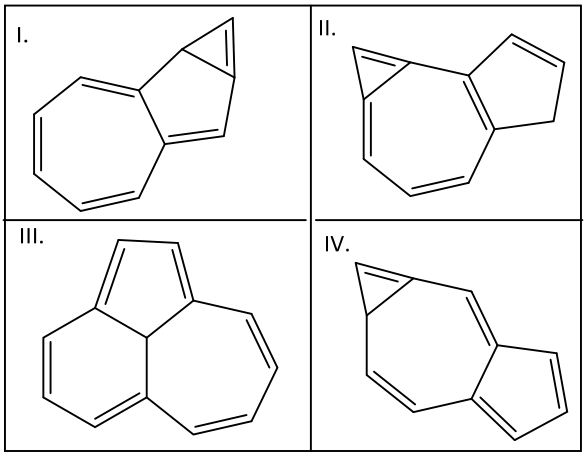
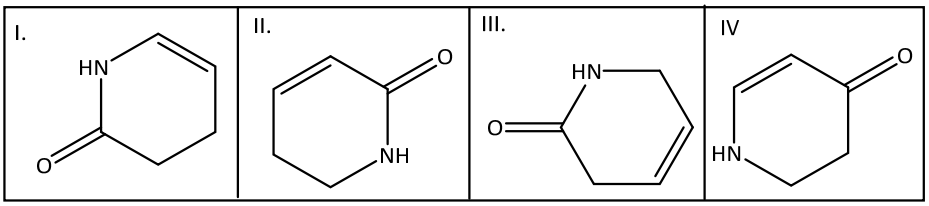
1. Which of the following compounds will give rise to an aromatic conjugate base? E



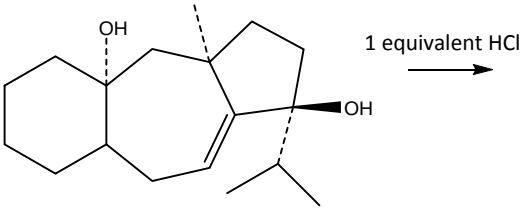
a) I only
b) II only
c) II & III
d) III & IV
e) I, II, III & IV

2. Rank the ***dienophiles*** below from most reactive to least reactive (most> least) in a Diels-Alder reaction. B

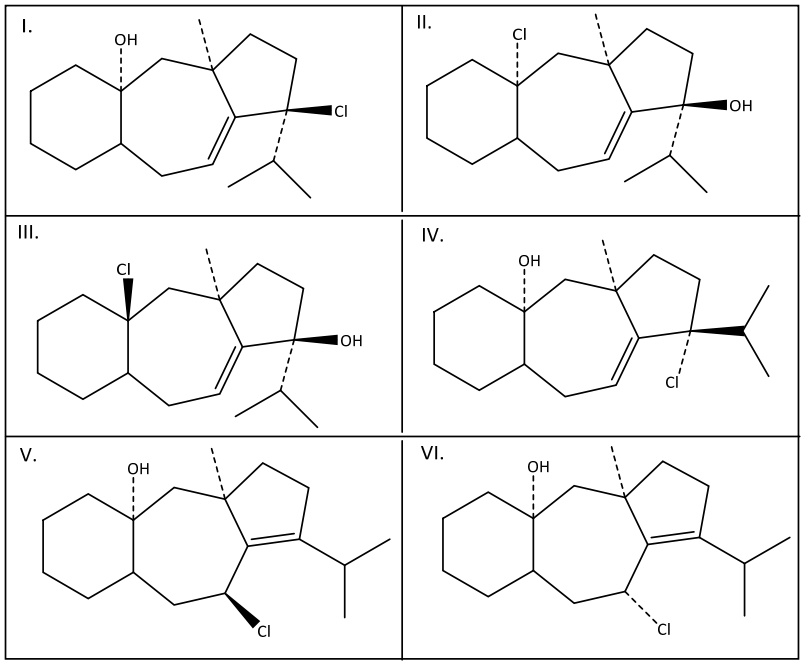


a) II = IV > I > III
b) II > IV > III > I
c) IV > II > I > III
d) I > III > IV > II
e) II > III > IV > I

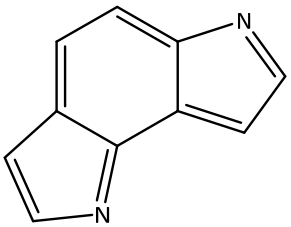
3. The major kinetic product(s) of the reaction below is (are): A



a) I & IV
b) II & III
c) V & VI
d) I, II, III & IV
e) I, II, III, IV, V & VI

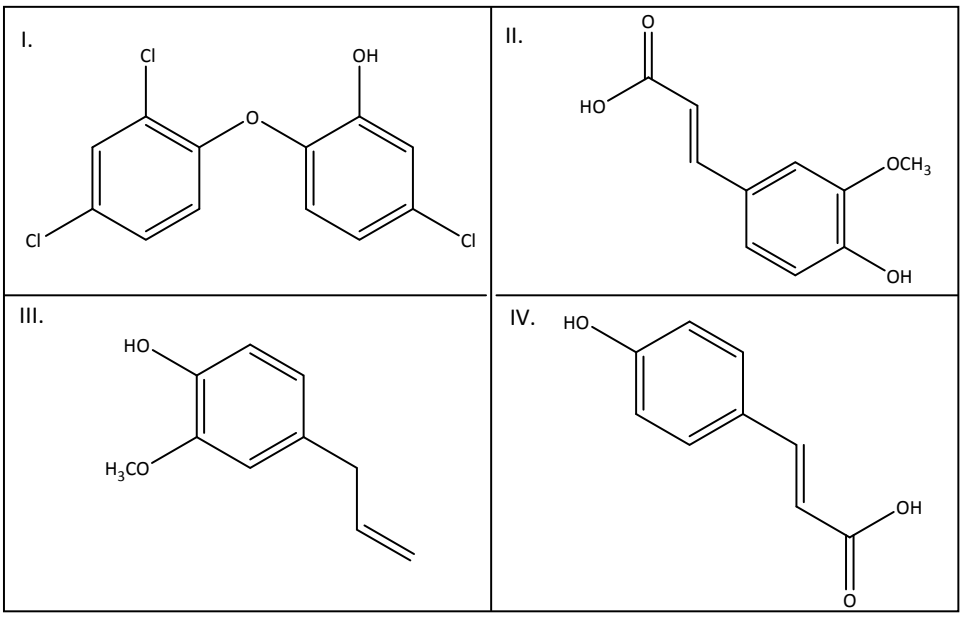


4. The number of π electrons in the ***aromatic system*** of the compound below is: E



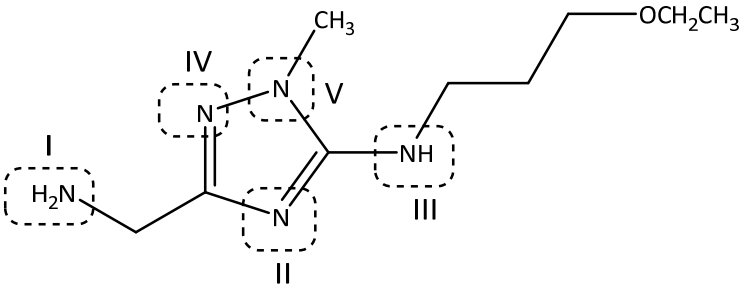
a) 6
b) 10
c) 12
d) 14
e) There is no aromatic system in this molecule

5. Rank the acidity of the phenols from most acidic to least acidic (most>least) in each of the compounds below. *Use sigma values to predict the ranking.* C



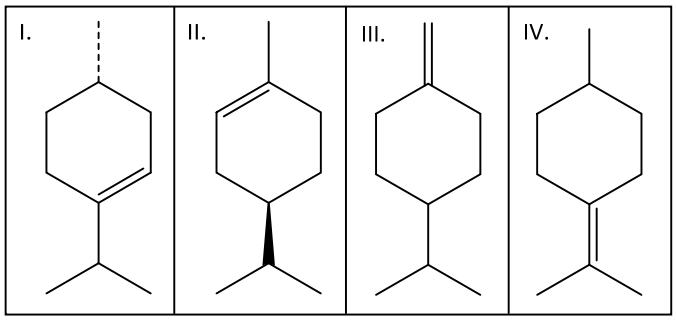
a) I > II > III > IV
b) IV > III > II > I
c) I > IV > II > III
d) I > II > IV > III
e) IV > II > I > III

6. Which nitrogen atom in the structure below has the highest pKb? C



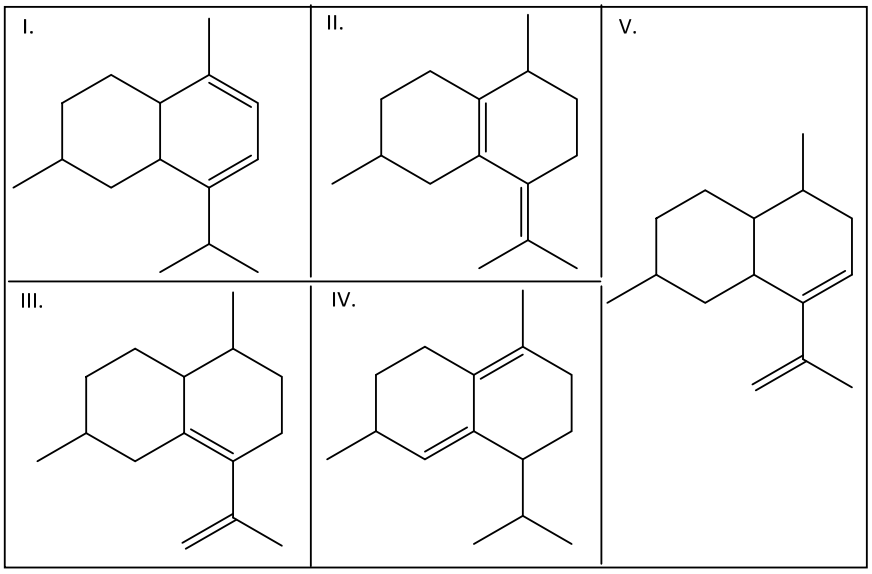
a) I
b) III
c) V
d) II & IV
e) I & III

7. Which of the following starting materials will provide *only one major product* upon reaction with 1. BH_3 2. H_2O_2, NaOH? E



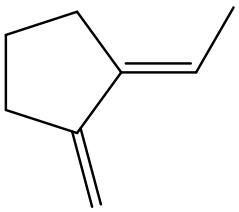
a) I
b) I & II
c) II
d) III & IV
e) III

8. A series of isomers of cadinene are shown below. Which of the isomers can serve as a diene in the Diels-Alder reaction? C



a) I & III
b) I, II & III
c) I, III & V
d) II & IV
e) I, II, III & IV

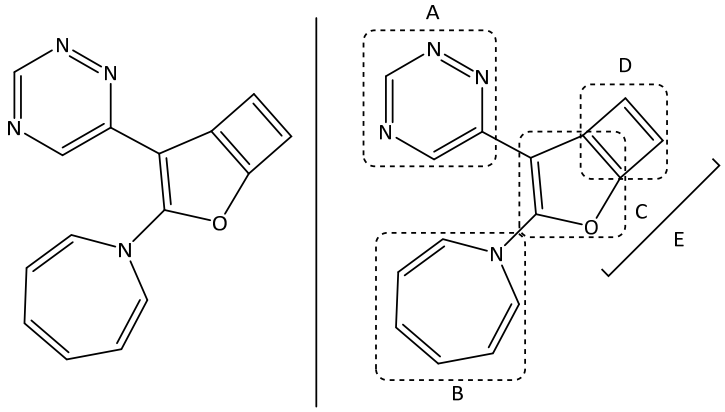
9. Which of the following statements is true as they relate to the compound below? D



I. The compound is a conjugated diene
II. The compound can serve as a dienophile in a Diels-Alder reaction
III. Treatment of this compound with one equivalent of H_3O^+ will provide two major kinetic products. Both kinetic products contain a disubstituted alkene.
IV. Treatment of this compound with one equivalent of H_3O^+ will provide two major thermodynamic products, one containing a primary alcohol and one containing a secondary alcohol. (Disregard stereochemistry when considering products)

a) I
b) I & II
c) I, II & III
d) I, II & IV
e) I, II, III & IV

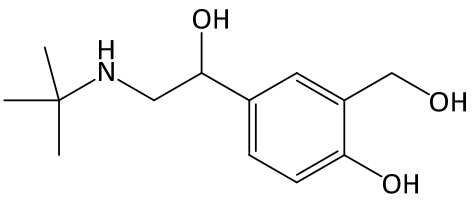
10. Five rings are highlighted in the molecule below and labeled as A, B, C, D and E (E is a combination of C and D). The structure on the left is provided without the highlighted boxes for clarity. Which of the following criteria for aromaticity (I, II, III, IV) is met for each ring system? B



CRITERIA FOR AROMATICITY
I. Cyclic
II. Planar
III. Continuous π system
IV. n = integer for Huckel Rule

a) A = I, II, III, IV ; B = I, II, III, IV; C = I, II, III, IV; D = I, II, III E = I, II, III
b) A = I, II, III, IV ; B = I, II, III; C = I, II, III, IV; D = I, II, III; E = I, II, III
c) A = I, II, III, IV ; B = I, II, III; C = I, II; D = I, II, III; E = I, II, III
d) A = I, II, III, IV ; B = I, II, III; C = I, II, III; D = I, II, III; E = I
e) A = I, II, III ; B = I, II, III; C = I, II, III, IV; D = I, II, III; E = I, II

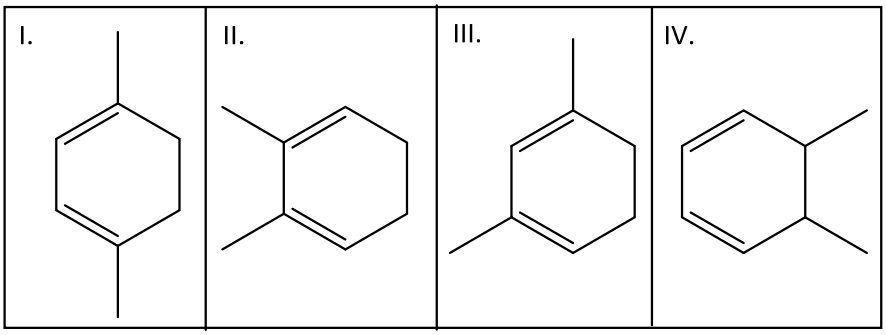
11. The structure of albuterol is given below. Albuterol contains one chiral center. Which set of the following reagents could be used to convert R- albuterol to *only* S albuterol? Assume an excess of reagent is available. E



I. 1. TsCl, pyr 2. H_3O^+
II. NaOH
III. 1. TsCl, pyr 2. NaOH
IV. 1. $SOCl_2$ 2. NaOH
V. 1. $POCl_3$, pyr 2. H_3O^+

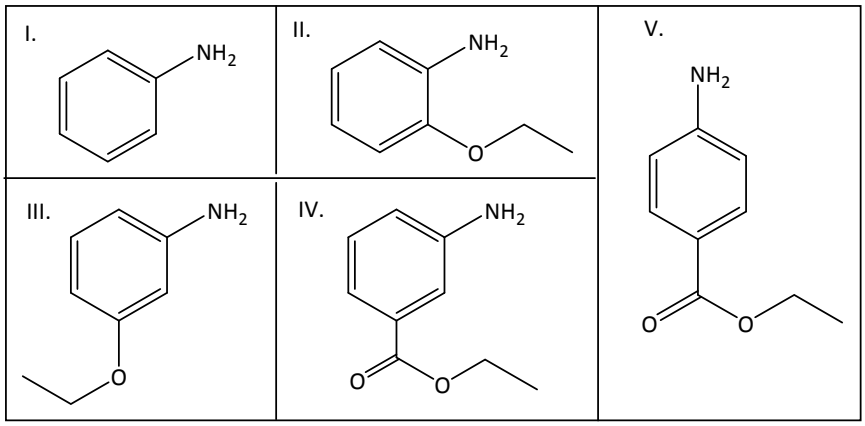
a) I only
b) II & III
c) II, III & IV
d) I & V
e) III only

12. Consider the reaction of each compound below with one equivalent of HBr. In which reaction is the major kinetic product(s) derived from *only* 1,2-addition and the major thermodynamic product(s) derived from *only* 1,4-additon? C



a) I only
b) I & II
c) II only
d) I, II, IV
e) II, III & IV

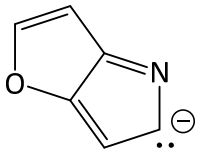
13. The pKa values for the conjugate acids of each of the substituted anilines are listed below. Match the pKa value (A, B, C etc..) to each structure. A

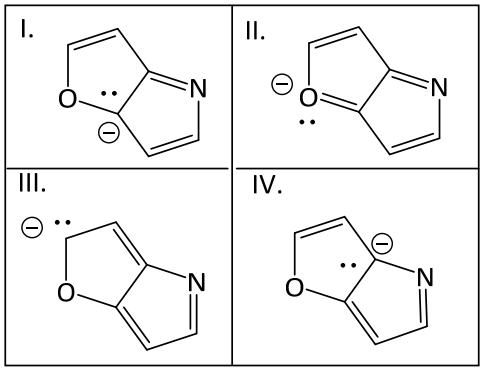


pKa Values
A =2.30
B = 3.56
C = 4.17
D = 4.64
E = 5.25

a) V = A; IV = B; III = C; I = D; II = E
b) V = A; IV = B; III = C; II = D; I= E
c) V = A; III = B; IV = C; I = D; II = E
d) IV = A; V = B; II = C; III = D; I = E
e) II = A; I = B; III= C; IV = D; V = E

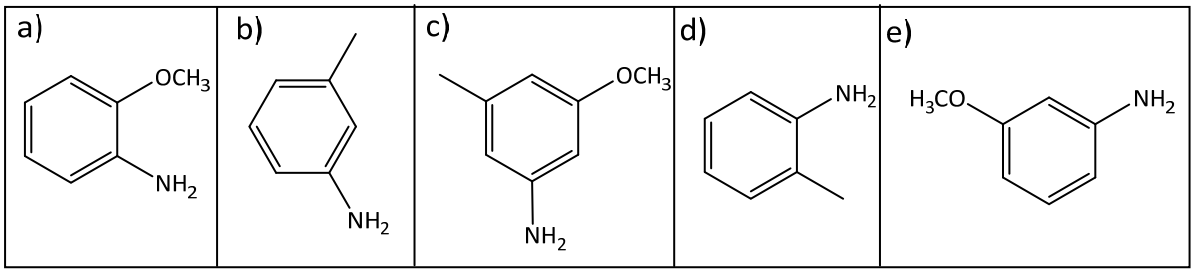
14. Which of the following structures represent resonance forms of the compound below? D



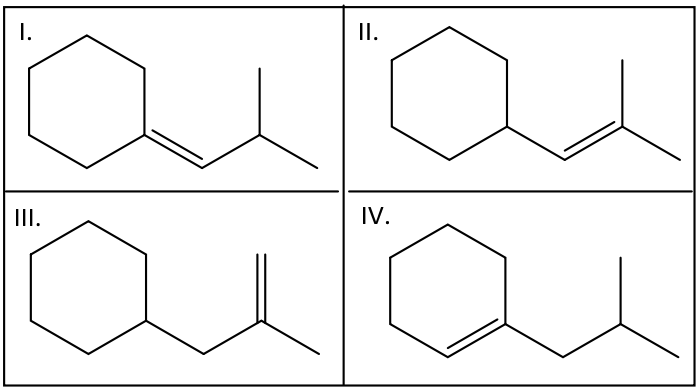


a) I, II, & III
b) I & III
c) II & IV
d) I, III & IV
e) IV

15. Which of the following structures represents m-aminoanisole? E



16. Which of the following starting materials will provide a mixture of enantiomers as major products upon reaction with 1. BH_3 2. H_2O_2, NaOH? A



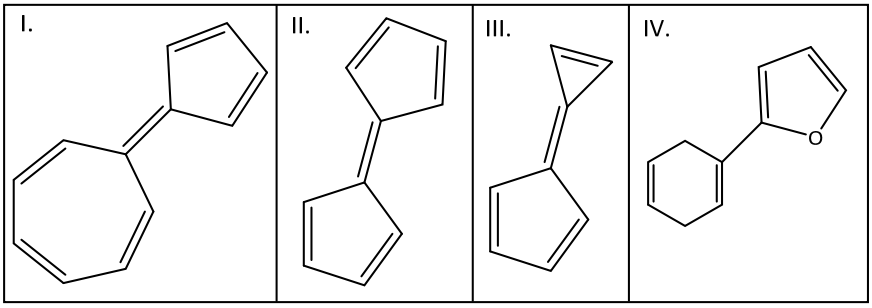
a) I, II, III & IV
b) I & II
c) III & IV
d) I, III & IV
e) IV only

17. Which of the following *starting materials* could be reacted with 1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$ to give 1-methyl-2-phenylcyclopentanol as *a major kinetic product* of the reaction? B

I. 3-methyl-4-phenylcyclopentene
II. 3-methyl-2-phenylcyclopentene
III. 2-methyl-3-phenylcyclopentene
IV. 1-methyl-2-phenylcyclopentene

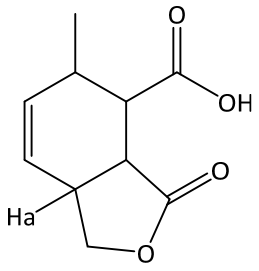
a) I only
b) III only
c) II only
d) III & IV
e) I, III & IV

18. Rank the relative rates of the reaction of each compound below with one equivalent of HCl from fastest to slowest (fastest>slowest). D



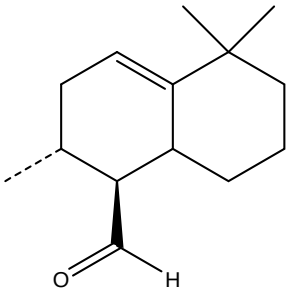
a) I > II > III > IV
b) IV > III > II > I
c) I > III > II > IV
d) I = III > II > IV
e) IV > I = III > II

19. In which chemical shift range would the protons labeled as Ha in the structure below appear in a proton NMR spectrum? B

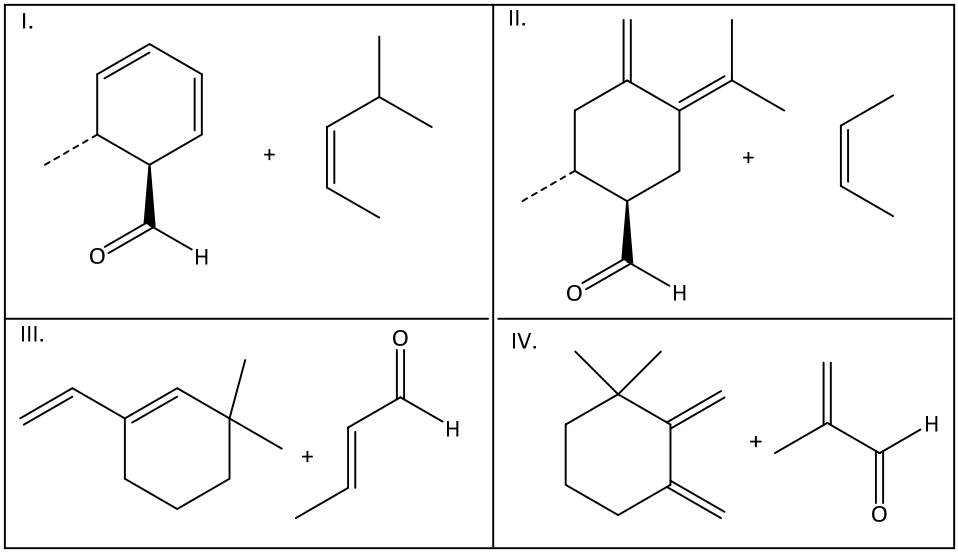


a) 0-1.5ppm
b) 1.5-2.5ppm
c) 2.5-4.5ppm
d) 4.5-6.5ppm
e) 6.5-8.5ppm

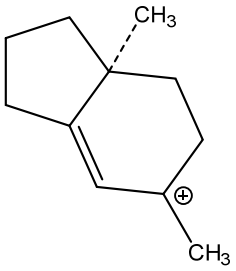
20. Which diene and which dienophile could be used to prepare the compound shown below in a Diels-Alder reaction? Credit for all answers



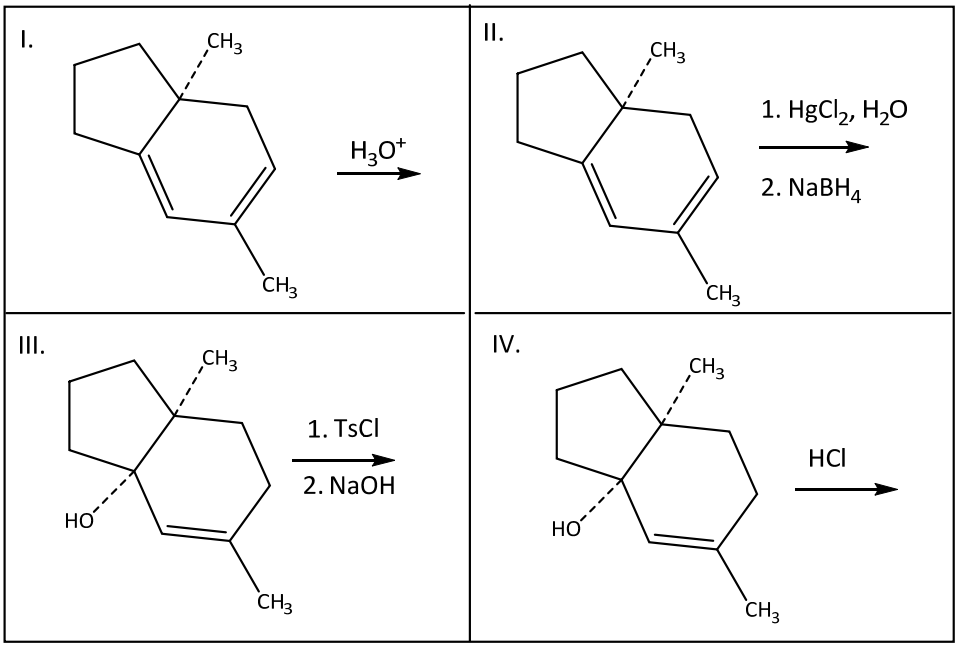
a) I only
b) II only
c) II & IV
d) III only
e) I & III



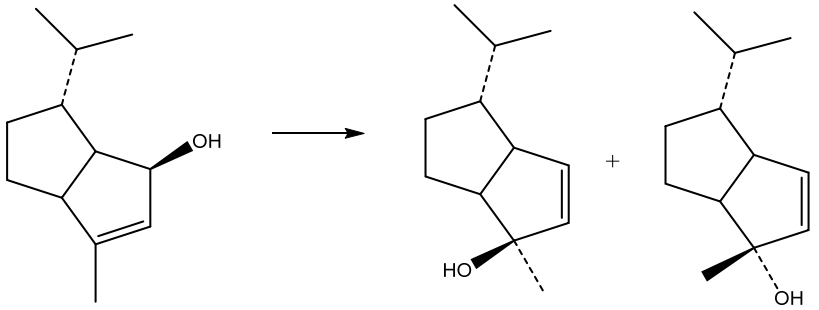
21. The reaction intermediate below can be generated in which of the following reactions? E



a) I & II
b) I, II & IV
c) II & III
d) I, II & III
e) I & IV

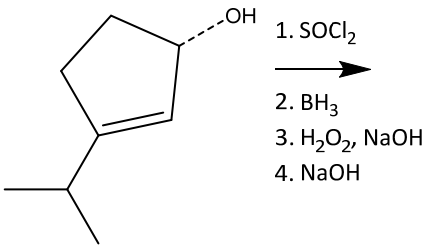


22. The mechanism of the reaction below is: A

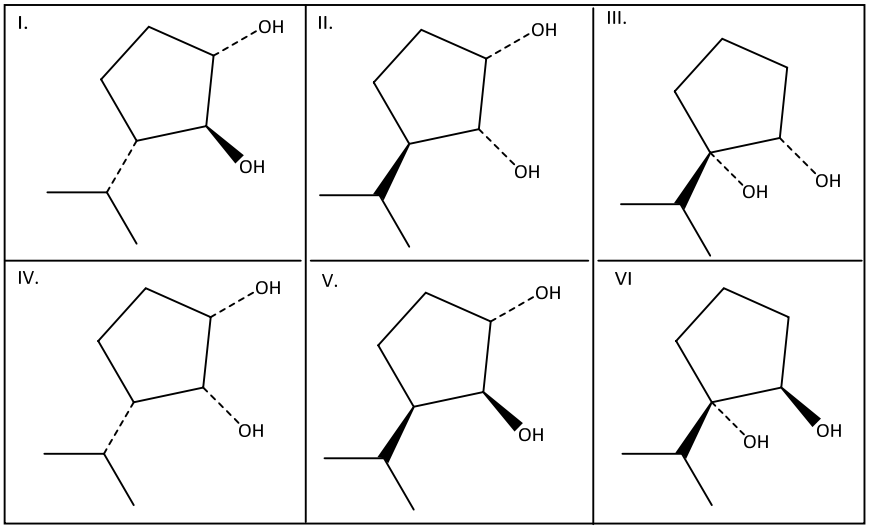


a) SN_1
b) SN_2
c) E_1
d) Electrophilic addition
e) None of these mechanisms

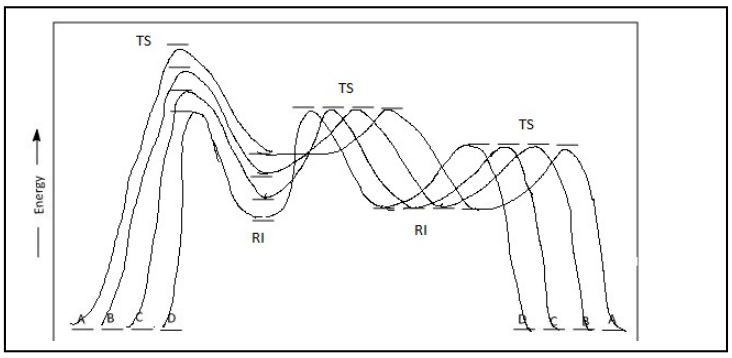
23. The major product(s) of the reaction below is (are): A

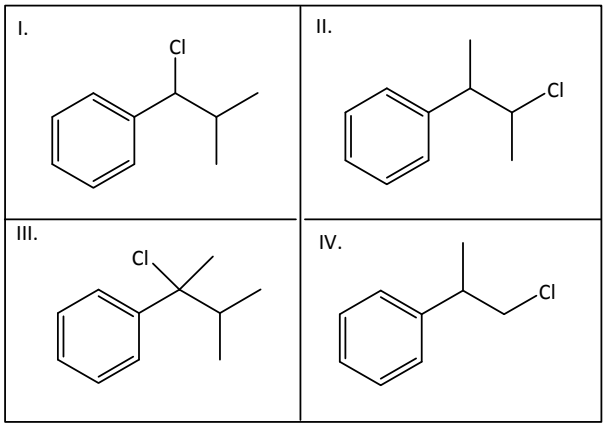


a) I & II
b) I & IV
c) IV & V
d) III & VI
e) I, II, IV & V



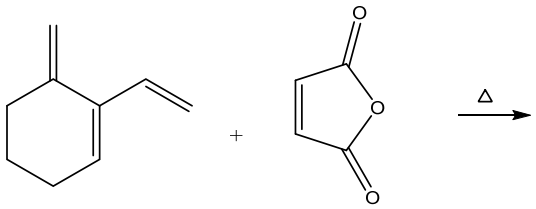
24. Assume each starting material (I, II, III, IV) is reacted with H_3O^+. Match each reaction pathway (A, B, C, D) in the reaction energy diagram below to each starting material. B



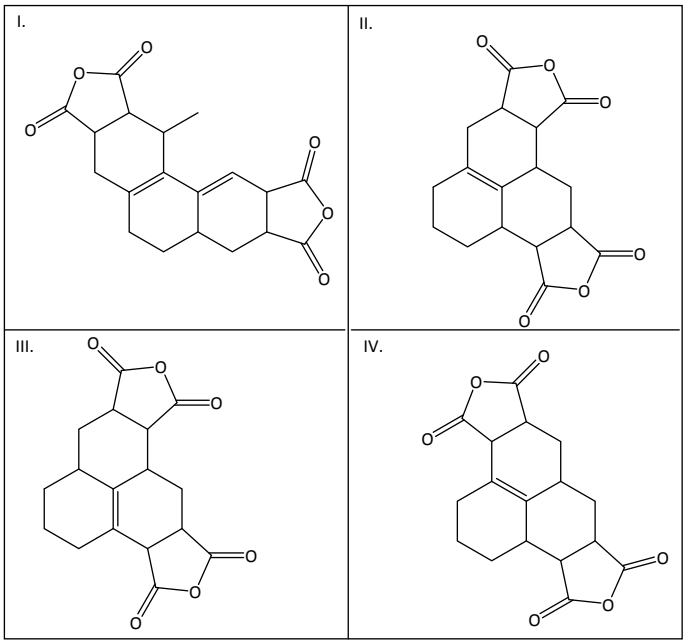


a) A = III B = I C = II D = IV
b) A = IV B = II C = I D = III
c) A = III B = II C = I D = IV
d) A = IV B = II C = III D = I
e) A = IV B = I C = II D = III

25. The triene below reacts with 2 equivalents of maleic anhydride. Which of the following structures represents the major product of this reaction? B



a) I
b) II
c) III
d) IV
e) None of these



Substituent	Abbreviation	σ meta	σpara
acetamido-	AcNH-	0.21	-0.02
acetoxy-	AcO-	0.39	-0.01
acetyl-	Ac-	0.38	0.50
alkenyl-	$-CH_2=CH_2$	0.05	-0.02
amino-	NH_2-	-0.16	-0.66
bromo-	Br-	0.39	0.23
tert-butyl-	$(CH_3)_3C$-	-0.10	-0.20
chloro-	Cl-	0.37	0.23
cyano-	NC-	0.56	0.66
ethoxy-	EtO-	0.10	-0.24
ethyl-	Et-	-0.07	-0.15
fluoro-	F-	0.34	0.06
hydrogen	H-	0.00	0.00
hydroxy-	HO-	0.12	-0.37
methoxy-	MeO-	0.12	-0.27
methyl-	Me-	-0.07	-0.17
nitro-	NO_2-	0.71	0.78
phenoxy-	PhO-	0.15	-0.21
phenyl-	Ph-	0.06	-0.01
trifluoromethyl	F_3C-	0.43	0.54
trimethylamino-	$(CH_3)_3N^+$-	0.88	0.82

Table 1: σ values for Various Substituents

Range	Kind of Proton
0-1.5 ppm	H atoms bonded to sp3 carbons where the sp3 carbons are only bonded to other sp3 carbons and hydrogen (alkanes)
1.5-2.5 ppm	H atoms bonded to sp3 carbons where the sp3 carbon is bonded to at least one sp2 carbon and no heteroatoms (allylic, benzylic,alpha-H)
2.5-4.5 ppm	H atoms bonded to an sp3 carbon that is also bonded to at least one heteroatom
4.5-6.5 ppm	H atoms bonded to sp2 carbons of alkenes (*not aromatic sp2 carbons*)
6.5-8.5 ppm	H atoms bonded to sp2 carbons of an aromatic ring
10-12 ppm	H atom bonded to an sp2 carbon atom of the carbonyl group of an aldehyde or H atom bonded to the sp3 oxygen of a carboxylic acid.
Anywhere	H atom directly bonded to a heteroatom other than the oxygen atom of a carboxylic acid. Show up as a broad singlet (eg. OH of alcohol or phenol; NH of amine or amide)

Table 2: Chemical Shift Ranges of Various Proton Types in Proton NMR Spectroscopy