## <u>Substitution Reactions – 2 types: S<sub>N</sub>1 and S<sub>N</sub>2</u>

#### S<sub>N</sub>2 reactions:

- S = Substitution
- N = nucleophilic
- 2 = bimolecular reaction (rate of reaction depends on 2 reagents)
  - stereospecific reaction
  - inversion of configuration
  - concerted reaction
  - rate depends on two reagent concentration: [Nu] and [SM]
  - favored for primary 1°& 2° carbons, Never 3° centres
  - polar aprotic solvents e.g; Dimethyl formamide(DMF), Dimethyl Sulfoxide (DMSO), acetonitrile.



nucleophile

$$R - x + Y$$
:  $\rightarrow R - Y + X^{\Theta}$ 

 $\begin{array}{l} R = Alkyl \\ X = Halides \\ I^{\Theta} > Br^{\Theta} > Cl^{\Theta} >> F^{\Theta} \\ never; OH^{\Theta}, OR^{\Theta}, NR^{\Theta} \end{array}$ 

# Other possible Leaving Groups – ACID required

O<sup>-H</sup>O<sup>-H</sup> (Need acid) H R

Eg.



# **Excellent to Good Leaving Groups**



The order of halide leaving group ability is due to solvation and size.

very good

poor

Eg.

Eg.





# **<u>S<sub>N</sub>1 reactions - Substitution Nucleophilic Unimolecular</u>**

- rate depends on 1 concentration: [SM]
- stepwise (not concerted)
- carbocation intermediate
- not stereospecific



Eg.



Eg.



Eg.



One reason is that the OH<sup>-</sup> is not a good leaving group.

S<sub>N</sub>1 -Best if 3° carbocation can form -Never on 1° alkyl halides -Leaving groups – same as S<sub>N</sub>2

- OR and OH work if strong acid is present; the HOR and HOH are the leaving groups.
- >  $S_N1$  and  $S_N2$  can compete with E1 and E2 (alkenes are formed)

Eg.

### ALKENES AND ALKYNES

<u>Alkenes and Alkynes</u> – Term olefin comes from: oleum facere Olefin "oil" + "to make"

Alkene (olefin) Alkyne (acetylene)

Alkenes – structure and nomenclature

H H ethylene (common name) H H H ethene (systematic name) replace "ane" of corresponding alkane name with "ene"

> propylene (common name) or propene(systematic name)

1-butene

- to name find longest chain containing maximum number of C=C with both multiply bonded carbons in chain

- number from end to give 1st carbon of C=C lowest number, prefix with number to indicate position of first double bonded carbon







cis-2-butene

trans-2-butene

Stereoisomers (Diastereomers)

- cis = two large groups on same side
- trans = two large groups on opposite side

These 2-butenes are structural isomers with respect to the 1-butene above