CHM102A Tutorial 5

Topics covered in lectures-12, 13 to be discussed in Tutorial 5

- Nucleophilic substitution reactions: S_N^1 , S_N^2 : Basic features with examples, reaction profile, stereochemistry, factors affecting S_N^1 , S_N^2 reactions, effect of substrate, nucleophile, solvent, stability of carbocations, comparison between S_N^1 , S_N^2 .
- Elimination reactions: E1, E2, Zaitsev rule, mechanism, energy-profile, regioslectivity, factors affecting E2/E1 reactions, comparison between S_N^1/S_N^2 and E1/E2, stereochemistry of E2 reactions, E2 reactions, dehydohalogenation in six-membered rings, E1cB reaction.
- 1. Rank the species below in order of increasing nucleophilicity in hydroxyl solvents: CH₃CO₂-, CH₃S-, HO-, H₂O

Ans: $H_2O < CH_3CO_2^- < HO^- < CH_3S^-$

2. Draw the structures of organic products formed with correct stereochemistry at the stereogenic centre (if any) in the following reactions.

(i)
$$Br \longrightarrow CH_3$$
 $CH_3S \longrightarrow CH_3$ acetone

(ii) $CH_3 \longrightarrow CH_3$ $CH_3 \longrightarrow CH_3$

Ans:

Br
$$CH_3$$
 CH_3 CH_3

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3

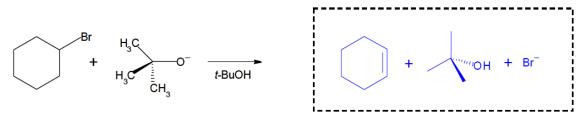
3. What product(s) would you expect from the following solvolyis reaction? Designate the type of reaction mechanism.

$$S_N^1$$
 OCH₃ OCH_3

Here α -carbon is tertiary, and thus in MeOH it should loose Br- to form tert. stable carbocation and proceed via S_N^1 reaction. Planarity of carbocation leads to two products.

4. For the following reaction, draw the product(s) of the major reaction(s). Clearly indicate any relevant stereochemistry.

Ans with justification



leaving group ability	strength of nucleophile	strength of base	electrophilic site
Br ⁻	$(H_3C)_3CO^{-}$	$(H_3C)_3CO^-$	2°
good	bad nucleophile;	basic enough for E2	has β hydrogen atoms
	too bulky	(too basic for E1*)	

E1? no	E2? major	S _N 1? no	S _N 2? no

^{*}Recall that carbocations cannot be formed in the presence of basic anions.

5. Deduce substrate and corresponding nucleophile to prepare following molecules using $S_{\rm N}{}^{\rm 1}$ reaction?

$$\bigcap_{H_3CO}$$

Ans:

6. Given that the following three molecules have the absolute configurations given, show how each reactant gives a different outcome by E2.

Ans:

7. Indicate the stereochemical outcome of the following S_N^2 reactions. Assume that all chiral centers are optically pure. Do these reactions all give racemic mixtures?

Ans:

8. What are the products of following E2 reactions:

Ans: