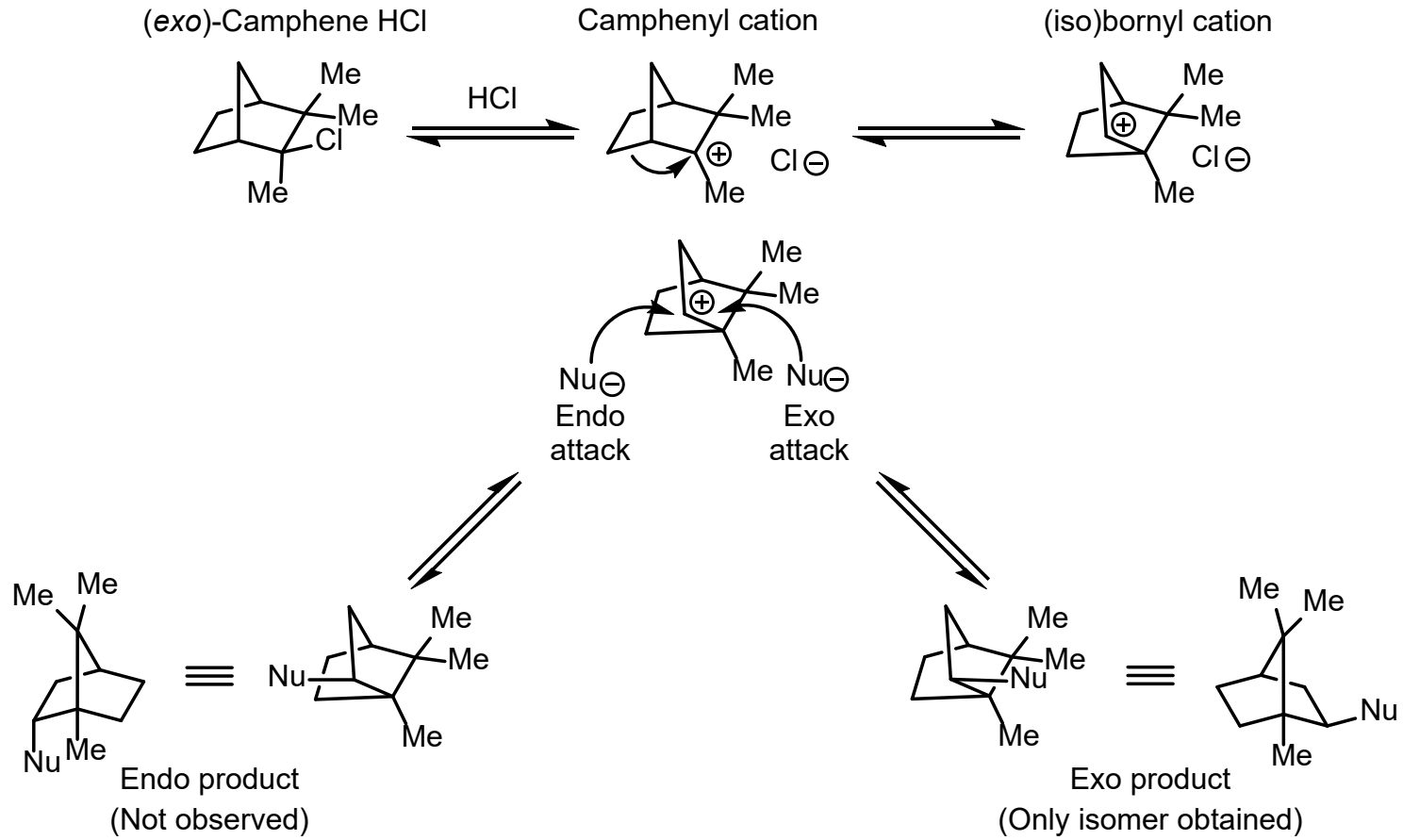
Hans Meerwein
(1879-1965)

Further exploration into the bicyclo-[2,2,1]-heptyl skeleton led to more questions than answers

Meerwein, H., van Emster, *Ber.*, **1920**, 53, 1815; Meerwein, H., *Ber.*, **1922**, 55, 2500.

Acid Catalyzed Bicyclo-[2,2,1]-heptyl Skeletal Rearrangements

Paul D. Bartlett
(1907-1997)



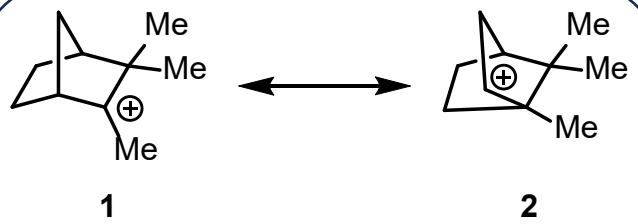
Two lingering questions:

1. Kinetics: Ionization occurred 10^5 faster with the *exo* starting material than *endo*
2. Stereochemical: When Nu = Cl^-, the reaction is highly diastereoselective

Bartlett, P. D.; Pockel, I. *J. Am. Chem. Soc.*, **1937**, 59, 820; Bartlett, P. D.; Pockel, I. *J. Am. Chem. Soc.*, **1938**, 60, 1585.

Wilson's Solution: σ-bond resonance

Christopher L. Wilson
(University College, London)



1 **2**

Rapidly interconverting species described by resonance structures (mesomerism)

Wilson's original drawing from 1939

"Although the intermediate ion **[1]** is represented as having the camphene structure, it is possible that it is mesomeric between this and the corresponding isobornyl structure **[2]**"
-Christopher L. Wilson, 1939

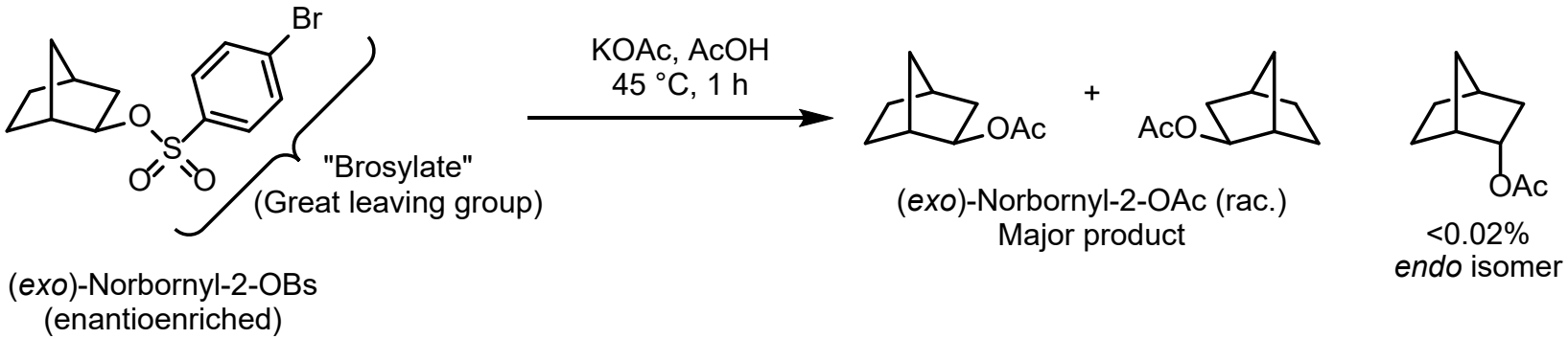
Further intrigue into the bicyclo-[2,2,1]-heptyl cation lay dormant until the Winstein experiment sparked true debate

Wilson, C. L., *J. Chem. Soc.*, **1939**, 1188-1199.

Norbornyl Sulfinate Acetolysis: Origin of the Problem

Saul Winstein (right), circa 1953
(1912-1969)

Winstein and Trifan, 1949:



(*exo*)-Norbornyl-2-OBs
(enantioenriched)

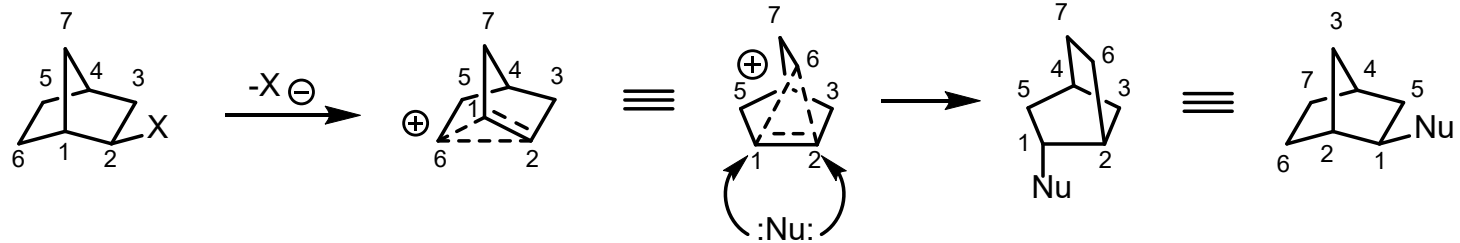
(*exo*)-Norbornyl-2-OAc (rac.)
Major product

Kinetic analysis:
exo vs *endo* rates of solvolysis

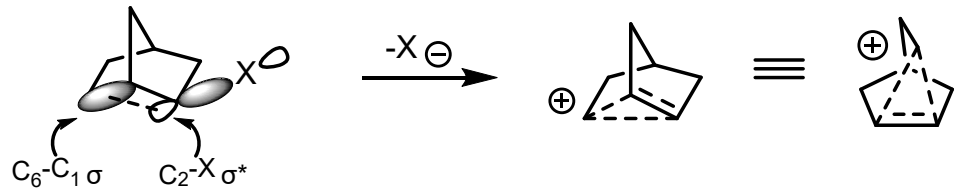
	(exo)-Norbornyl-2-OBs	(endo)-Norbornyl-2-OBs
K_{rel}	350	1

Winstein's proposed solution: Carbonium ion

Stereochemical rationale: Why solvolysis products are racemic and *exo*



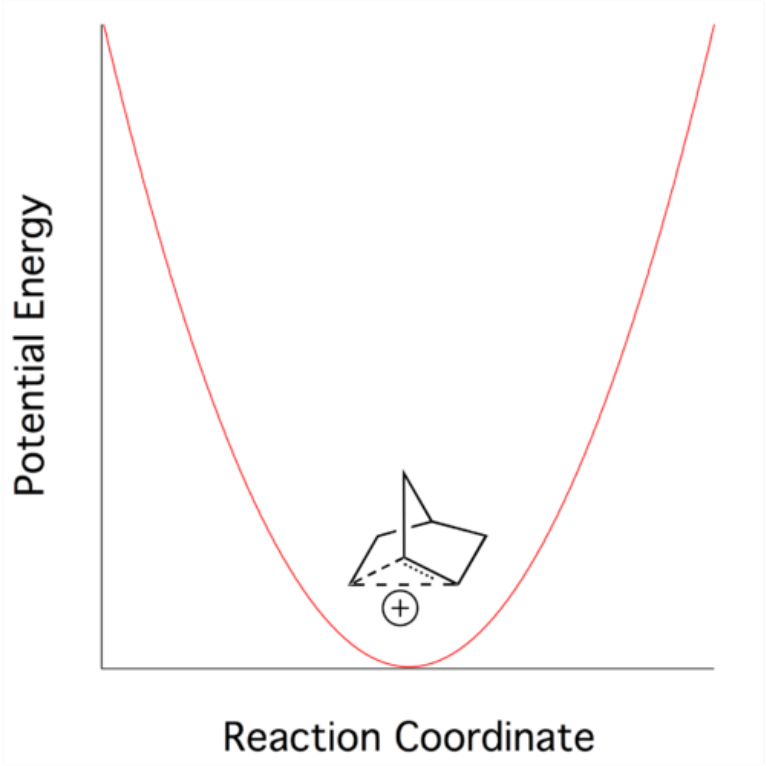
Kinetic rationale: Why the *exo* diasteromer ionizes faster

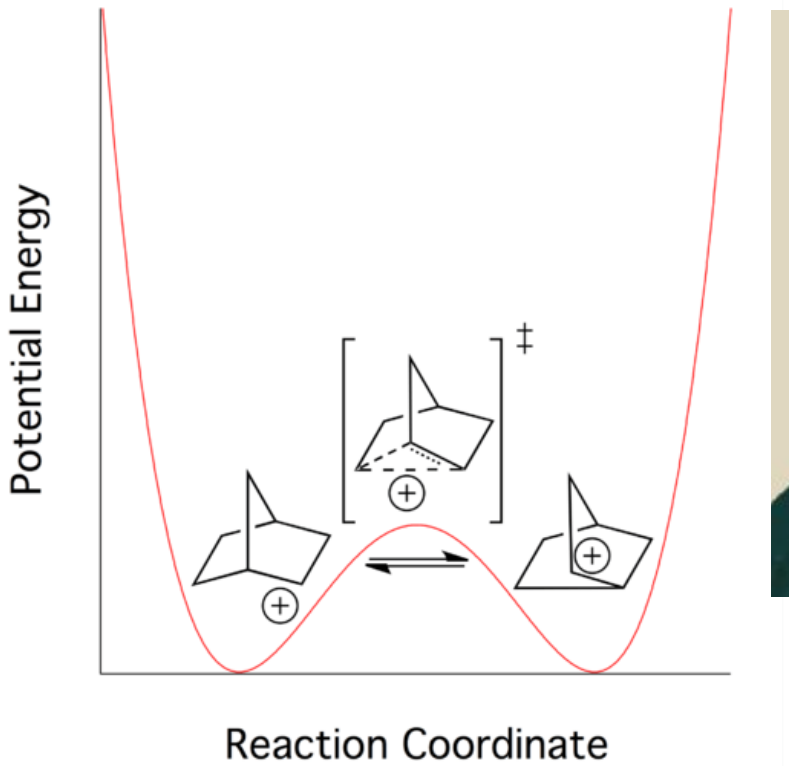


S. Winstein, *J. Am. Chem. Soc.*, **1949**, 71, 8, 2953. Photo from: https://cen.acs.org/articles/90/i47/Celebrating-Saul-Winsteins-Legacy-Organic.html

Both Sides of the Debate: Non-classical vs Classical

G. A. Olah





H. C. Brown

Crucial aspects argued by either side:

1. Non-classical σ-donation forms a "carbonium" or pentavalent carbon.

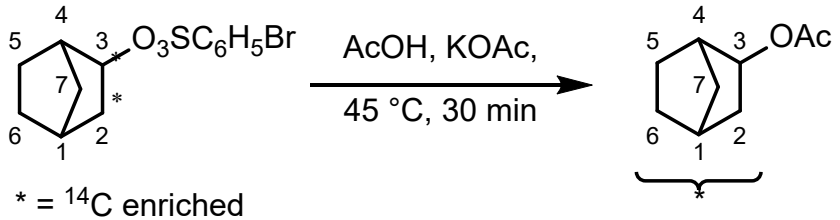
2. Reaction coordinate is an energy minimum, offering added stability over rapidly equilibrating cation species

1. Sterics explain rate differences in solvolysis (Neighboring group/bond participation does not assist in ionization)

2. Non-classical cation delocalization affords negligible added stabilization, thus, it must not be a low energy minimum

Isotopic Labelling and Degradation Studies: John D. Roberts

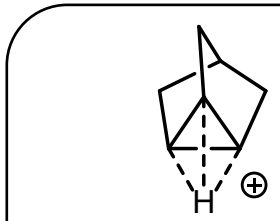
John D. Roberts: ^{14}C labeling reveals cation equilibration:



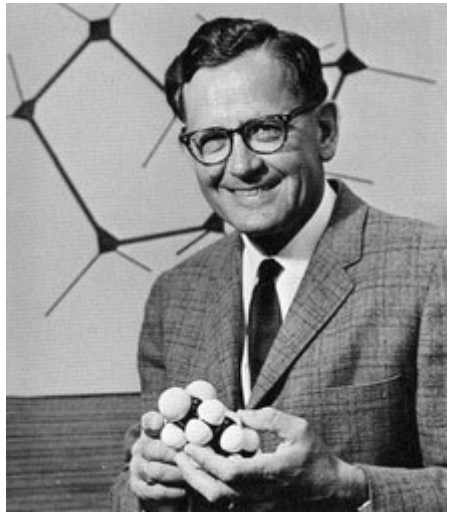
* = ^{14}C enriched

100% ^{14}C activity

Taken forward to careful degradation studies

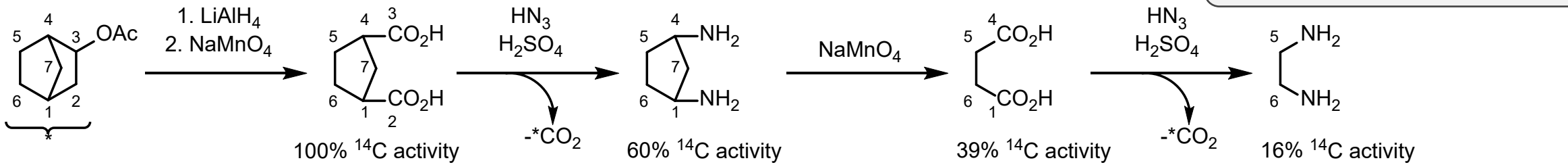


J. D. Robert's propsed structure "Nortricyclonium ion"



John D. Roberts in 1967 (1918-2016)

First person to coin the term "Non-classical" cation



100% ^{14}C activity

60% ^{14}C activity

39% ^{14}C activity

16% ^{14}C activity

Thus: C_3 and C_2 contained a total of 40% activity

Thus: C_7 contained a total of 21% activity

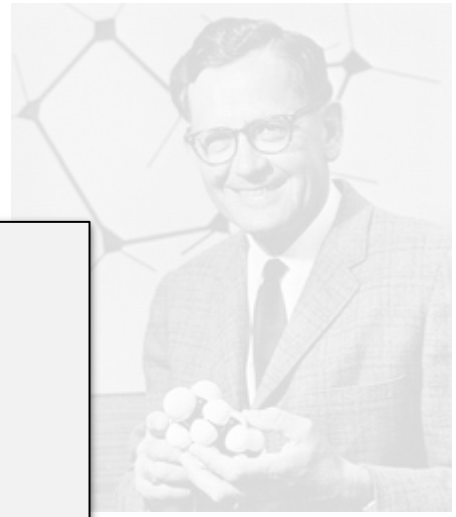
Thus: C_1 and C_4 contained a total of 23% activity

Thus: C_5 and C_6 contained a total of 16% activity

Roberts, J. D.; Lee, C. C. *J. Am. Chem. Soc.*, **1951**, 73, 5009., Photo from: https://en.wikipedia.org/wiki/John_D._Roberts, faculty yearbook photo from Cal. Tech.

Group Problem

John D. Roberts: ^{14}C labeling reveals cation equilibration:



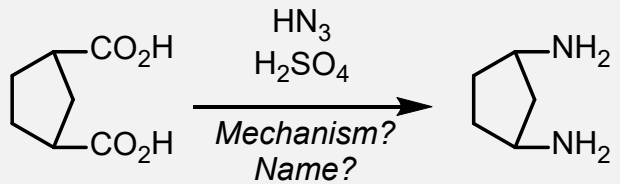
D. Roberts in 1967
(1918-2016)

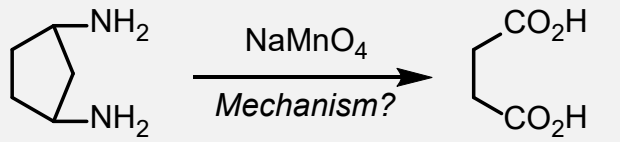
* = ^{14}C enriched

Taken forward t

erson to coin the term
n-classical" cation

Propose mechanisms for the following transformations:





100% ^{14}C activity

-*CO_2

60% ^{14}C activity

39% ^{14}C activity

-*CO_2

16% ^{14}C activity

Thus:
C_3 and C_2 contained
a total of 40% activity

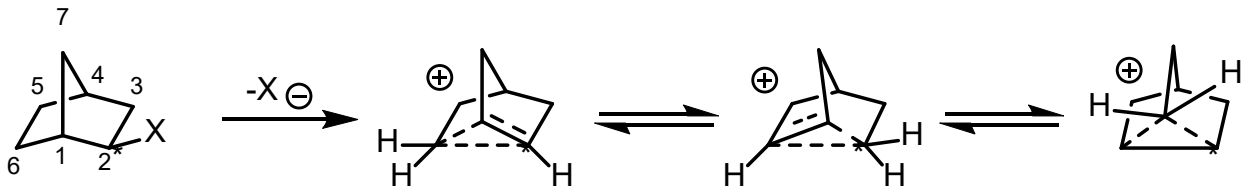
Thus:
C_7 contained
a total of 21% activity

Thus:
C_1 and C_4 contained
a total of 23% activity

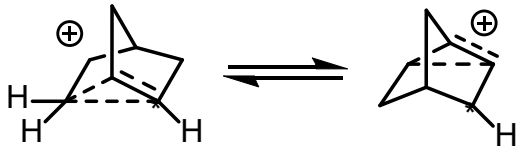
Thus:
C_5 and C_6 contained
a total of 16% activity

Roberts, J. D.; Lee, C. C. *J. Am. Chem. Soc.*, **1951**, 73, 5009., Photo from: https://en.wikipedia.org/wiki/John_D._Roberts, faculty yearbook photo from Cal. Tech.

Degenerate Carbocations: Hydride Shifts and Rearrangements

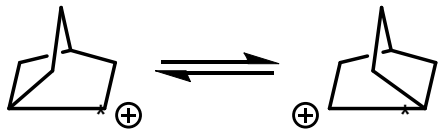


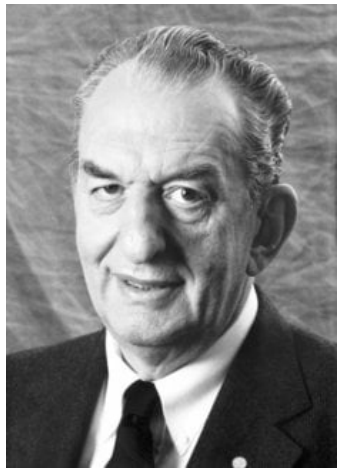
6, 1, 2-hydride shift
ΔG° = 5.9 kcal/mol



3, 2-hydride shift
ΔG° = 10.8 kcal/mol

Brown's proposed Wagner-Meerwein Rearrangement:
ΔG° = ??? kcal/mol

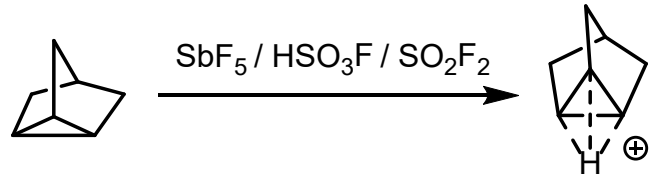




George A. Olah
(1927-2017)

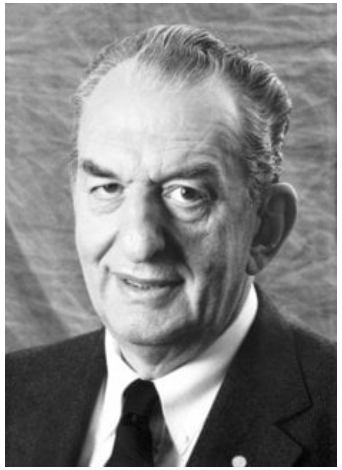
Expert at obtaining carbocation ^{1}H and ^{13}C NMR spectra in non-nucleophilic solvents.

"Magic Acid" mediated formation of 2-norbornyl cation:

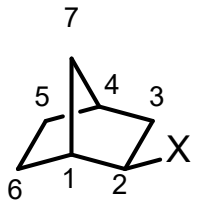


Olah, G. A., et. al, *J. Am. Chem. Soc.*, **1982**, 104, 7105-7108., *J. Am. Chem. Soc.*, **1970**, 92, 15, 4627–4640

Freezing Out Degenerate Shifts: Olah's Spectroscopic Evidence

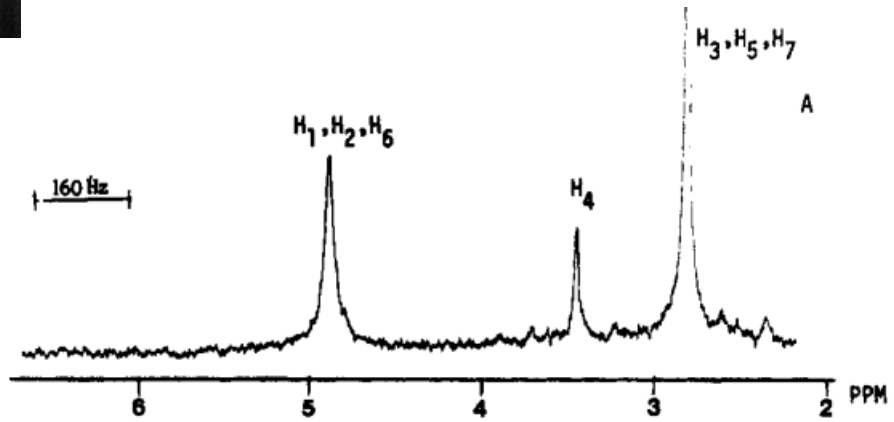


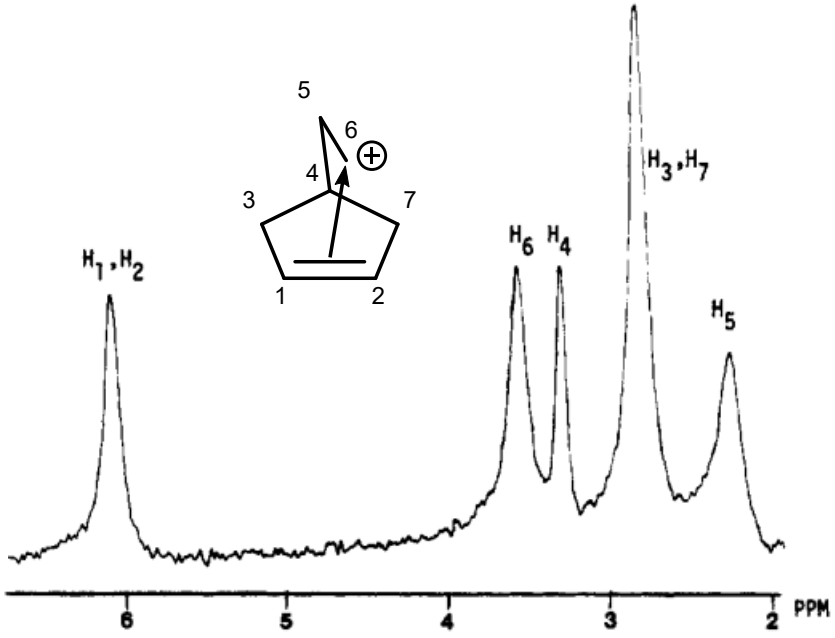
23 °C:
1 peak by ^{1}H NMR
Broad singlet at 3.10 ppm



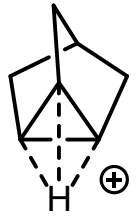
-158 °C:
6, 1, 2-Hydride shifts frozen out on the NMR timescale

-100 °C:
3,2-Hydride shifts frozen out on the NMR timescale





At -100 °C, the ^{1}H NMR signal begins to resemble Robert's original depiction of the non-classical ion:



"Nortricyclonium"
Roberts (1951)

Olah concludes:
If there is any form of W-M rearrangement, then it must be lower barrier than 5.9 kcal/mol

Olah, G. A., et. al, *J. Am. Chem. Soc.*, **1982**, 104, 7105-7108., *J. Am. Chem. Soc.*, **1970**, 92, 15, 4627–4640.

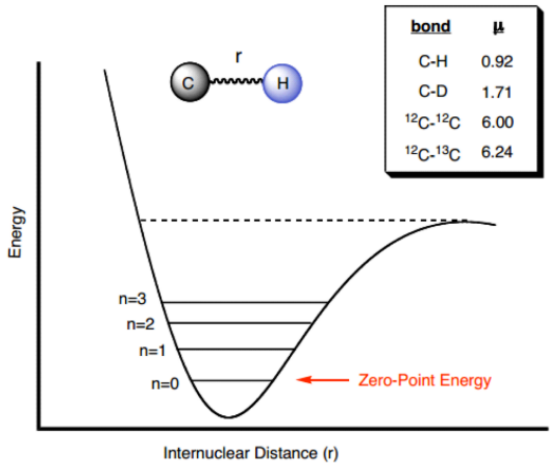
Saunders and Kates: Isotopic Breaking of Degeneracy

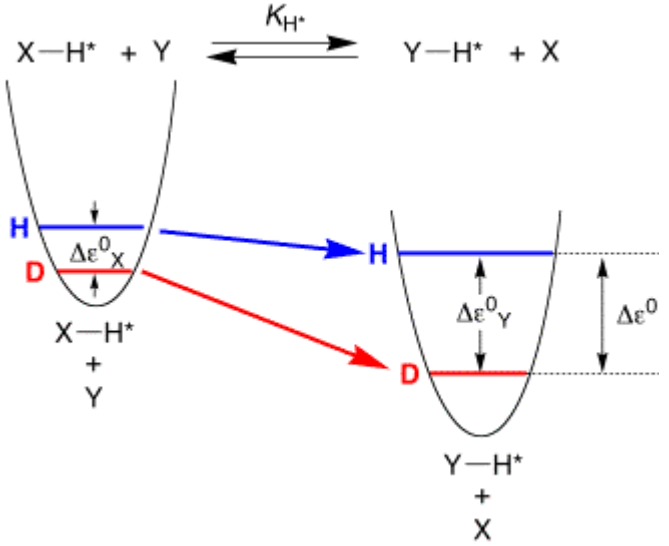
Isotope Labeling: Shifts Equilibria Position

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Reduced mass (increases with H to D or ^{12}C to ^{13}C)

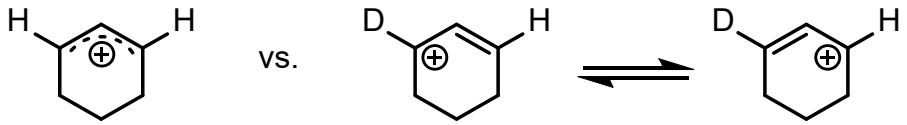
"Deuterium prefers the stronger bond" i.e. C(sp^2)-H/D versus C(sp^3)-H/D



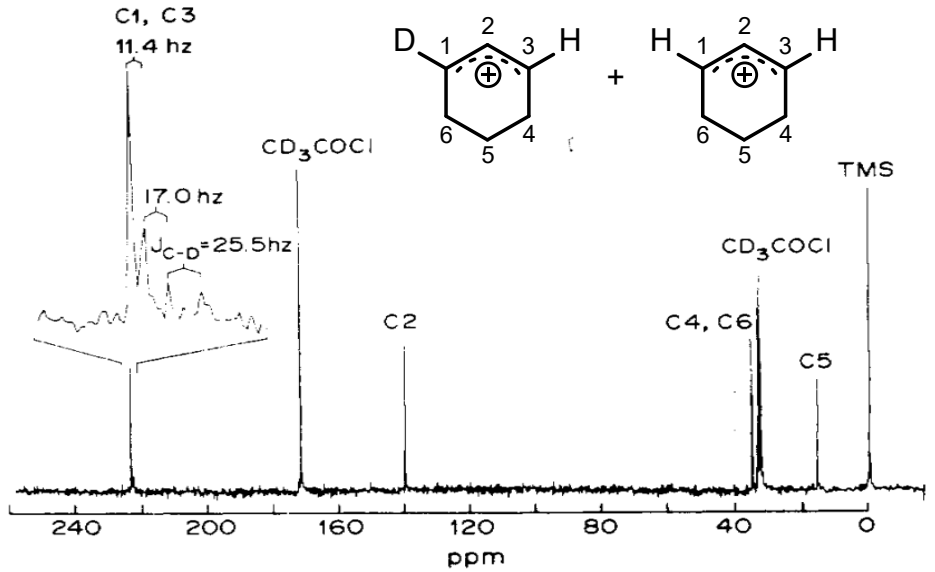


"Deuterium prefers the side of the equilibrium with the larger ZPE difference"

Saunders and Kates: Isotopic labeling (D, ^{13}C and CD_3) used to break the symmetry of degenerate nuclei in NMR



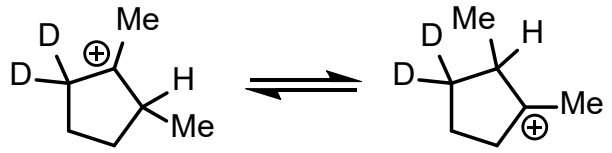
Δ = 11.4 Hz (0.163 ppm) indicates a high degrees of cation symmetry and a minimal equilibrium isotope effect



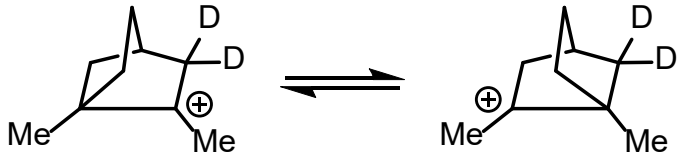
Saunders, M., *J. Am. Chem. Soc.*, **1977**, 99, 24, 8070–8071., Saunders, M., *J. Am. Chem. Soc.*, **1980**, 102, 6867-6868.

Saunders and Kates: Isotopic Breaking of Degeneracy

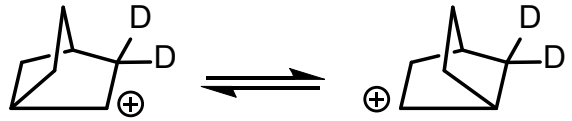
Basis for comparison:
other cationic species



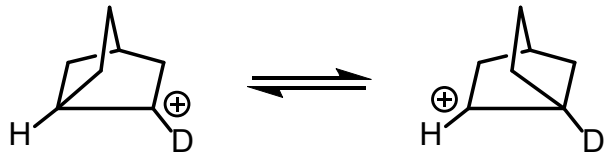
Δ ^{13}C = 104 ppm (!!!)



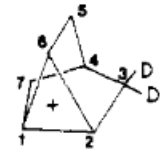
Δ ^{13}C = 23.9 ppm



Δ ^{13}C = 2.1-2.4 ppm



Δ ^{13}C = <2 ppm



^{13}C = ~125 ppm

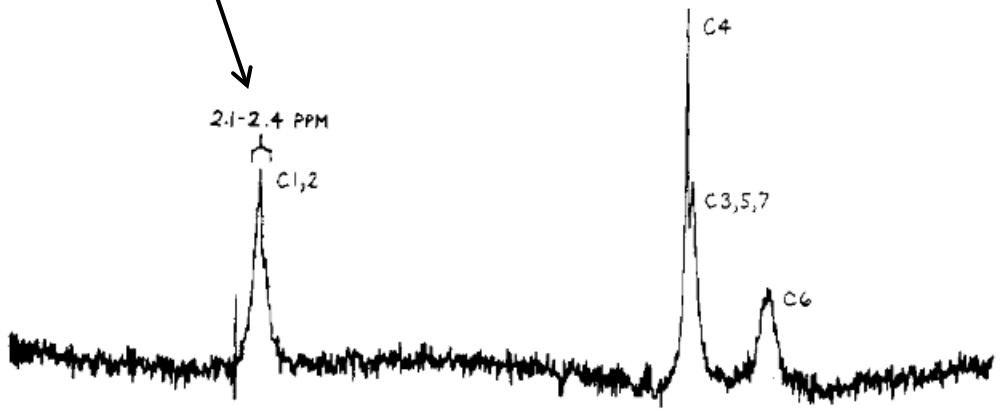


Figure 1. 67.9-MHz ^{13}C NMR spectrum of VIII at about −150 °C.

^{2}H NMR taken of the sample showed negligible scrambling from hydride shifts

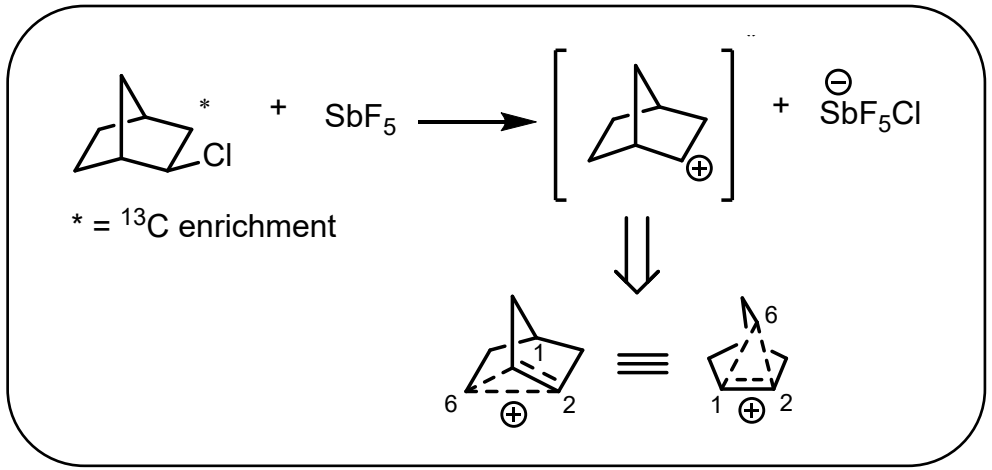
Small equilibrium isotope effect indicates C_1 and C_2 are nearly chemically equivalent

Saunders, M., *J. Am. Chem. Soc.*, **1980**, 102, 6867-6868.

Spectroscopic Evidence: Solid State NMR down to 5 Kelvin

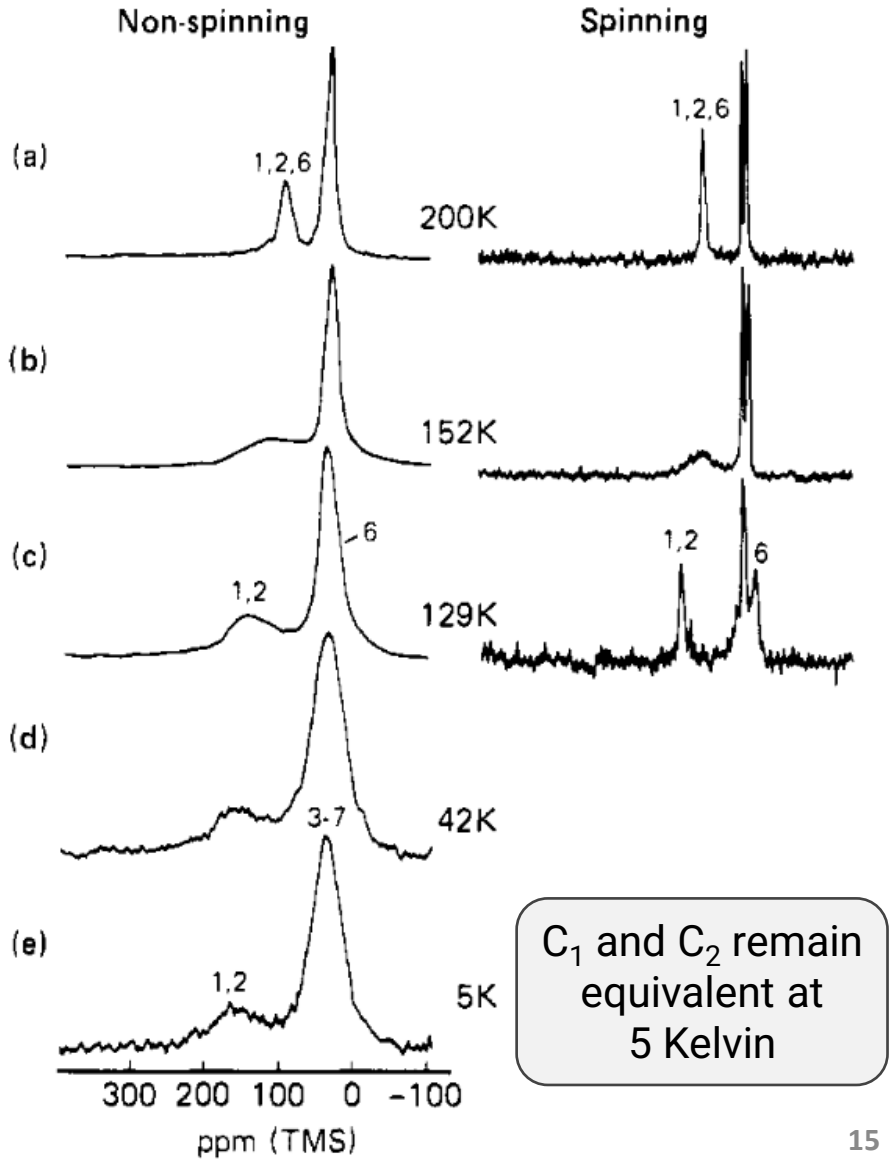
Costantino S. Yannoni (IBM Lab) & Philip C. Myhre (Harvey Mudd College):

Low Temperature Solid State ^{13}C NMR Experiments



If you agree with the author's conclusions:

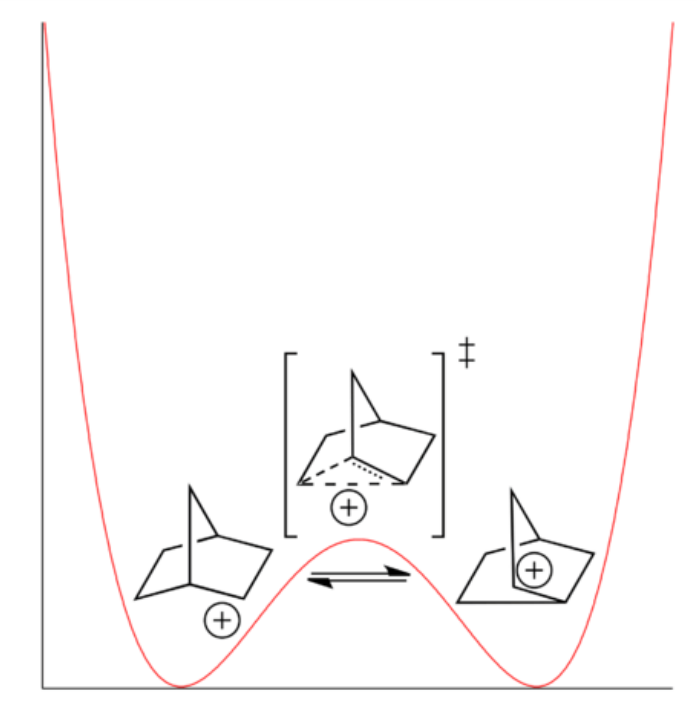
C_1 and C_2 being chemically equivalent at 5 Kelvin indicates an interconversion barrier of <***0.2 kcal/mol (!!!)***



C_1 and C_2 remain equivalent at 5 Kelvin

Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.*, **1982**, 104, 7380.

Spectroscopic Evidence Summary and Brown's Argument



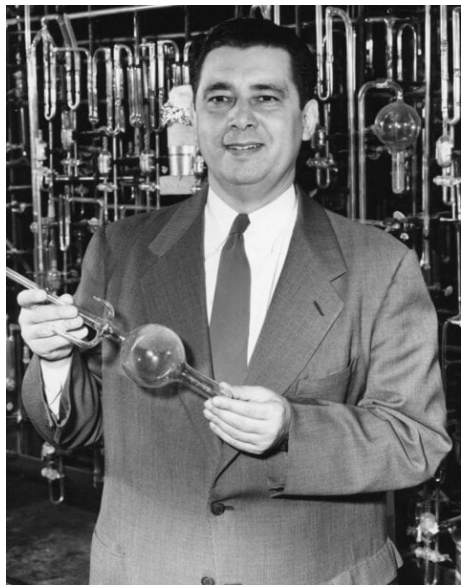
1. If there is any barrier, it must be very low in energy
2. Pragmatists argue that such a low barrier is effectively meaningless

1. Steric factors explain rate differences in solvolysis

2. Non-classical cation stabilization energy is over-stated and invoked improperly

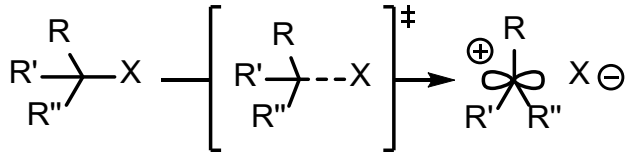
Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.*, **1982**, 104, 7380.

Critical Naysayer: H. C. Brown

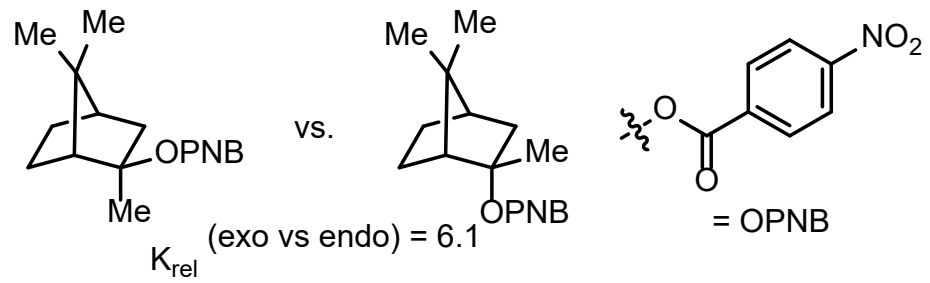


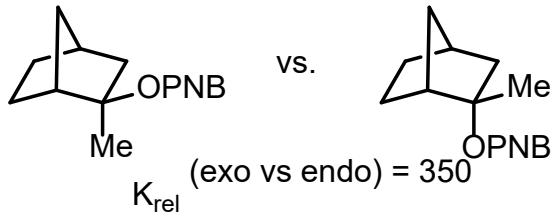
H. C. Brown

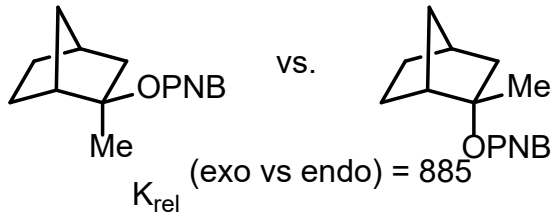
Steric factors explain rate differences in solvolysis: ("Backside" Strain)

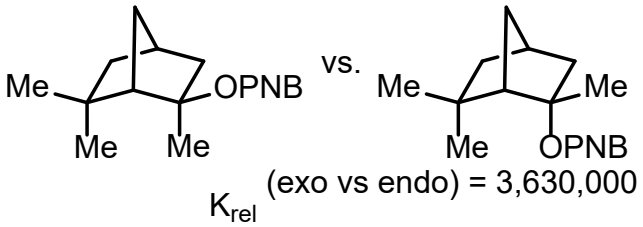


"Many phenomena which today are recognized as resulting from steric forces were attributed to the operation of purely electronic factors.... attention to the role of steric effects in organic chemistry sank to a very low ebb."
-H. C. Brown, 1962







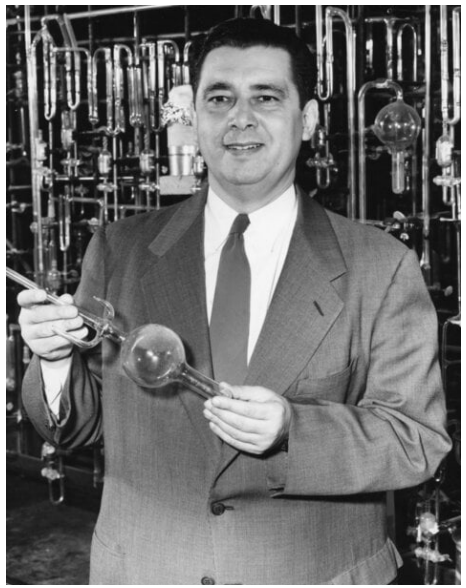


A-values:

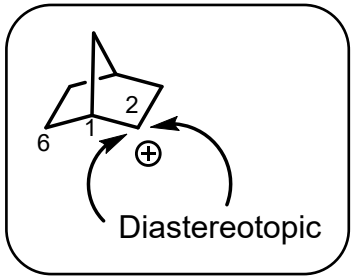
Ph	3.0 kcal/mol
CH_3	1.8 kcal/mol
OTs	0.7 kcal/mol
OAc	0.7 kcal/mol

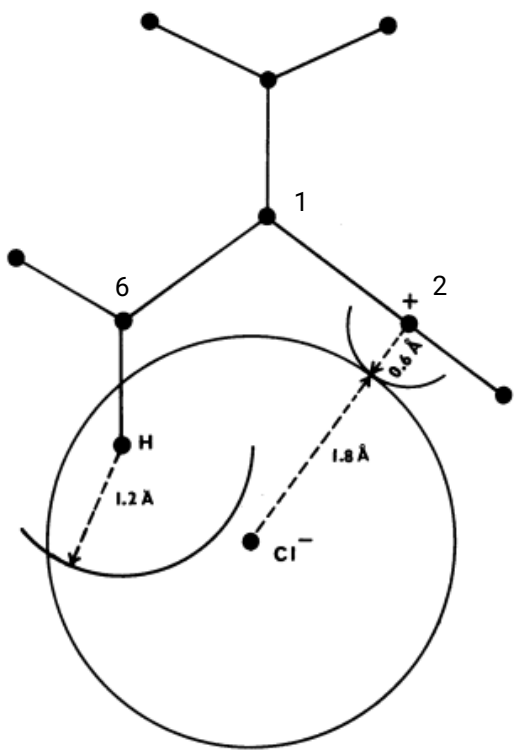
Brown H.C. *Science*, **1946**, 103, 385-7. Brown, H. C. *Acc. Chem. Res.*, **1983**, 16, 432-440. Photo from https://www.nobelprize.org/prizes/chemistry/1979/brown/photo-gallery/

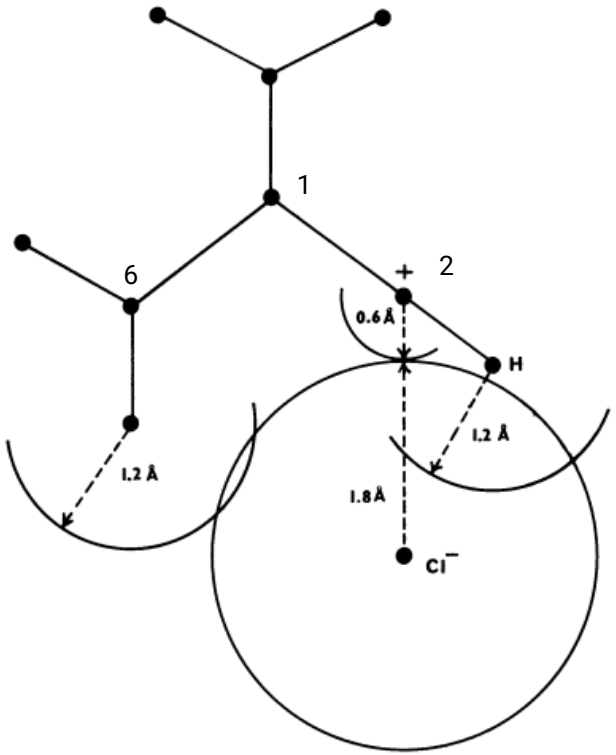
H. C. Brown: Explanation of *Exo* vs *Endo* Rates of Ionization/Capture



H. C. Brown



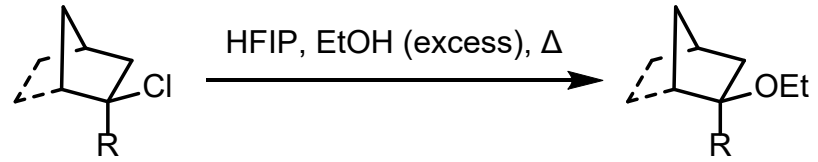




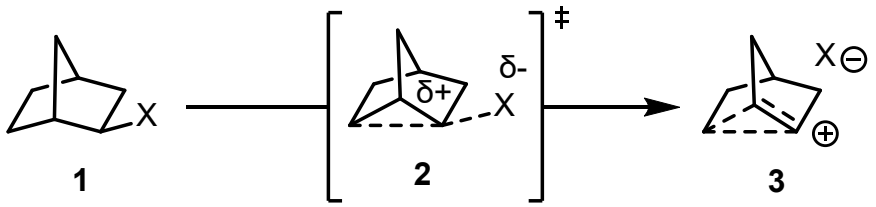
Nucleophilic attack ***and*** anion departure into / from C_2 is blocked by C_6-H or C_2-H
Structures that compress the C_6-C_1-C_2 angle exacerbate this phenomenon

Brown, H. C., *Chem. Soc. Spec. Pub. 16*, London, **1962**, 140-162., Brown, H. C., *Acc. Chem. Res.*, **1983**, 16, 432-440.

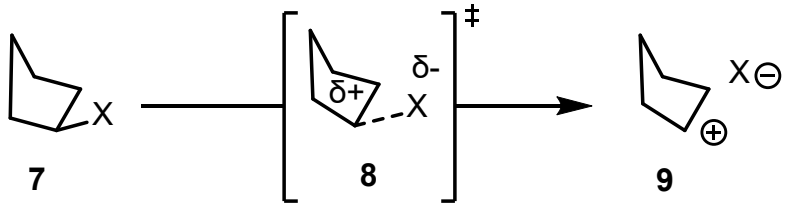
H. C. Brown: “Where is the non-classical stabilization energy?”



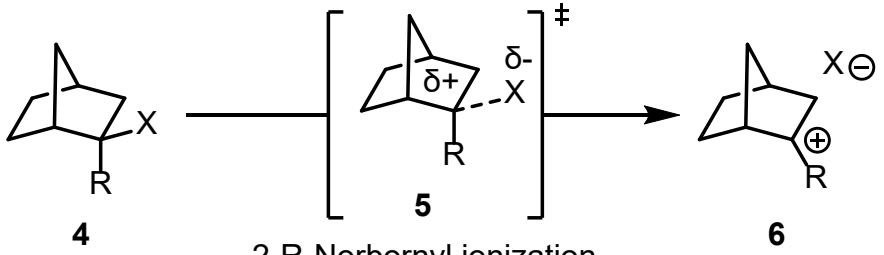
R = Me, Ph



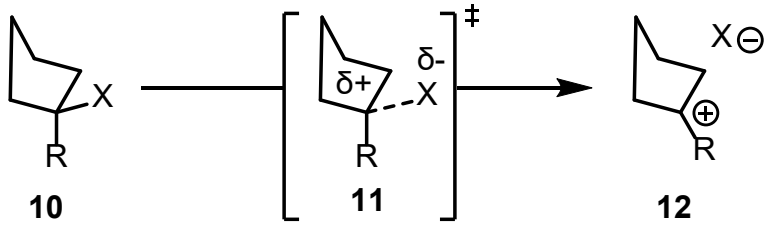
Norbornyl ionization



Cyclopentyl ionization



2-R-Norbornyl ionization



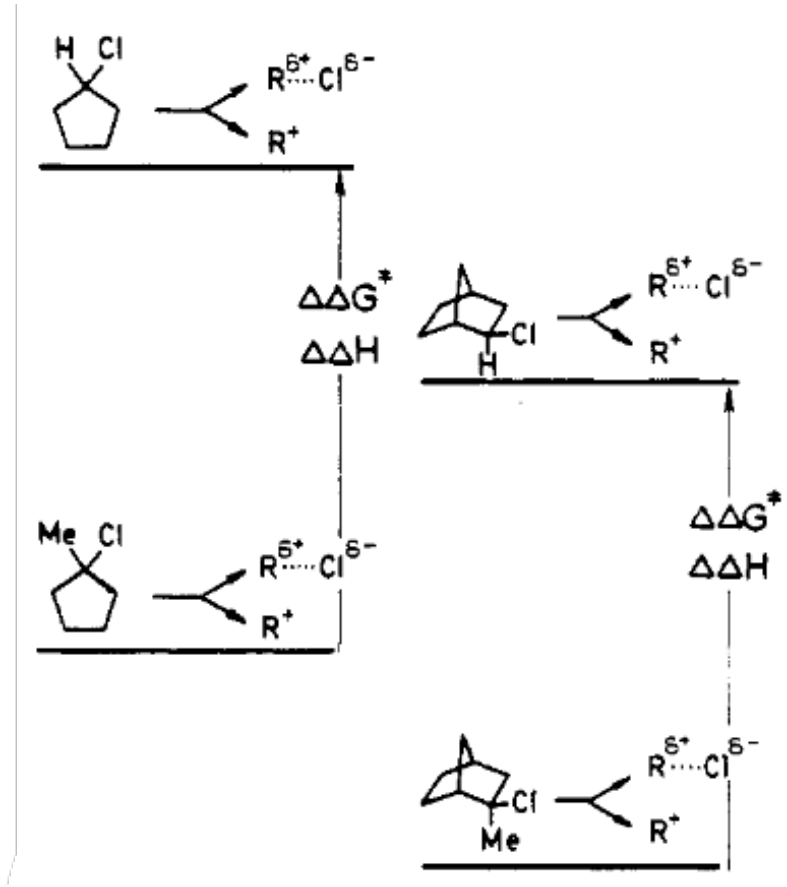
R-Cyclopentyl ionization

If the non-classical theory holds true:
$\Delta\Delta G^{\ddagger}$(**2** vs **5**) < $\Delta\Delta G^{\ddagger}$(**8** vs **11**)

Brown, H. C., *Acc. Chem. Res.*, **1983**, 16, 432-440.

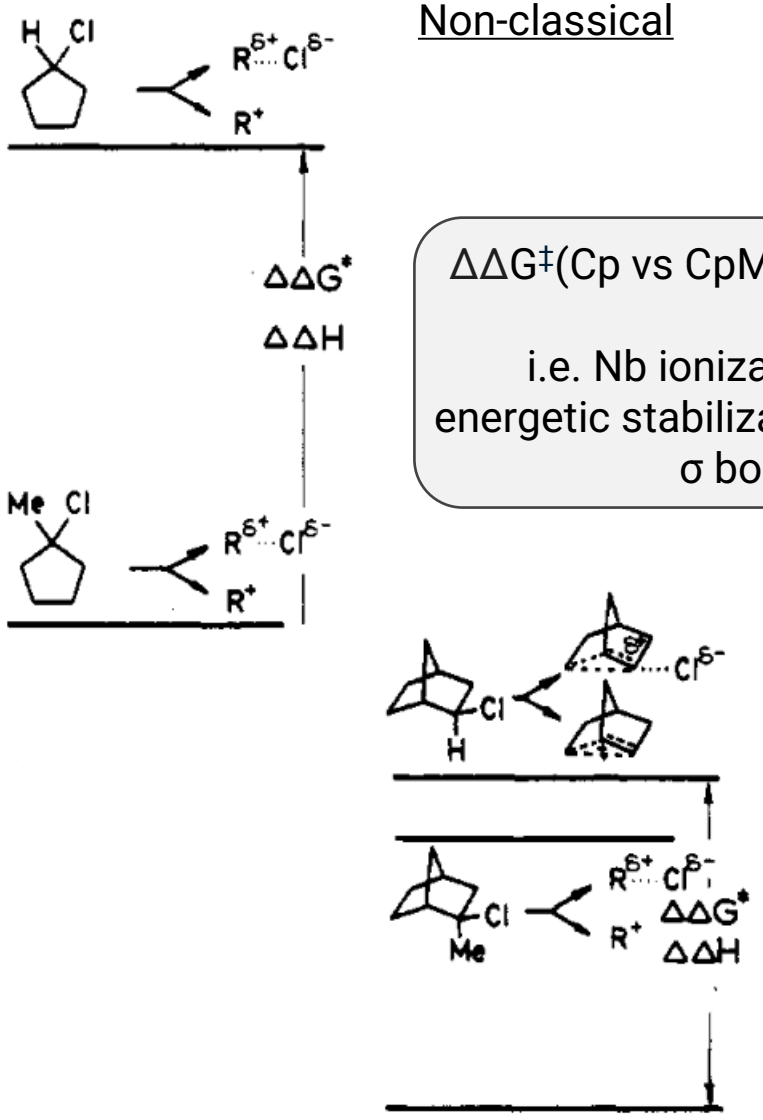
H. C. Brown: “Where is the non-classical stabilization energy?”

Classical



ΔΔG‡(Cp vs CpMe) = ΔΔG‡(Nb vs NbMe)

Non-classical

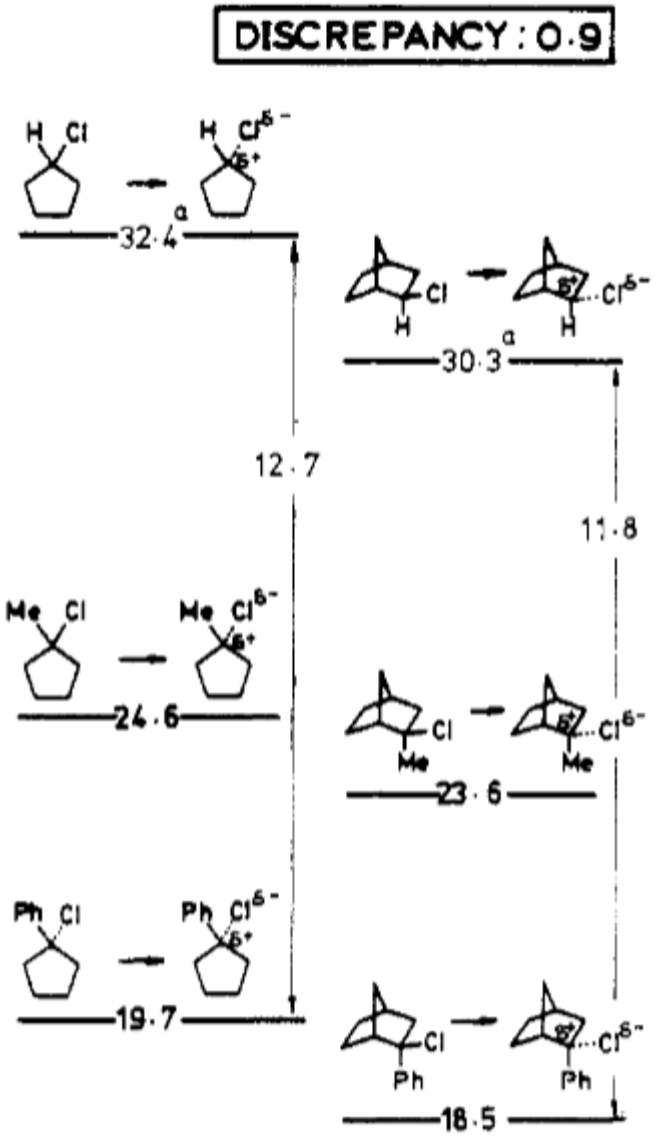


ΔΔG‡(Cp vs CpMe) > ΔΔG‡ (Nb vs NbMe)

i.e. Nb ionization should enjoy an energetic stabilization due to the proposed σ bond donation.

Brown, H. C., *Acc. Chem. Res.*, **1983**, 16, 432-440.

H. C. Brown: “Where is the non-classical stabilization energy?”



ΔΔG‡(Cp vs CpMe) > ΔΔG‡ (Nb vs NbMe) by only 0.9 kcal/mol

i.e. Nb ionization energy is minimally (0.9 kcal/mol) stabilized by any non-classical effects (bridging, delocalization)

Brown deems this evidence as proof that the non-classical depiction is over-stated

Grob argues:
If bridging is occurring, then substituents at the 6 position should have an electronic impact on the rates of ionization

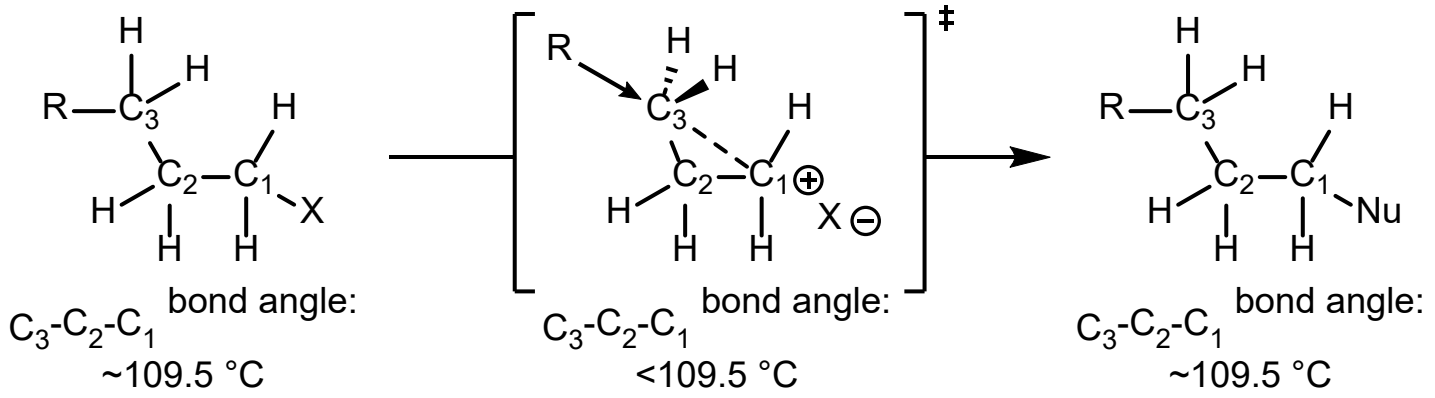
Cyril Grob
(1917–2003)

Brown, H. C., *Acc. Chem. Res.*, **1983**, 16, 432-440.

Grob: Bridging In Carbocations

Cyril Grob
(1917–2003)

"Bridging is a through space interaction"



Rules for bridging:

1. Nucleophilic attack at the backside of C_1 must be hindered or impossible. (to avoid S_N2 invertive displacement)

2. The R group at C_3 should be an electron donor to help disperse the δ+ formed.

3. Both C atoms involved in bridging should be able to adopt the trigonal-bipyramidal configuration favored by pentacoordinate atoms.

Deviations from this preferred arrangement will lead to a strained transition state and hence reduce bridging.

Grob, C., *Acc. Chem. Res.*, **1983**, 16, 426-431.

Exo versus *Endo* Rate Differences: Correlated by ρ values

Linear-Free Energy Relationship:
Electronic induction vs. Rate

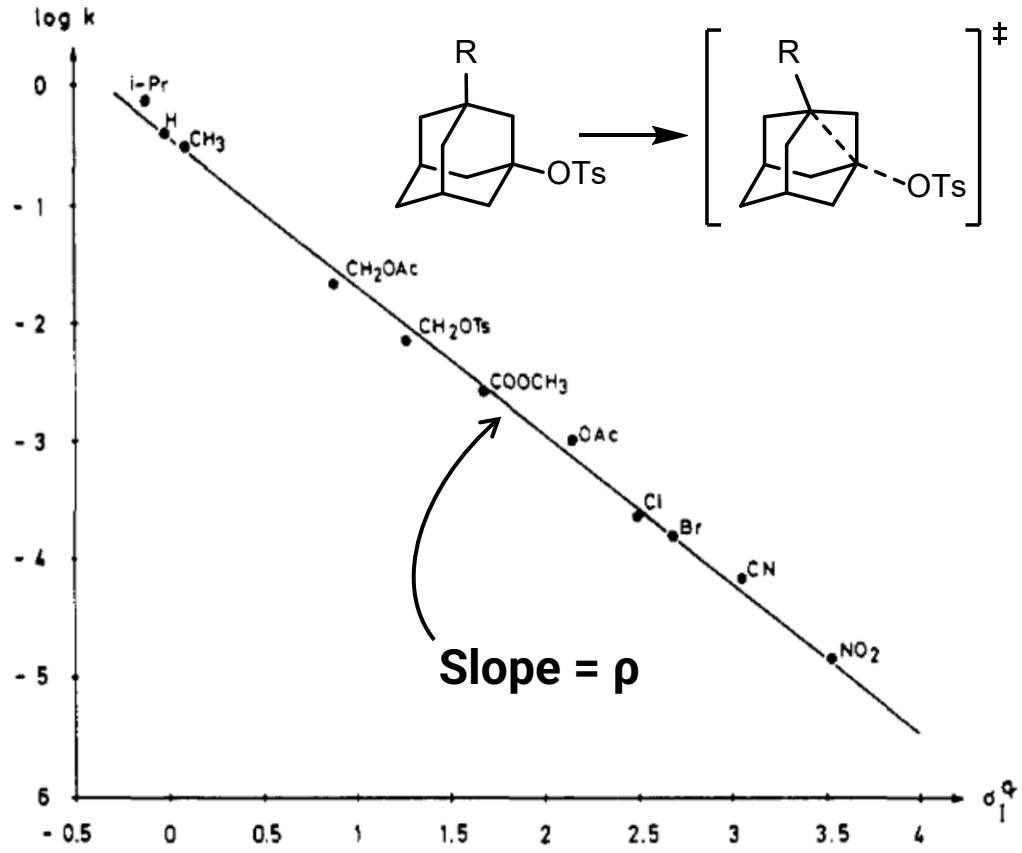
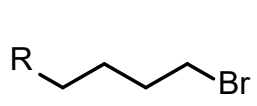
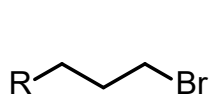


Figure 1. Plot of log *k* for 3-substituted-1-adamantyl tosylates **18** vs. inductive substituent constants σ_I^q.

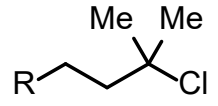
ρ values of different carbon scaffolds:



ρ = 0.0

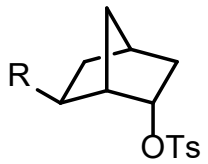


ρ = -0.12



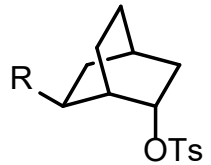
ρ = -0.71

ρ = -2.0

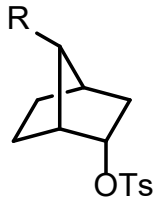


ρ = -0.78

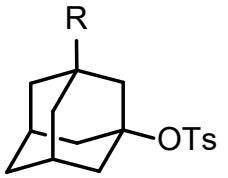
ρ = -1.5



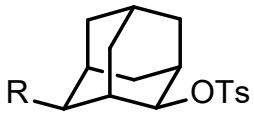
ρ = -1.0



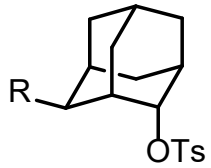
ρ = -0.72



ρ = -1.26



ρ = -0.82



ρ = -0.51

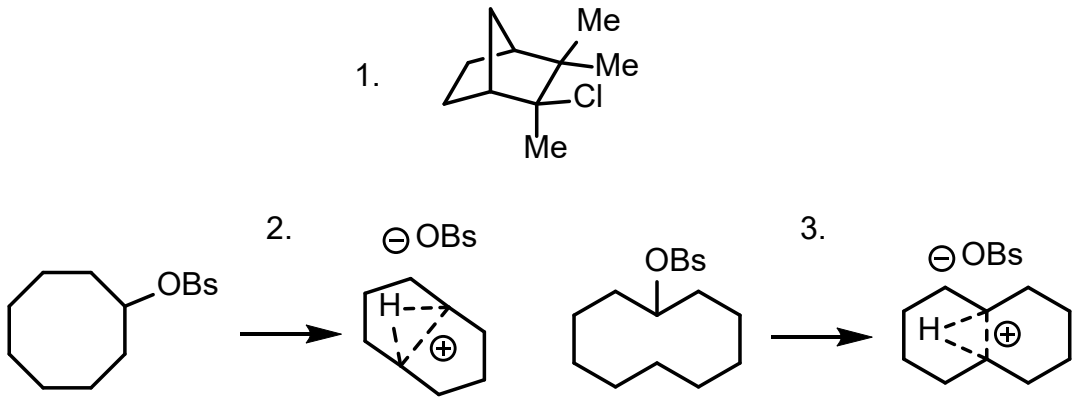
ρ values indicate norbornyl ionization is highly dependent on the electronic density at C_6

Grob, C., *Acc. Chem. Res.*, **1983**, 16, 426-431.

Key Takeaways from the Debate: Looking Back at the Evidence

It is puzzling that nonclassical supporters have often stated that all secondary cations possess the same stability, with only 2-norbornyl being exceptional.
–H. C. Brown, 1983

Retracted examples:



For some 20 years I have been carefully examining many pieces of evidence purporting to support the formation of a highly stabilized 2-norbornyl cation. Invariably, the arguments and evidence have crumpled after careful study.[1b]

Citation 1b:
Brown: "The Nonclassical Ion Problem" 1977.

Key takeaways:

1. Olah's spectroscopic evidence cannot rule out a very low energy barrier of interconversion

2. Saunders spectroscopic evidence relied on the assumption that a classical cation must have no *s* character
"Thou shall not direct s character toward vacant orbitals"
-Eschenmoser group 11th Commandment

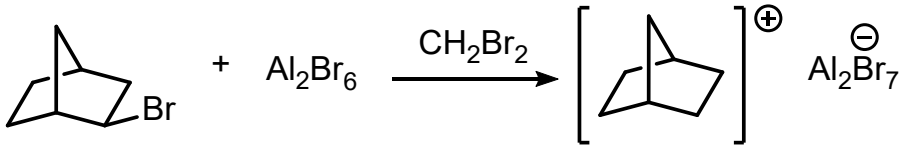
3. Brown's missing stabilization energy may be due to weak bridging in 2-substituted Nb scaffolds

4. Grob's justification of a pentacoordinate carbon TS is the best explanation for the rate data of 6-substituted Nb scaffolds

Quote: Brown, H. C., *Acc. Chem. Res.*, **1983**, 16, 432-440.
Articles correcting claims of non-classical cations: 1. Brown, H. C., *J. Am. Chem. Soc.,* **1963**, 85, 2322., 2. and 3. H. J. Schneider, *J. Am. Chem. Soc.* **1983**, 105, 3556.

X-Ray Crystallography: The End of the Debate

Krossing and Meyer, Science, 2013:
Direct X-Ray Evidence

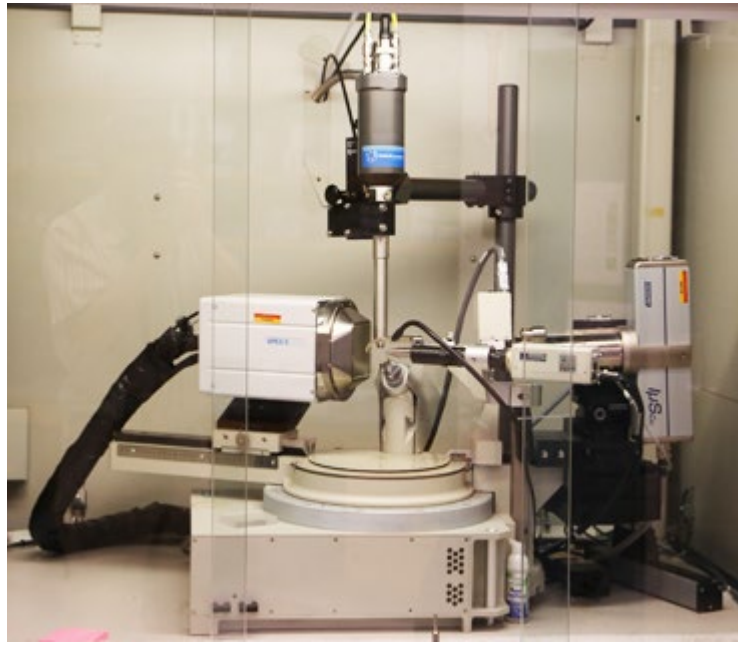


"Crystals turned out to be extremely labile towards room temperature and atmosphere… numerous crystals were inspected under the microscope under cooling in protective perfluoropolyalkylether oil and nitrogen atmosphere and were tested on the diffractometer."

"Finally, a total of seven single crystals were selected and used for XRD studies…" Krossing and Meyer

Spontaneous crystallization after four days at 245 K (-28 °C)

Crystals coated in a protective oil layer



Crystals subjected to X-ray analysis

Scholz, F., Meyer, K., & Krossing, I. *Science*, **2013**, 341, 6141, 62–64.

Obtaining a Crystal Structure: Struggles along the way

At 120 K (-153 °C):

At 40 K (-233 °C):

Karsten Meyer:
"The crystallography was a tour de force… the procedure is insane – it put us through torture"

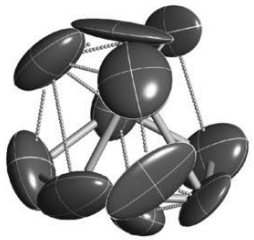
10 careful annealing/cooling cycles to maintain crystal lattice without cracking/breaking

Helium-cooled diffractometer was required (final temp 30 K)

Meyer, K., & Krossing, I. *Science*, **2013**, 341, 6141, 62–64.

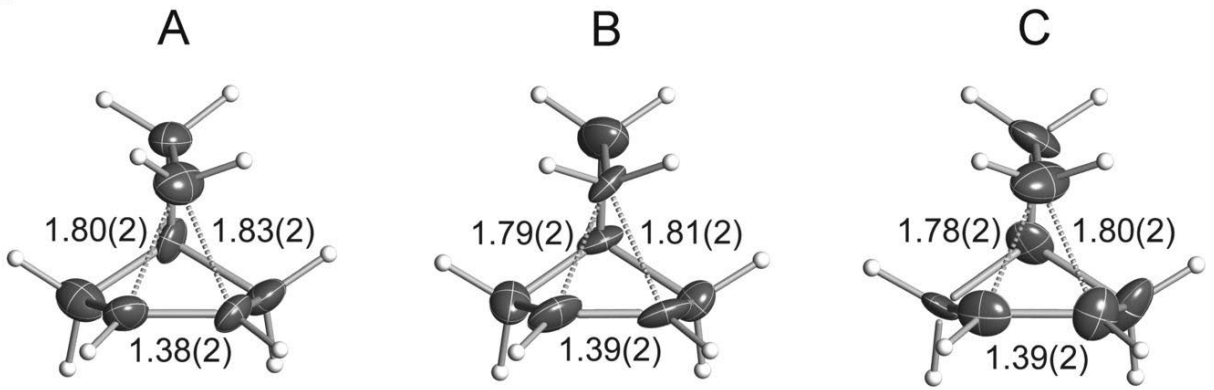
Bond Lengths: Direct Evidence of the Non-Classical Cation

@120K:



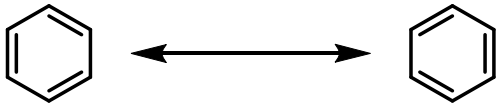
Disordered structure at 120 K

@ 40K:

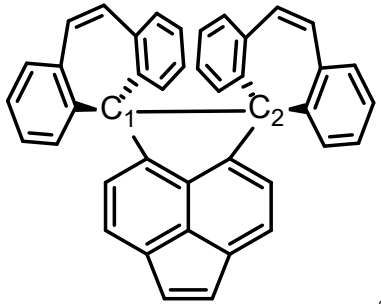


Mean value of all six C···C, x-ray: 1.80 Å (MP2: 1.825 Å)
Mean value of all three C=C, x-ray: 1.39 Å (MP2: 1.393 Å)

Bond Length Comparison:



Average C-C bond length = 1.39 Å
C-C bond order = 1.5



C_1-C_2 bond length = 1.806 Å

J. D. Roberts (aged 95) on whether the 2013 crystal structure would have caused Brown to reconsider his position:

"Herb would be Herb no matter what happened."

Scholz, F., Meyer, K., & Krossing, I. *Science*, **2013**, 341, 6141, 62–64. Longest reported C-C single bond: Suzuki, T., *Chem*, **2018**, 4, 795–806.

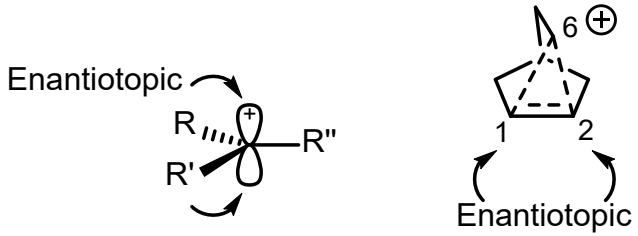
“Reverse Winstein Experiment”: Enantioselective Nucleophile Capture

Chiral imidodiphosphorimidate (IDPi) catalysts differentiate enantiotopic cation faces:

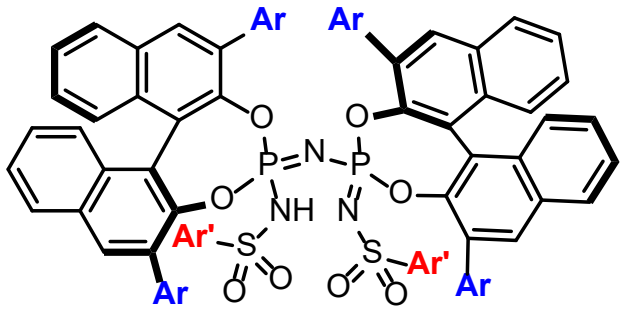
Main challenge:
Catalyst binding to a delocalized positive charge across 3 atoms

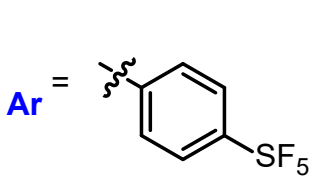
Easily tunable to change steric and electronic parameters (enzyme-like)

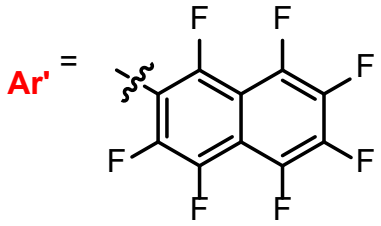
Very weakly Lewis basic, thus, highly acidic (able to protonate olefins and cyclopropanes)



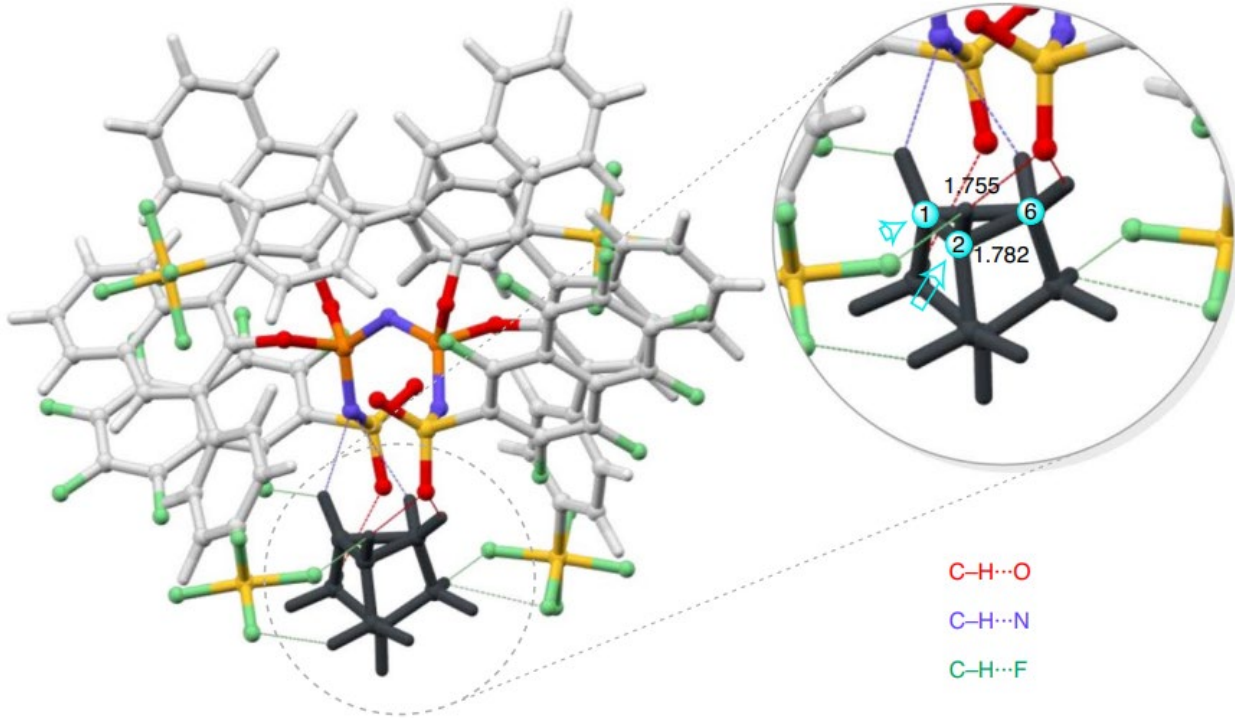
Optimized catalyst structure:







Lowest energy catalyst-substrate binding model:

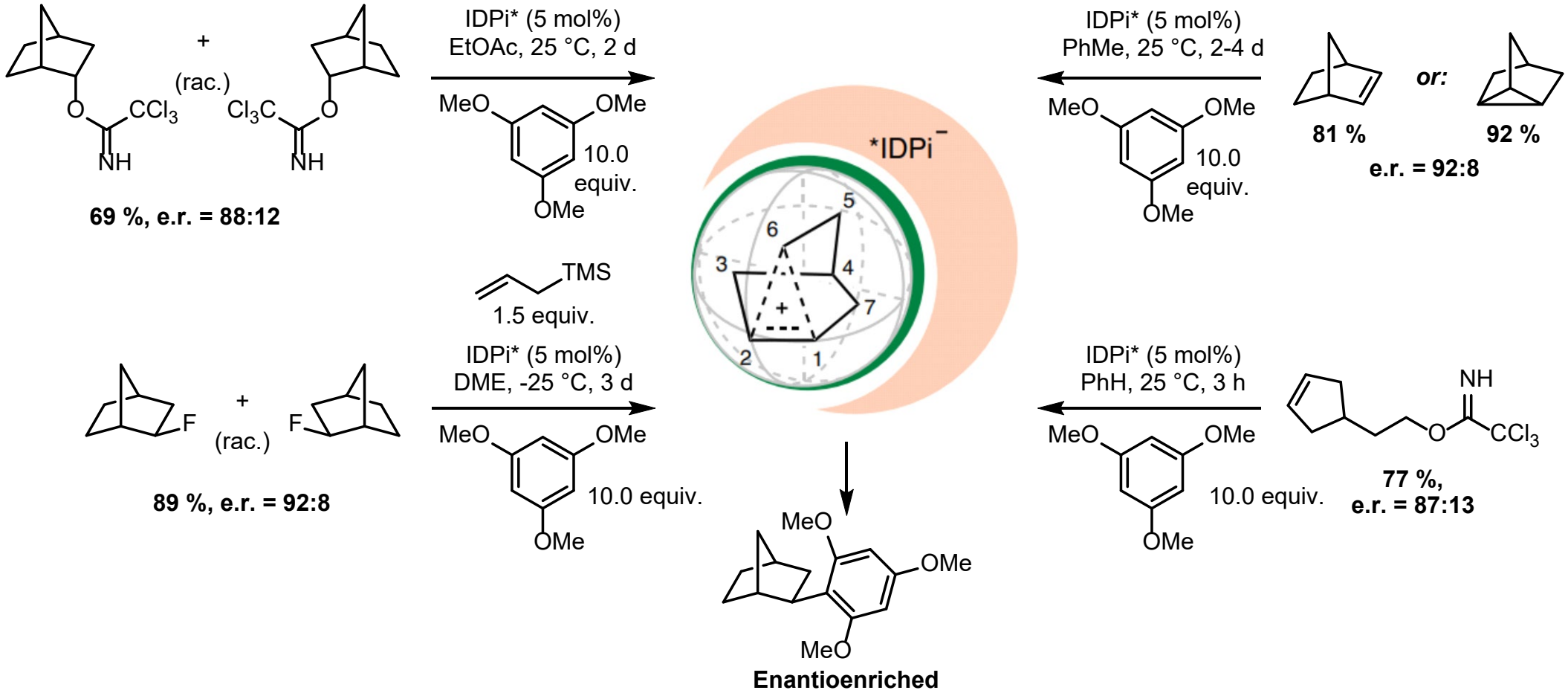


Level of theory: PB-D3(BJ)/def2-SVP)

List, B., *Nat. Chem.*, **2020**, 12, 1174–1179.

List and co.: Enantioselective cation capture

Fine control of cation formation and nucleophile trapping rates led to good yield and e.r. under optimized conditions:



List, B., *Nat. Chem.*, **2020**, 12, 1174–1179.

Additional Readings

1.) Acc. Chem. Res. (Vol. 16, Number 12, Dec. 1983)

ACCOUNTS OF CHEMICAL RESEARCH®

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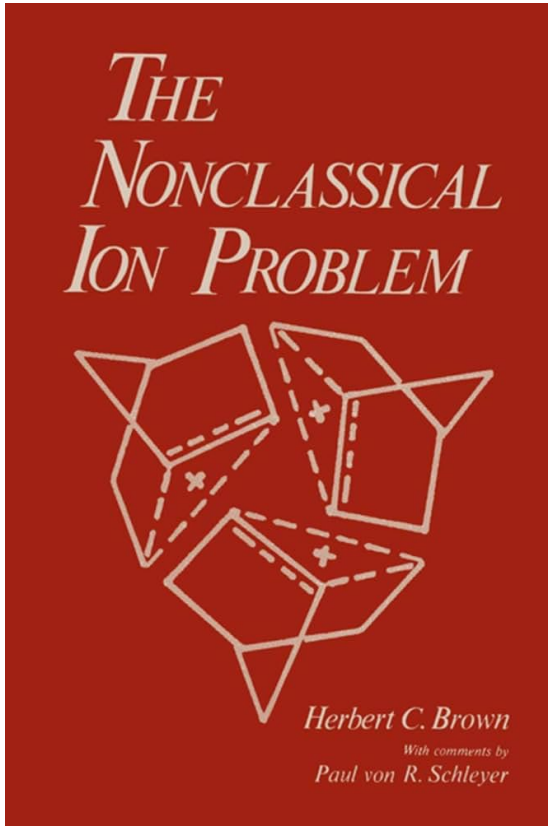
VOLUME 16 NUMBER 12 DECEMBER, 1983

EDITOR
JOSEPH F. BUNNETT

ASSOCIATE EDITORS

The Great Carbocation Problem

2.) The Nonclassical Ion Problem



Dean Tantillo and co.: Computational analysis

3.) *J. Org. Chem.*, **2007**, 72, 8877.

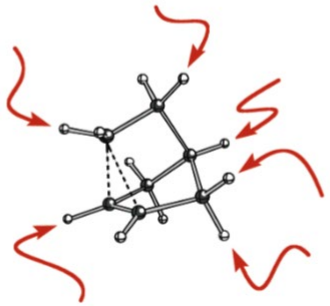
Perturbing the Structure of the 2-Norbornyl Cation through C−H···N and C−H···π Interactions

Young J. Hong and Dean J. Tantillo*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

tantillo@chem.ucdavis.edu

Received July 12, 2007



4.) *Chem. Sci.*, **2024**, 15, 15577–15587.

Chemical Science

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Cite this: *Chem. Sci.*, 2024, **15**, 15577

All publication charges for this article have been paid for by the Royal Society of Chemistry

Revisiting a classic carbocation – DFT, coupled-cluster, and *ab initio* molecular dynamics computations on barbaralyl cation formation and rearrangements†

Wentao Guo, ‡ Wang-Yeuk Kong ‡ and Dean J. Tantillo *

Density functional theory computations were used to model the formation and rearrangement of the barbaralyl cation ($C_9H_9^+$). Two highly delocalized minima were located for $C_9H_9^+$, one of C_s symmetry and the other of D_{3h} symmetry, with the former having lower energy. Quantum chemistry-based NMR predictions affirm that the lower energy structure is the best match with experimental spectra. Partial scrambling was found to proceed through a C_2 symmetric transition structure associated with a barrier of only 2.3 kcal mol^{-1}. The full scrambling was found to involve a C_{2v} symmetric transition structure associated with a 5.0 kcal mol^{-1} barrier. *Ab initio* molecular dynamics simulations initiated from the D_{3h} $C_9H_9^+$ structure revealed its connection to six minima, due to the six-fold symmetry of the potential energy surface. The effects of tunneling and boron substitution on this complex reaction network were also examined.

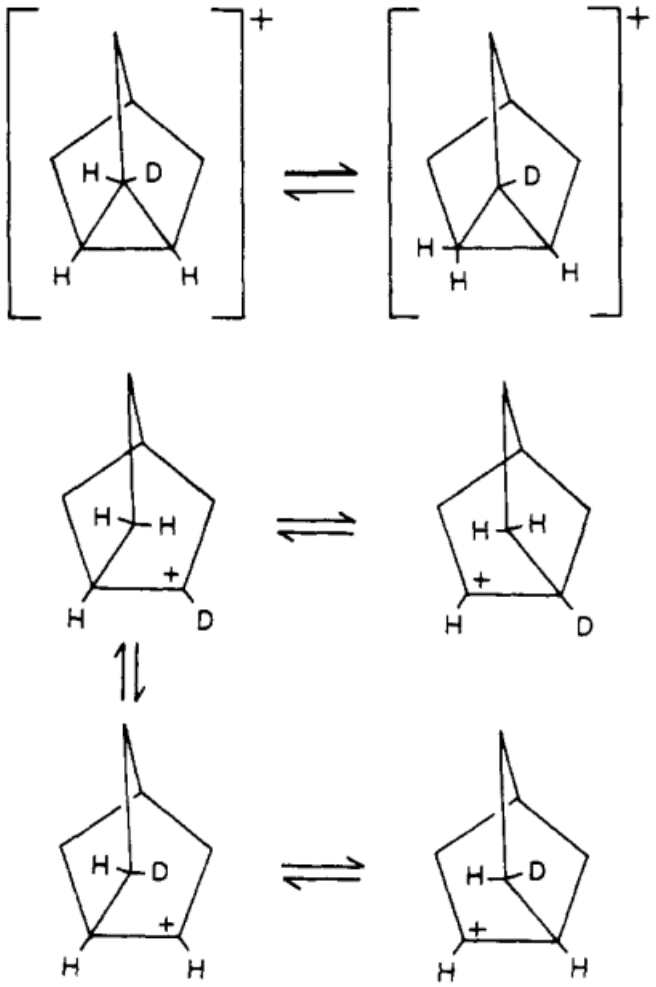
Received 20th July 2024
Accepted 26th August 2024

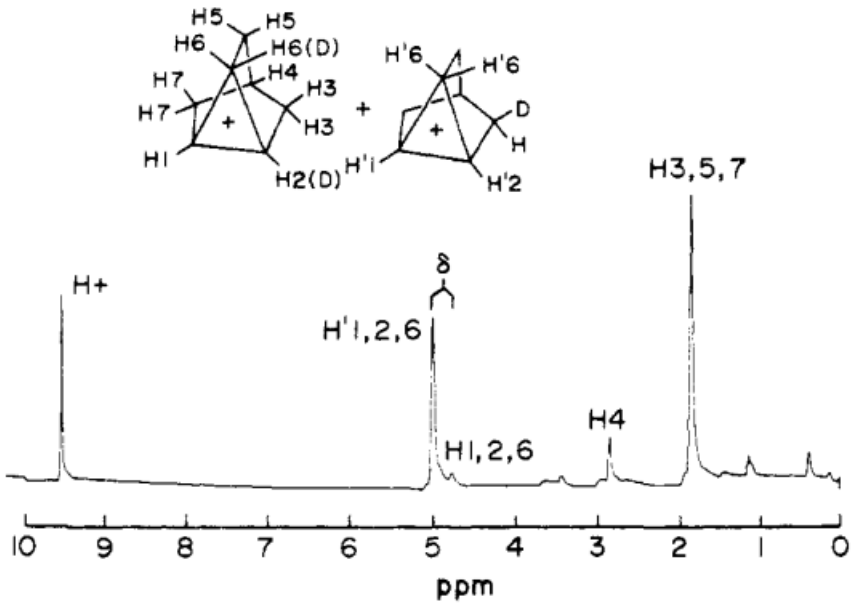
DOI: 10.1039/d4sc04829f

rsc.li/chemical-science

Questions?

Backup Slide – Saunders and Kates, 1983

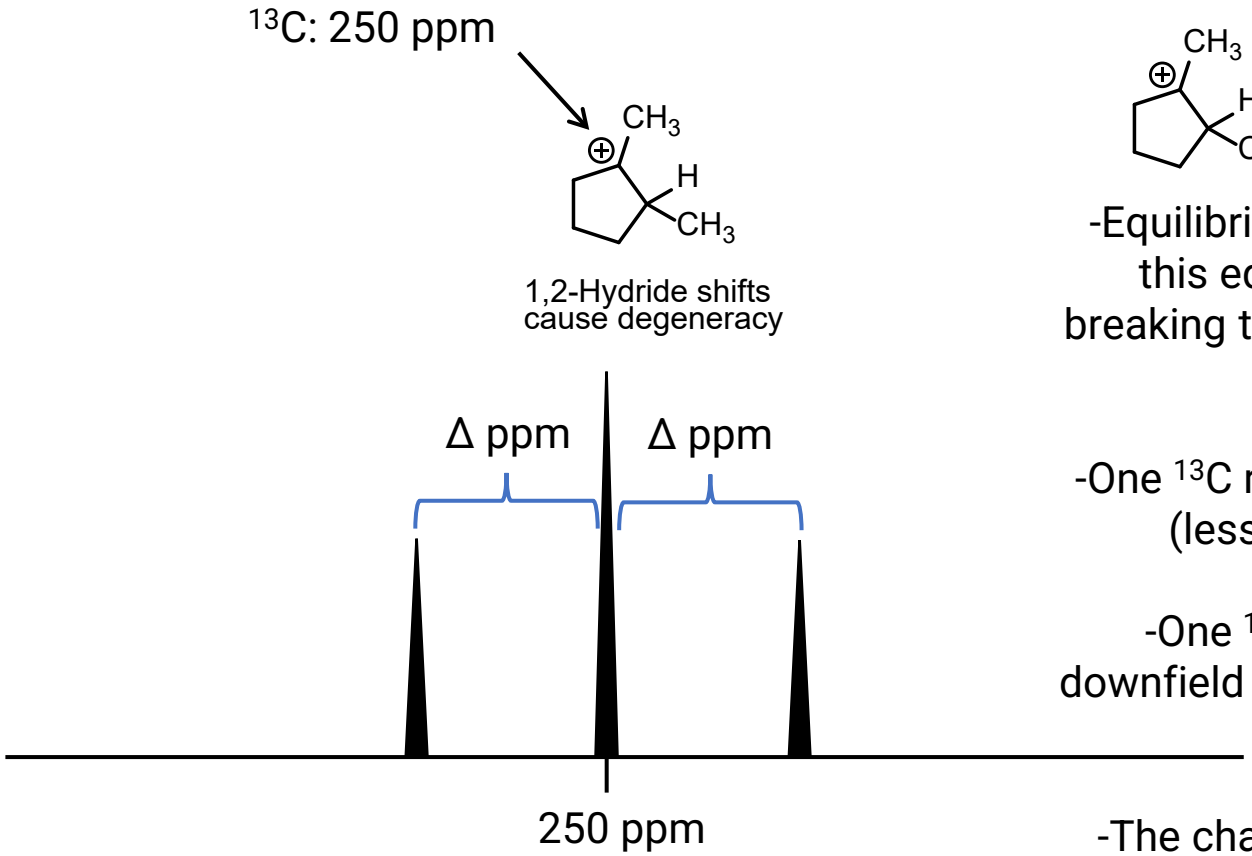


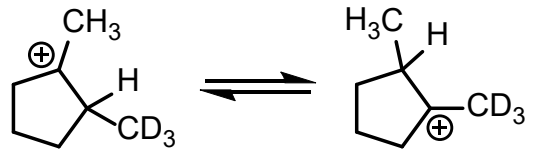


Upfield 1H NMR shift (More deuterium bound to cationic carbon)

Assuming an exponential temperature dependence in order to extrapolate the kinetic isotope effects to −43 °C, we predict an isotopic shift of 0.059 ppm *downfield* on the basis of this classical model through the use of a computer program that calculates the average frequencies weighted by the above isotope effects. This is clearly incompatible with the observed shift of 0.146 ppm *upfield*.

Backup Slide – Saunders and Kates, 1980





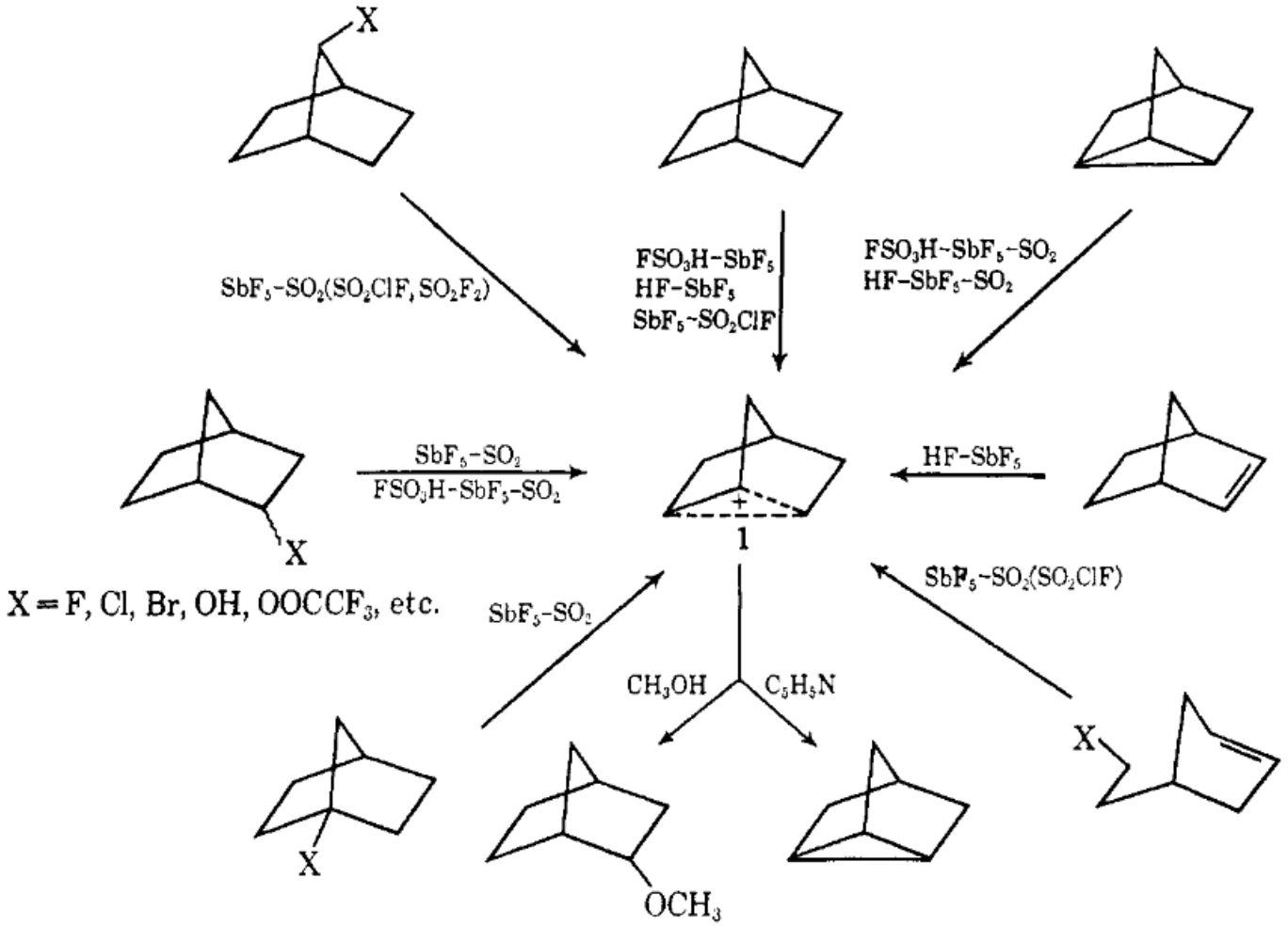
-Equilibrium isotope effect shifts this equilibrium to the right, breaking the degeneracy of the two carbon atoms

-One ^{13}C resonance moves upfield (less cationic character)

-One ^{13}C resonance moves downfield (more cationic character)

-The change in chemical shift is represented by Δ ppm

Backup Slide: Olah's Ways of forming 2-Nb cation



J. Am. Chem. Soc., **1970**, 92, 15, 4627–4640

Crystal Packing, Meyer, Science, 2013

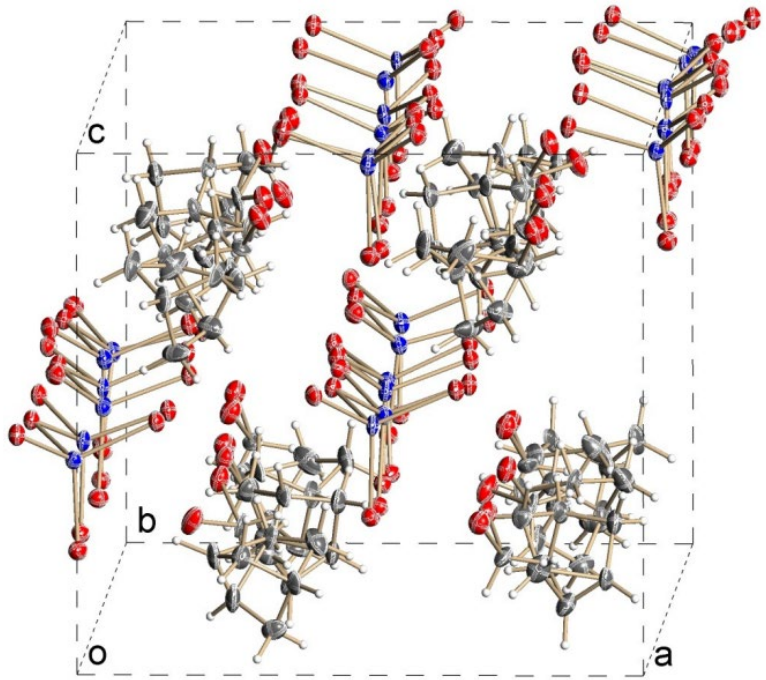


Fig. S17. Packing diagram of crystalline **1** (crystal #1) at 40K along the crystallographic b axis (thermal ellipsoids at 50 % probability, hydrogen atoms as spheres of arbitrary size; C – grey, H – white, Al – blue, Br – red).

Packing diagrams along the axis a, b, and c

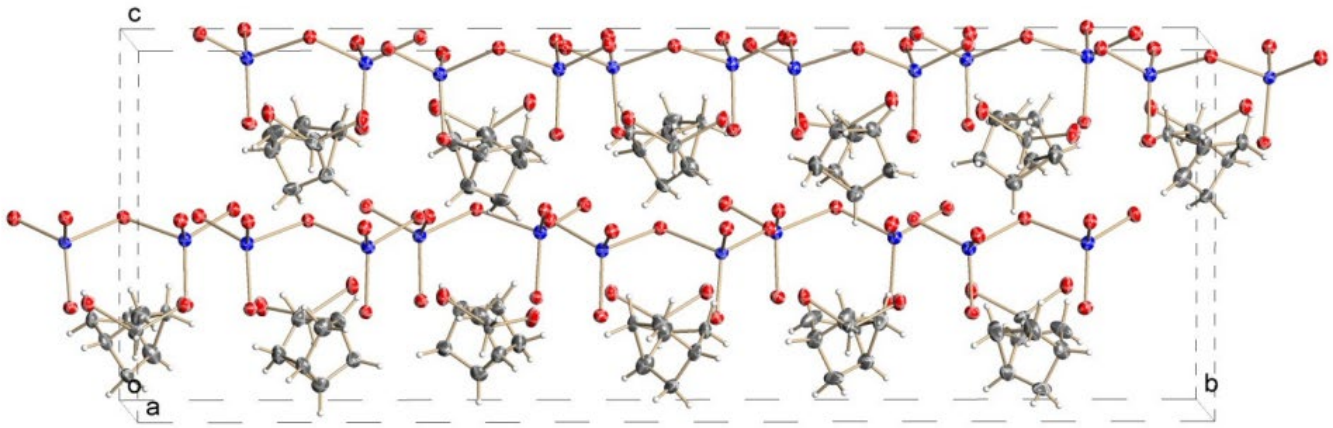
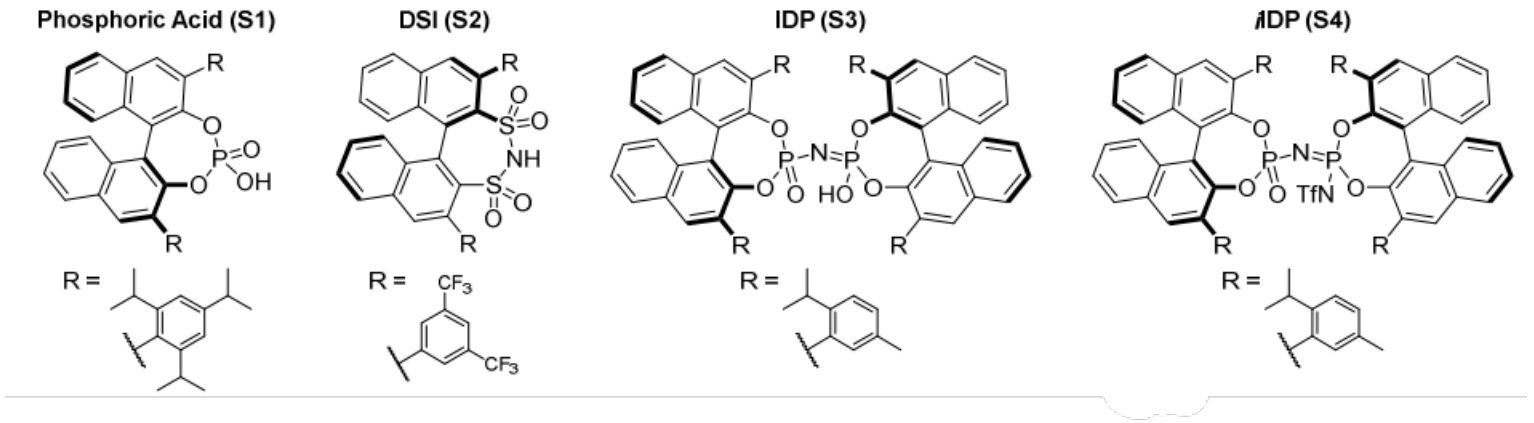


Fig. S16. Packing diagram of crystalline **1** (crystal #1) at 40 K along the crystallographic a axis (thermal ellipsoids at 50 % probability, hydrogen atoms as spheres of arbitrary size; C – grey, H – white, Al – blue, Br – red).

Backup Slide – Failed chiral bronsted acid catalyst, List and co.



Backup Slide

and Kates' original paper.[30] Second, if equilibration is between two strongly bridged ions, as should be the case here, the cation is closer to an sp^3 hybrid and the isotope effect should be reduced. Such cases are known, but they do not approach the small splitting found here. In short I think the situation is much the same as with low-temperature NMR. The data are consistent with a single symmetric structure but do not rule out equilibration between two *very* strongly bridged species separated by a *very* small barrier.