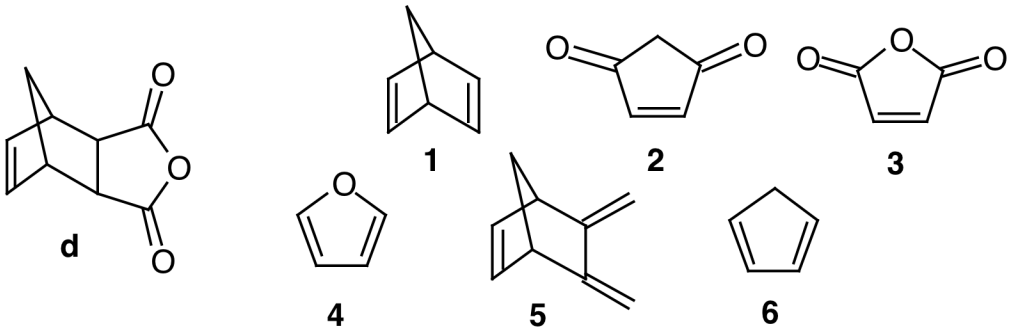
"Grade or Education" = 1

CHEM 2261/01
Summer 11
Exam 3
Chapters 7-9

1. Pick the choice which correctly indicates the structure of the diene and dienophile which could be used to prepare the compound with the structure labelled d.



__ A. The compounds with structures 3 and 5 could be used to prepare compound d.

__ B. The compounds with structures 3 and 6 could be used to prepare compound d.

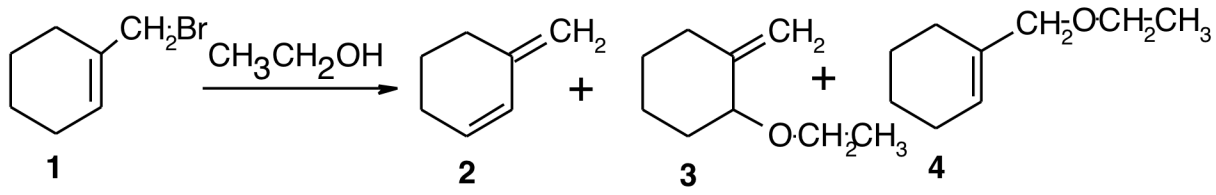
__ C. The compounds with structures 2 and 4 could be used to prepare compound d.

__ D. The compounds with structures 1 and 3 could be used to prepare compound d.

__ E. The compounds with structures 4 and 6 could be used to prepare compound d.

Rationale:
Chapter 7 Problem 75d

2. When the compound with structure 1 shown below undergoes solvolysis in ethanol, three products are obtained. These products have structures 2, 3, and 4, shown below. Figure out the mechanism which accounts for the formation of these products and pick the CORRECT statement regarding this mechanism from the multiple choices.



1 **2** **3** **4**

__ A. If a base pulls off a H from the southernmost carbon of structure 1 a carbanion is formed on this carbon; this carbanion is delocalized, with some negative charge located on the northeasternmost carbon in the six-membered ring; the lone pair of electrons carrying the negative charge can attack the carbon bearing the Br atom from the backside, forming a pi bond between the northeastern six-membered-ring carbon and the non-ring carbon, and breaking the C-Br bond; this process forms structure 2.

__ B. Structure 3 is generated when the initially-formed primary carbocation rearranges to a more stable secondary carbocation via a 1,2 shift of a pi bond; this secondary carbocation reacts with ethanol to form structure 3.

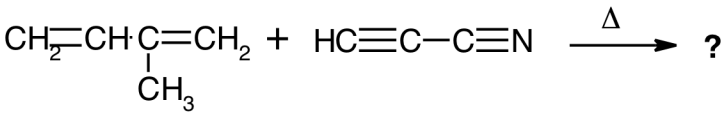
__ C. $CH_3CH_2O^-$ is formed from CH_3CH_2OH; this acts as a nucleophile, attacking the backside of the carbon bearing the Br in structure 1, and substituting OCH_2CH_3 for Br in an S_N2 reaction, generating structure 4.

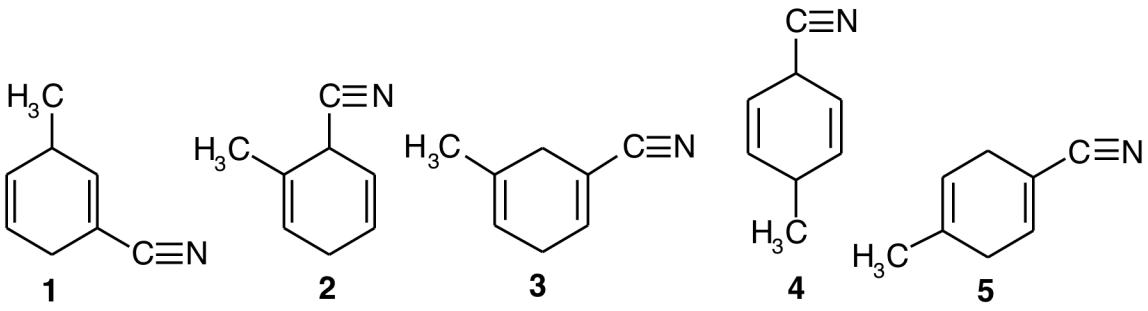
__ D. A 1,4 addition of HBr to structure 2 generates structure 1; structure 2 is formed from structure 1 by the reverse process.

__ E. When the Br leaves structure 1 it forms a delocalized carbocation with some positive charge located on the southeasternmost carbon of the six-membered ring; if a base then pulls off a hydrogen atom from the southernmost carbon atom of the ring the electron pair which was the C-H bond becomes a C-C pi bond generating structure 2.

Rationale:
Chapter 9 Problem 46

3. Find both products of the Diels-Alder reaction shown below.





__ A. This reaction yields products having structures 1 and 4.

__ B. This reaction yields products having structures 2 and 4.

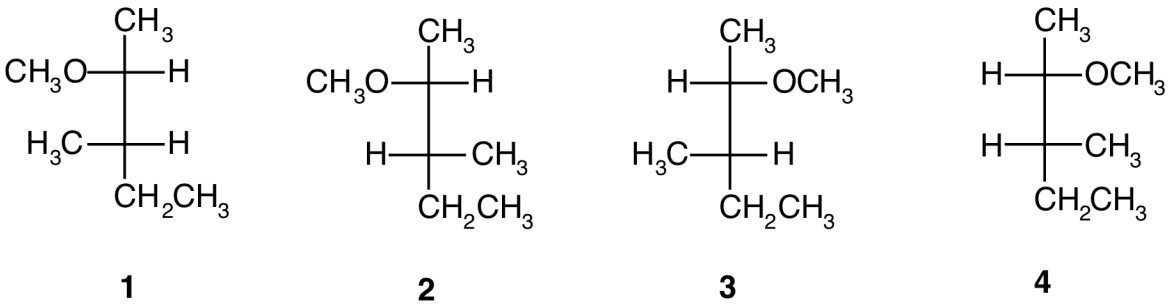
__ C. This reaction yields products having structures 1 and 4.

__ D. This reaction yields products having structures 1 and 2.

__ E. This reaction yields products having structures 3 and 5.

Rationale:
Chapter 7 Problem 36b

4. Find the substitution product(s) of the reaction of (2R,3R)-2-chloro-3-methylpentane + high concentration of CH_3O^- from among the numbered structures shown below. Choose the CORRECT statement from the multiple choices.



__ A. 2 is the sole product of this reaction.

__ B. 1 is the sole product of this reaction.

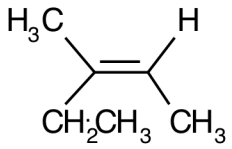
__ C. 3 is the sole product of this reaction.

__ D. 2 and 4 are both products of this reaction.

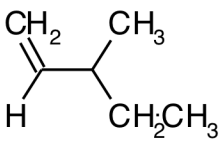
__ E. 4 is the sole product of this reaction.

Rationale:
Chapter 8 Problem 52d

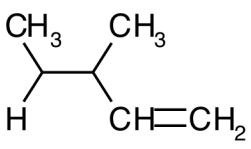
5. Find the elimination product(s) of (2R,3R)-2-chloro-3-methylpentane + high concentration of CH_3O^- among the numbered structures below. Choose the CORRECT product(s) of this reaction.



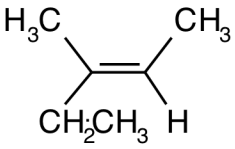
1



2



3



4

__ A. 4 is the product of this reaction.

__ B. 2 is the product of this reaction.

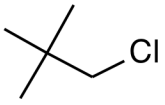
__ C. 1 is the product of this reaction.

__ D. 1 and 3 are both products of this reaction.

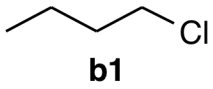
__ E. 3 is the product of this reaction.

Rationale:
Chapter 9 Problem 48d

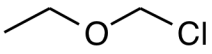
6. Use the numbered structures shown below to choose the CORRECT statement from the multiple choices.



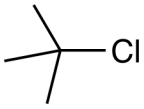
a



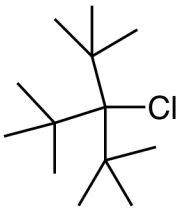
b1



b2



c1



c2

__ A. b2 will not react with HO^-.

__ B. c2 will react with H_2O faster than c1 will.

__ C. $(CH_3)_3CBr$ will react faster with CH_3CH_2OH than it will with H_2O.

__ D. b1 will react with HO^- faster than b2 will.

__ E. $(CH_3)_2CHS^-$ will react faster with a than CH_3S^- will.

Rationale:
Chapter 8 Problem 48

7. Choose the correct statement about nucleophilicity from the multiple choices.

__ A. Cl^- is a better nucleophile than Br^- in DMSO.

__ B. HO^- is a better nucleophile than $^-NH_2$ in H_2O.

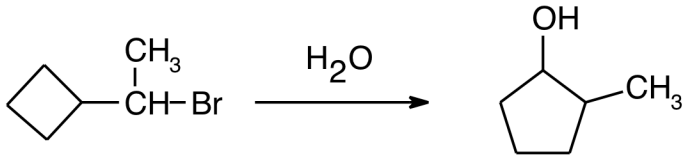
__ C. CH_3OH is a better nucleophile than CH_3O^- in DMSO.

__ D. Cl^- is a better nucleophile than Br^- in H_2O.

__ E. HO^- is a better nucleophile than $^-NH_2$ in DMSO.

Rationale:
Chapter 8 Problem 7

8. Work out the mechanism for the reaction shown below and pick the statement which is CORRECT about this mechanism from the multiple choices.



__ A. When the four-membered ring rearranges to form a five-membered ring a tertiary carbocation is formed.

__ B. In the first step of this mechanism a water molecule acting as a nucleophile replaces the bromine atom via an S_N2 reaction.

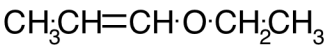
__ C. In one of the steps in this mechanism the methyl (CH_3) group undergoes a 1,2 shift converting a secondary carbocation into a more stable tertiary carbocation.

__ D. In one of the steps in this mechanism a secondary carbocation rearranges to form a more stable tertiary carbocation via a 1,2-hydride shift.

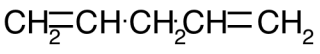
__ E. In one of the steps in this mechanism a lone pair of electrons on the oxygen atom of an H_2O molecule attacks a secondary carbocation on a five-membered ring, forming a carbon-oxygen bond.

Rationale:
Chapter 8 Problem 62a

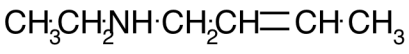
9. Which of the following compounds have delocalized electrons?



b

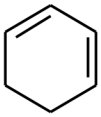


g



h

i



k

__ A. The compounds with structures g, g, i, and k have delocalized electrons.

__ B. None of the compounds shown have delocalized electrons.

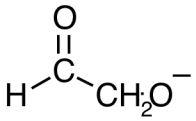
__ C. All of the compounds shown have delocalized electrons.

__ D. The compounds with structures h and i have delocalized electrons.

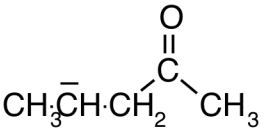
__ E. The compounds with structures b and k have delocalized electrons.

Rationale:
Chapter 7 Problem 41(b,g,h,i,k)

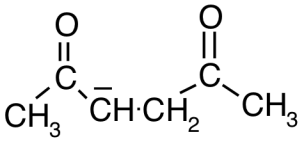
10. By referring to the labelled structures below pick the choice which is CORRECT.



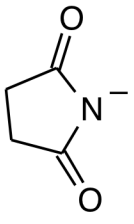
a1



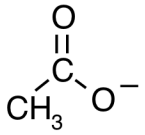
b1



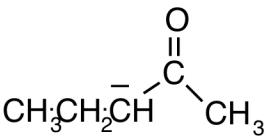
c1



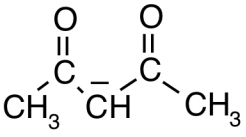
d1



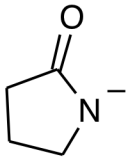
a2



b2



c2



d2

__ A. d2 is more stable than d1.

__ B. None of the other choices is correct.

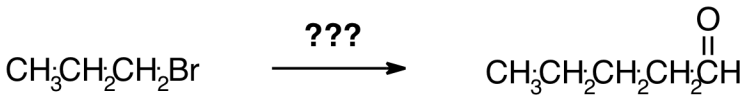
__ C. c1 is more stable than c2.

__ D. b1 is more stable than b2.

__ E. a1 is more stable than a2.

Rationale:
Chapter 7 Problem 58

11. Pick the choice which correctly describes how the synthesis implied in the figure below could be carried out.



__ A. First react the bromide with $CH_3CO_2^-$. Next react the product of this reaction with H_2SO_4, $HgSO_4$, and H_2O.

__ B. First react the bromide with $CH_3CO_2^-$. Next react the product of this reaction with: 1. BH_3/THF, then 2. HO^-, H_2O_2, H_2O.

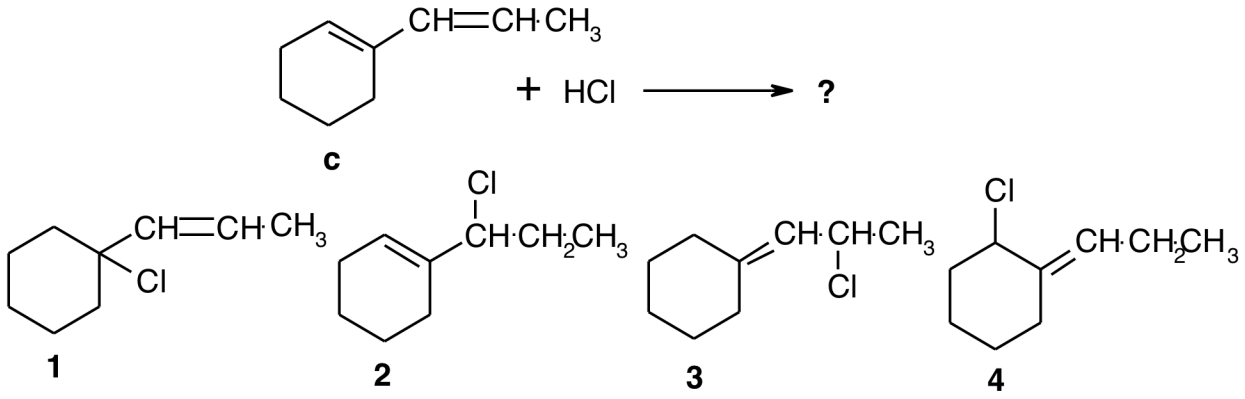
__ C. First react the bromide with $HC{\equiv}C^-$. Next react the product of this reaction with H_2 and Lindlar catalyst. Finally react the product of this reaction with RCO_3H.

__ D. First react the bromide with $HC{\equiv}C^-$. Next react the product of this reaction with H_2SO_4, $HgSO_4$, and H_2O.

__ E. First react the bromide with $HC{\equiv}C^-$. Next react the product of this reaction with: 1. BH_3/THF, then 2. HO^-, H_2O_2, H_2O.

Rationale:
Chapter 8 Problem 54c

12. Find the structure of the major 1,2-addition product, the major 1,4-addition product, the kinetic product, and the thermodynamic product resulting from the reaction of the compound with structure c shown below with one equivalent of HCl



__ A. The 1,2-addition reaction yields the thermodynamic product with structure 2 and the 1,4-addition reaction yields the kinetic product with structure 4.

__ B. The 1,2-addition reaction yields the kinetic product with structure 3 and the 1,4-addition reaction yields the thermodynamic product with structure 2.

__ C. The 1,2-addition reaction yields the kinetic product with structure 2 and the 1,4-addition reaction yields the thermodynamic product with structure 4.

__ D. The 1,2-addition reaction yields the kinetic product with structure 1 and the 1,4-addition reaction yields the thermodynamic product with structure 3.

__ E. The 1,2-addition reaction yields the thermodynamic product with structure 1 and the 1,4-addition reaction yields the kinetic product with structure 3.

Rationale:
Chapter 7 Problem 31c

13. Pick the statement which CORRECTLY indicates which compound in a pair will give a higher substitution-product to elimination-product ratio when it reacts with isopropyl bromide.

__ A. Ethoxide ion will give a higher substitution-to-elimination ratio than tert-butoxide ion.

__ B. None of the other choices is correct.

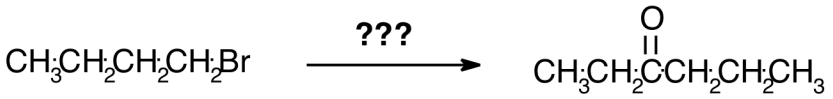
__ C. ^{-}OCN will give a higher substitution-to-elimination ratio than ^{-}SCN.

__ D. CH_3O^{-} will give a higher substitution-to-elimination ratio than CH_3S^{-}.

__ E. Cl^{-} will give a higher substitution-to-elimination ratio than Br^{-}.

Rationale:
Chapter 9 Problem 41

14. Select the choice which gives a CORRECT way to carry out the synthesis suggested by the figure below.



__ A. First treat the alkyl bromide with $C{\equiv}C^{-}$; finally react with: 1. BH_3/THF, followed by 2. HO^{-}, H_2O_2, H_2O.

__ B. First treat the alkyl bromide with tert-BuO^{-}; next treat the product of this reaction with Br_2; next react with excess $^{-}NH_2$ (3 equivalents), followed by CH_3CH_2Br; finally react with RCO_3H.

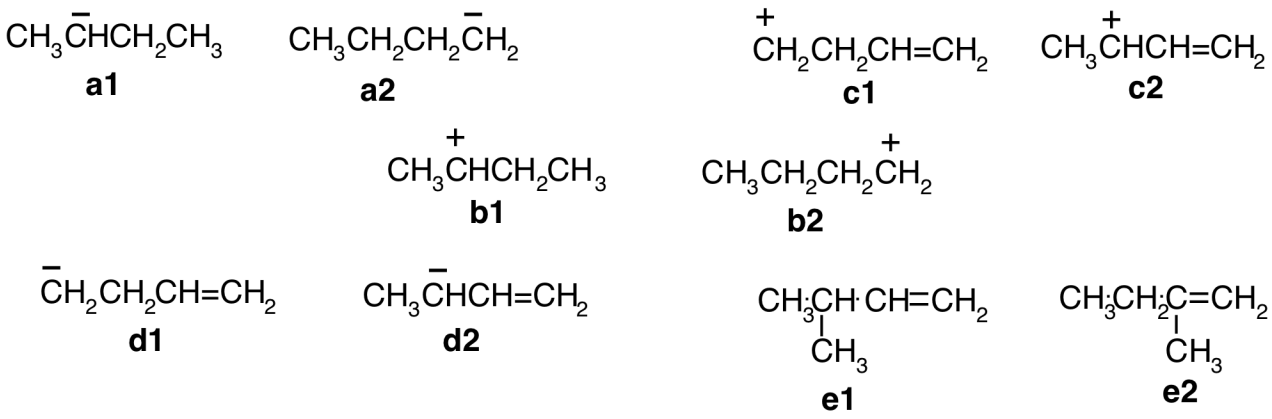
__ C. First treat the alkyl bromide with $C{\equiv}C^{-}$; finally react with H_2O, H_2SO_4, and $HgSO_4$.

__ D. First treat the alkyl bromide with tert-BuO^{-}; next treat the product of this reaction with Br_2; next react with excess $^{-}NH_2$ (3 equivalents), followed by CH_3CH_2Br; finally react with: 1. BH_3/THF, followed by 2. HO^{-}, H_2O_2, H_2O.

__ E. First treat the alkyl bromide with tert-BuO^{-}; next treat the product of this reaction with Br_2; next react with excess $^{-}NH_2$ (3 equivalents), followed by CH_3CH_2Br; finally react with H_2O and H_2SO_4.

Rationale:
Chapter 9 Problem 54a

15. Figure out which speciec in each of the pairs shown below is more stable. Pairs of structures share the same letter, like a1 and a2. Pick the CORRECT statement from the multiple choices.



__ A. e1 is more stable than e2.
__ B. d2 is more stable than d1.
__ C. a1 is more stable than a2.
__ D. b2 is more stable than b1.
__ E. c1 is more stable than c2.

Rationale:
Chapter 9 Problem 35(a,b,c,d,e)

Answer Key

"Grade or Education" = 1

CHEM 2261/01
Summer 11
Exam 3
Chapters 7-9

1. B
2. E
3. E
4. E
5. A
6. B
7. A
8. E
9. E
10. B
11. E
12. D
13. A
14. ERROR
15. B