# S<sub>N</sub>1 Displacement At sp<sup>3</sup> Centers

from chapter(s)	in the recommended tex

# A. Introduction

## **B. Types Of Nucleophilic Substitutions**

## **Negatively Charged Nucleophiles**

$$N_3^-$$
 + MeI = MeN<sub>3</sub> + I<sup>-</sup> 2 AcO<sup>-</sup> + CI = AcO OAc + 2 CI<sup>-</sup>

#### **Neutral Nucleophiles**

$$Et_3N + MeI = Et_3N + MeI = Et_3N + CI$$

$$2 Te + CI$$

$$CI = Te + CI$$

$$CI$$
 +  $S$  =  $S$  +  $CI$  BnBr + PPh<sub>3</sub> = BnPPh<sub>3</sub> + Br

$$Et_2NH + 1 MeI = Et_2NMe + HI$$
 $Ph$ 
 $SH + CI$ 
 $Ph$ 

$$Ph \underbrace{CI} \quad + \quad HO \underbrace{O} \quad + \quad HCI \\ \qquad \qquad Me_3O^+ \quad + \quad I^- \quad = \quad Me_2O \quad + \quad MeI$$

#### **Charges On Leaving Groups**

$$CI$$
 +  $N=N+=N^-$  =  $N_3$  +  $CI^-$  MeI + NaSCN = MeSCN + NaI

$$N^{+}Ph_{3}$$
 +  $NC^{-}$  =  $N^{+}Ph$  +  $Lil$  =  $N^{-}$  +  $Lil^{+}$ 

$$LiO \longrightarrow S^{+} CI^{-} = O \longrightarrow + LiCI$$

(intramolecular)

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

## C. S<sub>N</sub>1

## **Introduction Into The Key Steps**

group replaces another.

nucleophile with first order kinetics.

#### mesylate

benzyl carbocation and <sup>-</sup>OMs

is the rate

## tosylate

## allyl carbocation and O<sup>-</sup>Ts

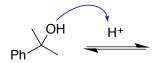
## allyl carbocation and hydrogen phosphate

an allyl carbocation and hydrogen phosphate

#### carbocation and hydroxide

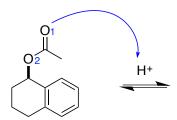
carbocation and water

<u>better</u> <u>right</u> <u>left</u> true.



#### protonated intermediate

carbocation intermediate



#### protonated intermediate

carbocation intermediate

#### Carbocations can

#### <u>cations</u>

## <u>racemic</u>,

 $sp^2$ 

flat and the nucleophile can

product

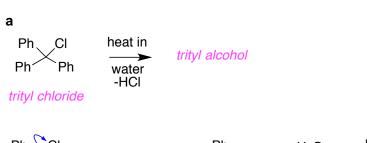
two intermediates.

one intermediates.

S<sub>N</sub>1 reaction of bromide with allyl chloride involves one

carbocation intermediate

product and HCI



b
$$\begin{array}{c|cccc}
O & CI \\
P & P \\
O & P \\
P & P \\$$

carbocation intermediate

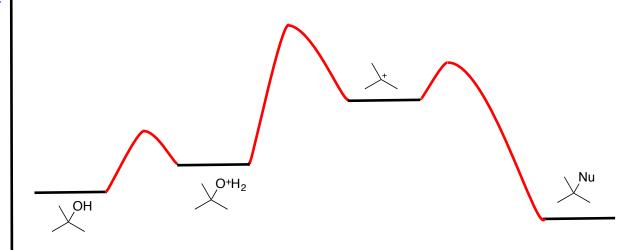
protonated amine

# Kinetics Of $S_N \mathbf{1}$

protonated intermediate

carbocation





reaction progress

rate is proportional to

[<sup>t</sup>BuOH]

rate =

k [†BuOH]

#### at the same rate the

## **Carbocation Stability**

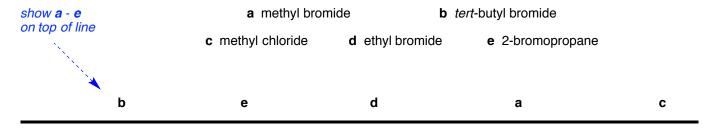
Rates of  $S_N 1$  reactions tend to <u>increase</u>

least stable most stable

$$\nearrow$$
 Br  $\bigcirc$  Br  $\bigcirc$  Br

fastest slowest





fastest slowest

towards from the

greater than that from hyperconjugation in Et<sup>+</sup>. *more* stable than many other primary carbocations.

# Stereochemistry And $S_N \mathbf{1}$

$$^{\dagger}Bu$$
  $\longrightarrow$   $^{\bullet}OH$   $\xrightarrow{HCN}$   $^{\bullet}Bu$   $\longrightarrow$   $^{\bullet}CN$ 

circle if optically active

circle if optically active

circle if optically active

