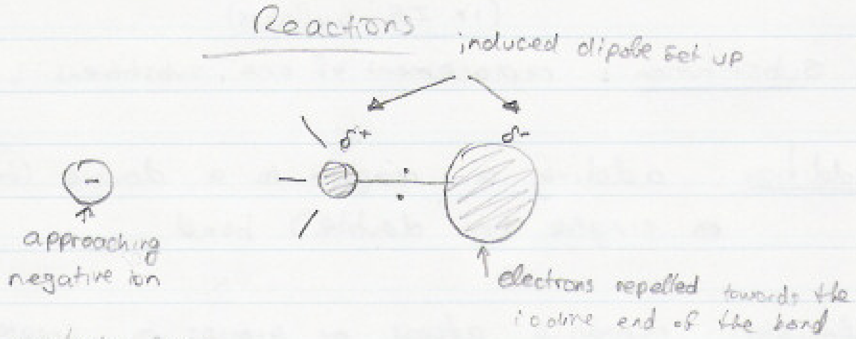
Nucleophilic Substitution Reactions

April 14th, 2005



has lone electron pairs, additional e's.

Attacking Reagents

- Nucleophile : "nucleus-loving"
  - attacks a location w/ high density of positive charge, i.e. carbon atom
  - contains an unshared pair of electrons with which it can form new bonds
  - Lewis base, usually a neutral molecule, as NH_3 or an anion as OH^-

- Electrophile : "electron-loving"
  - attacks a location with high density of negative charge, i.e. C=C
  - contains a vacant orbital in order to form a new bond
  - Lewis acid, often a cation, such as H^+

- Free Radical : the reagent contains one unpaired electrons.

Modes of Bond Breaking

$$A \overset{\curvearrowright}{-} B \longrightarrow A^{+} + :B^{-}$$

- Heterolytic : bond breaks to give two ions (B- has taken both electrons from the bond)

$$\overset{\curvearrowright}{A}-\overset{\curvearrowright}{B} \longrightarrow A\cdot + \cdot B$$

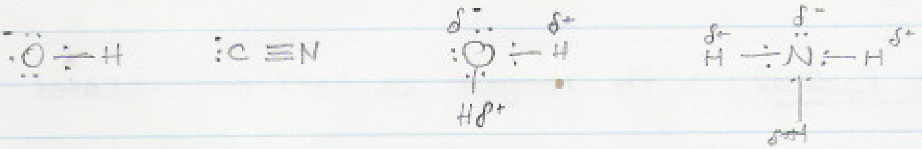
- Homolytic : Bond breaks to give two uncharged species, each with one unpaired electron (both are free radicals) condensation, dehydration — Elim.

Types of Reactions
(in IB syllabus)

- Substitution: replacement of one substituent by another
- Addition: adding a reagent to a double (or triple) bond, forming a single (or double) bond
- Elimination removing atoms or groups to create multiple bond
  → same as condensation & dehydration, but use Elimination instead for a term
- Oxidation & Reduction

Nucleophile

- A nucleophile is a species (an ion or a molecule) which is strongly attracted to a region of positive charge in something else.
- Nucleophiles are either fully negative ions or else have a strongly negative charge on a molecule

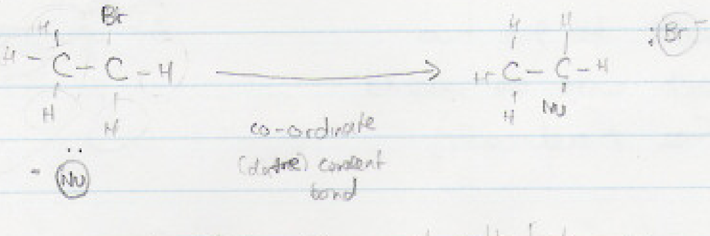


S_N2 reaction

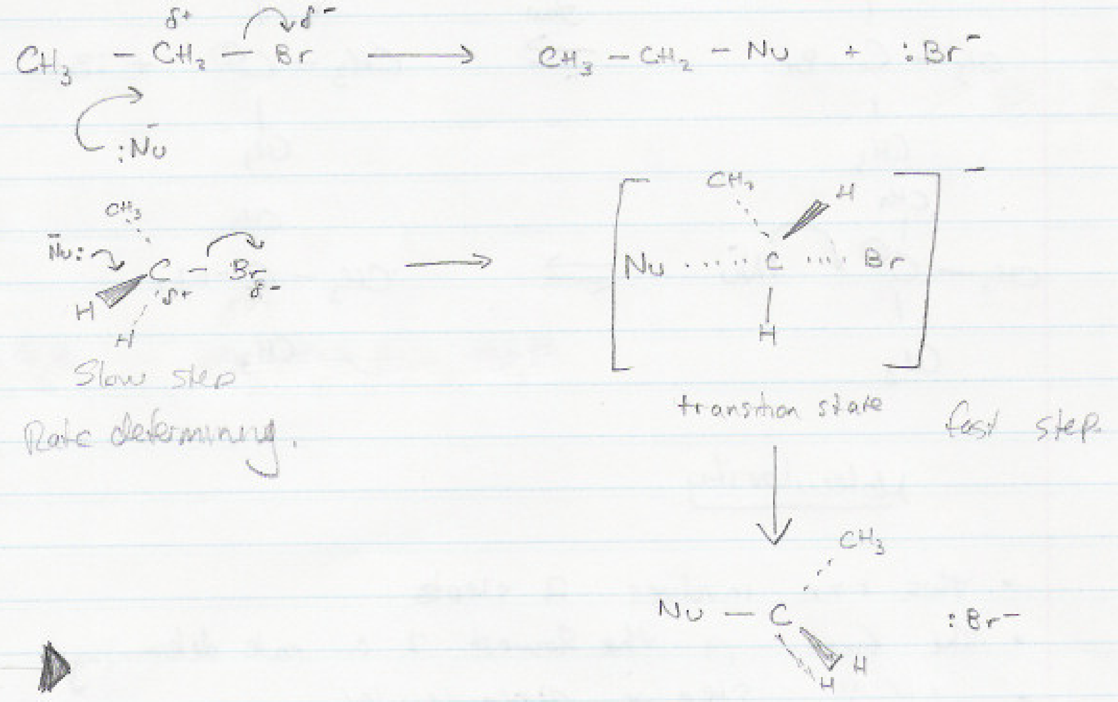
2 hydrogens on carbon too.

- S = substitution
- N = Nucleophile
- 2 = # of species
  Bimolecular

- Bromoethane: 1° halogenalkane ie. has only one alkyl group on central carbon
- [Nucleophile (Nu^-): ion w/ a lone electron pair]



unstable. Nu must attach as soon as Br leaves



Slow step

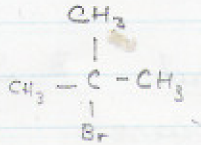
Rate determining.

transition state

fast step

S_N1 reaction

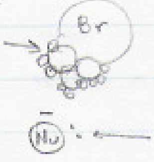
- 2-bromo-2-methylpropane



$CH_3-C(CH_3)(Br)-CH_3$

. Tertiary halogenalkane: carbon Contains three Alkyl groups.

-stable. Can exist as a carbocation for short period of time



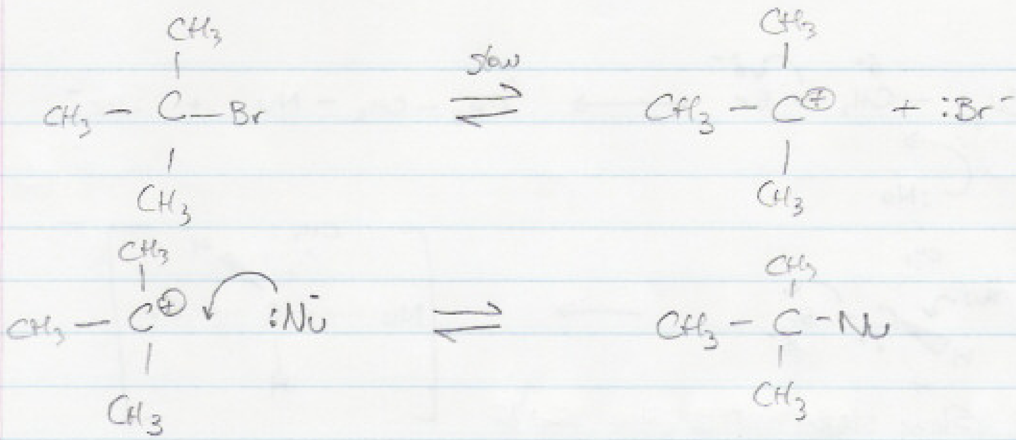
Back of molecule Clustered w/ CH3 groups

lone pair on nucleophile Can't get @ the δ+ carbon

Molecularity

- The reaction mechanism involves two steps
- the first is the rate determining (slowest & is bimolecular
- Rate = K[R-Br][Nu]

S_N1 Occurs in two stages

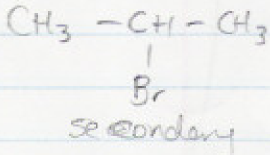


Molecularity

- This rxn involves 2 steps
- The first is the slowest & ∴ rate determining
- " " " step is unimolecular
- Note a tertiary carbocation is more stable than a primary carbocation ∴ S_N1 is preferred here.

S_N1 & S_N2

- 2-bromopropane
- Secondary Halogenalkane
- Either S_N1 or S_N2 can occur.
- Halogenalkane.



$CH_3-CH(Br)-CH_3$

secondary halogenalkane

1° 2° 3° ⟶

increasing stability of Carbocation.

Nature of Halogen affects the rate

- As the halogen changes from F to Cl to I → the bond polarity decreases. Nucleophile more attracted to F!
- Polarity decrease, also decreases the + Charge on the central carbon ∴ decreasing the Rate of Rxn.