Problem Set 8: Substitution Reactions

Chemistry 260

Organic Chemistry

1. Which of the following species are nucleophiles?

- (1) CN⁻
- (2) Na⁺
- $(3) I^{-}$
- (4) Ca²⁺
- (5) NH₃

2. For each of the compounds below, indicate whether it is a nucleophile, an electrophile, or neither.

(a)

CH₄

(c)



(b)

NH₃

(d)

CH₂CH₂

(e)

CH₃ CH₃-C-CH₃ (f)

CH₃

3. Circle the nucleophilic atom in the compounds below.

(a

H₃C, CH₃

(b)

H H-C-NH₂ H

(c)

H₃C CH₃

(d)

H₃N, C-O

4-6. Which is the most reactive in an S_N2 reaction?

- 4. (1) HS-
- (2) HO-
- 5. (1) Cl-
- (2) Br

(3) I -

- 6. (1) CH₃-I

7. Which is the most reactive in an S_N2 reaction?

(1)

(2)

(3)

3)
$$CH_3$$
 I $CH_2CH_2CH_3$ I CH_3 I CH_3

(4)

8. Which of the following statements applies to the S_N2 reaction of optically pure (-)-2-bromooctane with dilute aqueous sodium hydroxide?

- (1) the product will be racemic 2-octanol
- (2) the product will be optically pure (+)-2-octanol
- (3) the product will be optically pure (-)-2-octanol
- (4) the product will be either optically pure (+) or (-)-2-octanol, but it is not possible to predict which
- (5) none of the above

9-12. Identify each of the alkyl halides below as: (1) 1°

10.

H

CH₂Br

(2) 2°

(3) 3°.

11.

9.

12.

$$CH_3CH_2$$
 CH_2CH_2CI
 $C=C$
 CH_3

13. Predict the products of each of the reactions below.

$$\begin{array}{c} \text{(a)}\\ \text{H}\\ \text{Br} \end{array} \xrightarrow[]{\text{NaCN}} \\ \text{CH}_{3}\text{-}\text{S}\text{-}\text{CH}_{3} \\ \text{(solvent)} \end{array}$$

Br
$$\xrightarrow{\text{NaOH}}$$
 $\xrightarrow{\text{NaOH}}$ $\xrightarrow{\text{O}}$ $\xrightarrow{\text{CH}_3-\text{S}-\text{CH}_3}$ (solvent)

(d)
$$\begin{array}{c}
R \\
R-C-Br \\
CH_{3}
\end{array}$$
R = any alkyl

14. What is the R/S configuration of the product of the S_N2 reaction below? Base your answer on the structure of the reactant and the mechanism of the reaction, not on the way the product is drawn.

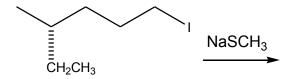
15. Choose the best statement regarding the reaction below.

- (a) The product will be optically pure.
- (b) The product will have no optical activity.
- (c) The product will have considerable optical activity, but will not be pure.
- (d) The extent of optical activity cannot be predicted.
- 16. Choose the best statement regarding the reaction below.

Optically Pure

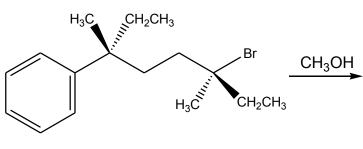
- (a) The product will be optically pure.
- (b) The product will have little or no optical activity.
- (c) The product will have considerable optical activity, but will not be pure.
- (d) The extent of optical activity cannot be predicted.

17. Choose the best statement regarding the reaction below.



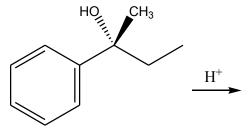
(S)-4-methyl-1-iodohexane

- (a) The product will have S configuration.
- (b) The product will have R configuration.
- (c) The product will be racemic.
- (d) Cannot predict the configuration of the product.
- 18. Choose the best statement regarding the reaction below.



Optically Pure

- (a) The product will be optically pure.
- (b) The product will have no optical activity.
- (c) The product will have some optical activity, but will not be optically pure.
- 19. Rationalize, in terms of a mechanism, the loss of optical activity of (R)-2-phenyl-2-butanol when dissolved in acidic solution.



(*R*)-2-phenyl-2-butanol

20. The following questions relate to the reaction shown below:

- (a) Why is little or no product **B** formed?
- (b) Optical activity of **A** is lost. Why?
- 21. For each reaction shown below, draw the structure of the major organic product(s). Show stereochemistry where appropriate.

(a)
$$H_3C \xrightarrow{H_3} H$$
 + NaSH \longrightarrow CI CH_3

22. Propose a mechanism for the reaction below:

23. Propose a mechanism for each reaction below.

(a)
$$O$$
 CH_3OH/H^+ Et OH

(b)
$$CH_3OH/H^+$$
 Et OCH_3

24. Answer the following questions with respect to the reaction below:

(a) Using the knowledge you have learned in Chem 123, how would you classify this reaction?

- (b) When the concentration of the methylcyclopentanol is doubled, what would be the effect on the reaction rate?
- (c) Assuming the reaction is reversible, if a dehydrating agent is added to the reaction mixture, which side of the equilibrium favour?
- (d) If the temperature is increased, what will be the effect on the equilibrium constant?
- (e) What would be the effect on the optical activity as this reaction proceeds?