Worksheet

Alkyl Halides, Nucleophilic substitution, Elimination

(Advanced Level)

Designed by

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Chemistry Affinity

Conceptual, Real World, Happy Learning

1. Chloroethane, C_2H_5Cl, does not react with methanol under mild conditions. What reagent could be added to the reaction mixture to increase the rate of substitution.?

A) HCl (conc.)
B) NaOH
C) NH_4OH
D) $AgNO_3$

2. Compound X reacts with HI. The product of this reaction, when treated with KOH in ethanol, gives Y (an isomer of X). Ozonolysis of Y (H_2O_2 workup) produces two compounds: a two carbon carboxylic acid, and a four carbon ketone. What is X?

A) 2-methyl-2-pentene
B) 4-methyl-1-pentene
C) 2,3-dimethyl-2-butene
D) 3-methyl-1-pentene

3. The S_N2 reaction of 1-chloro-3-methylbutane with sodium methoxide is relatively slow, but can be accelerated by the addition of a small amount of NaI. How is this catalysis best explained?

A) The sodium cation helps pull off the chloride anion
B) The iodide anion activates the methoxide nucleophile
C) S_N2 reaction of iodide ion converts the alkyl chloride to the more reactive alkyl iodide
D) The NaI changes the mechanism to S_N1

4. Synthesis of hexane-3,4-diol from *trans*-3-hexene may be accomplished in two ways:
(i) OsO_4 hydroxylation & (ii) $C_6H_5CO_3H$ epoxidation followed by NaOH opening of the epoxide ring.
Which of the following statements about the products from these reactions is correct?

A) the two methods give the same product
B) (i) gives a chiral isomer, (ii) gives an achiral isomer
C) (i) gives an achiral isomer, (ii) gives a chiral isomer
D) two different isomers are formed, but both are chiral

5. Reaction of 1,4-dibromobutane with Mg turnings in ether gives the bis-Grignard reagent, $BrMgCH_2CH_2CH_2CH_2MgBr$. What is the product from the reaction of meso-2,3-dibromobutane with Mg under the same conditions?

A) *trans*-2-butene
B) *cis*-2-butene
C) meso-$CH_3CH(MgBr)CH(MgBr)CH_3$
D) racemic-$CH_3CH(MgBr)CH(MgBr)CH_3$

6. In the S_N2 reaction of cyanide ion with $(CH_3)_2CHCH_2CH_2X$ what is the relative order of reactivity for the following X substituents?

I. X = F II. X = Cl III. X = Br IV. X = I

A) I > II > III > IV
B) IV> III > II > I
C) III > I > II > IV
D) II > III > IV > I

7. How is the following reaction best classified?

$(CH_3)_3CBr + (CH_3CH_2)_3N \text{ -----> } (CH_3)_2C{=}CH_2 + (CH_3CH_2)_3NH^{(+)}\ Br^{(-)}$

A) S_N2 substitution
B) E1 elimination
C) electrophilic addition
D) cationic rearrangement

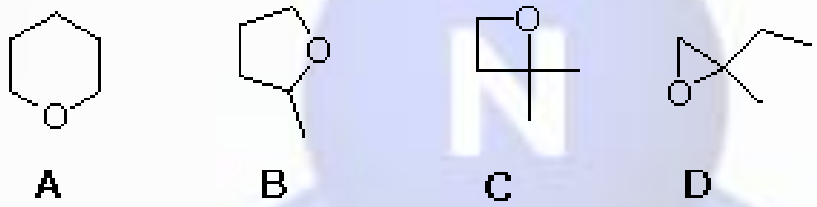
8. Which of the following isomeric chlorides will undergo S_N2 substitution most readily?

A) 4-chloro-1-butene
B) 1-chloro-1-butene (cis or trans)
C) 1-chloro-2-butene (cis or trans)
D) 2-chloro-1-butene

9. Which reagent would be best for achieving an E2 elimination of 3-chloropentane?

A) C_2H_5ONa
B) CH_3CO_2Na
C) $NaHCO_3$
D) NaI

10. A chiral $C_5H_{10}O$ ether reacts with hot HI to give a $C_5H_{10}I_2$ product Treatment of this with hot KOH in ethanol produces 1,3-pentadiene. What is the structure of the original ether?



11. A $C_7H_{13}Br$ compound reacts with KOH in ethanol to form 3-methylcyclohexene as the major product. What is a likely structure for the starting alkyl bromide?

A) *cis*-4-methylcyclohexyl bromide
B) *trans*-3-methylcyclohexyl bromide
C) *cis*-2-methylcyclohexyl bromide
D) *trans*-2-methylcyclohexyl bromide

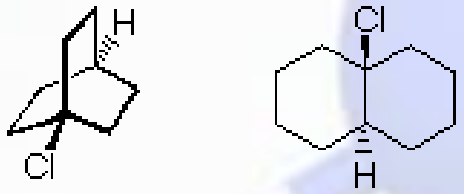
12. A synthesis of 2,5-dimethyl-2-hexanol from 2-methylpropene requires the formation of two four-carbon intermediates, X and Y. These intermediates combine to give the desired product after the usual hydrolysis work-up. Select appropriate methods of preparing X and Y from 2-methylpropene

A) X add HBr, then react with Mg in ether Y add water, acid-catalysis
B) X add HBr (peroxides), then react with Mg in ether Y react with $C_6H_5CO_3H$ in CH_2Cl_2
C) X add HOBr Y add B_2H_6in ether, then NaOH
D) X add HOBr Y add HBr (peroxides) ,then react with Mg in ether

13. All of the following alkyl bromides react by S_N2 substitution when treated with sodium cyanide in methanol.
Which one does not undergo an inversion of configuration?

A) (R)-1-bromo-2-methylbutane
B) (S)-2-bromo-3-methylbutane
C) (R)-1-bromo-3,3-dimethylcyclohexane
D) *cis*-4-ethyl-1-bromocyclohexane

14. The structures of two 3°-bicyclic chlorides (I and II) are shown below



I

II

Which of the following statements is correct?
A) on treatment with KOH in ethanol, both compounds undergo E2 elimination.
B) on treatment with KOH in ethanol, I undergoes substitution and II undergoes elimination.
C) I is more reactive than II for both substitution and elimination
D) II is more reactive than I for both substitution and elimination

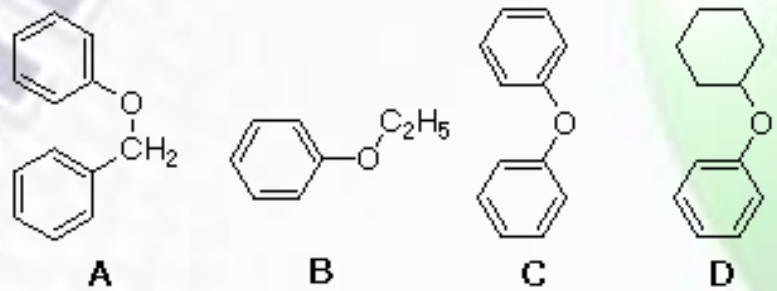
15. A $C_6H_{12}O$ compound does not react with Br_2 in CCl_4, produces a flammable gas on treatment with $LiAlH_4$, and reacts with H_2CrO_4 changing the color from orange to green Which of the following compounds best agrees with these facts?

A) 1-methylcyclopentanol
B) methoxycyclopentane
C) 2-cyclopropyl-2-propanol
D) 2-cyclobutylethanol

16. What reagents and conditions are used for the Simmons-Smith reaction?

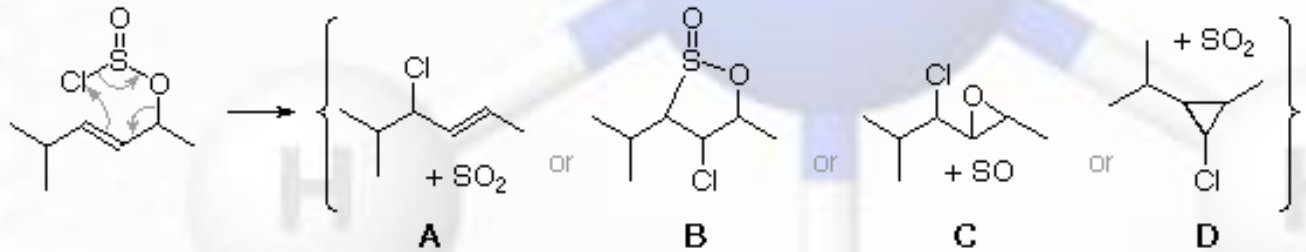
A) CH_3I + Mg in ether
B) CH_2I_2 + Zn (Cu) in ether
C) $BrCH_2CH_2Br$ + Zn in ether
D) CBr_4 + Zn (Cu) in ether

17. Which of the following ethers is unlikely to be cleaved by hot conc. HBr?



A B C D

18. Which of the following is the most likely product from the reaction illustrated by the curved arrows in the formula on the left?



A B C D

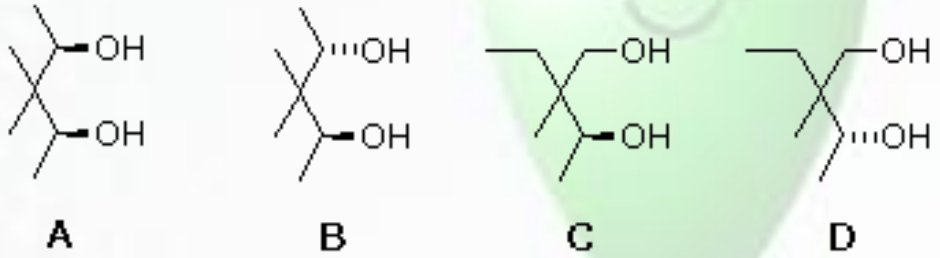
19. Reaction of 1,1-dibromopentane with three equivalents of $NaNH_2$ in ether is followed by treatment with 0.1M HCl at 0° C.
What is the product?

A) cyclopentene.
B) 1,2-pentadiene.
C) 2-pentyne.
D) 1-pentyne.

20. What is the product from the acid catalyzed addition of methanol to 2,2-diethyloxirane?

A) 3,3-dimethoxypentane
B) 2-ethyl-1-methoxy-1-butanol
C) 2-ethyl-1-methoxy-2-butanol
D) 2-ethyl-2-methoxy-1-butanol

21. A chiral $C_7H_{16}O_2$ diol is oxidized by PCC in CH_2Cl_2 to an achiral $C_7H_{12}O_2$ compound. Which of the following would satisfy these facts?



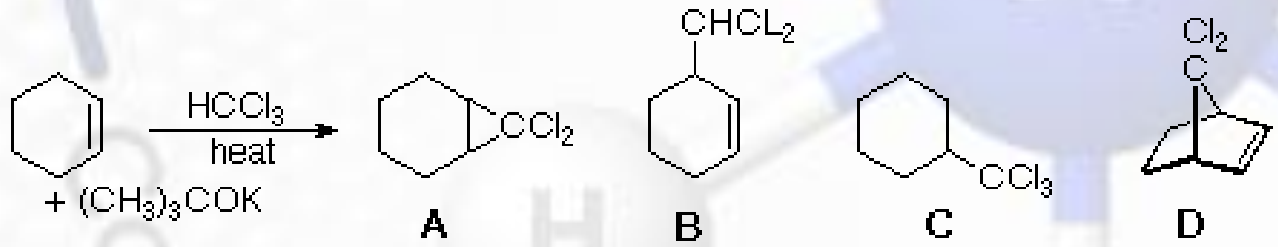
22. Which of the following organic halides will undergo an E2 elimination on heating with KOH in alcohol?

A) 2,2-dimethyl-1-bromopropane
B) 2,2-dimethyl-1-bromocyclohexane
C) benzyl chloride ($C_6H_5CH_2Cl$)
D) 2,5-dimethyl-1-bromobenzene

23. Reaction of (R)-2-chloro-4-methylpentane with excess NaI in acetone gives racemic 2-iodo-4-methylpentane
How can this be explained?

A) the reaction mechanism changes to S_N1
B) the reaction proceeds via a rapidly inverting radical intermediate
C) the substitution is S_N2, but repeated attack by iodide anion (with inversion) leads to racemization
D) iodide anion preferentially attacks chlorine, giving a rapidly inverting carbanion intermediate

24. What is the chief product from the following reaction?



25. Consider the S_N1 solvolysis of the following 1°-alkyl chlorides in aqueous ethanol.

I $CH_3CH_2CH_2Cl$ II $CH_2=CHCH_2Cl$ III CH_3OCH_2Cl IV $CF_3CF_2CH_2Cl$

What is the order of decreasing reactivity?

A) III > II > I > IV
B) II > I > III > IV
C) IV > III > II > I
D) I > II > III > IV

26. In the S_N2 reaction of iodide ion with $(CH_3)_2CHCH_2CH_2X$ what is the order of decreasing reactivity for the following X substituents?

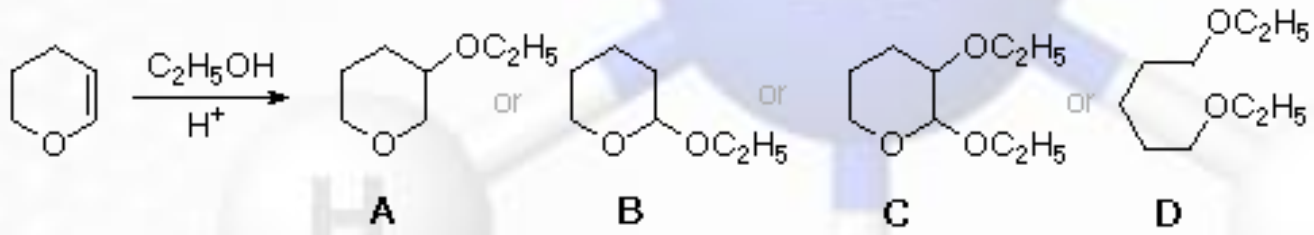
I. X = -OH II. X = CH_3CO_2- III. X = CF_3SO_3- IV. X = CCl_3CO_2-

A) I > II > III > IV
B) IV > III > II > I
C) III > II > IV > I
D) III > IV > II > I

27. Which of the following reaction sequences would best serve to convert 2-methyl-1-bromopropane to 4-methyl-1-iodopentane?

A) (i) Mg in ether; .(ii) ethylene oxide (C_2H_4O); (iii) HI & heat
B) (i) NaC≡CH in ether; .(ii) H_2 + Lindlar catalyst; (iii) HI
C) (i) KOH in alcohol; . (ii) $C_6H_5CO_3H$ in CH_2Cl_2; (iii) NaC≡CH in ether ; (iv) 2 H_2 + Pt catalyst
D) (i) NaC≡CH in ether; .(ii) H_3O^+ + $HgSO_4$; (iii) HI & heat

28. Which of the following is the product from ethanol addition to dihydropyran (shown on the left below)?



29. What product(s) are expected from the following reaction?

A) $2CH_3CH_2I$, (B) $2ICH_2CH_2OH$, (C) $2ICH_2CH_2I$, (D)$CH_3CH_2I + CH_3CH_2OH$

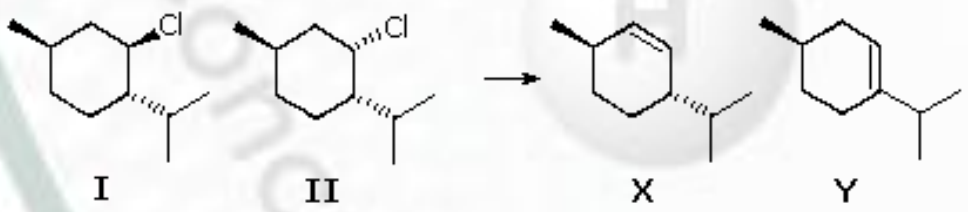
30. Which of the following reagents and conditions would best serve to convert 1-butyne to 1-bromo-1-butene?

A) 1 equivalent of HBr, no peroxides.
B) 1 equivalent of HBr, with peroxides.
C) 1 equivalent of Br_2, followed by 1 equivalent of KOH.
D) 2 equivalents of HBr, followed by 1 equivalent of KOH

31. A chiral $C_5H_{10}O$ alcohol is reduced by catalytic hydrogenation to an achiral $C_5H_{12}O$ alcohol. The original alcohol is oxidized by activated MnO_2 to an achiral carbonyl compound (C_5H_8O). Which of the following might be the chiral alcohol?

A) 1-penten-3-ol
B) 4-penten-2-ol
C) 3-methyl-2-buten-1-ol
D) 2-methyl-2-buten-1-ol

32. Stereoisomers I and II undergo E2 elimination on treatment with sodium ethoxide in ethanol. One isomer reacts 500 times faster than the other. Also, one isomer gives X as the only product, whereas the other gives Y together with some X. Which of the following statements provides the best assignment of I and II?



A) II reacts faster and gives both Y & X
B) II reacts faster and gives only X
C) I reacts faster and gives both Y & X
D) I reacts faster and gives only X

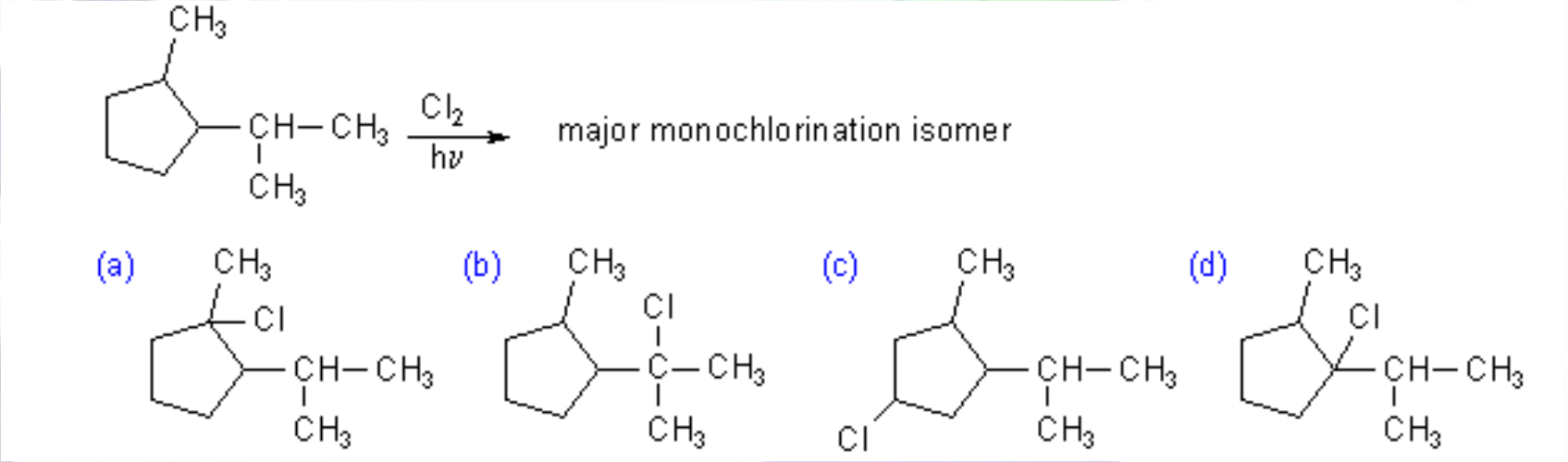
33. A water soluble $C_6H_{14}O_2$ compound is oxidized by lead tetraacetate (or periodic acid) to a single C_3H_6O carbonyl compound. Which of the following would satisfy this fact?

A) meso-2,3-dimethoxybutane
B) 1,2-diethoxyethane
C) meso-2,5-hexanediol
D) meso-3,4-hexanediol

34. If the rate of reaction of [0.1 M] sodium cyanide with [0.1M] 1 bromoethane is 1.4×10^{-4}, what effect will an increase in NaCN concentration to [0.3] and alkyl bromide concentration to [0.2] have on the overall reaction rate?

A) increase by 2 times
B) increase by 3 times
C) iincrease by 6 times
D) increase by 1.5 times

35. Which of the these compounds represents the major monochlorination isomer formed in the following reaction?



36. How many <u>dichlorinated</u> isomers can be formed by the halogenation of $CH_3CH_2CH_2CH_3$ with Cl_2 in the presence of light?

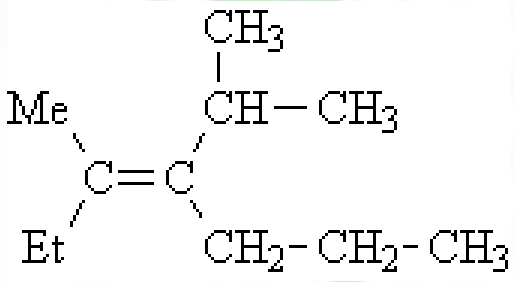
(A), 2, (B) 3, © 5, (D) 6

37. Which of the following compounds would have the highest boiling point?

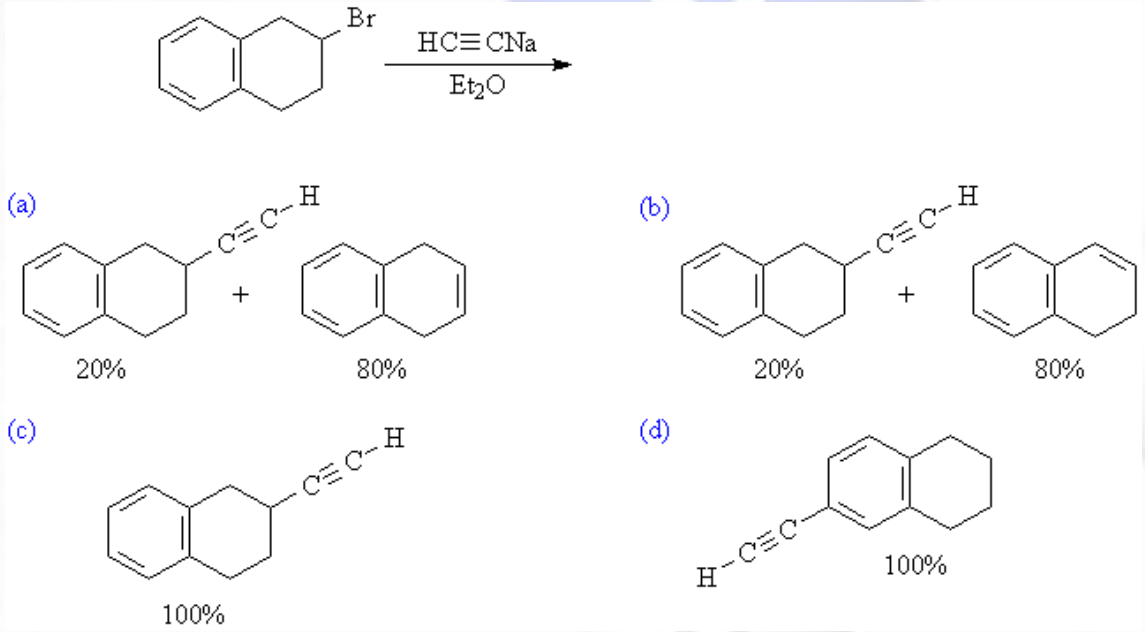
(A) $CH_3CH_2CH_2CH_3$, (B) CH_3NH_2, © CH_3OH, (D) CH_2F_2

38. The best nomenclature for the following compound is

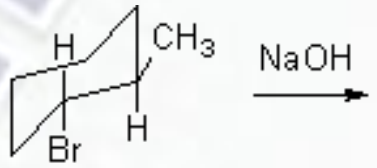
(A) cis, (B) trans, © E, (D) Z



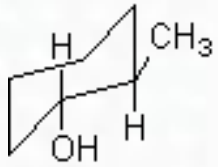
39. What are the products obtained from the following reaction?



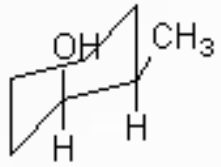
40. The E2 product of the following reaction will be _?_ and the S_N2 product will be _?_.



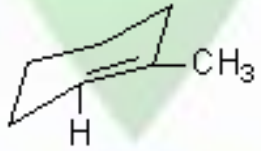
NaOH



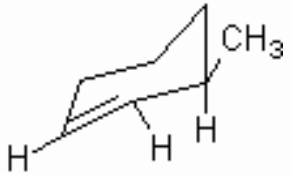
A



B



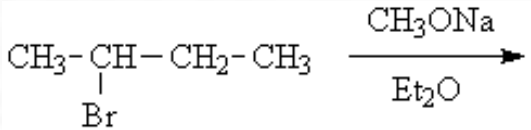
C



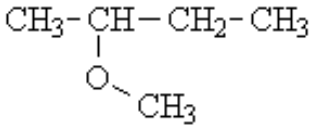
D

(A) C and A, (B) D and A© C and B, (D) D and B

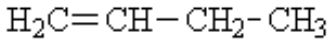
41. What is the major product obtained from the following reaction?



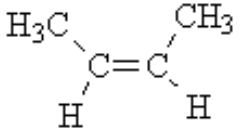
(a)



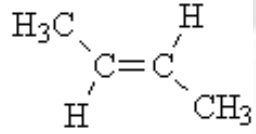
(b)



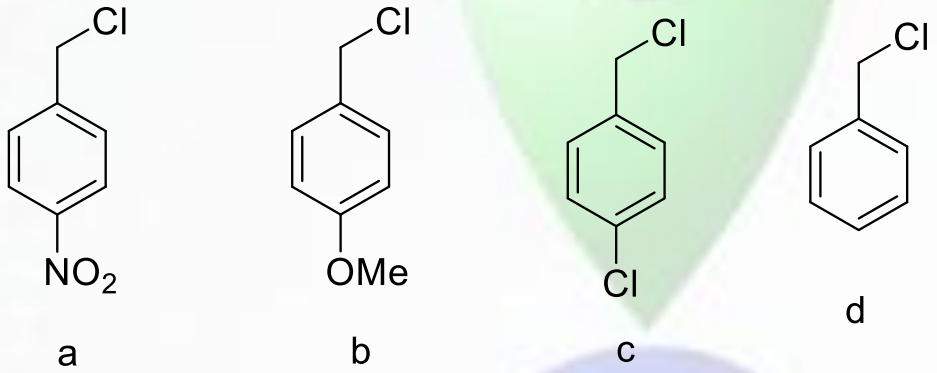
(c)



(d)



42. Write down the decreasing order towards SN1 reaction for the following compounds.



a b c d

43. Assertion A : Hydrolysis of an alkyl chloride is a slow reaction but in the presence of NaI, the rate of the hydrolysis increases.

Reason R : I^- is a good nucleophile as well as a good leaving group.
In the light of the above statements, choose the correct answer from the options given below

1. **A is true, R is false**
2. **A is false bur R is true**
3. **Both A and R are true but R is the correct explanation of A**
4. **Both A and R are true but R is not the correct explanation of A**

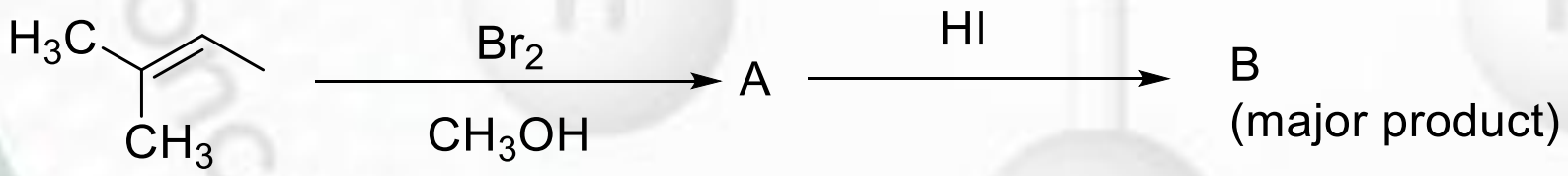
44. Among the following which has the highest boiling point.

a. CH3CH2CH2CH2Br,
b. (CH3)3CBr,
c. (CH3)2CHCH2Br.
d. (CH3)CH2CH(CH3)Br

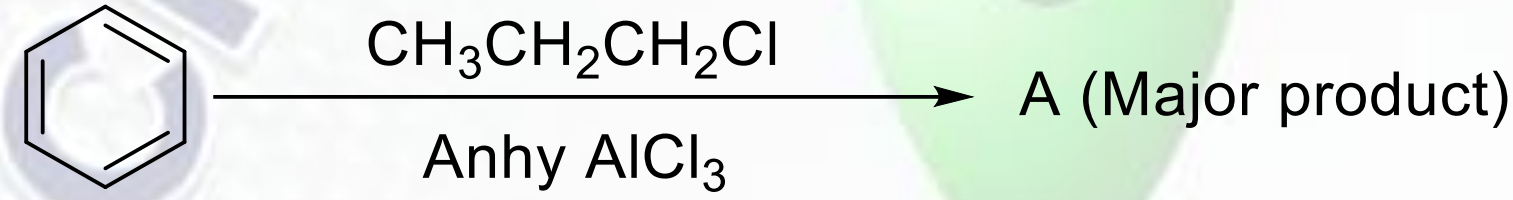
45. What should be the correct IUPAC name for diethylbromomethane?

i. 1-Bromo-1,1-diethylmethane
ii. 3-Bromopentane
iii. 1-Bromo-1-ethylpropane
iv. 1-Bromopentane

46. Write down A and B

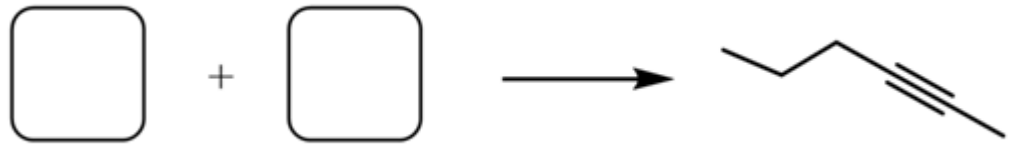


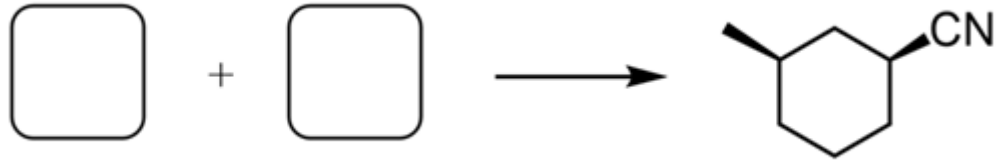
47. Write down major product with proper explanation

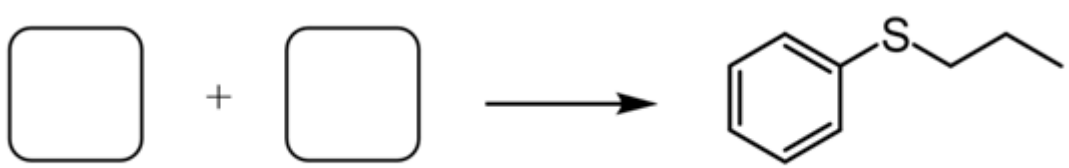


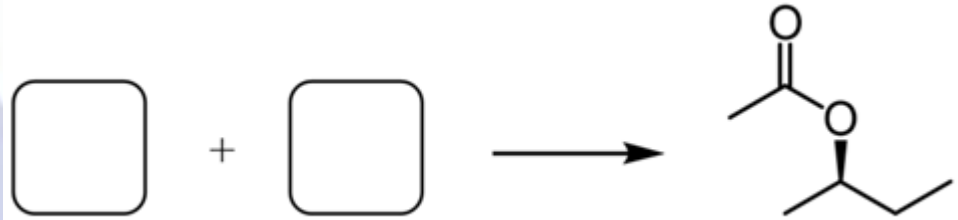
48. Write down intermediate and the product

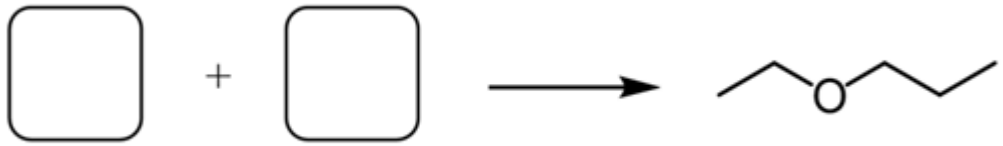
49. Identify the alkyl halide and the nucleophile that would lead to each product.

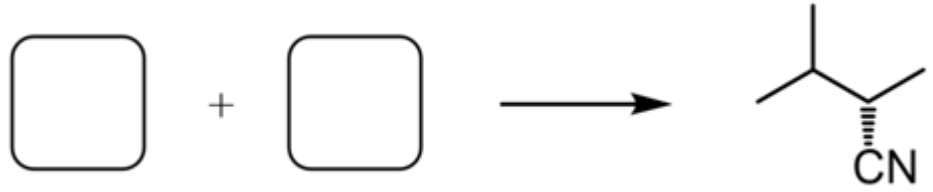
1. 

2. 

3. 

4. 

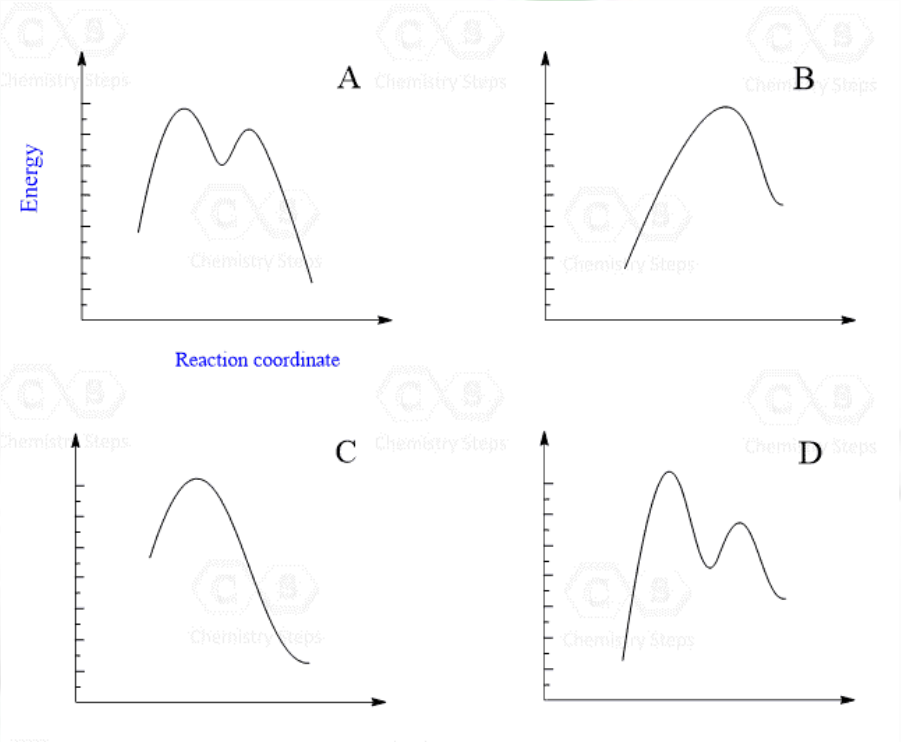
5. 

6. 

Question is taken from : https://www.chemistrysteps.com/sn2-mechanism-practice-problems/

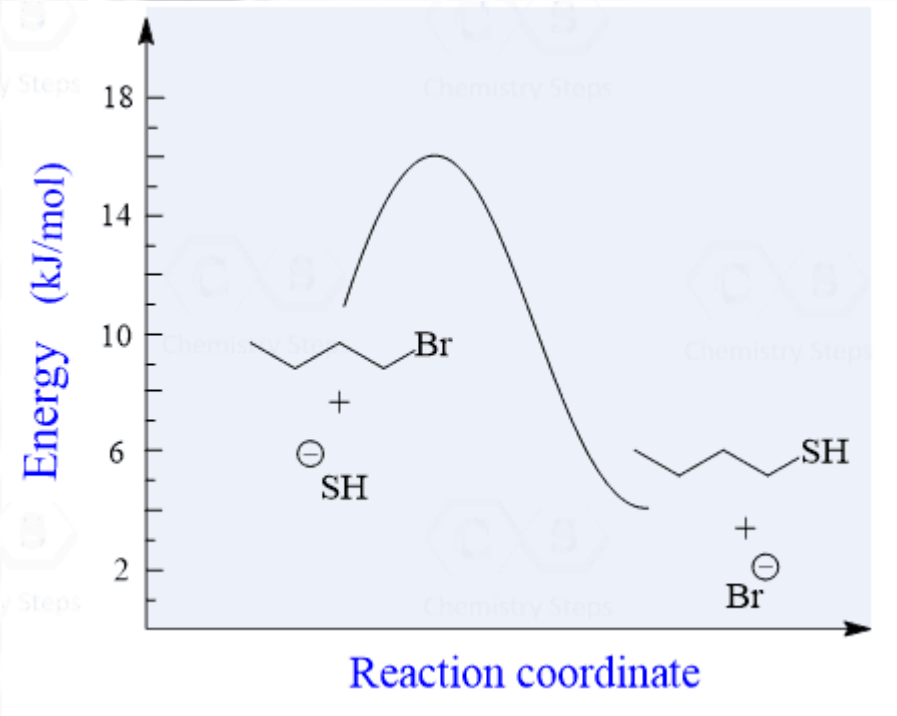
50. Draw the energy diagram for the below reaction

51. Which of the following energy diagrams represents an exothermic S_N2 reaction?



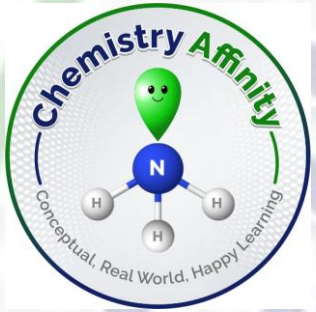
Question is taken from : https://www.chemistrysteps.com/sn2-mechanism-practice-problems/

52. Consider the SN2 reaction between 1-Bromobutane and the cyanide ion. Energy diagram of the reaction is given in below with the *hypothetical* values. Based on the energy diagram answer the following questions.



a) Label the reactants and products
b) label the substrate and the nucleophile
c) Label the transition state
d) Label the Activation energy E_a, and ΔH°
e) Is the reaction endothermic or exothermic?
f) How many kJ/mol is the E_a, and ΔH°?
g) Is the reaction mechanism S_N1 or S_N2?
h) What is the rate equation of the reaction?
i) What is the overall order of the reaction?

Question is taken from : https://www.chemistrysteps.com/sn2-mechanism-practice-problems/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All the best