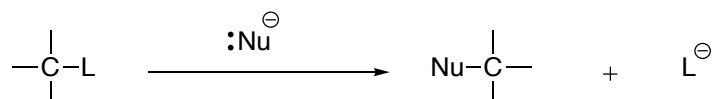


Stereospecific reactions: stereochemistry of starting material determines stereochemistry of product. All concerted reactions are stereospecific but not all stereospecific reactions are concerted. Examples of concerted stereospecific rxns include:

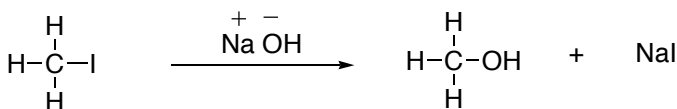
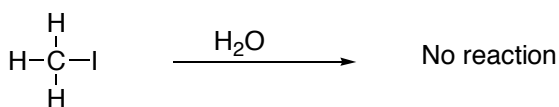
- E2 – elimination reaction
- S_N2 – substitution reaction

i) S_N2 reaction:

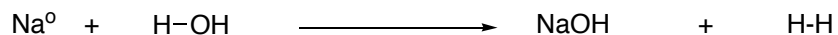


L = leaving group – partially negative (eg. TsO (tosylate, a sulfonate) , Cl, Br, I)

Nu = Nucleophile – a substance (molecule) that seeks a positive center (usually carbon)

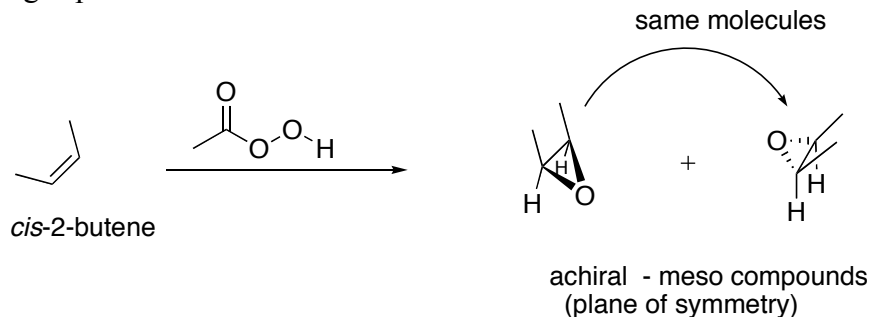


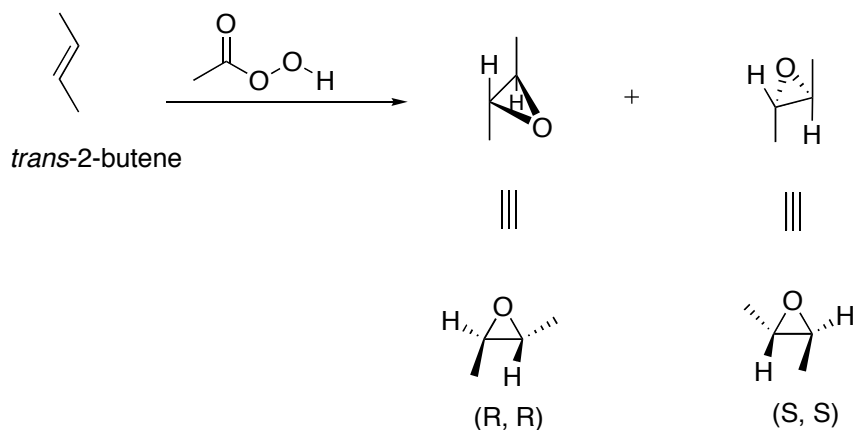
Making NaOH from H₂O : Demo



Stereospecific addition reaction: (see reactions of alkenes)

Eg. Epoxidation:





- both starting materials are achiral (not chiral), but each of the products can be chiral
 - however they are formed as a 1:1 mixture of enantiomers – racemic mixture
- Generally get pure (or partially pure) chiral products only if one of the reagents is chiral

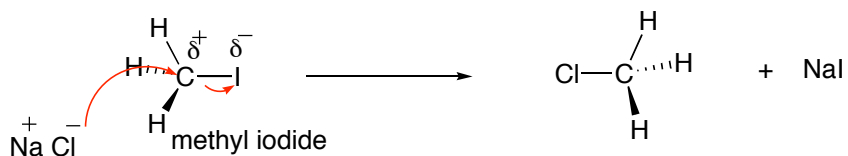
Substitution Reactions:

1) S_N2 reaction:

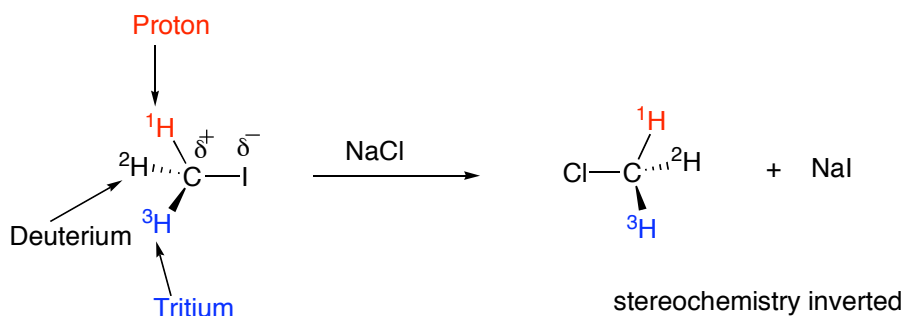
S = Substitution

N = nucleophilic

2 = bimolecular reaction (rate of reaction depends on 2 reagents)



- stereochemistry of product is inverted (attack from the opposite side as leaving group)
- WALDEN INVERSION

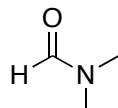


S_N2 Reaction:

- concerted reaction – all bonds break and form at the same time
- stereospecific – inversion of configuration
- rate depends on [Cl⁻] & [CH₃I] – bimolecular process (two molecules are involved)

Influences on S_N2 reaction:

- works best if 1° carbon attached to leaving group
- with 2° carbon the reaction goes okay, with 3° carbon fails (too bulky)
- with reactive nucleophile reaction goes best
- for leaving group – best if the leaving group is electron withdrawing (solvation factor also affects leaving group ability)
- solvent – polar-aprotic solvents are best, such as DMF, DMSO
 - aprotic – no hydrogen (proton) attached to oxygen in the molecule

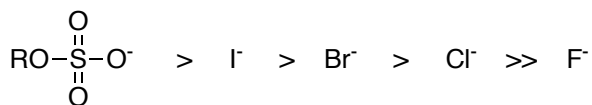


dimethylformamide (DMF)



dimethylsulfoxide (DMSO)

- leaving groups:

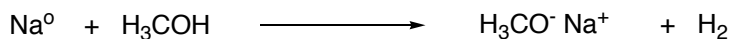
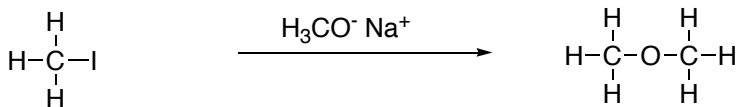


very good

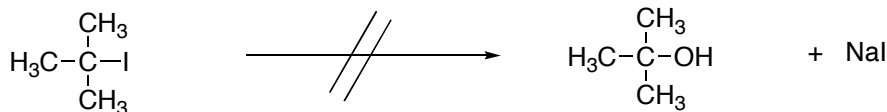
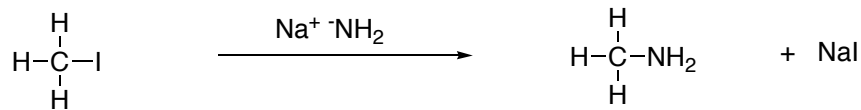
poor

The order of halide leaving group ability is due to solvation

- groups that could never be leaving group in substitution reaction:
OH⁻, OR⁻, NHR⁻



- in the reaction to form dimethyl ether shown above, the reverse reaction would not occur, since ⁻OCH₃ is a very poor leaving group



$\text{Na}^+ \text{OH}^-$

3° carbon, so no S_N2 reaction

2) S_N1 Reaction:

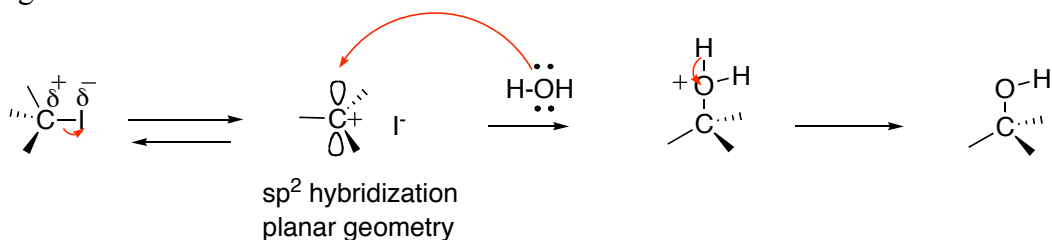
S = Substitution

N = Nucleophilic

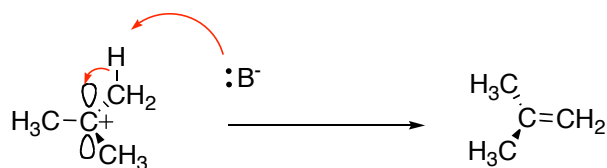
1 = unimolecular reaction – rate of the reaction depends on only one reagent

- nucleophilic substitution reaction
- rate depends on one reagent's concentration
- step-wise reaction (not concerted)
- carbocation intermediate is observed
- favoured if leaving group is at 3° carbon center
- non-stereospecific
- best if leaving group is attached to 3° carbon center
- never occurs if 1° carbon is attached to leaving group

eg.



- the carbocation intermediate may undergo elimination in the presence of base:



Sample questions:

