S_N1 Displacement At sp^3 Centers

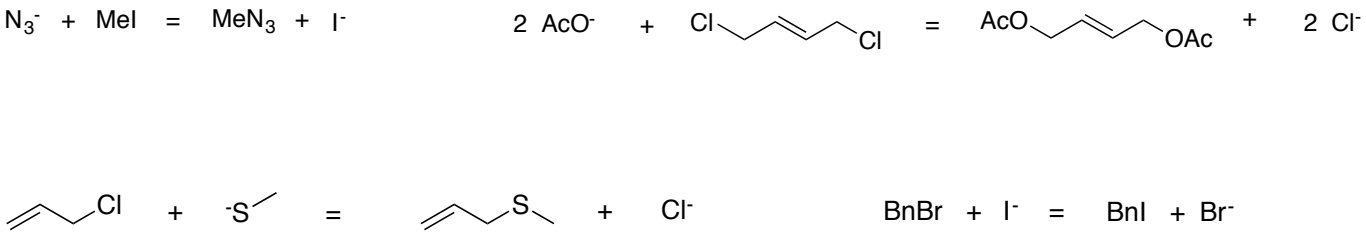
from chapter(s) _____ in the recommended text

A. Introduction

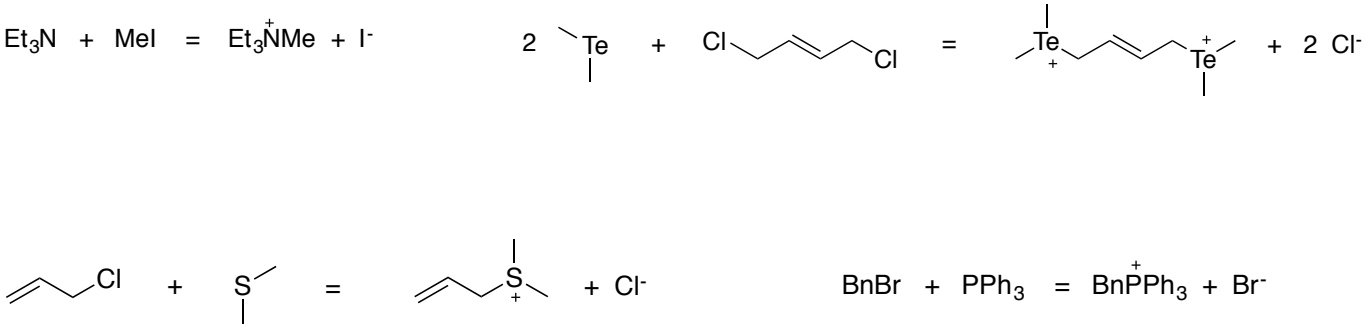
.

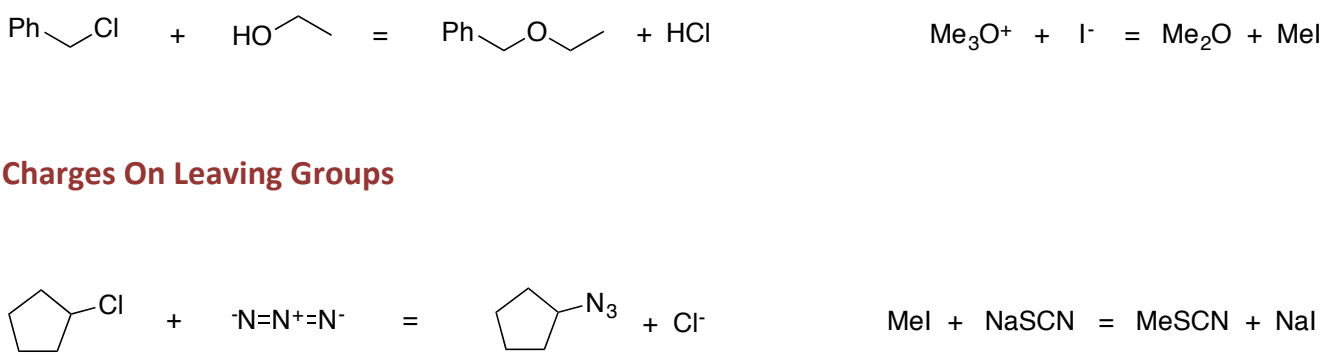
B. Types Of Nucleophilic Substitutions

Negatively Charged Nucleophiles

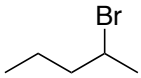


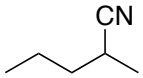
Neutral Nucleophiles





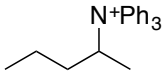
Charges On Leaving Groups

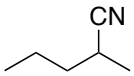


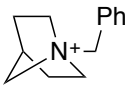
+ NC^- = 

+ Br^-

^{t}BuCl + LiI = ^{t}BuI + LiCl



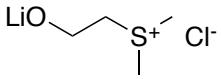
+ NC^- = 

+ NPh_3 

+ LiI = 

+ 

+ Li^+



= 

+ 

+ LiCl

(*intramolecular*)

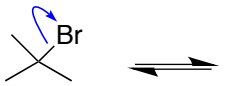
$Ph_3P^+Me\ Cl^-$ + NaSEt = PPh_3 + MeSEt + NaCl

C. S_N1

Introduction Into The Key Steps

group *replaces another*.

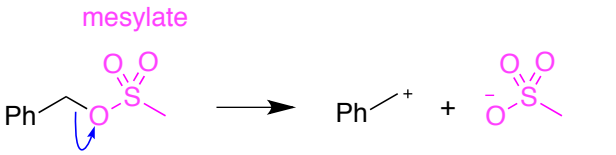
nucleophile *with first order kinetics*.



+ Br^-

+ I^-

carbocation and bromide



benzyl carbocation and $^-$OMs

is the rate

tosylate

allyl carbocation and O^-Ts

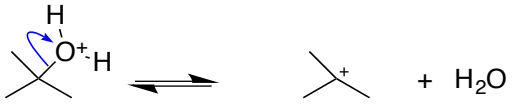
hydrogen phosphate

allyl carbocation and hydrogen phosphate

geraniol hydrogen phosphate

an allyl carbocation and hydrogen phosphate

carbocation and hydroxide

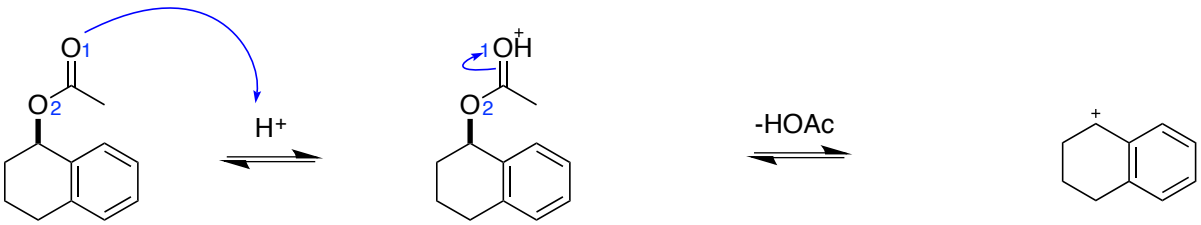


carbocation and water

better
right
left
true.

protonated intermediate

carbocation intermediate

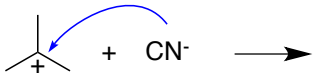


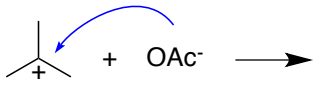
protonated intermediate

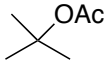
carbocation intermediate

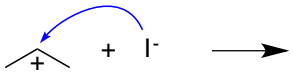
O[1] is

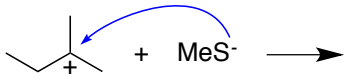
Carbocations *can*





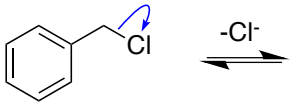


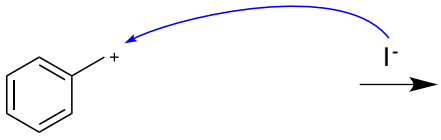


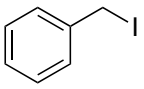


cations

racemic,
sp^2
flat and the nucleophile can

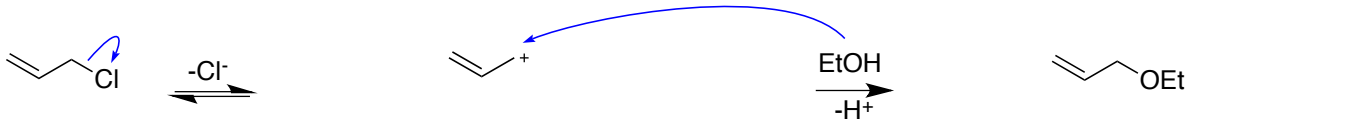






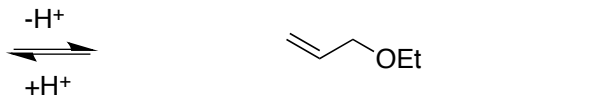
intermediate

product



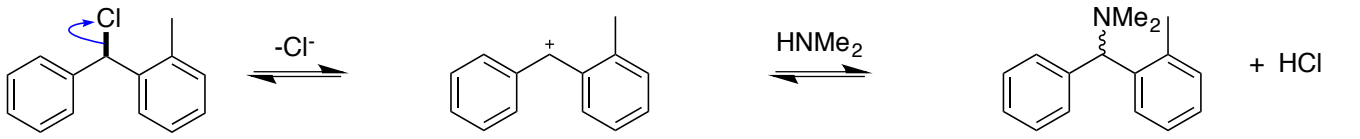
intermediate *product*

intermediate *protonated intermediate*



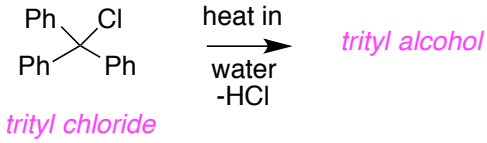
product

two intermediates.
one intermediates.
S_N1 reaction of bromide with allyl chloride involves *one*

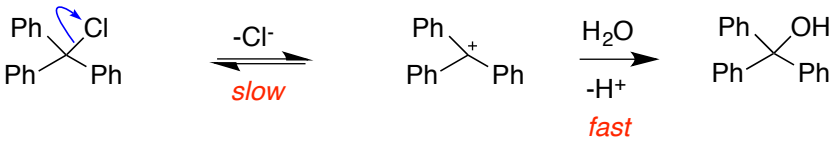


carbocation intermediate *product and HCl*

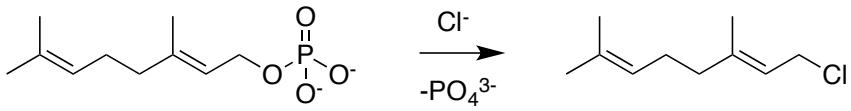
a



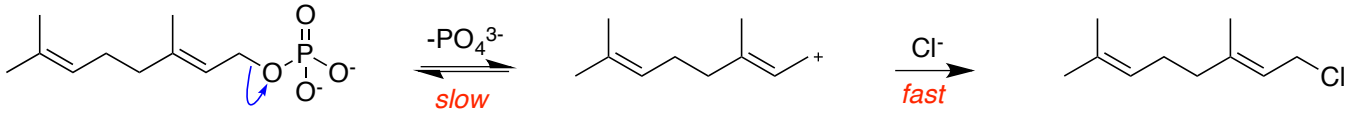
trityl chloride *trityl alcohol*

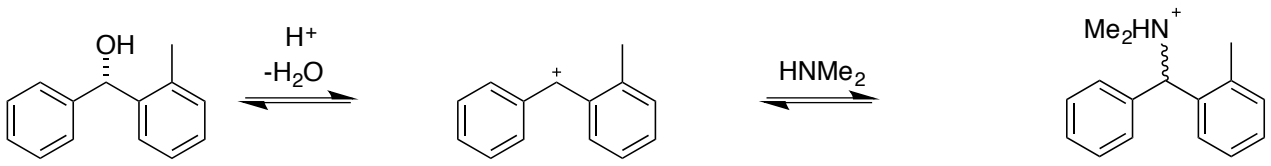


b



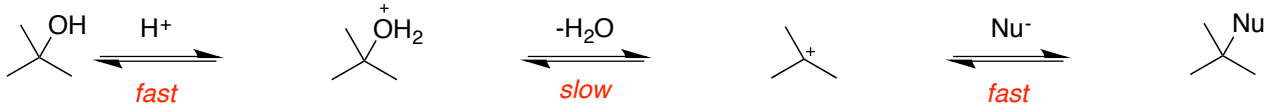
geranyl phosphate *geranyl chloride*



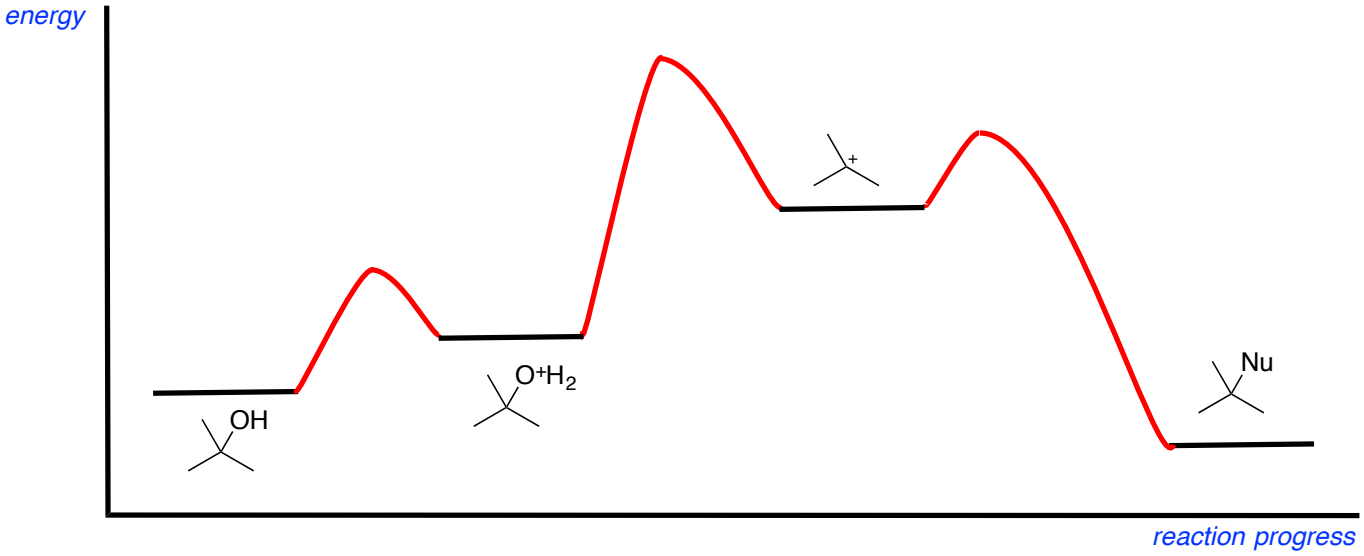


carbocation intermediate *protonated amine*

Kinetics Of S_N1



protonated intermediate *carbocation*



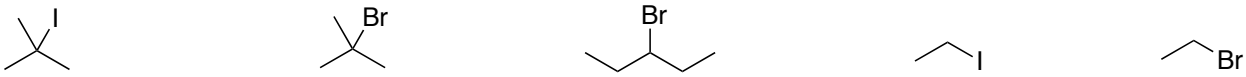
rate is proportional to [^{t}BuOH] rate = k [^{t}BuOH]

at the same rate the

Carbocation Stability

Rates of S_N1 reactions tend to *increase*

most stable *least stable*



fastest *slowest*

show 3°, 1°, 2°, Me on top of line

Me	1°	2°	3°
least stable			*most stable*
0	1	2	3

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

*show **a** - **e** on top of line*

a methyl bromide **b** *tert*-butyl bromide

c methyl chloride **d** ethyl bromide **e** 2-bromopropane

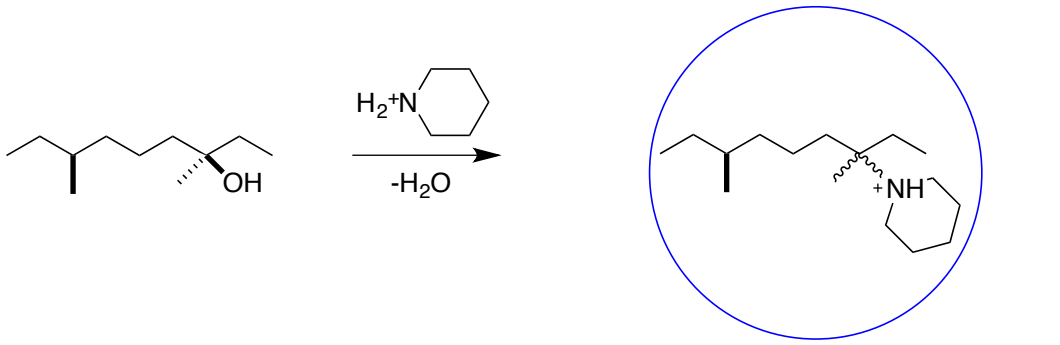
b **e** **d** **a** **c**

fastest *slowest*

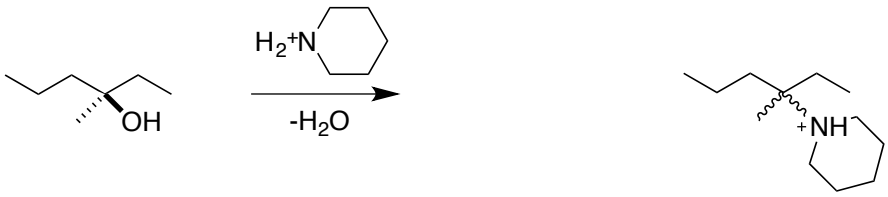
towards from the
increases the overlap

greater than that from hyperconjugation in Et^+.
more stable than many other primary carbocations.

Stereochemistry And S_N1

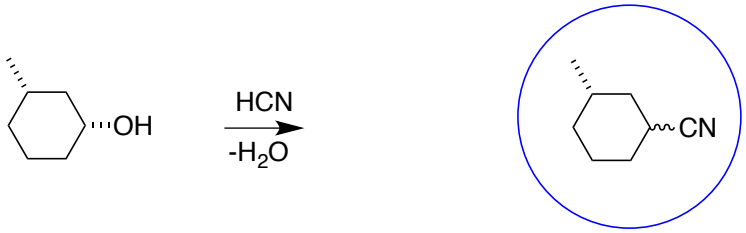


circle if optically active

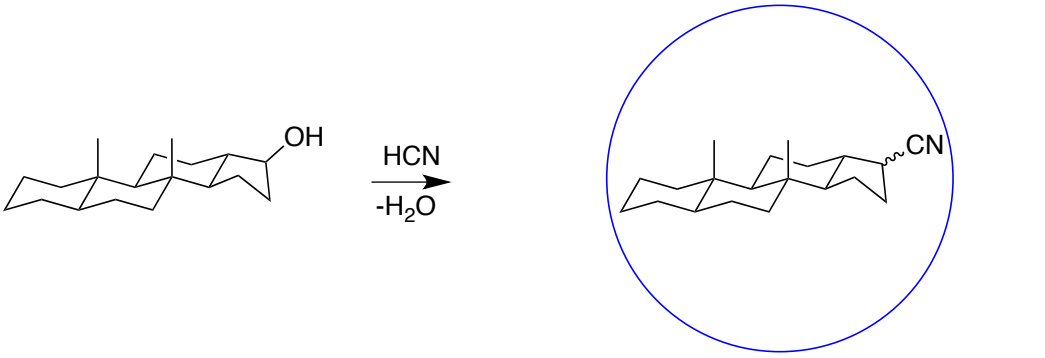


circle if optically active

circle if optically active



circle if optically active



circle if optically active