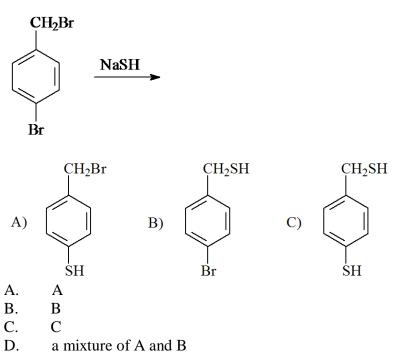
ACS Review Nucleophilic Substitution

- 1. Which of the following undergoes a substitution reaction with sodium cyanide in DMSO at the fastest rate?
 - A. CH₃CH₂F
 - B. CH_3CH_2Cl
 - C. CH₃CH₂Br
 - D. CH₃CH₂I
- 2. 1-Chloro-4-fluorobutane is reacted with one equivalent of sodium iodide in acetone. During the reaction a precipitate forms. What is the precipitate?
 - A. FCH₂CH₂CH₂CH₂L
 - B. ClCH₂CH₂CH₂CH₂I
 - C. NaCl
 - D. NaF
- 3. The rate law for the following reaction is:

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CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl + NaCN _____
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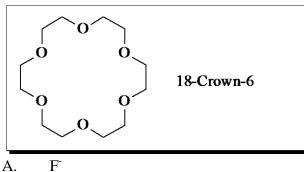
- A. rate = $k[CH_3CH_2CH_2CI]$
- B. rate = $k[CH_3CH_2CH_2Cl][NaCN]$
- C. rate = $k[CH_3CH_2CH_2CI][NaCN]^2$
- D. rate = k[NaCN]
- 4. Which of the following reacts the fastest by the $S_N 2$ mechanism?
 - A. CH₃Br
 - B. CH₃CH₂Br
 - C. (CH₃)₂CHBr
 - D. $(CH_3)_3CBr$
- 5. Give the product(s) of the following reaction?



6. Which halide ion reacts the fastest with cyclopentyl *p*-toluenesulfonate in ethanol/water?

OTs A) I^{Θ} B) Br[⊖] C) Cl^{Θ} D) F^{Θ} A. А B. В C. С D. D

Which one of the following species forms the strongest ion-dipole attraction with 18-crown-6? 7.



- \mathbf{K}^+ Β.
- $Cr_2O_7^{2-}$ C.
- D. Br_2

8. Identify the major product(s) in the reaction of (R)-2-bromopentane with sodium cyanide in DMSO? (R)-2-cyanopentane A.

- B. (S)-2-cyanopentane
- racemic mixture of 2-cyanopentane C.
- trans-2-pentene D.
- Which of the following reacts fastest with methanol by the S_N1 mechanism? 9.

A) CH₃CH₂CH₂CH₂CH₂Br

B) CH₃CH₂CH₂CHCH₃

Br

C) (CH₃)₂CCH₂CH₃ Br

D) (CH₃)₃CCH₂Br

- A A.
- В Β.
- C. С

D. D

10. A pentacoordinate carbon is a transient species in the _____ mechanism.

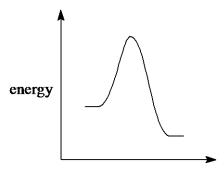
- A. $S_N 1$
- B. $S_N 2$
- C. E1
- D. E2

11. What is the leaving group in the following reaction?

$CH_3CH_2OH + HC1 \longrightarrow CH_3CH_2C1 + H_2O$

- A. OH
- B. H_2O
- C. $CH_3CH_2^+$
- D. C1⁻

12. Considering the S_N1 , S_N2 , E1, and E2 mechanisms, the energy diagram shown below corresponds to:



rxn coordinate

- A. only the $S_N 1$ mechanism
- B. only the $S_N 2$ mechanism
- C. both the S_N1 and E1 mechanisms
- D. both the $S_N 2$ and E2 mechanisms

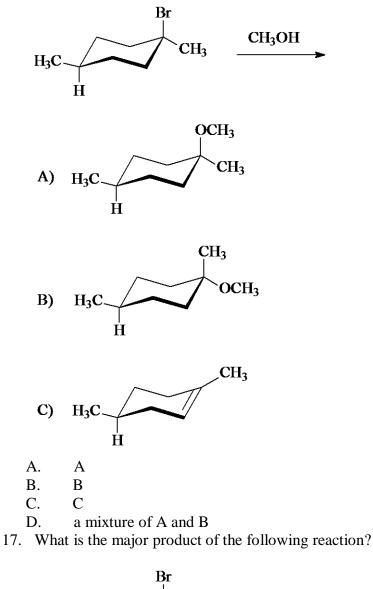
13. Which of the following is the rate law for the S_N1 mechanism of an alkyl halide with a nucleophile?

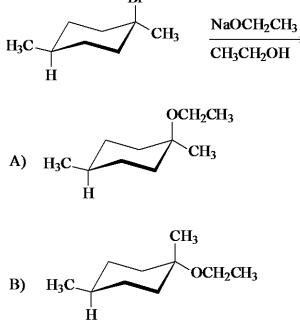
- A. rate = k[alkyl halide]
- B. rate = k[nucleophile]
- C. rate = k[alkyl halide][nucleophile]
- D. rate = $k[alkyl halide]^{2}[nucleophile]$

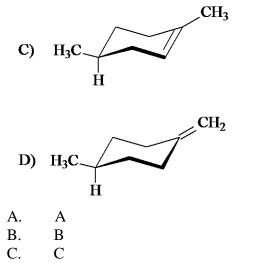
14. Which of the following bases works best to maximize the E2 product in the reaction shown below?

$(CH_3)_2CHCH_2CH_2CH_2Br + base \longrightarrow (CH_3)_2CHCH_2CH=CH_2$

- A. KOCH₂CH₃
- B. NaOCH₂CH₃
- C. NaOC(CH₃)₃
- D. NaOH
- 15. Which of the following does <u>not</u> correctly describe S_N2 reactions of alkyl halides?
 - A. Tertiary halides react faster than secondary halides.
 - B. Rate of reaction depends on the concentrations of both the alkyl halide and the nucleophile.
 - C. The mechanism consists of a single step with no intermediates.
 - D. The transition state species has a pentavalent carbon atom.
- 16. Identify the substitution product(s) in the following reaction.







D. D

18. Starting with 1-hexene, which synthetic sequence below gives 2-cyanohexane?

A.	(1) H ₂ SO ₄ (cat.), H ₂ O	(2) NaCN
B.	(1) HBr/peroxide	(2) NaCN
C.	(1) HBr	(2) NaCN
D.	(1) Br_2 , H_2O	(2) NaCN

19. Which sequence of reactions below gives the highest yield of ethyl isopropyl ether?

	CH ₃ CH ₂ OCH(CH ₃) ₂	ethyl isopropyl ether
A)	(1) $CH_3CH_2OH + Na$	(2) (CH ₃) ₂ CHBr
B)	(1) (CH ₃) ₂ CHOH + Na	(2) CH_3CH_2Br
C)	(1) (CH ₃) ₂ CHOH + Na	$(2) CH_3 CH_2 OH$
D)	$(1) CH_3 CH_2 OH + Na$	(2) (CH ₃) ₂ CHOH
A.	А	
B.	В	

- B.
- C. С
- D. D

20. In the solvolysis of *t*-butyl chloride, a minor product is 2-methylpropene, which results from the:

(CH₃)₃CC1 + H_2O $(CH_3)_3COH + (CH_3)_2C=CH_2$

major

minor

E2 mechanism with OH⁻ acting as the base. A.

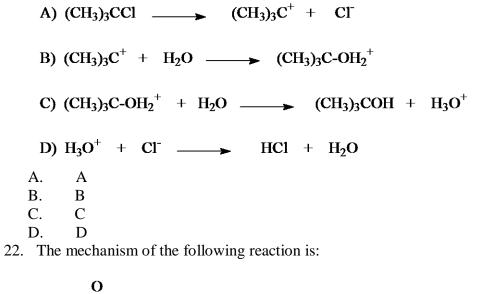
Β. E2 mechanism with H₂O acting as the base.

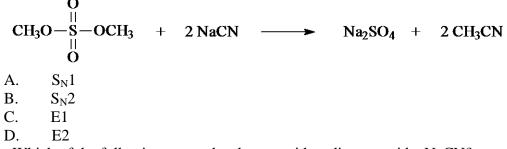
E1 mechanism with OH⁻ acting as the base. C.

E1 mechanism with H₂O acting as the base. D.

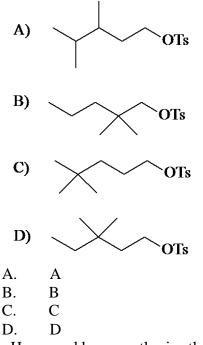
21. What is the rate limiting step in the following reaction?

 $(CH_3)_3CC1 + H_2O$ $(CH_3)_3COH + HC$





23. Which of the following reacts the slowest with sodium cyanide, NaCN?

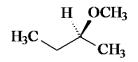


24. How would you synthesize the following compound starting with optically pure (R) or (S)-2-butanol?

H_{3C}	
A) (1) (R)-2-butanol + TsCl B) (1) (S)-2-butanol + TsCl	

(2) NaCN/DMSO
(2) NaCN/DMSO

- A. A
- B. B
- C. C
- D. D
- 25. Starting with optically pure (R) or (S)-2-butanol which method below would give the best yield of the following ether?



A) (1) (R)-2-butanol + TsCl	(2) CH ₃ ONa
B) (1) (S)-2-butanol + TsCl	(2) CH ₃ ONa
C) (1) (R)-2-butanol + Na	(2) CH ₃ I
D) (1) (S)-2-butanol + Na	(2) CH ₃ I

- A. A
- B. B
- C. C
- D. D

26. Which of the following conditions favor the S_N1 mechanism as opposed to the S_N2 mechanism?

- I. tertiary alkyl halide
- II. primary alkyl halide
- III. polar solvent
- A. only I
- B. only II
- C. I and III
- D. II and III

27. The species shown below represents the transition state for the:

$$\begin{array}{c} CH_2CH_3 \\ \downarrow \\ HO \cdots C \cdots Br \\ \delta & \uparrow \Lambda & \delta \\ H & H \end{array}$$

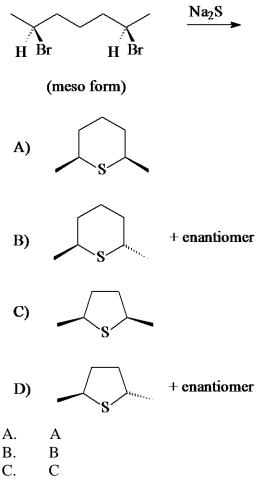
- A. reaction of 1-propanol with HBr.
- B. reaction of 1-bromopropane with OH⁻.
- C. elimination of HBr from 1-bromopropane.
- D. addition of HBr to propene with peroxides.

28. The species shown below represents the transition state for the:

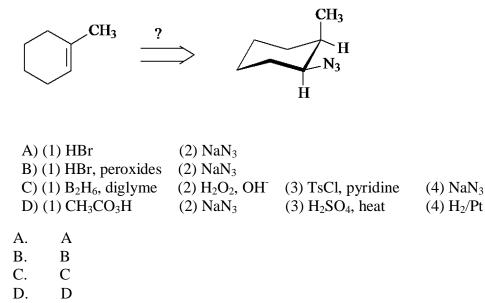
$$\begin{array}{c} CH_2CH_3 \\ | \\ H_2O \cdots C \cdots Br \\ \delta^+ & \lambda & \delta^- \\ H & H \end{array}$$

- A. reaction of 1-propanol with HBr.
- B. reaction of 1-bromopropane with OH⁻.

- C. addition of HOBr to 1-propene.
- D. addition of HBr to propene with peroxides.
- 29. Which of the following is the double substitution product of the reaction below?



- D. D
- 30. Starting with 1-methylcyclohexene, which of the following reaction sequences is the best synthesis of the azide shown below?

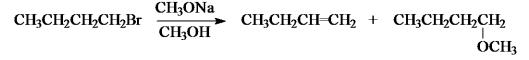


31. Rank the following in decreasing order of leaving group ability.

$H_{3}C - \left\langle \begin{array}{c} & O \\ & \parallel \\ & - \\ & - \\ & - \\ & - \\ & 0 \\ & O \\$	O CH₃CO⁻	Cl	ΌΗ
Ι	П	Ш	IV
A. $I > III > IV > II$			

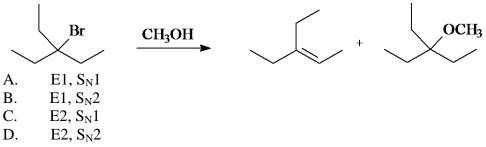
- $C. \qquad III > II > I > IV$
- D. II > I > III > IV

32. Identify the mechanistic pathways, respectively, for the products in the following reaction.

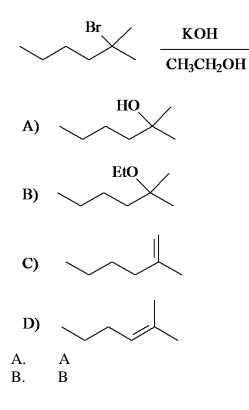


- A. E1, S_N1
- B. E1, S_N2
- C. E2, S_N1
- D. E2, S_N2

33. Identify the mechanistic pathways, respectively, for the products in the following reaction.



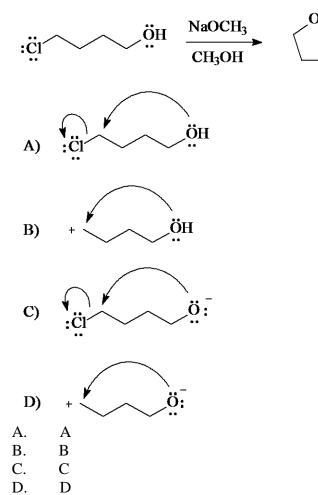
34. What is the major product in the following reaction?



C. C

D. D

35. Which of the following mechanistic steps is the most likely route for the formation of the cyclic ether shown?



36. In which of the solvents below would the reaction shown take place at the fastest rate?

$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}Br + NaCN \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CN + NaBr$

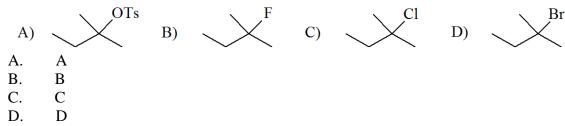
- A. ethanol
- B. acetic acid
- C. dimethyl sulfoxide
- D. water
- 37. Consider the reaction of each of the following with 1-bromopentane. Which one would have the highest elimination/substitution ratio?
 - A. NaOCH₂CH₃, ethanol, 55° C
 - B. NaSH, ethanol-water, 25°C
 - C. KOC(CH₃)₃, (CH₃)₃COH, 55^oC
 - D. KCN, DMSO, 40°C

38. Which one of the following correctly depicts the reaction below?

$$H \xrightarrow{CH_3} H \xrightarrow{NaSCH_3} ethanol-water$$

<u>Mechanism</u> A) S _N 1	<u>Rate Law</u> rate = k [(S)-2-bromobutane]	Steriochemistry not stereospecific, but more inversion than retention of configuration
B) S _N 1	rate = k [(S)-2-bromobutane][NaSCH ₃]	stereospecific, retention of configuration
C) S _N 2	rate = k [(S)-2-bromobutane]	not stereospecific, but more inversion than retention of configuration
D) S _N 2	rate = k [(S)-2-bromobutane][NaSCH ₃]	stereospecific, inversion of configuration
A. A B. B C. C D. D		J

39. Which of the following undergoes S_N1 solvolysis in ethanol/water at the fastest rate?



40. The major product of the following reaction is an alcohol. Which of the following best describes this reaction?

Br H₃C CH_2CH_3 H_2O , acetone CH₂CH₂CH₃

- A. $S_N 2$ with inversion of configuration
- B. $S_N 2$ with racemization
- C. $S_N 1$ with inversion of configuration
- D. $S_N 1$ with racemization

ACS Review Nucleophilic Substitution $_{\underline{KEY}}$

1. D 2. C 3. B 4. A 5. B 6. A 7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
3. B 4. A 5. B 6. A 7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
4. A 5. B 6. A 7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
5. B 6. A 7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
 6. A 7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
7. B 8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
8. B 9. C 10. B 11. B 12. D 13. A 14. C 15. A
9. C 10. B 11. B 12. D 13. A 14. C 15. A
10. в 11. в 12. d 13. а 14. с 15. а
11. в 12. d 13. а 14. с 15. а
12. d 13. a 14. c 15. a
13. a 14. c 15. a
14. с 15. а
15. A
16 -
16. D
17. с
18. с
19. в
20. d
21. А
22. в
23. в
24. А
25. d
26. с
27. в
28. a
29. a
30. с
31. в
32. d
33. a
34. d
35. C
36. C
37. с
38. D
39. A
40. D