

CHEM 221 section 01

LECTURE #13

Tues., Oct.18, 2005

Midterm exam: Tues.Oct.25 during class
Ch.1, 7.2-7.5, 7.10, 2, 3.1-3.5

ASSIGNED READINGS:

TODAY'S CLASS: Sections 4.1 - 4.6

NEXT CLASS: rest of Ch.4...

<http://artsandscience.concordia.ca/facstaff/P-R/rogers>

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Chapter 4: Reactions of Alkenes

Chapter Goals

To learn the typical reaction of π -systems: electrophilic addition

- Learn how various electrophiles react with alkenes
- Understand the factors that determine product distribution
- Understand the relative stabilities of alkenes
- Begin to think about synthesizing molecules of interest

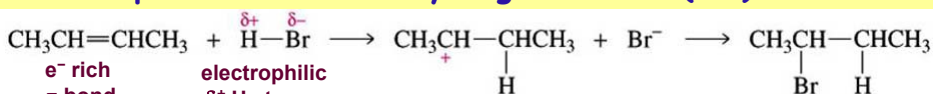
- 4.1 Addition of hydrogen halides
- 4.2 Carbocation stabilities
- 4.3 Structure of the transition state
- 4.4 Regioselectivity of electrophilic addition reactions
- 4.5 Addition of water & alcohols
- 4.6 Carbocation rearrangements
- 4.7 Addition of halogens

(4.8 in Chem222: Oxymercuration-reduction & alkoxymercuration-reduction)

- 4.9 Addition of borane: hydroboration-oxidation
- 4.10 Addition of radicals
- 4.11 Addition of hydrogen: relative stabilities of alkenes
- 4.12 Reactions & synthesis

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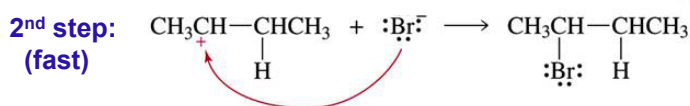
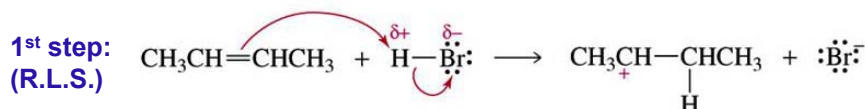
4.1 Hydrohalogenation: a route to alkyl halides electrophilic addition of hydrogen halides (HX) to alkenes



- All hydrogen halides (HF, HCl, HBr, HI) react this way with alkenes
- Rxn faster as acidity increases \Rightarrow because H is more electrophilic...

General mechanism for electrophilic additions:

- π -electrons attack electrophilic atom \rightarrow yields carbocation
- carbocation (after rearranging?) reacts with a nucleophile



- Rxn performed in polar "noncoordinating" solvents (*i.e.*, non-nucleophilic) \Rightarrow so only nucleophile encountered by carbocation is the X^-

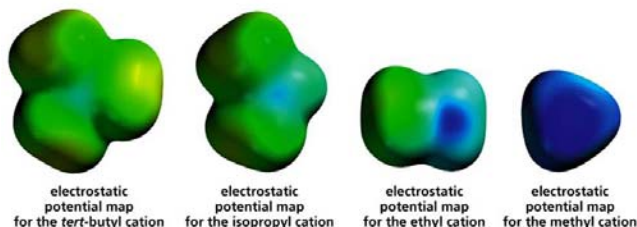
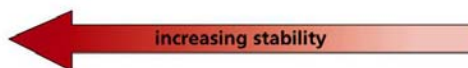
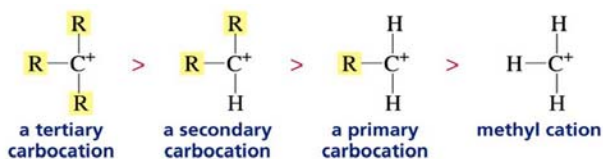
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4.2 Carbocation stabilities: more stable \Rightarrow easier to form

Alkyl groups stabilize carbocations:

- decrease density of + charge at the carbocationic centre
- via inductive electron donation
- alkyl groups are "EDG"s (*not* EWG's...)

How can alkyl groups stabilize a carbocation?



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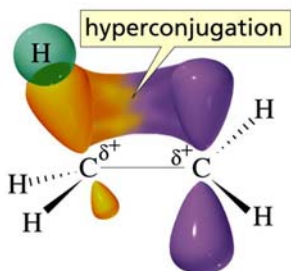
Hyperconjugation: Partial delocalization of electrons

Can rationalize via inductive stabilization by electron-rich R groups, but orbitals give a more concrete explanation (also applies to radicals)

Consider methyl cation CH_3^+ ← planar (sp^2 -hyb. C, empty p-orbital)
C already bonded to all available e⁻s

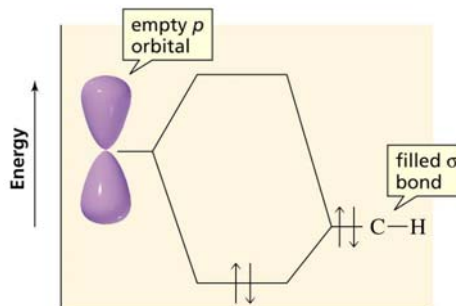
vs. ethyl cation CH_3CH_2^+

Can adopt conformation where adjacent σ -bonds line up with empty p-orbital:

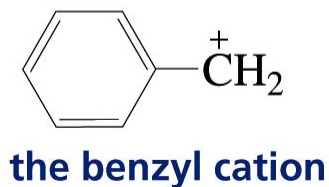
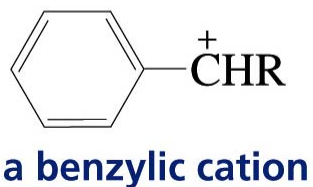
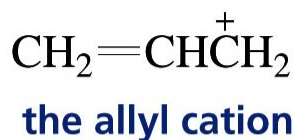
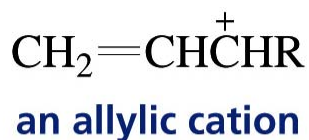


(5) Bruice Fig.4.1

Fig. 4.2 M.O. diagram showing orbitals on neighbouring C's in an alkyl-substituted carbocation

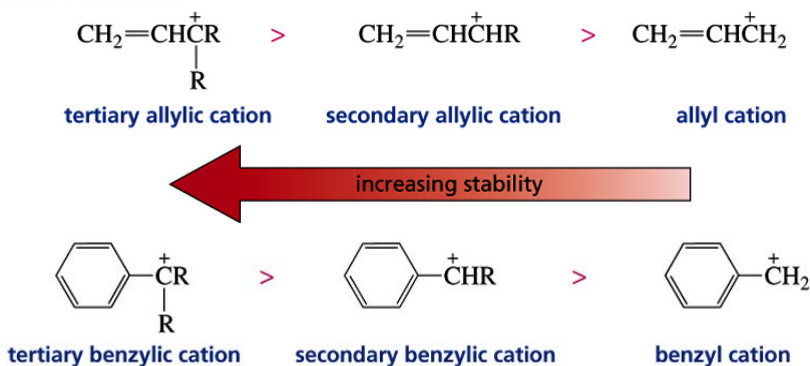


Even better stabilization: via full delocalization
Resonance-Stabilized Cations (see Ch.7.7)



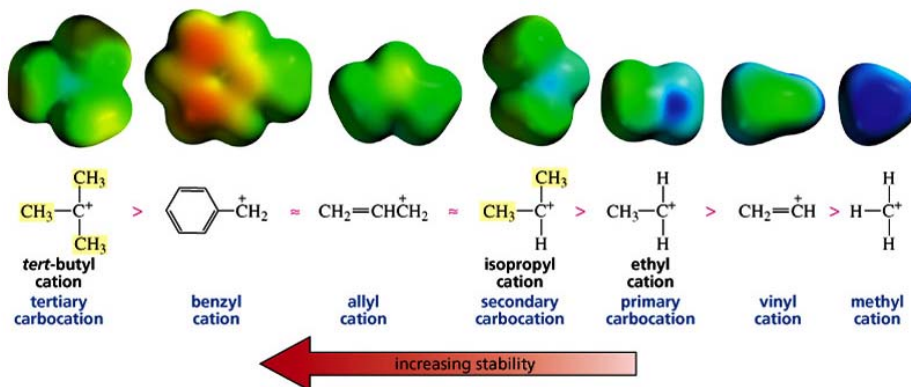
**With these, see combinations of both effects:
Electron-donation from R groups + resonance**

Relative stabilities of allylic and benzylic cations:
more R groups on cationic C \Rightarrow more stable



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Summary: Relative Stabilities of Carbocations



WHY IS THIS IMPORTANT?

The more stable the carbocationic intermediate, the easier it is to form.
i.e., the lower the ΔG^\ddagger required to reach \ddagger leading to that carbocation...
& therefore, the faster it will form

\Rightarrow we can start to predict which product we will get when ≥ 2 are possible

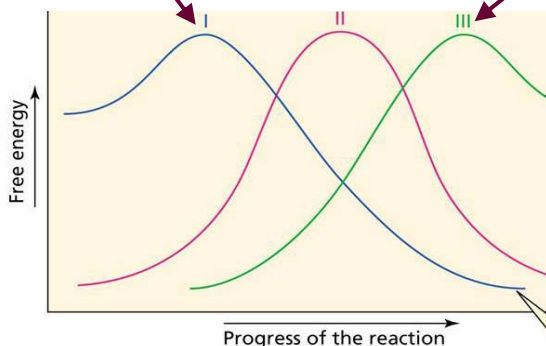
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4.3 The structure of the electrophilic addition ‡ : RLS's ‡ resembles the carbocation intermediate

The Hammond postulate: *think about what needs to happen to form the ‡*
A rxn's transition state will resemble the species (reactant or product) to which it is energetically closer (*i.e.*, structurally similar)

An exergonic rxn:
‡ resembles reactant
"early transition state"

An endergonic rxn:
‡ resembles product
"late transition state"

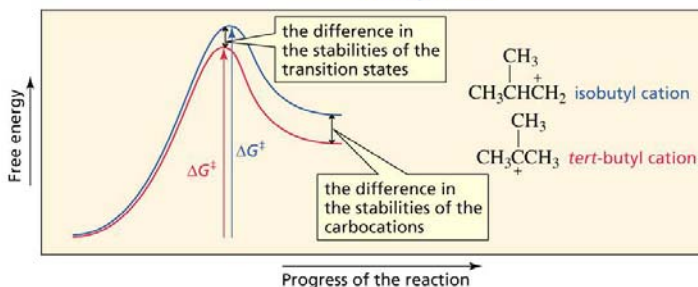
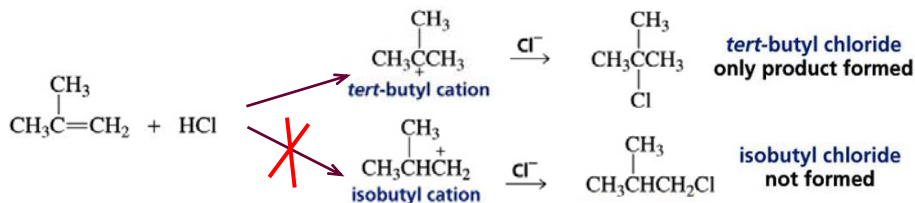


If reaction could lead to 2 different carbocations, the ‡ leading to the more stable carbocation will be easier to form...
→ faster rxn via that route
→ major product...

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THUS: Regiochemistry of electrophilic addition (4.4) is determined by carbocation stability

"Regio" refers to the site in the molecule where the rxn takes place
e.g., if more than C could end up bonded to the electrophile,
then you must worry about which "regiochemistry" is preferred



2 constitutional isomers possible as products...
but only 1 forms
⇒ rxn is "regioselective"

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Predicting regiochemistry: Markovnikov's rule

The H bonds to the sp^2 C that is bonded to a larger # of Hs.

This "rule" is based on: observations of product distributions made long before carbocations were understood!

Markovnikov's rule for predicting the major product works when:

- the electrophile is a δ^+ H atom
- THUS: 1st step = H forming bond to the less highly substituted sp^2 C
- leaves the carbocationic centre on the more highly substituted sp^2 C

"MARKOVNIKOV ADDITIONS": H adds where more H's were...

- any electrophilic additions where the electrophile is an H atom
e.g., addition of HX, water, alcohols... (see 4.5)

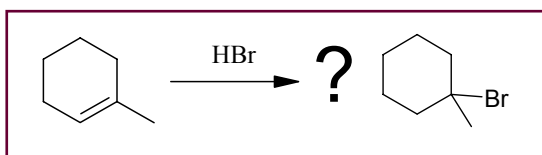
"ANTI-MARKOVNIKOV ADDITIONS": H adds where fewer H's were

- any electrophilic addition where H ends up bonded to the MORE highly substituted sp^2 C
- occurs when H does not act as the electrophile in the 1st step!
*e.g., hydroboration (4.9): involves "B-H" bond adding across the C=C
B is open-shell, more electrophilic than H...*

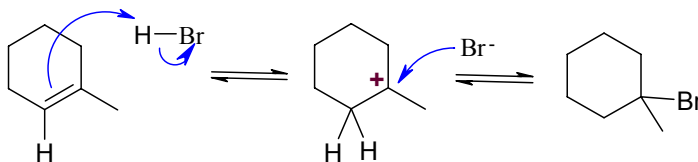
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Predicting regiochemistry: Markovnikov's rule

The H bonds to the sp^2 C that is bonded to a larger # of Hs.



Formed by attack of Nu on carbocation



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4.5 Addition of water (acid-catalyzed hydration) & addition of alcohols

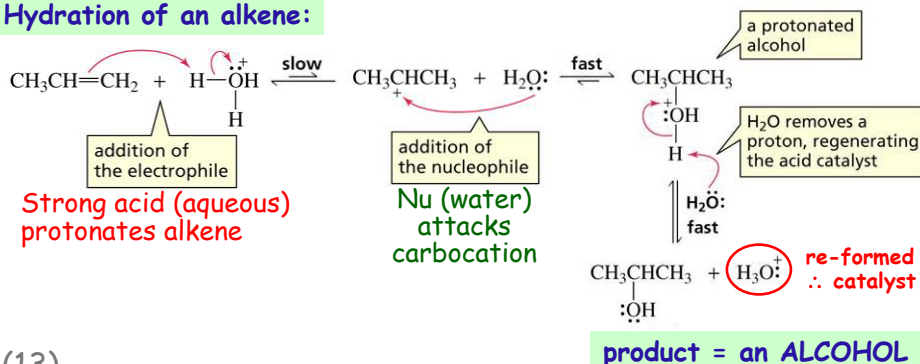
Markovnikov addition: occurs in acid; electrophile = H⁺

NET RESULT: Add H-OH or H-OR across the C=C bond

MECHANISM: *acid-catalyzed... (& won't happen without it!)*

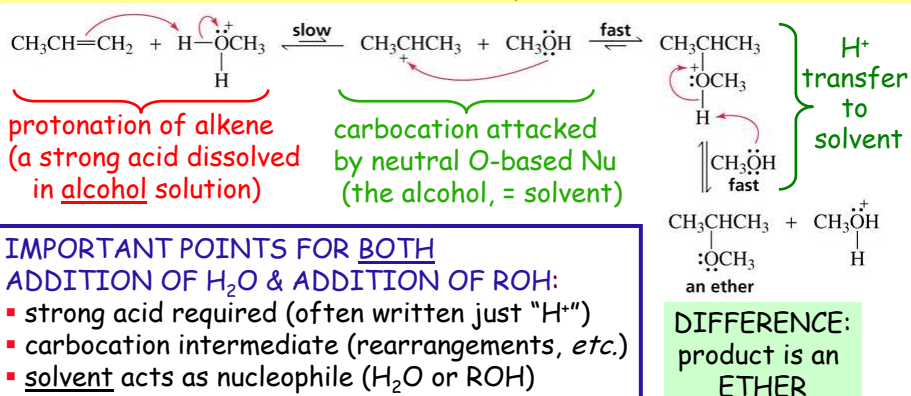
- 1.) strong acid protonates C=C bond ⇒ carbocation intermediate
- 2.) nucleophile (water or alcohol) attacks carbocationic centre
- 3.) H⁺ transfer to solvent ⇒ neutral alcohol or ether product

Hydration of an alkene:



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Same mechanism for acid-catalyzed addition of alcohols



IMPORTANT POINTS FOR BOTH ADDITION OF H₂O & ADDITION OF ROH:

- strong acid required (often written just "H⁺")
- carbocation intermediate (rearrangements, etc.)
- solvent acts as nucleophile (H₂O or ROH)

WHICH ACID? ⇒ NOT HYDROHALIC ACIDS (lead to hydrohalogenation)

- want acid's conjugate base to be less nucleophilic than water or ROH
 - ⇒ so solvent acts as nucleophile! (solvent = H₂O or ROH)
 - ⇒ for now: the less basic a species is, the less nucleophilic it is too
- common choices: H₂SO₄ / H₂O, H₃PO₄ / H₂O, H₂SO₄ / MeOH, etc.
 Not HX because Cl⁻, Br⁻ etc are good Nu's!

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4.6 Carbocations rearrange: to form most stable C+ possible

Carbocations are HIGHLY REACTIVE open-shell species

They do whatever they can to "solve their problem"

2 options: 1.) "search within themselves" \Rightarrow REARRANGE
(always happens first)

2.) "find solace in others" \Rightarrow REACT WITH A Nu
(slower - requires collision with something else)

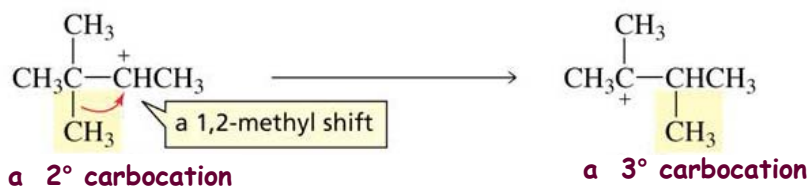
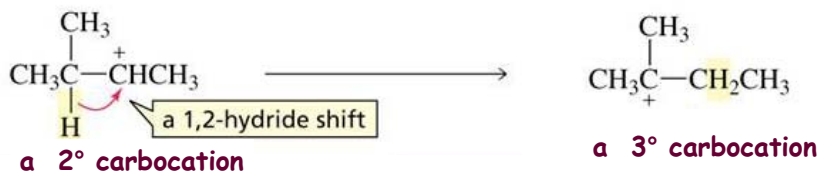
NOTE: rearrangement only occurs if more stable C+ results

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TWO kinds of rearrangements: (same mechanism) hydride shifts & alkyl shifts from adjacent C

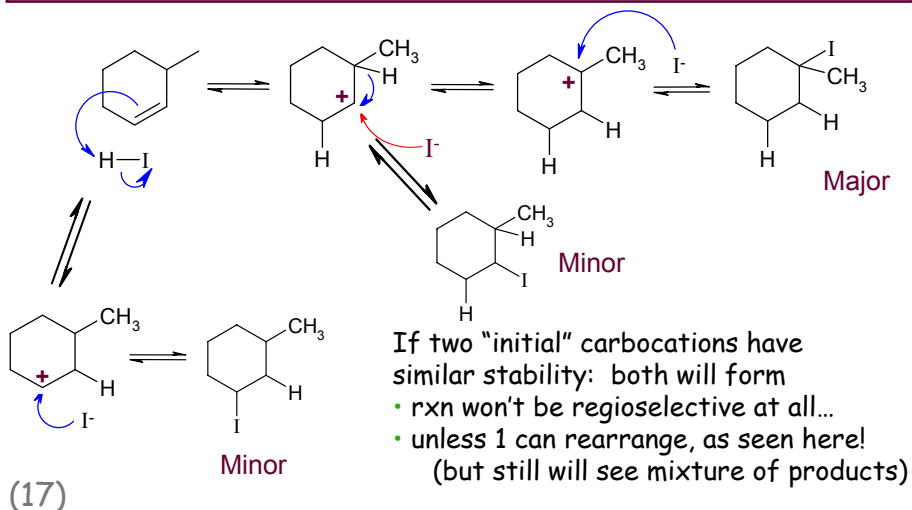
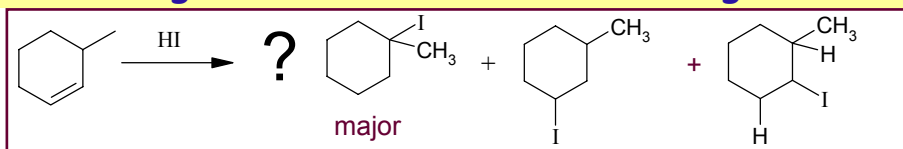
Mechanism: sort of like "extreme hyperconjugation"

- a bonding pair from the adjacent C is "stolen" by the C+ centre
 \Rightarrow a substituent shifts over onto C+ centre, creating a new C+ centre

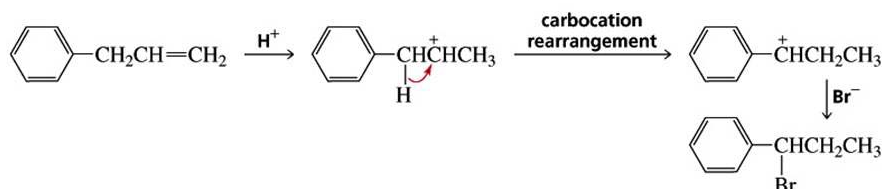


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Don't forget to consider cation rearrangements

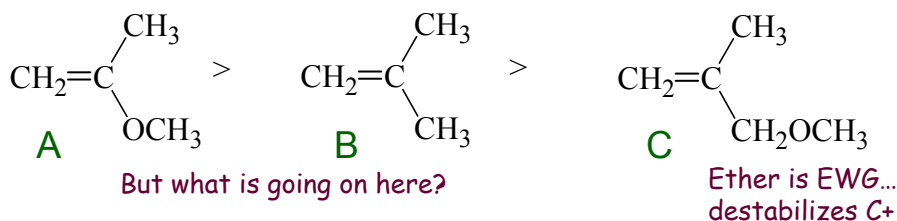


Rearrangements will definitely occur if they lead to a resonance-stabilized carbocation



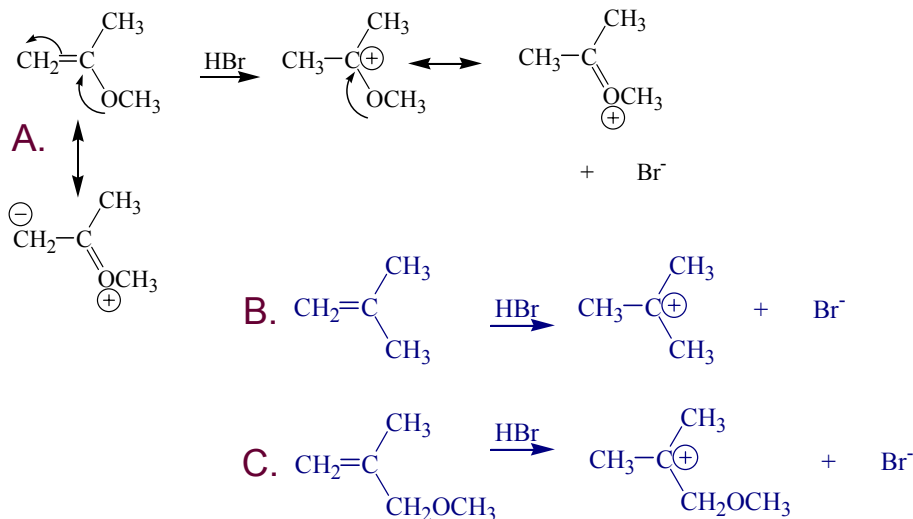
Delocalized electrons can affect the reactivity of a compound

Justify this relative reactivity toward HBr:



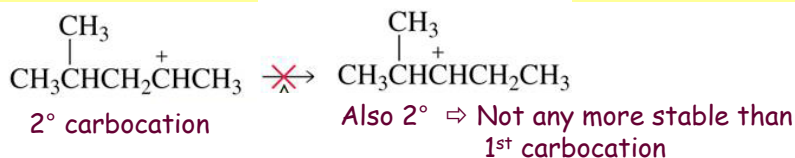
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Compound A is the most reactive because:
 it has a resonance form with enhanced reactivity
AND the resulting carbocation is resonance stabilized



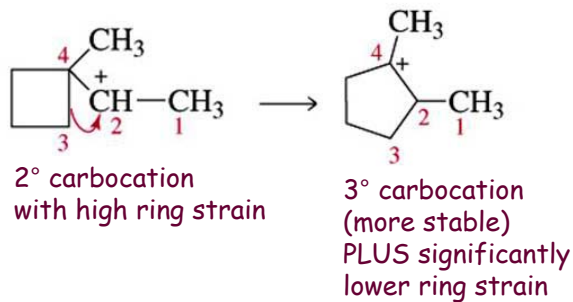
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Carbocations do not always rearrange ...



Carbocation rearrangement can lead to "Ring Expansion" (driven by relief of ring strain)

Keep on the watch for:
 carbocationic centres
 1 bond away from a ring
 & then see if the
 ring-expanded product
 has significantly lower
 ring strain or not



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ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: Ch.4 up to 4.6

Practice: writing mechanisms & predicting products