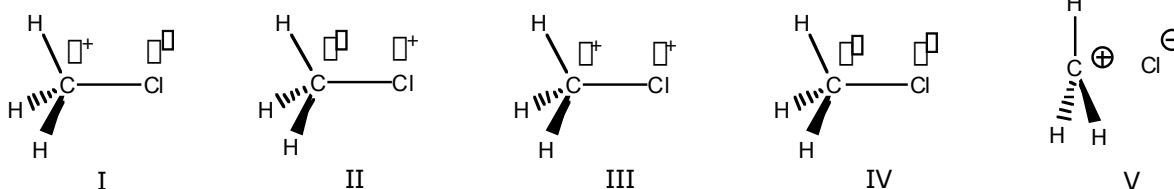
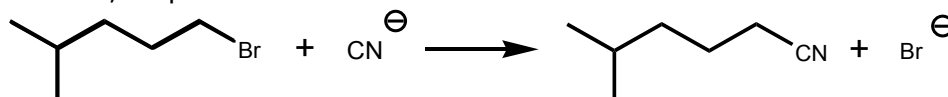


ORGANIC CHEMISTRY I – PRACTICE EXERCISE  
**Sn1 and Sn2 Reactions**

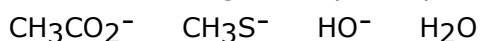
1) Which of the following best represents the carbon-chlorine bond of methyl chloride?



2) Provide a detailed, stepwise mechanism for the reaction below.



3) Rank the species below in order of increasing nucleophilicity in hydroxylic solvents:



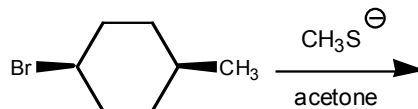
4) Give a stereochemical structure of the product from the reaction between (*S*)-2-iodopentane and KCN in DMF (dimethyl formamide, a good polar solvent for ionic reagents).

5) Consider the reaction of  $(\text{CH}_3)_3\text{CO}^-$  with iodomethane. Will the reaction rate increase, decrease, or remain the same if the concentration of iodomethane is increased? Explain.

6) Which of the following compounds will undergo an  $\text{S}_{\text{N}}2$  reaction most readily?

- A)  $(\text{CH}_3)_3\text{CCH}_2\text{I}$
- B)  $(\text{CH}_3)_3\text{CCl}$
- C)  $(\text{CH}_3)_2\text{CHI}$
- D)  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{I}$
- E)  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Cl}$

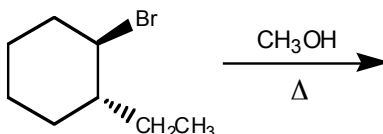
7) What is the major organic product in the following reaction?



8) Would 2-chloropropane or 1-chloro-2,2-dimethylpropane undergo substitution faster with  $\text{Na}^+ \text{ } ^-\text{CCH}$ ? Give the structure of the substitution product.

9) *t*-butyl chloride undergoes solvolysis in 70% water/30% acetone at a rate slower than in 80% water/20% acetone. Explain.

10) Provide the major organic product of the reaction below and a detailed, stepwise mechanism which accounts for its formation.



11)  $S_N2$  reactions involving chiral electrophiles usually proceed with:

- A) inversion of configuration
- B) slightly more inversion than retention.
- C) slightly more retention than inversion.
- D) retention of configuration.
- E) equal amounts of inversion and retention of configuration.

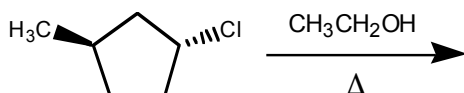
12) Which compound undergoes solvolysis in aqueous ethanol most rapidly and why?  
Remember: solvolysis refers to ionization of the molecule aided by the solvent.

cyclohexyl bromide    isopropyl chloride    methyl iodide

3-chloropentane    3-iodo-3-methylpentane

13) Why does  $\text{CH}_2=\text{CHCHBrCH}_3$  undergo solvolysis much more rapidly than 2-bromobutane?

14) Provide the structure of the major organic products which result in the reaction below.



15) What combination of reactants would be best to prepare  $\text{CH}_3\text{OCH}(\text{CH}_3)_2$  by an  $S_N2$  reaction?

16) The reaction between 2-iodohexane and ethanol to give a substitution product most likely follows an \_\_\_\_\_ mechanism.

17) Which of the following alkyl halides is most likely to undergo rearrangement in an  $S_N1$  reaction?

- A) 3-bromopentane
- B) 2-chloro-3,3-dimethylpentane
- C) 3-chloropentane
- D) bromocyclohexane
- E) 1-bromo-4-methylcyclohexane

18) Which compound is most nucleophilic? A)  $\text{CH}_3\text{SH}$  B)  $\text{CH}_3\text{OH}$  C)  $\text{H}_2\text{O}$  D)  $\text{CH}_3\text{CO}_2\text{H}$  E)  $\text{BF}_3$

19) Which halide has the smallest dipole moment?

A)  $\text{CH}_3\text{F}$     B)  $\text{CH}_3\text{Cl}$     C)  $\text{CH}_2\text{I}_2$     D)  $\text{CH}_2\text{Cl}_2$     E)  $\text{CF}_4$

20) When 2,2-dimethylbutane is subjected to free-radical chlorination, \_\_\_\_\_ distinct monochlorinated products are possible and \_\_\_\_\_ of these contain asymmetric carbon atoms.

A) 4, 2    B) 5, 0    C) 3, 0    D) 5, 2    E) 4, 0

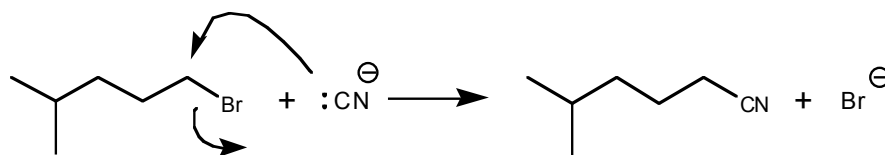
21) Arrange the substrates in order of increasing  $S_N2$  reactivity with  $\text{NaCN}$ : Bromoethane, 1-chloro-3,3-dimethylpentane, 1-chloro-2,2-dimethylpentane, and 2-bromo-2-methylpentane.

22) Arrange the following compounds in order of increasing reactivity toward ethanol solvolysis: *t*-butyl bromide, *t*-butyl iodide, isopropyl chloride, and methyl iodide.

## ANSWERS

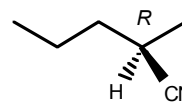
1) I

2)



3)  $\text{H}_2\text{O} < \text{CH}_3\text{CO}_2^- < \text{HO}^- < \text{CH}_3\text{S}^-$

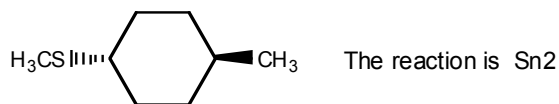
4)



5) This is an  $\text{S}_{\text{N}}2$  reaction. Rate =  $k[(\text{CH}_3)_3\text{CO}^-][\text{CH}_3\text{I}]$ . The rate increases as  $[\text{CH}_3\text{I}]$  increases.

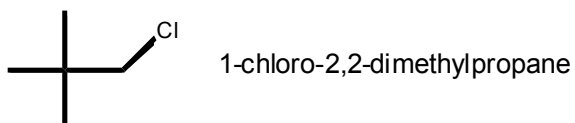
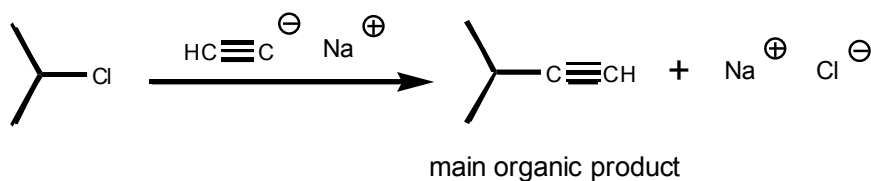
6) D

7)



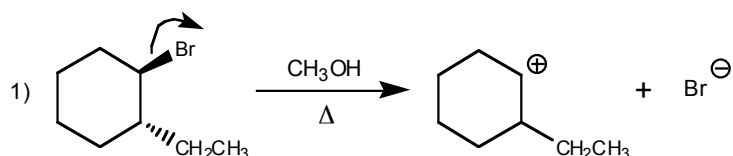
8)

2-Chloropropane. The reaction is  $\text{S}_{\text{N}}2$ , and even though 1-chloro-2,2-dimethylpropane is a primary chloride, it is more sterically hindered than 2-chloropropane, which is secondary.

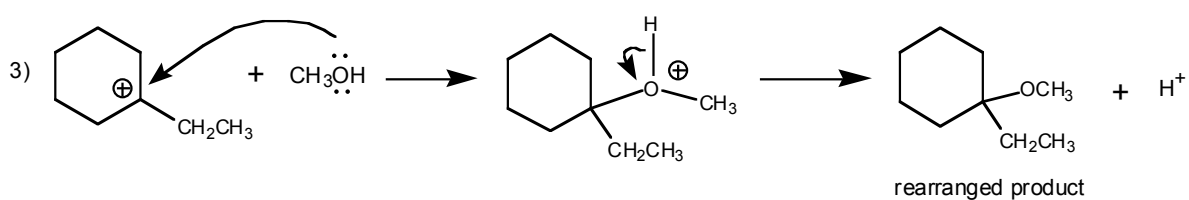
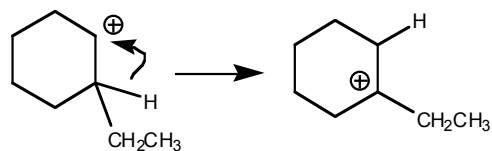


9) This is purely a solvent effect. The greater the percentage of water in this solvent mixture, the more polar the solvent. The more polar the solvent, the more easily solvated the developing carbocation and the more rapidly it is formed.

10)

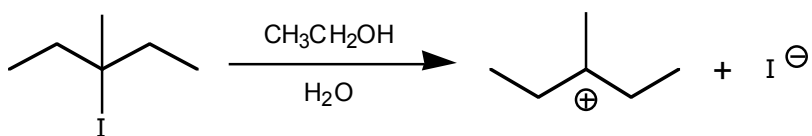


2) carbocation rearrangement from secondary to tertiary by means of a hydride shift



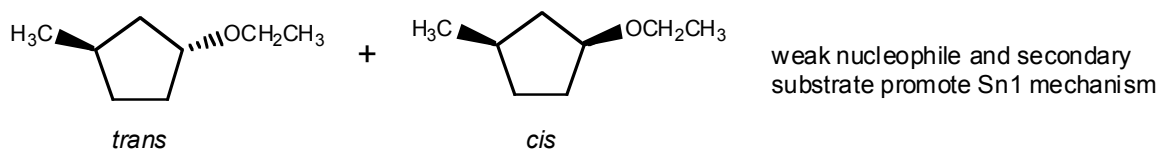
11) A

12) 3-Iodo-3-methylpentane. This molecule forms the most stable cation (tertiary).

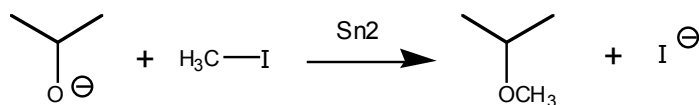


13) The intermediate carbocation is resonance stabilized (allylic). Can you draw the resonance structures?

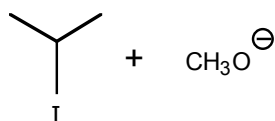
14)



15)



The following combination might also work, but less effectively. The substrate is more sterically hindered than methyl iodide.



16) S<sub>N</sub>1 - secondary substrate plus weak nucleophile.

17) B

18) A

19) E

20) A

21) 2-bromo-2-methylpentane < 1-chloro-2,2-dimethylpentane < 1-chloro-3,3-dimethylpentane  
< bromoethane

22) methyl iodide < isopropyl chloride < *t*-butyl bromide < *t*-butyl iodide

Again, solvolysis means ionization aided by the solvent. The substrate that can make the most stable cation will be most reactive. In this case there are two tertiary substrates. The one with the best leaving group (iodide) will be most reactive.