

S_N1 Displacement At sp³ Centers

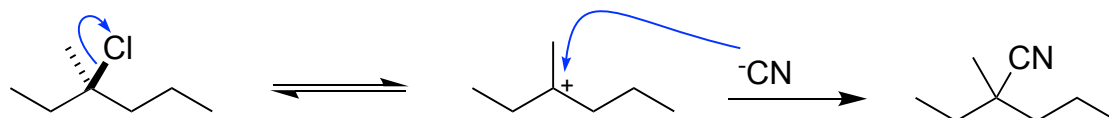
from chapter(s) _____ in the recommended text

A. Introduction

B. Fundamentals

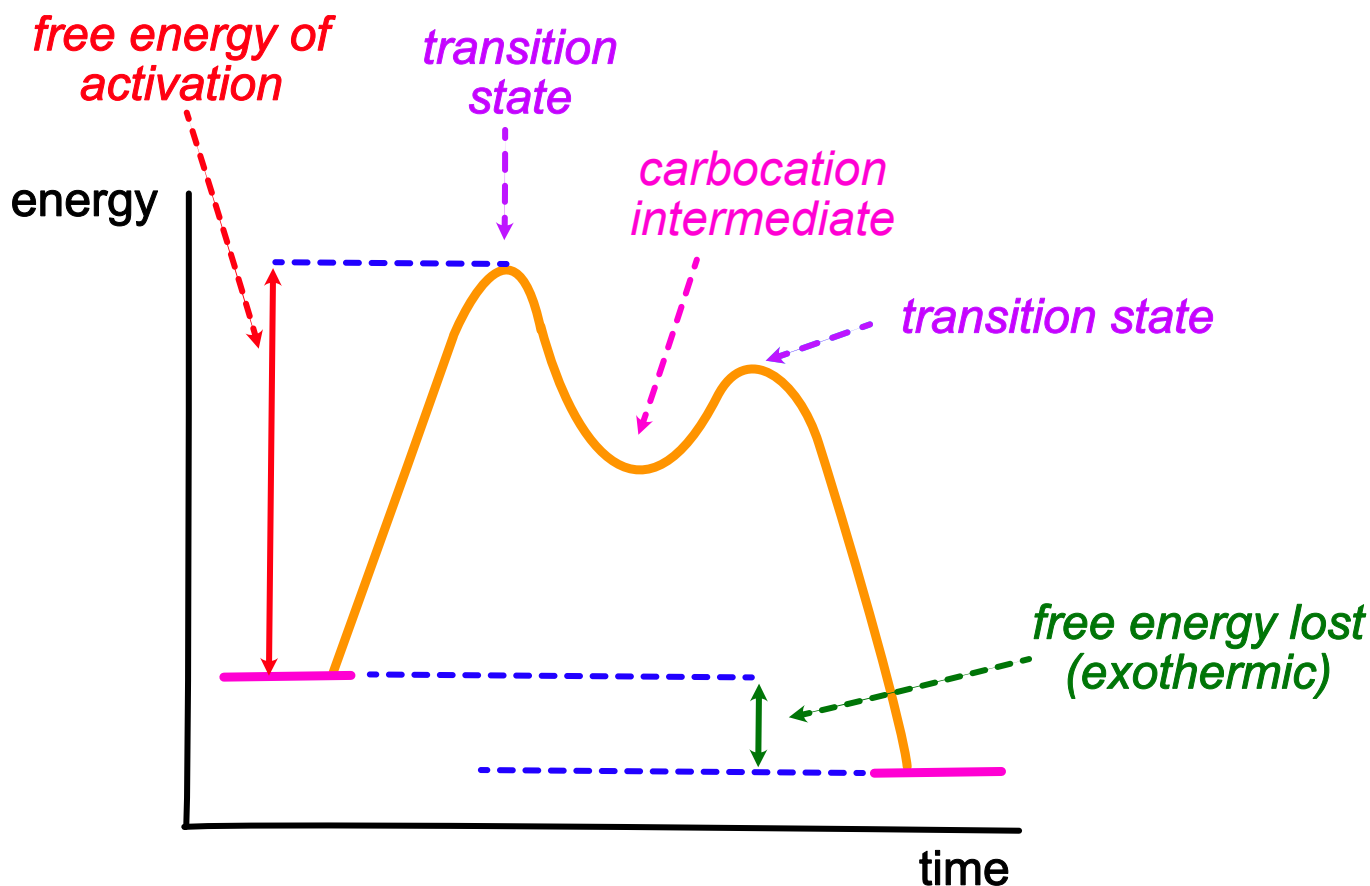
It takes *more / less* energy to separate most neutral molecules into cation-anion pairs than it does to combine cations with anions because of electrostatic forces.

Assuming this is true for the following reaction, formation of the carbocation *requires* energy from the system. Even so, carbocations *can* be isolated so they *are* stable intermediates.



movement of electrons from cyanide to the empty *p*-orbital of the carbocation.

Reactions like this are usually *more* favorable when a tertiary (3°) carbocation is formed since these tend to be *more* stable than secondary (2°) or primary (1°) ones.



Dissociation of chloride in this reaction hence the first transition state is *higher* energy

The carbon of the carbocation intermediate is sp^2 hybridized and groups are arranged around in in a *triangular* shape.

Approach of nucleophiles, like cyanide, on that carbocation will involve *the same* energies for the *pro-R* and *pro-S* faces. Consequently, if the starting material is one pure enantiomer then the product will have *0* % enantiomeric excess

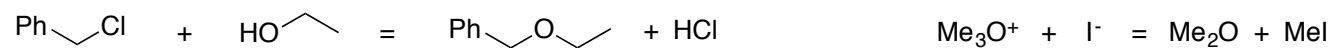
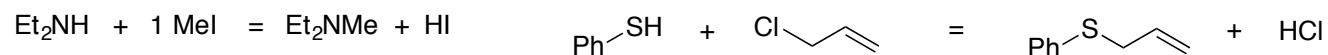
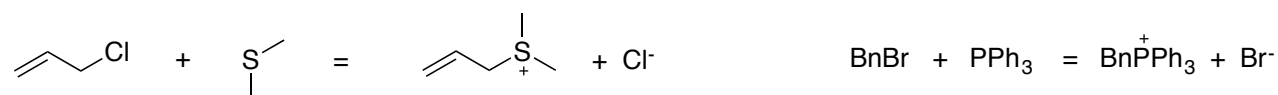
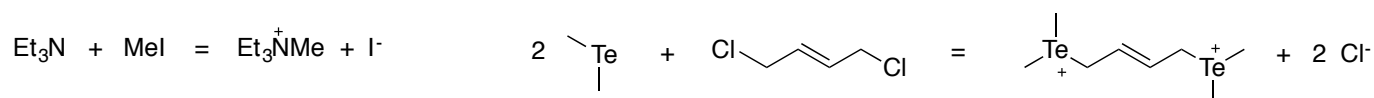
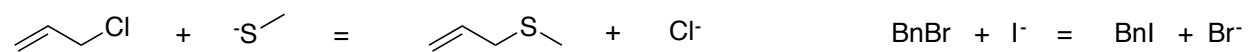
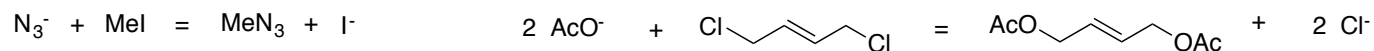
Nucleophiles *are* involved in the dissociative step of S_N1 reactions so their reaction rates are proportional to *only the substrate* concentrations.

Represent the rate of S_N1 reactions using the symbol k to represent the *rate* constant,

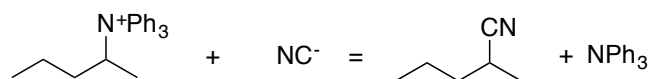
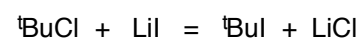
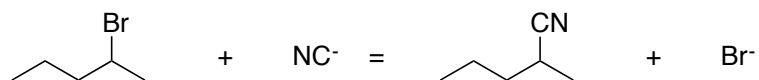
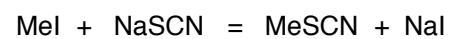
$$\text{rate} = k[\text{substrate}]$$

C. Charges On Nucleophiles And Leaving Groups

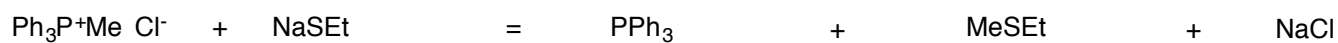
Nucleophiles



Leaving Groups



(intramolecular)



D. S_N1 Slow Formation Of Carbocations

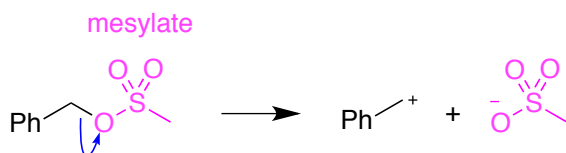
Key Steps

Substitution describes reactions in which one group *replaces another*.

S_N1 stands for substitution by a nucleophile *with first order kinetics*.



carbocation and bromide



*benzyl carbocation
and -OMs*

formation of a carbocation *is* the rate limiting step.





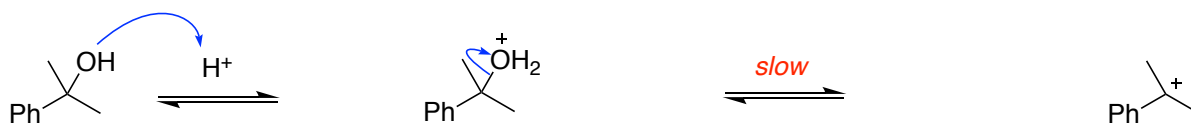
carbocation and hydroxide



carbocation and water

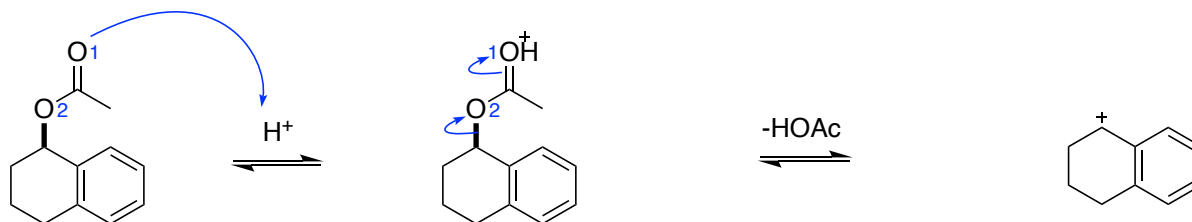
Water is a much *better* leaving group than hydroxide
 pathway on the *right* is more favorable
 the one on the *left* does not proceed at all.

Some poor *leaving groups* can be converted into better ones by protonating them: *true*



protonated intermediate

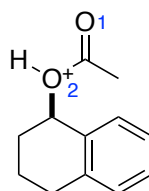
carbocation intermediate



protonated intermediate

carbocation intermediate

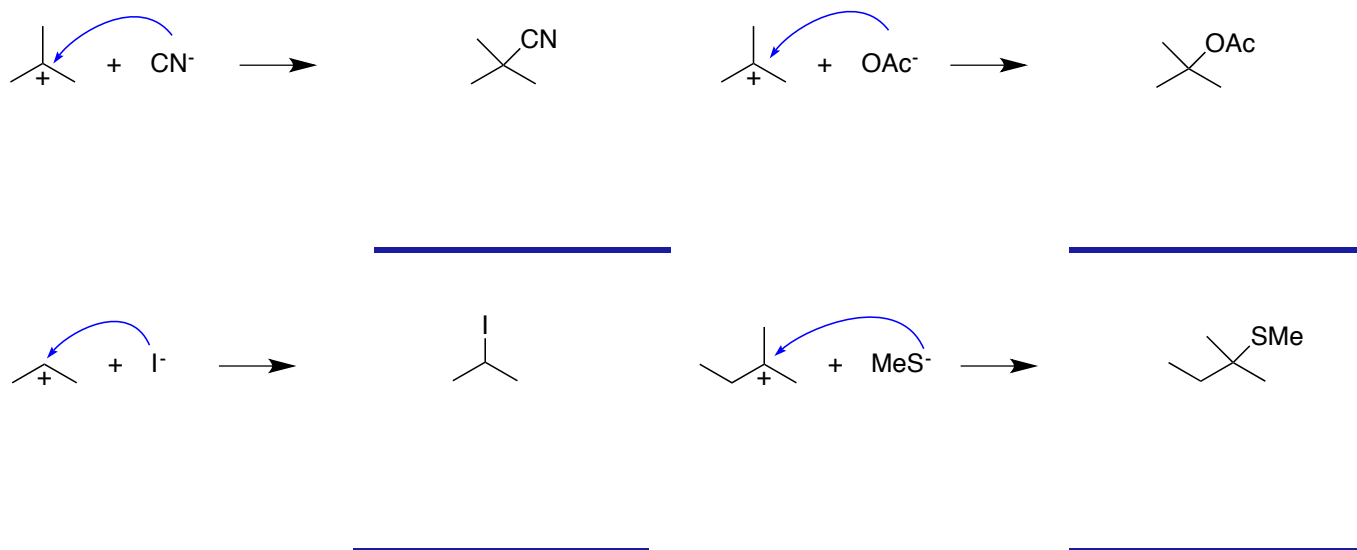
only protonation of O^1 is stabilized by resonance from the other oxygen.



*this cannot be
 stabilized by resonance*

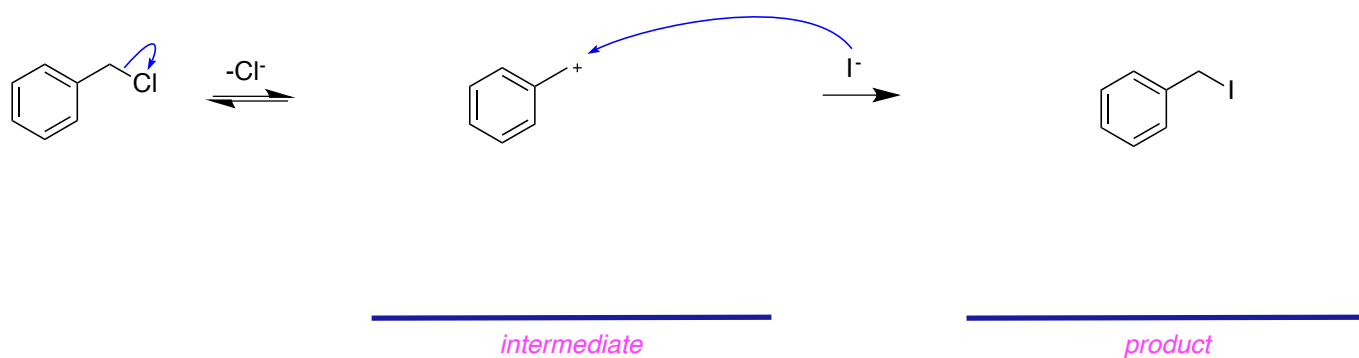
E. S_N1 Fast Combination Of Cations With Nucleophiles

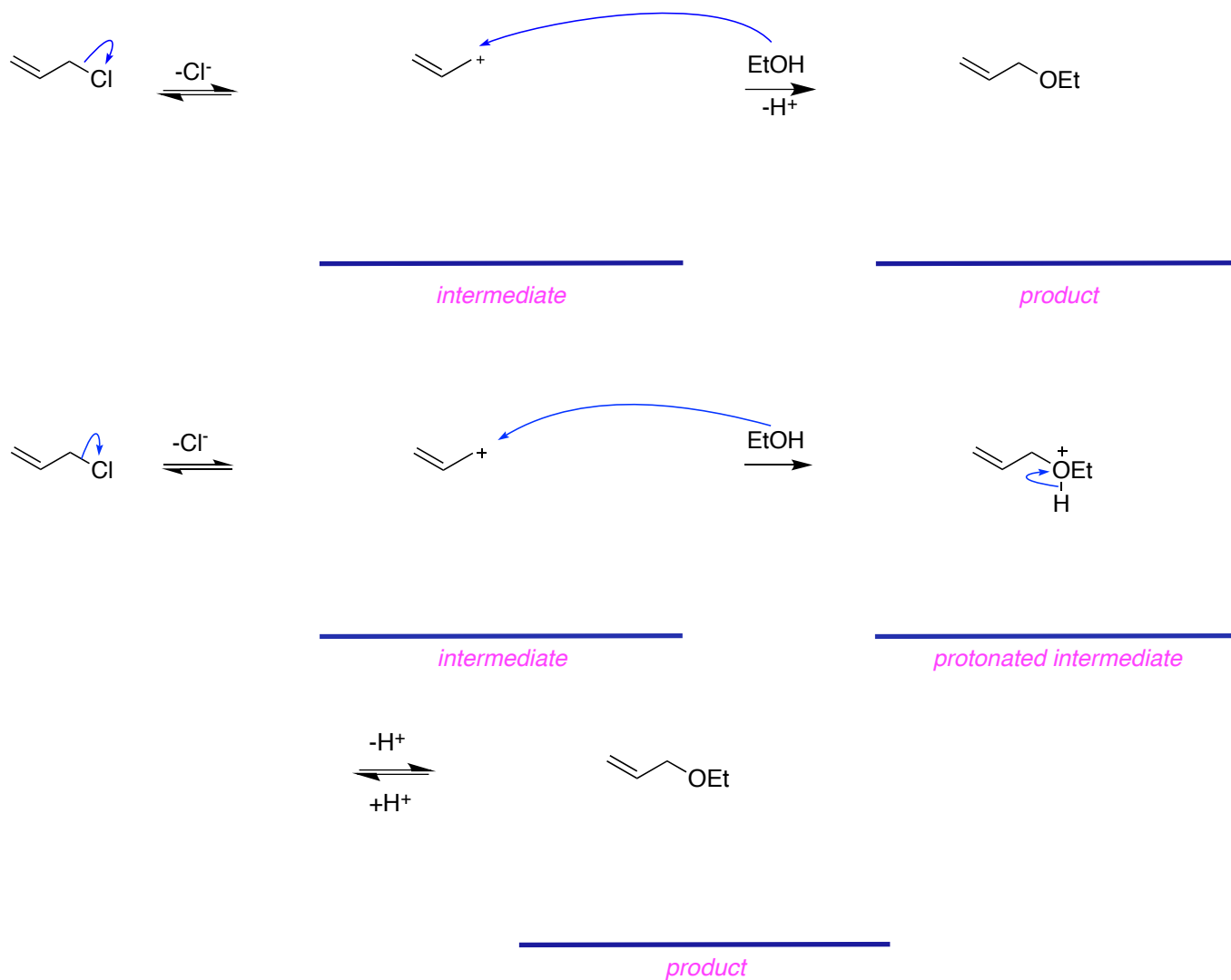
Carbocations *can* combine with negatively charged nucleophiles to produce neutral molecules.



When carbocations combine with *neutral* nucleophiles they form *cations*

the products will be *racemic*, because the intermediate, sp^2 -hybridized carbocations, are *flat*

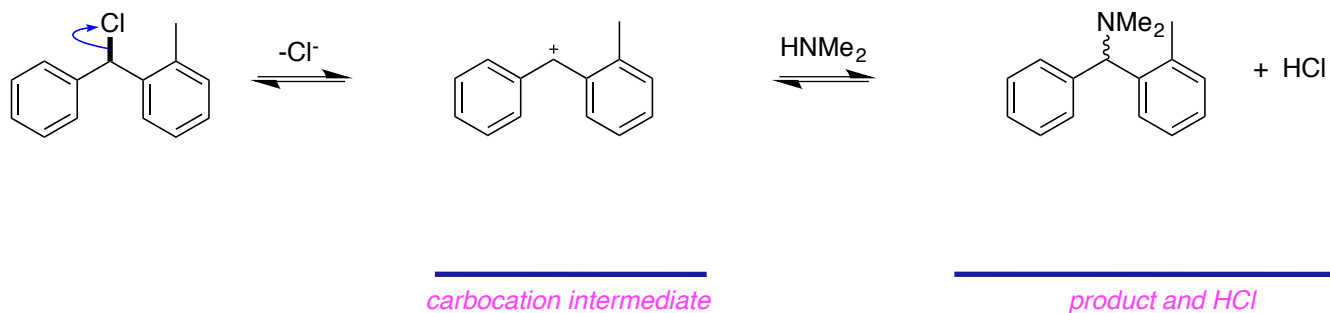
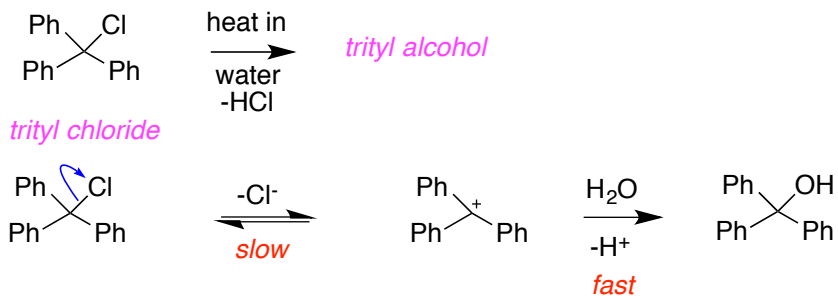
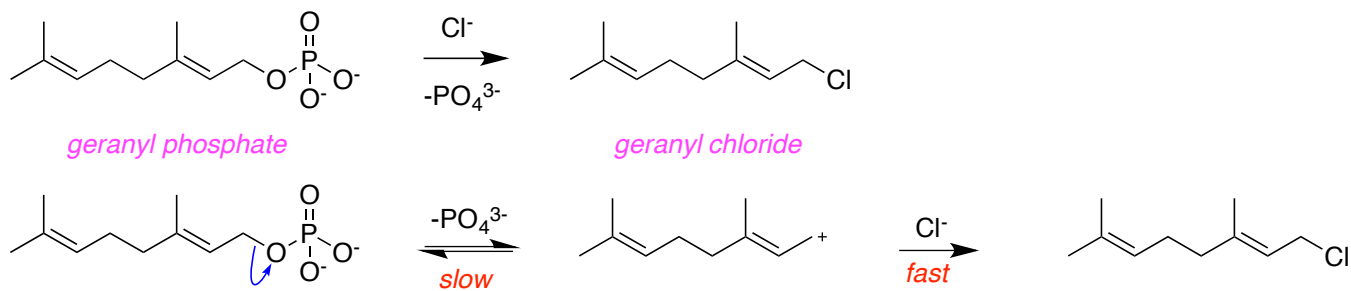


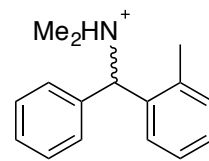
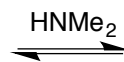
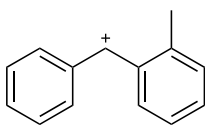
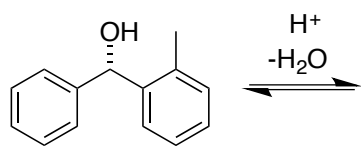


S_N1 reaction of *tert*-butyl chloride with water involves *two* intermediates.

S_N1 reaction of *tert*-butyl bromide with acetate (MeCO_2^-) involves *one* intermediate.

S_N1 reaction of bromide with allyl chloride involves *one* intermediate.

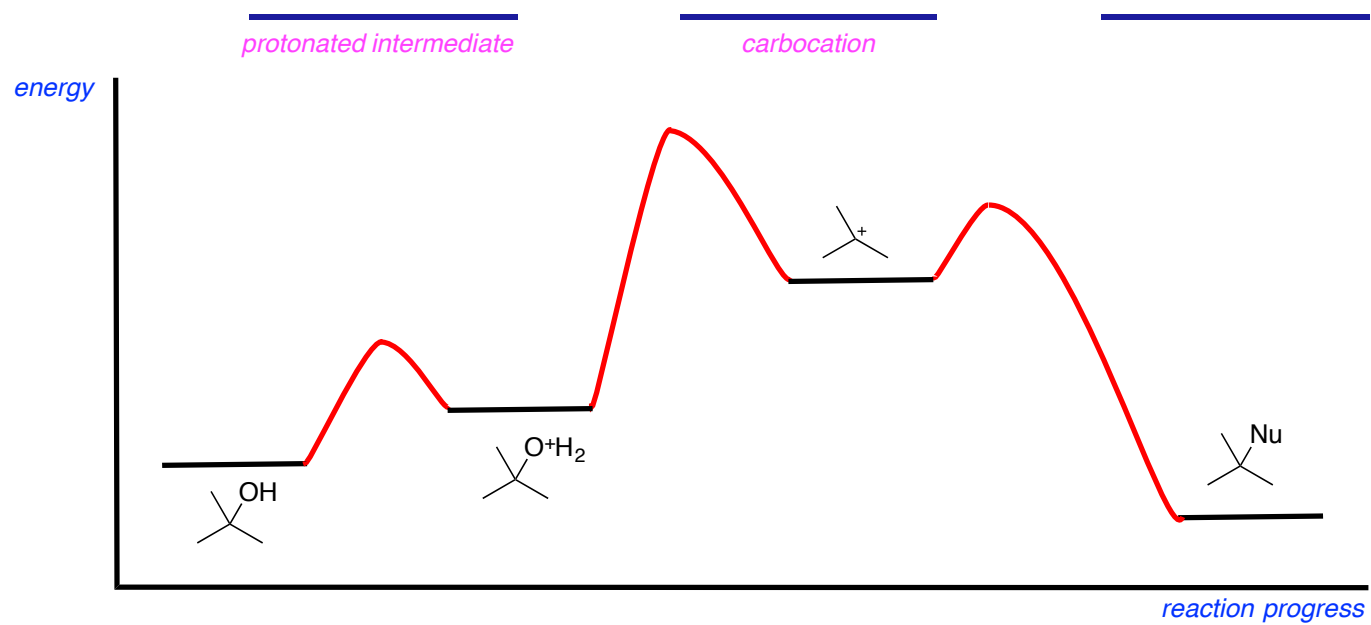
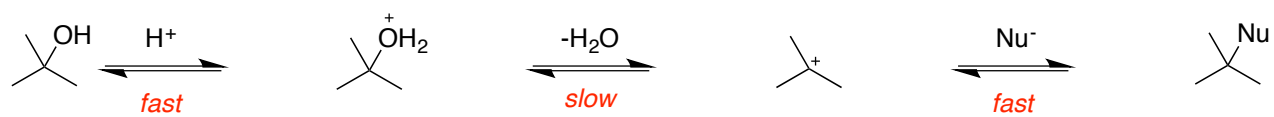
**a****b**



carbocation intermediate

protonated amine

F. S_N1 Kinetics



the rate of the reaction above *is* proportional to the concentration

rate is proportional to

[^tBuOH]

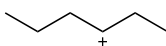
rate =

k [^tBuOH]

triphenylmethyl chloride with sodium cyanide proceeds *at the same rate* if the concentration of the cyanide salt is doubled

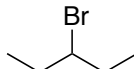
G. Carbocation Stabilities Govern S_N1 Reaction Rates

Rates of S_N1 reactions tend to *increase* with stabilities of carbocation intermediates.



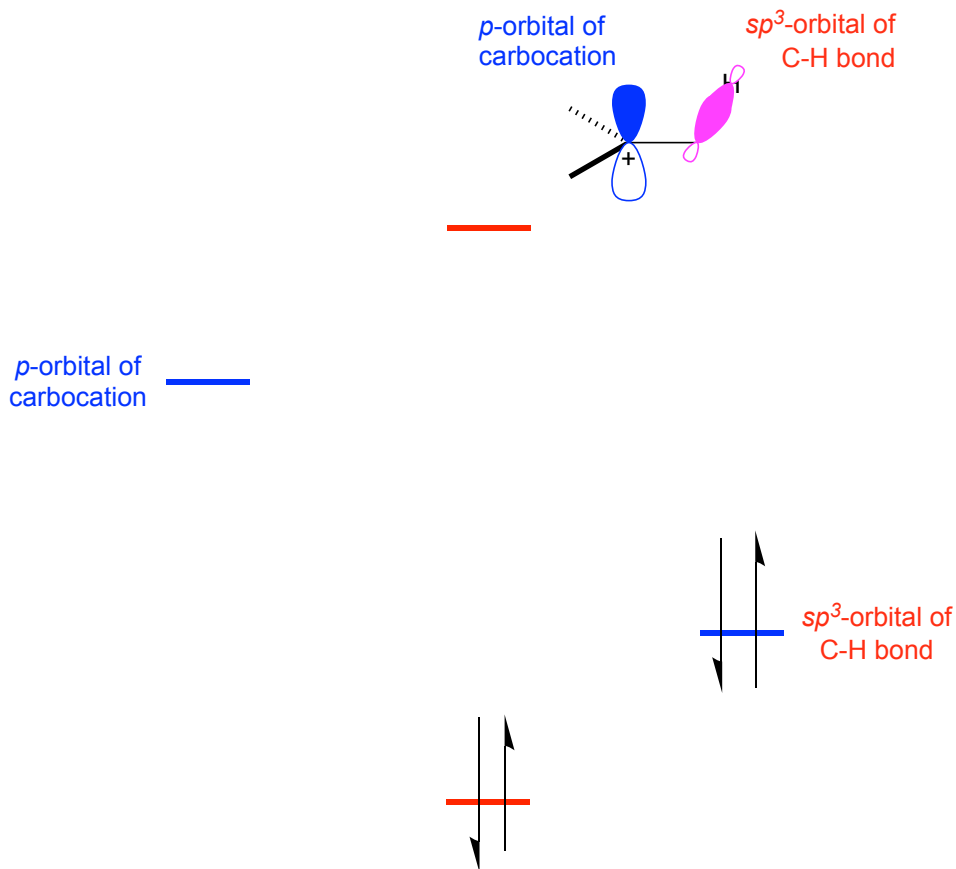
most stable

least stable



fastest

slowest



There are **3** times more of these interactions in the ^tBu cation than in Me⁺.

In Et⁺ the sp³ orbitals of the methyl group are tilted a bit *away from* the empty p-orbital of the cation, thus the overlap, and therefore the stabilization, is *less* than a situation in which the orbitals were completely parallel.

system overall is *greater* than that from hyperconjugation in Et⁺.

Allyl cations are *more* stable than many other primary carbocations.

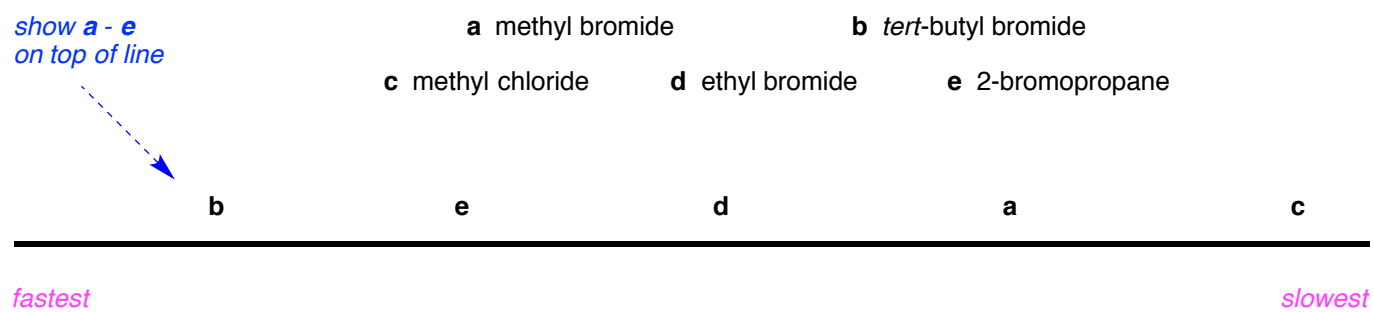
secondary molecular orbital interactions between an *empty* p-orbital and appropriately aligned C-H σ-orbitals

*show 3°, 1°, 2°, Me
on top of line*

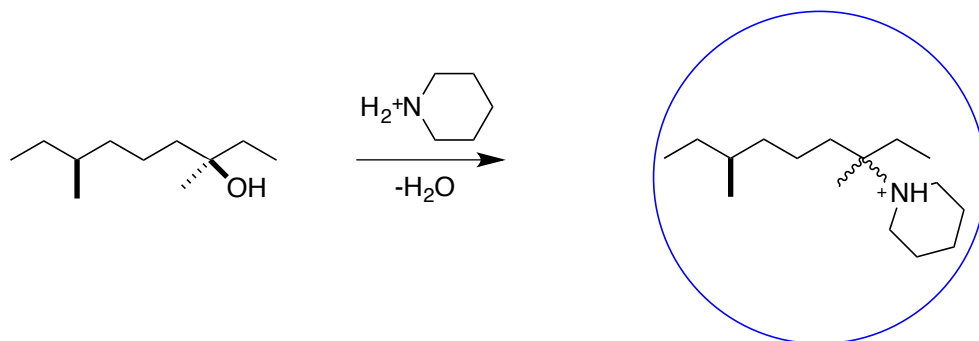
	Me	1°	2°	3°
<i>least stable</i>	0	1	2	3
<i>most stable</i>	0	1	2	3

*on bottom of line
show number of p-to-σ interactions*

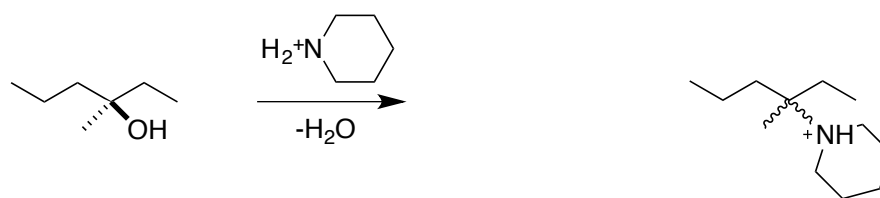
show a - e
on top of line



H. Relative Stereochemistry In S_N1



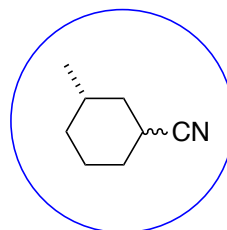
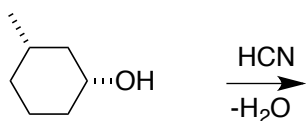
circle if optically active



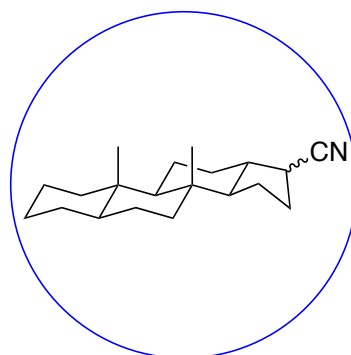
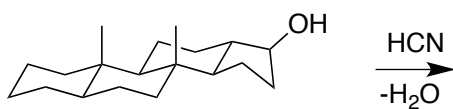
circle if optically active



circle if optically active



circle if optically active



circle if optically active