

## Bonding and Structure of Reactive Intermediates

A major goal of physical organic chemistry is to explain reactivity, i.e. the role of REACTIVE INTERMEDIATES (RI)

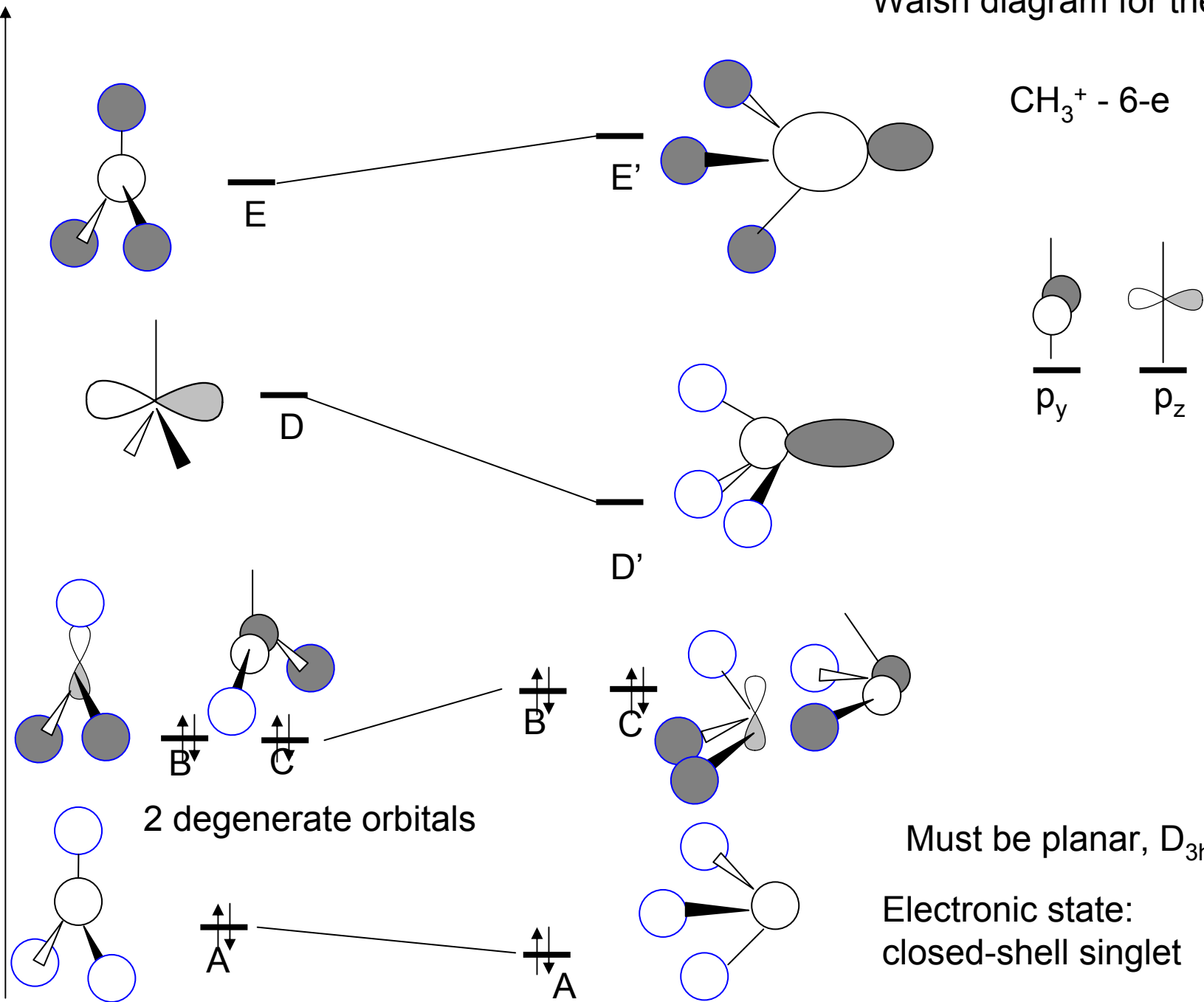
RI- some form of carbon, which does not have 4 bonds around, or has less than octet, or is highly strained (say, planar tetracoordinated)

Most common types of RI:

1. Carbocations
  - a) Carbenium ions ( $\text{CH}_3^+$ ), typical of condensed phases
  - b) Carbonium ions ( $\text{CH}_5^+$ ), typical of the gas phase
2. Carboanions,  $\text{CH}_3^-$
3. Radicals,  $\text{CH}_3^\bullet$ , with odd number of electrons
4. Carbenes ( $\text{CH}_2$ - even number of electrons, could be closed shell singlet or triplet)

# Walsh diagram for the $AH_3$

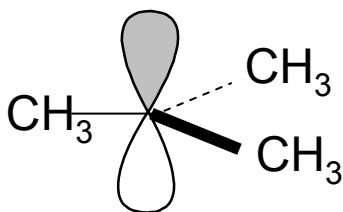
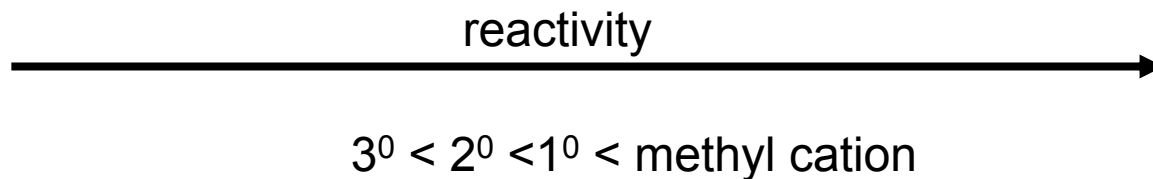
$CH_3^+ - 6-e$



$D_{3h}$   $\text{CH}_3^+$  is about 30 kcal/mol lower in energy than the  $C_{3v}$  form

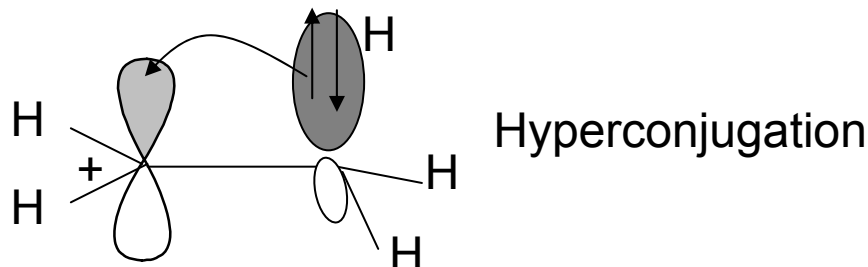
Carbocations are highly reactive.

Alkyl substituents stabilize carbocations and make them less reactive

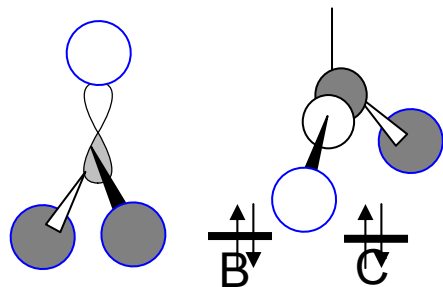


$\text{CH}_3$  is a  $\sigma$ - and  $\pi$ -donor. Donating of electron density to vacant orbital is favorable

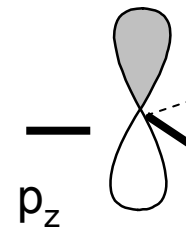
Valence bond theory:



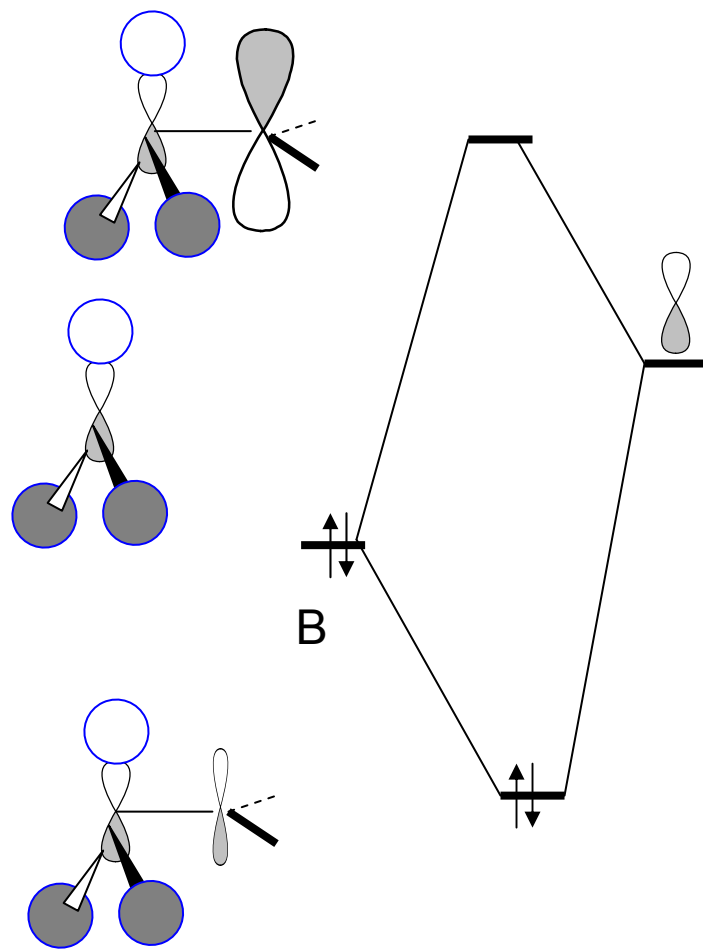
# Explain the trend in reactivity in terms of QMOT: ethyl carbenium cation



CH<sub>3</sub> fragment



LUMO of the CH<sub>2</sub> fragment



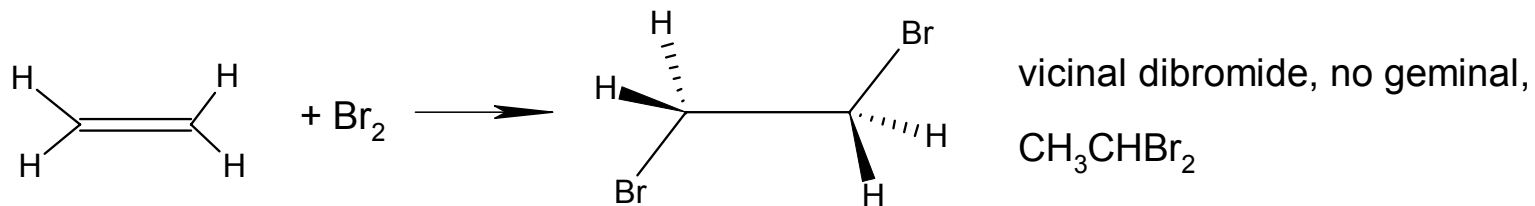
HOMO of CH<sub>3</sub> is mixing well with LUMO of CH<sub>2</sub>

It is always favorable to mix empty and filled orbitals

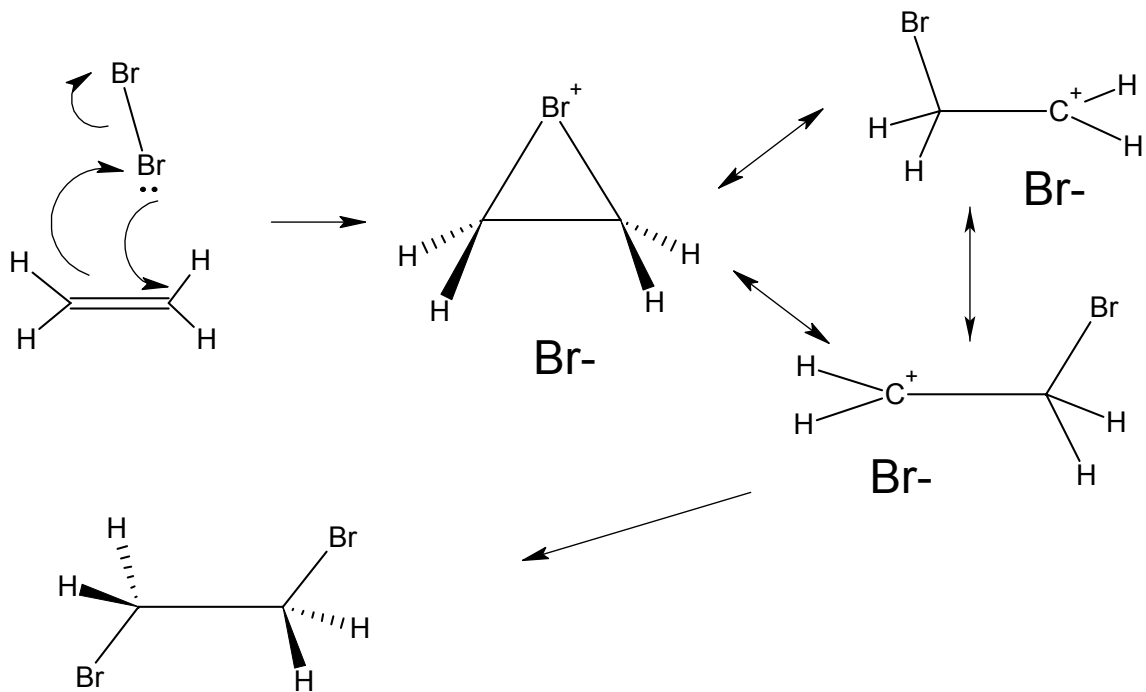
Remember: interaction of two filled orbitals is repulsive

# Examples of the reactions involving carbenium cations as RI

## 1. Bromination of ethylene:



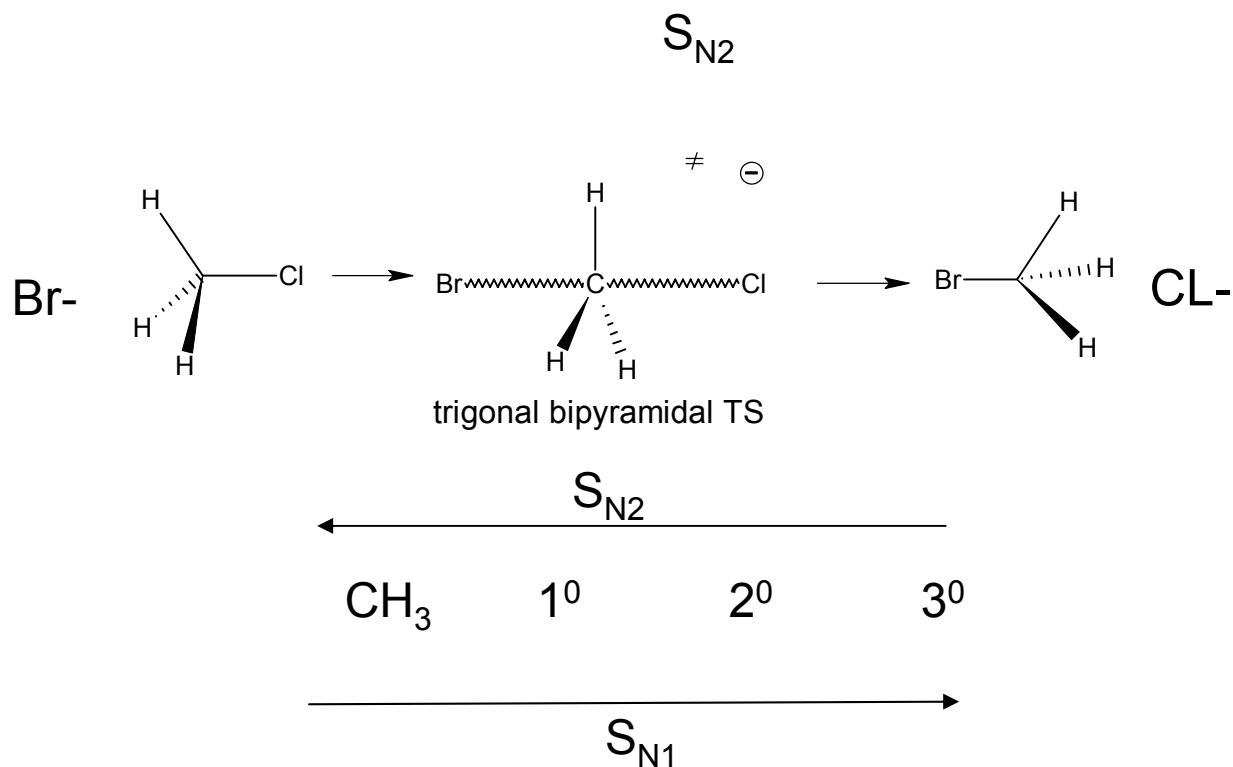
### Proposed mechanism:



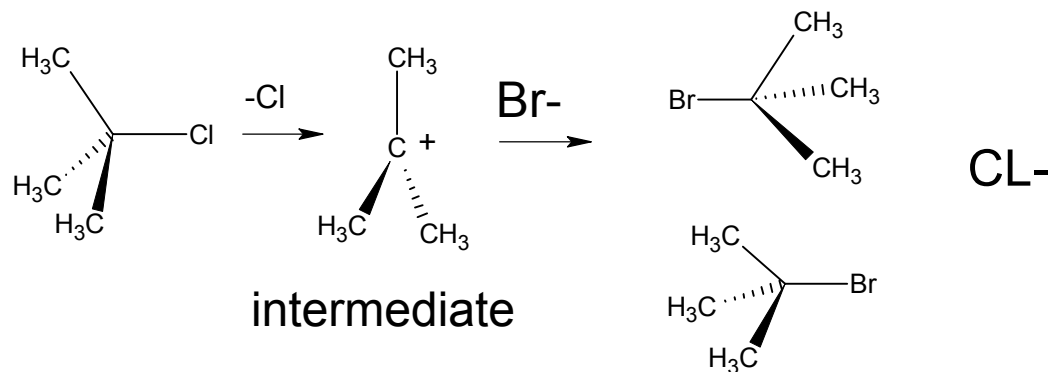
## $S_{N1}$ mechanism

For nucleophilic substitutions there are two mechanisms: (1) concerted (one step) via 5-coordinated carbon, with inversion of configuration and kinetics of 2<sup>nd</sup> order,  $S_{N2}$  mechanism

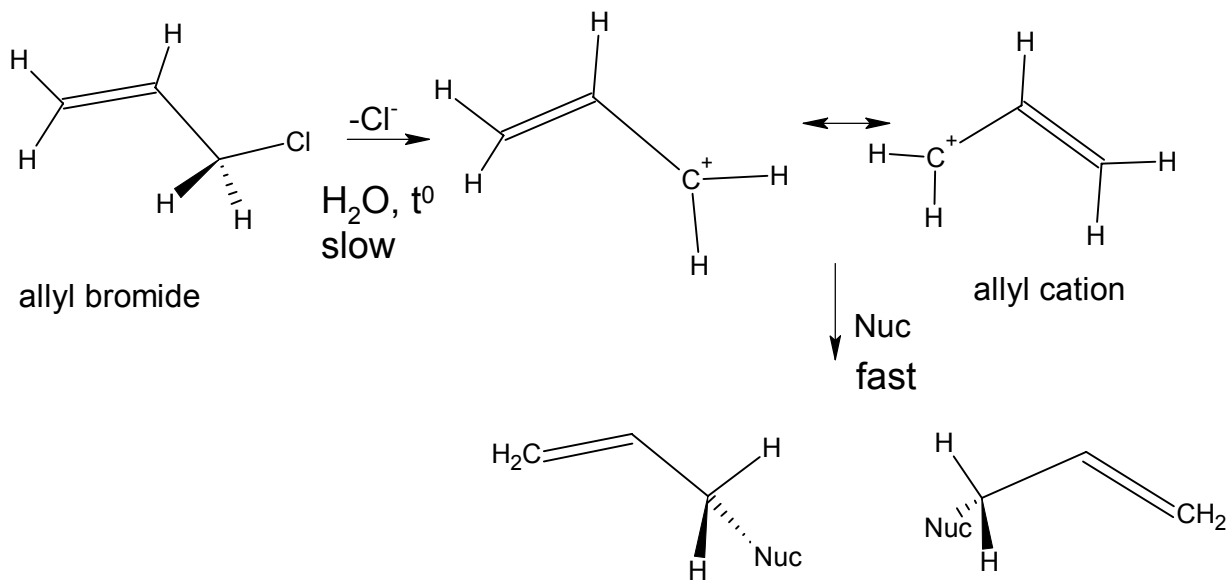
(2) Stepwise via carbenium cation, with 50:50 mixture of enantiomers and kinetics of the 1<sup>st</sup> order,  $S_{N1}$

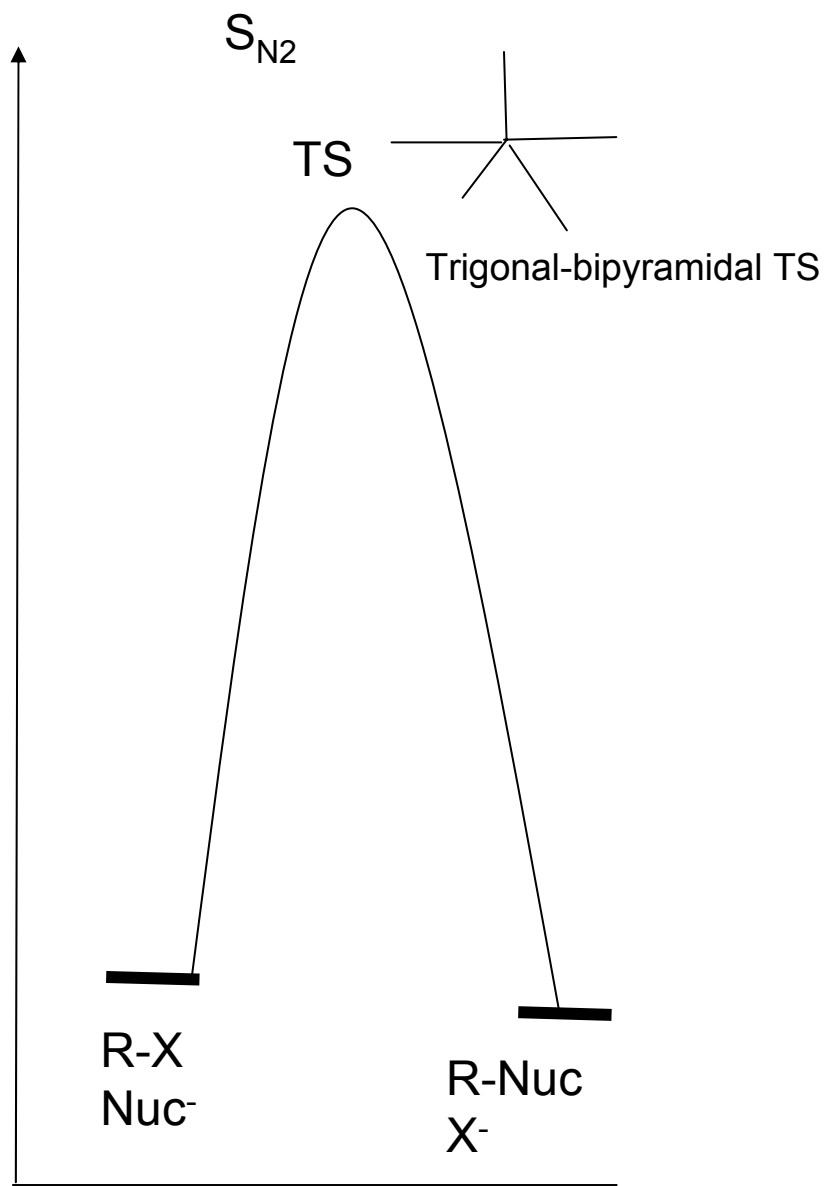
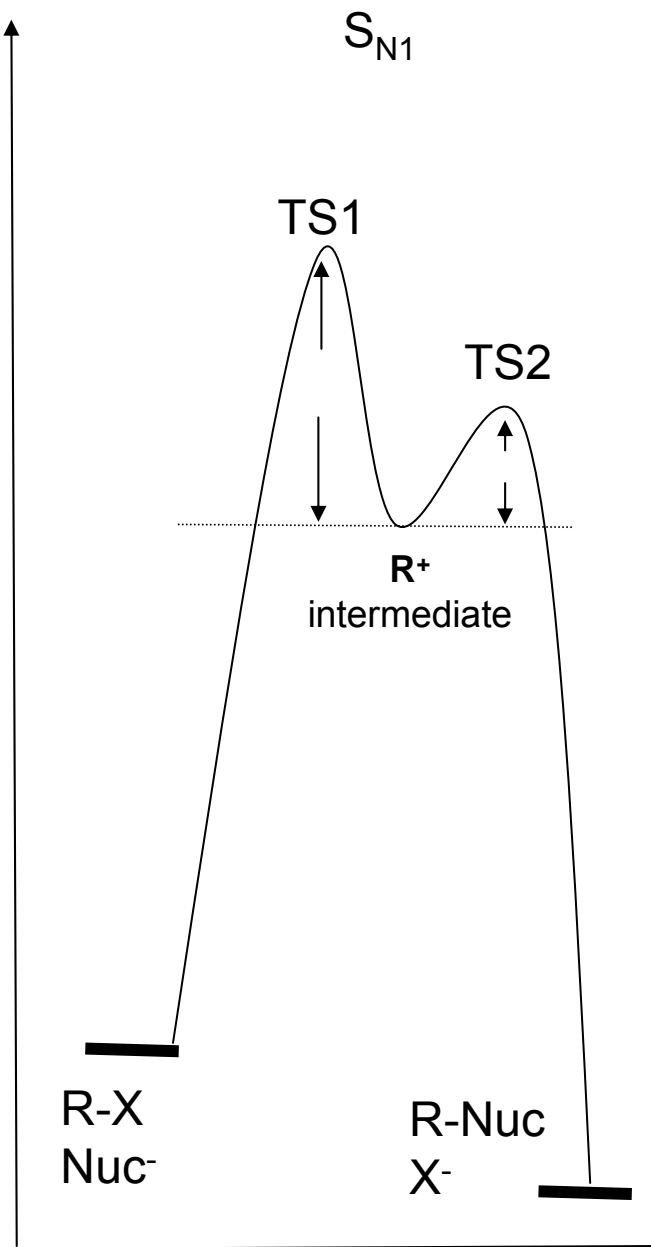


$S_{N1}$



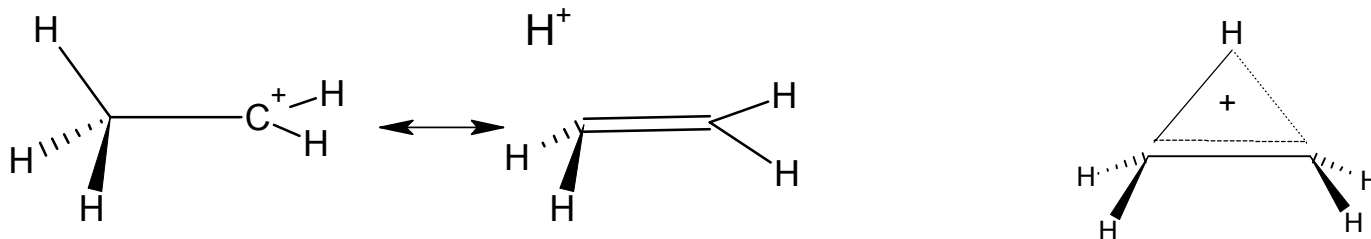
Steric effect? Perhaps. Lets eliminate the steric effect







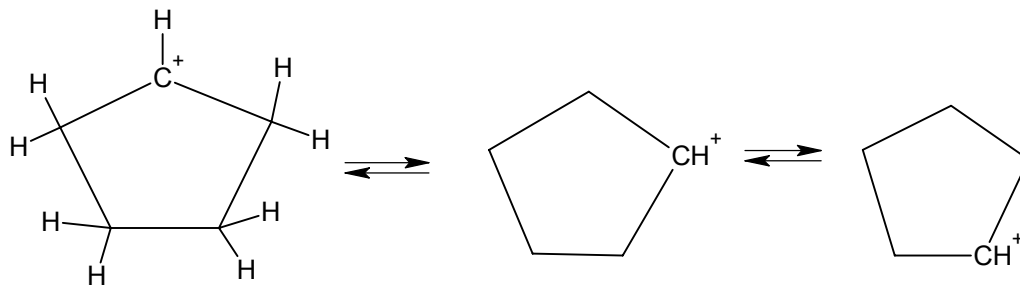
Resonance structures:



no-bond resonance

It is typical of a carbenium ion to have many isomers, which are close in energy, with very small interconversion barriers.

$\text{H}^+$  migrates very fast in carbenium ions



Could we see these isomers ?

-70<sup>0</sup>, HNMR- one signal for H

C<sup>13</sup> NMR- 1 signal for C<sup>13</sup> coupled with 9 equivalent H

NMR- 10<sup>-7</sup> sec

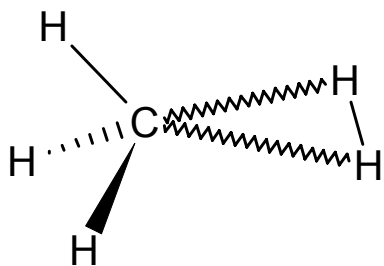
Need faster method

XPS (X-ray photoelectron spectroscopy) Another name-  
ESCA- electron spectroscopy for chemical analysis

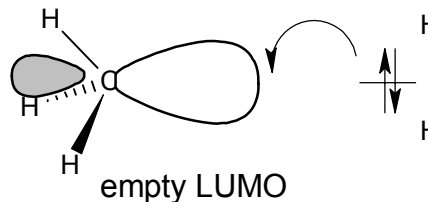
XPS- 10<sup>-16</sup>s

Indicates one C<sup>+</sup> and 4 neutral C.

Carbonium ion,  $\text{CH}_5^+$



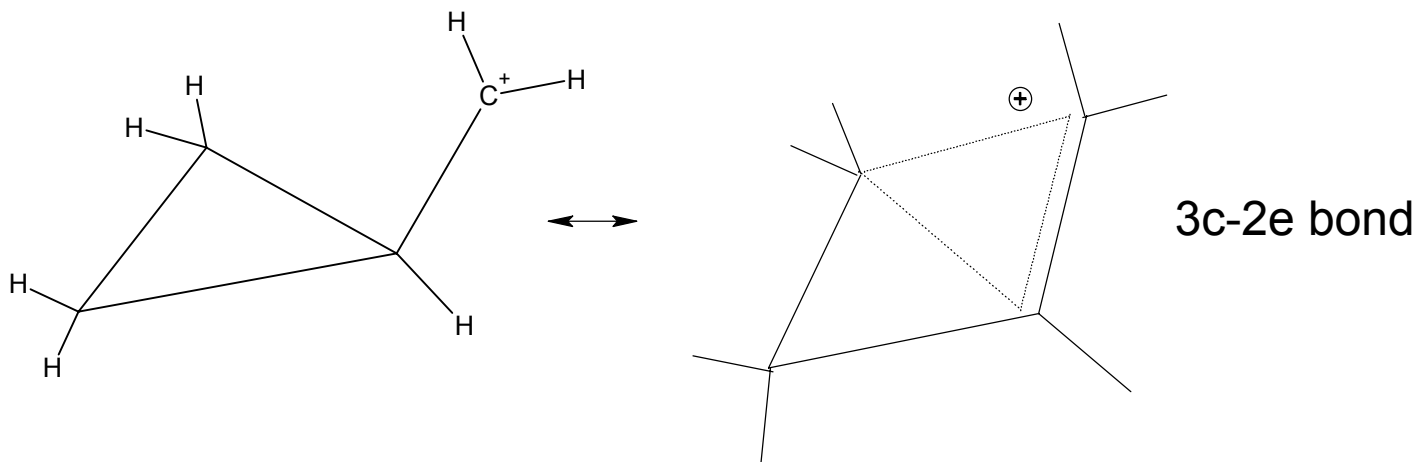
Not a well-defined structure.



3-center-2-electron bond

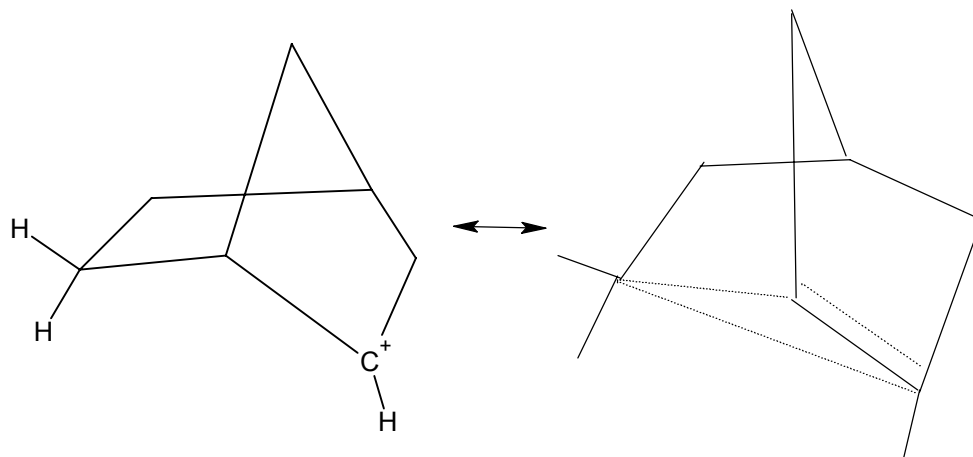
$\text{R}_5\text{C}^+$  - bridging structures with hypervalent carbon

There are many bridging carbocations with hypervalent carbon, which are classified as carbonium ions, or non-classical cations



Cyclopropylcarbonyl cation

# Norbornyl cation



3c-2e bond