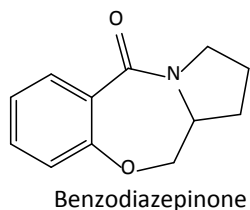
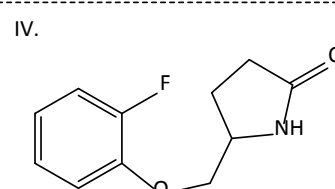
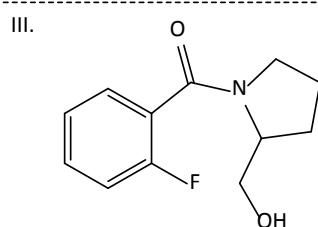
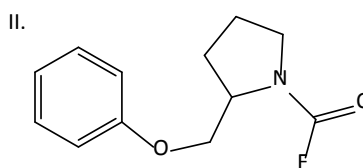
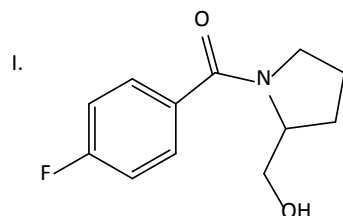


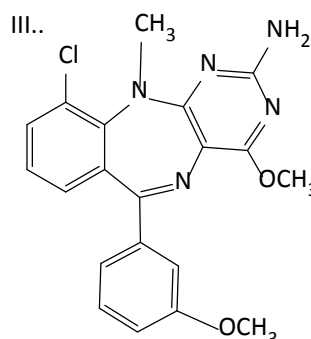
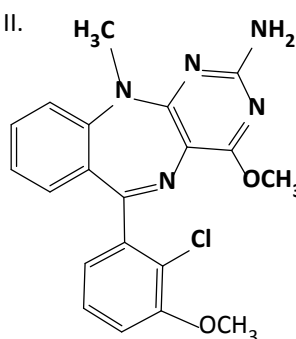
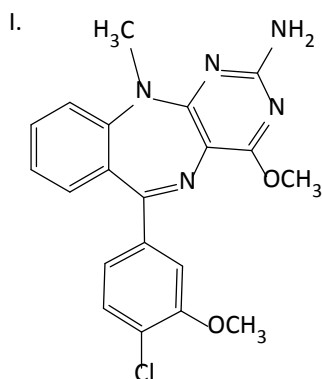
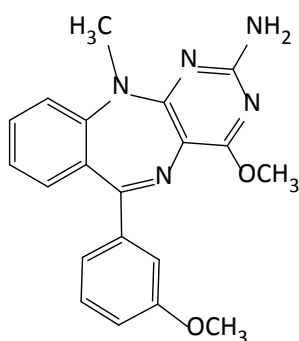
1. Benzodiazepinones contain the core structure of a number of psychoactive drugs. Benzodiazepinones can be formed in an *intramolecular* nucleophilic aromatic substitution. Which of the following starting materials could be used to form the benzodiazepinone compound shown below? **C**



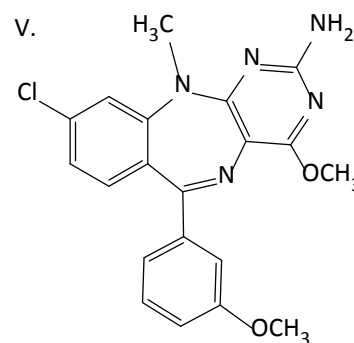
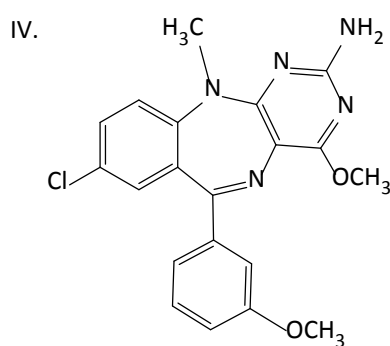
- a) I only
b) II only
c) III only
d) IV only
e) II & IV



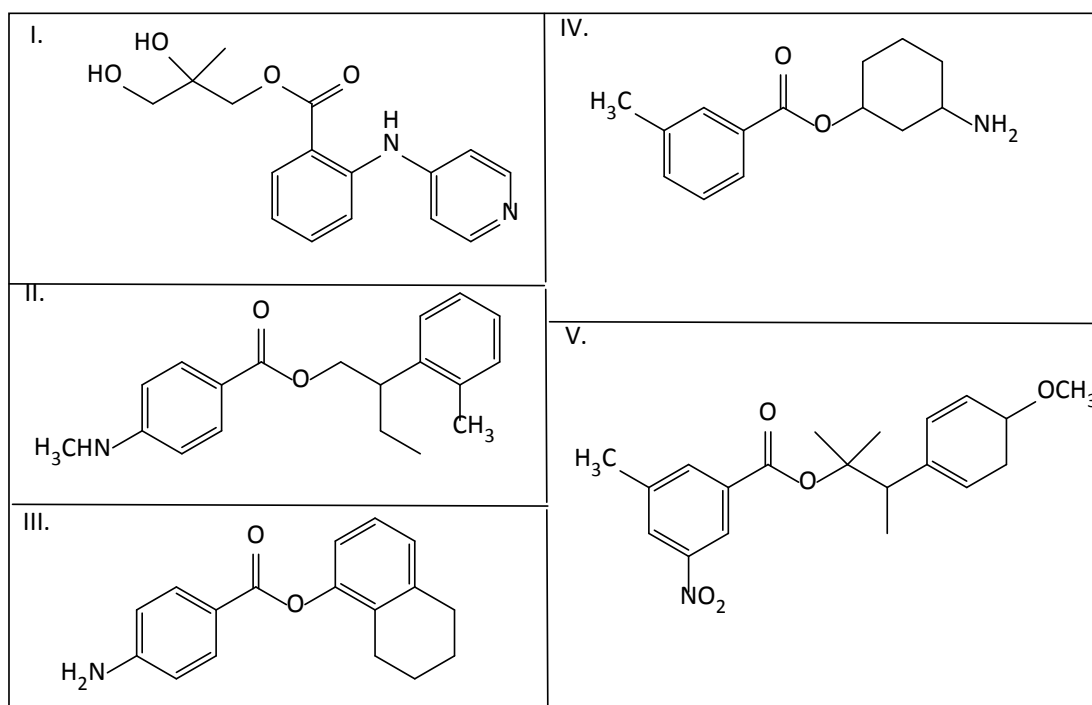
2. Reaction of the benzodiazepine analog below with Cl_2 , FeCl_3 will provide which of the following as the major product(s) of the reaction? **D**



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



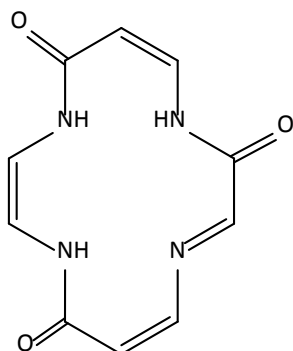
3. How many major products form in the Friedel-Crafts dialkylation of 1,2-dimethoxybenzene with t-butyl chloride and AlCl_3 ? **C**
- 1
 - 2
 - 3
 - 4
 - 5
4. Compound A undergoes base-catalyzed hydrolysis relatively slowly. The resulting products of base-catalyzed hydrolysis of compound A are a carboxylic acid and a secondary alcohol. Treatment of compound A with KMnO_4 provides a product that undergoes base-catalyzed hydrolysis faster than compound A itself. Which of the following structures could be Compound A? **E**



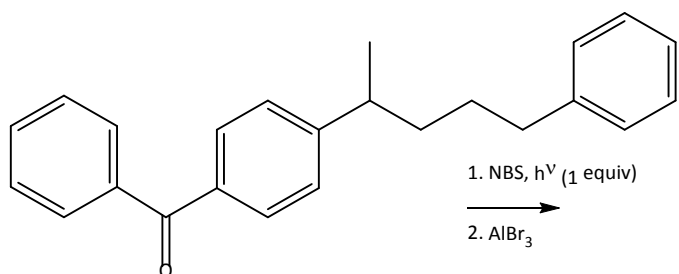
- a) I & II
b) III & IV
c) V only
d) I, II & IV
e) IV only

5. $4n + 2 = \underline{\hspace{2cm}}$ for the structure given below? **B**

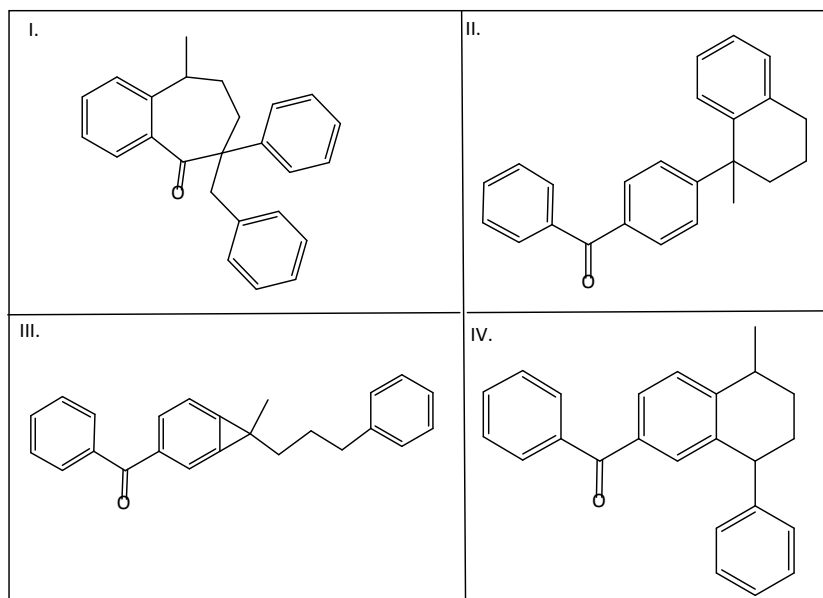
- 4
- 14
- 16
- 18
- 22



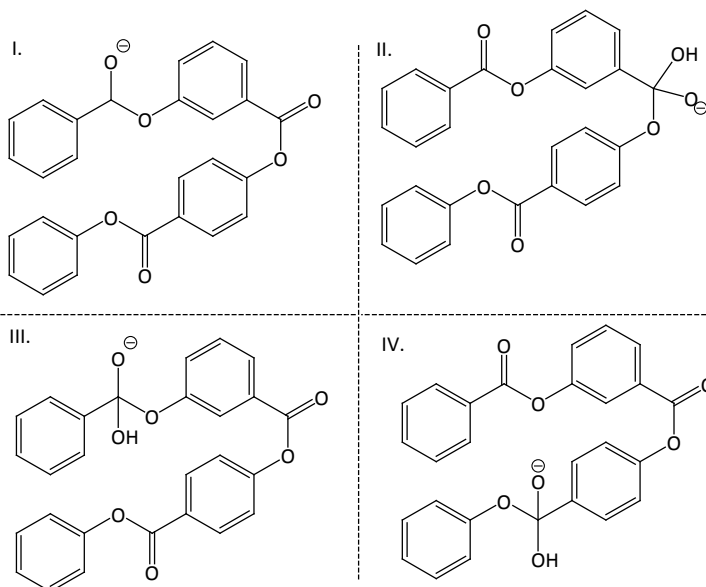
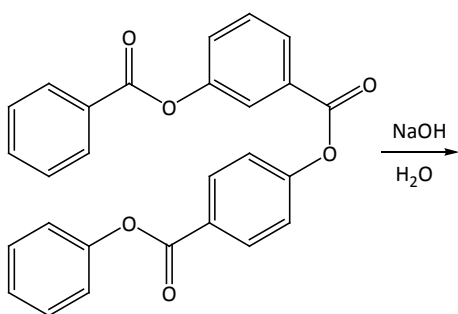
6. The overall major kinetic product(s) of the reaction below is (are): **B**
(Overall mean after step 2 of the reaction)



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



7. Which of the following reaction intermediates will form the fastest in the reaction below? **A**



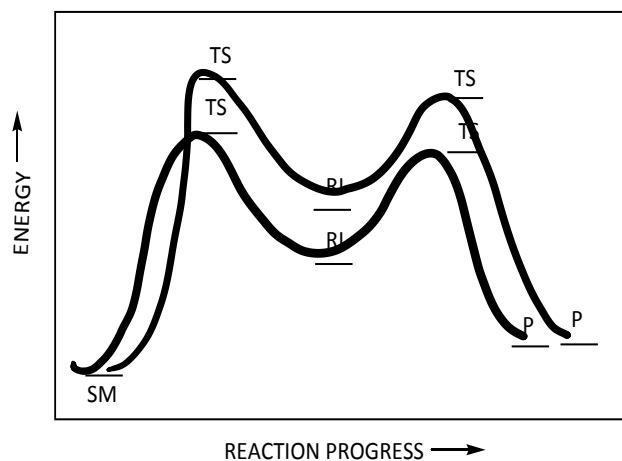
- a) II only
b) III only
c) II & III
d) II & IV
e) I only

8. Which of the following reactions could be used to prepare 2-amino-1-chloro-4-ethylbenzene? (Note: mixtures of isomers may form). **D**

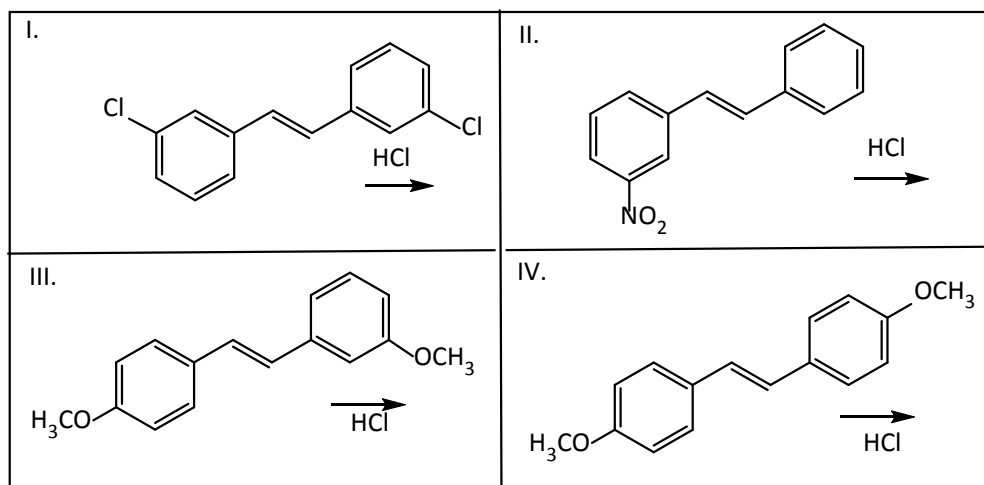
<p>I.</p> <p>Nitrobenzene</p> <p>1. $\text{Cl}_2, \text{FeCl}_3$</p> <p>2. ethylchloride, AlCl_3</p> <p>3. $\text{KOH}, \text{H}_2\text{NNH}_2$</p>	<p>II.</p> <p>Benzaldehyde</p> <p>1. H_2, Pt</p> <p>2. $\text{Cl}_2, \text{FeCl}_3$</p> <p>3. $\text{HNO}_3, \text{H}_2\text{SO}_4$</p> <p>4. H_2, Pd</p>
<p>III.</p> <p>Bromobenzene</p> <p>1. $\text{HNO}_3, \text{H}_2\text{SO}_4$</p> <p>2. $\text{Cl}_2, \text{FeCl}_3$</p> <p>3. AlCl_3</p> <p>4. H_2, Pd</p>	<p>IV.</p> <p>Aniline</p> <p>1. KMnO_4</p> <p>2. ethyl chloride, AlCl_3</p> <p>3. $\text{Cl}_2, \text{FeCl}_3$</p> <p>4. H_2, Pt</p>

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

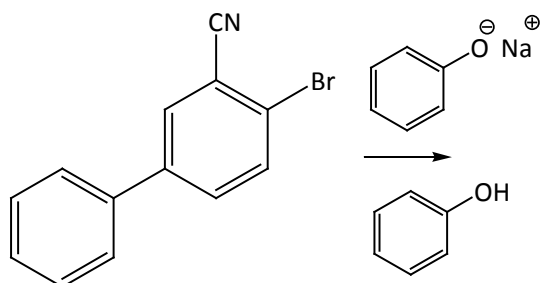
9. Which of the following reactions corresponds to the reaction energy diagram below? **A**



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



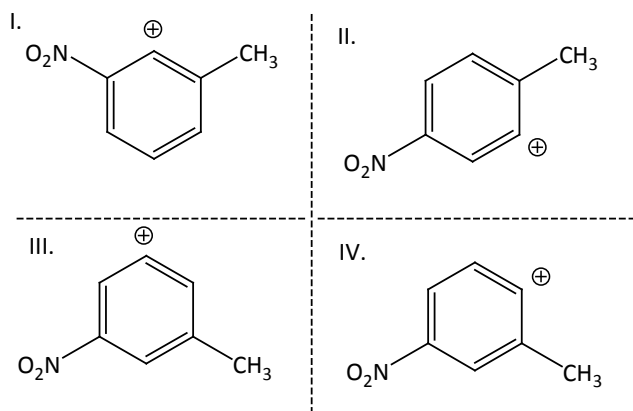
10. The major product(s) of the reaction below is (are): **A**



- I. 2-cyano-1-phenoxy-4-phenylbenzene
 II. 1-cyano-2-phenoxy-3-phenylbenzene
 III. 3-cyano-1-phenoxy-4-phenylbenzene
 IV. 4-cyano-1-phenoxy-2-phenylbenzene

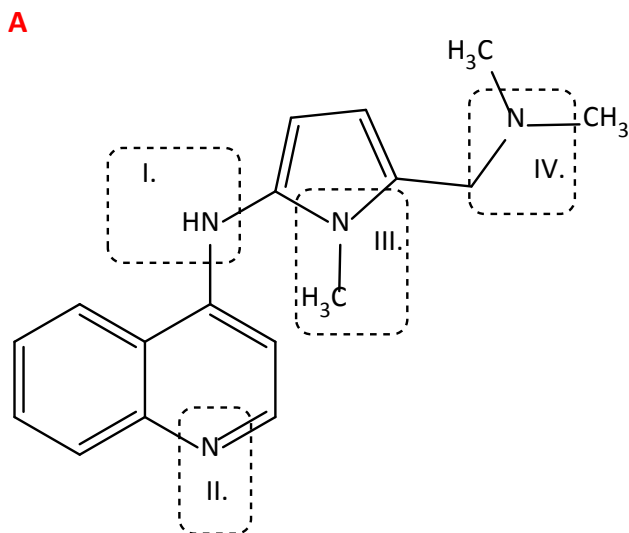
- a) I only
 b) I & III
 c) II only
 d) I, III & IV
 e) IV only

11. Which of the following reaction intermediate(s) give(s) rise to the major product(s) of the reaction of 2-fluoro-5-nitrotoluene with KNH_2 , NH_3 ? **C**



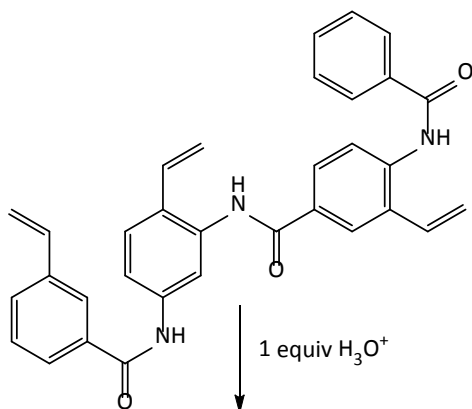
- a) I only
 b) II only
 c) III & IV
 d) III only
 e) I, III & IV

12. Rank the nitrogen atoms in the structure below from strongest base to weakest base (strongest > weakest)

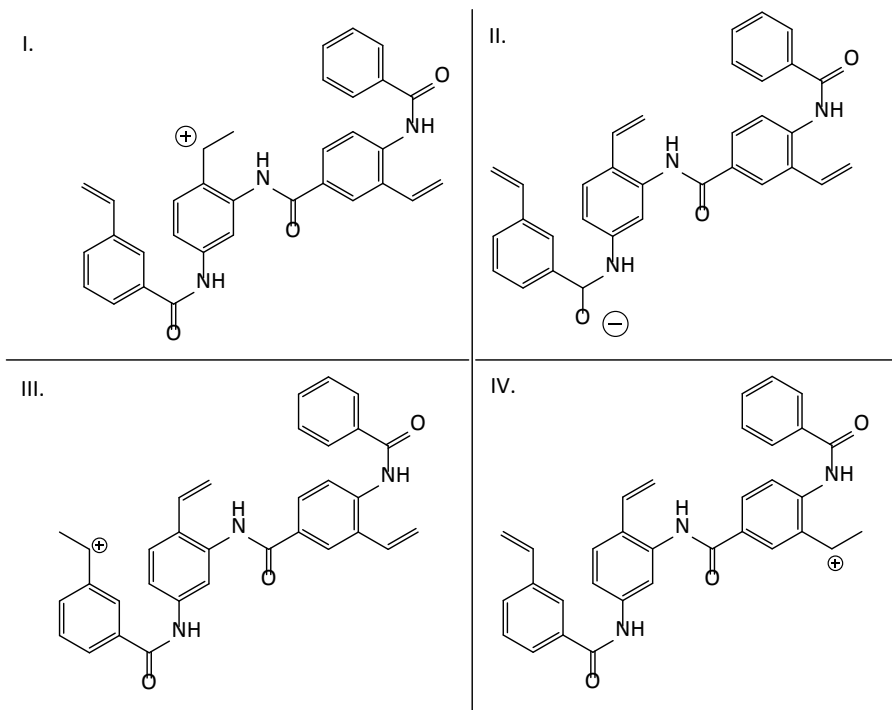


- a) IV = II > I > III
 b) IV > I > II > III
 c) IV = II > III > I
 d) III > I > IV > II
 e) IV > II > III > I

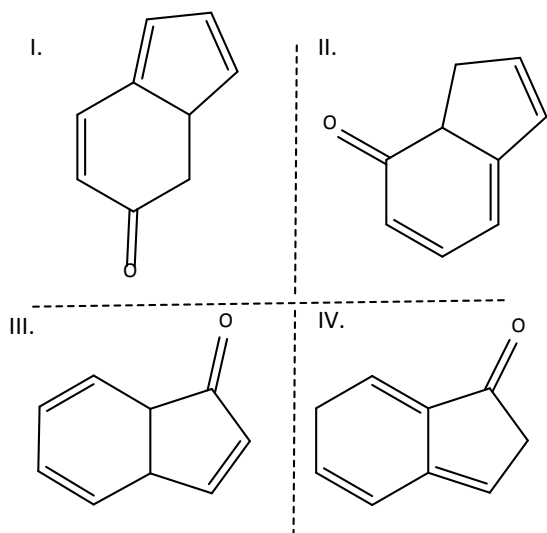
13. Which of the following reaction intermediates will form the fastest in the reaction outlined below? **E**



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

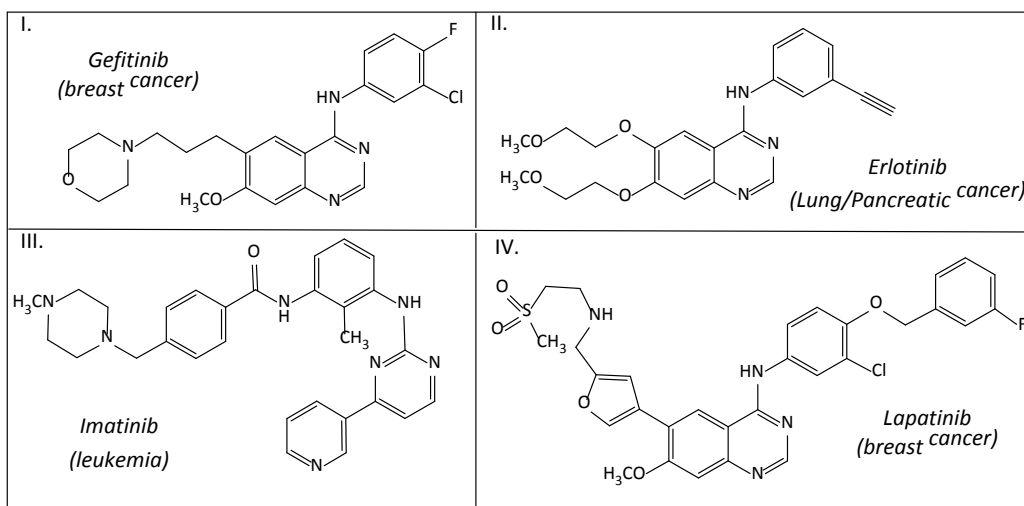


14. Enolates usually react with electrophilic reagents to give substitution at the α -carbon. However, in some cases, reaction occurs to give substitution on the oxygen atom as the major thermodynamic product. Which of the following reactions will result in substitution on the oxygen as the major thermodynamic product? **C**



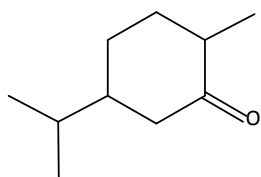
- | |
|---|
| <ul style="list-style-type: none"> a) I only b) I & II c) II only d) III & IV e) I, II, III & IV |
|---|

15. The four anticancer drugs below all contain a substituted aniline as part of its structure. Rank the pKa values of the aniline nitrogen from highest pKa to lowest pKa in these four structures. **B**

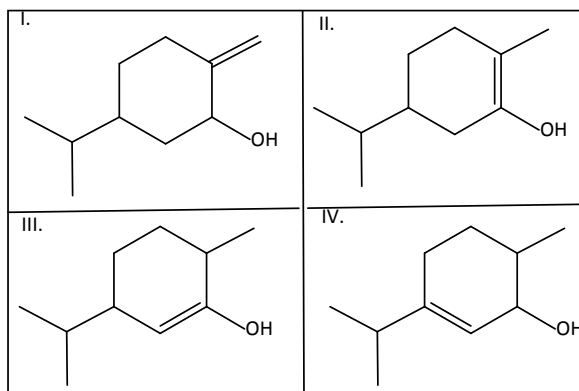


- | |
|----------------------|
| a) I > IV > II > III |
| b) III > II > IV > I |
| c) II > I > III > IV |
| d) III > IV > II > I |
| e) III > IV > I > II |

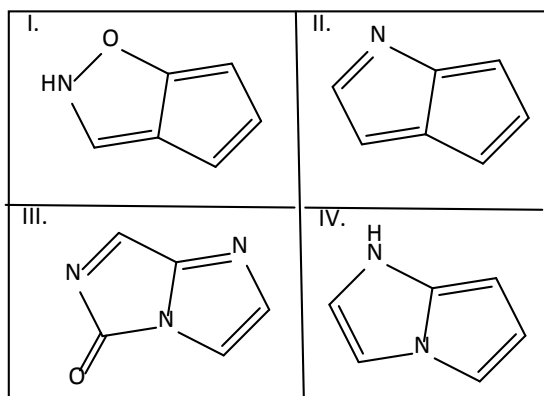
16. The enol(s) generated upon treatment of the compound below with acid is (are): **E**



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

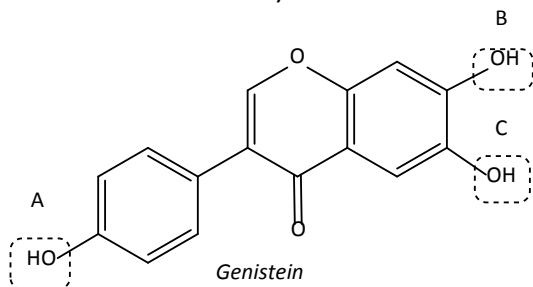


17. Which of the following compounds are aromatic? **D**



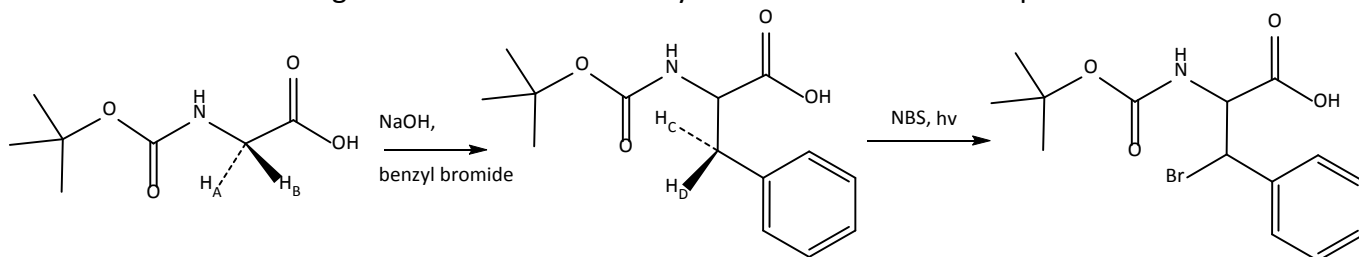
- | |
|----------------|
| a) I only |
| b) I & II |
| c) I, II & III |
| d) I & IV |
| e) IV only |

18. The pKas of the phenols of genistein are 7.2, 10 and 13.1. Match the pKa to the phenols (Labeled as A, B and C in the structure). **C**



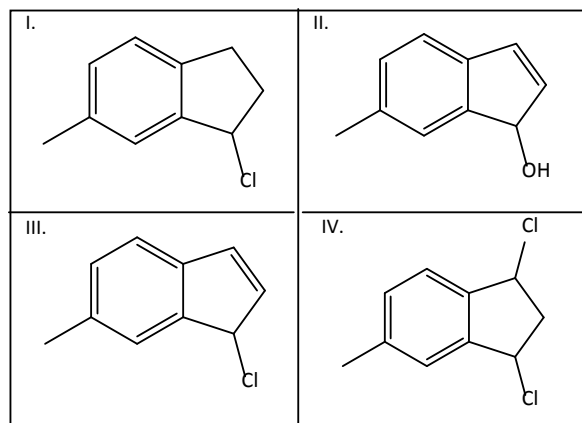
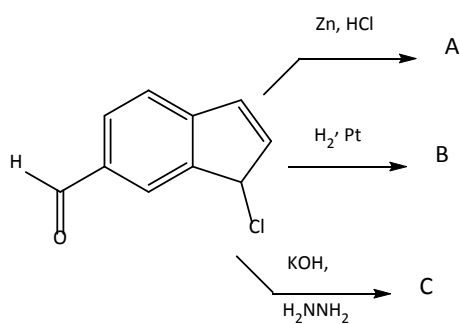
- a) A = 7.2 B = 10 C = 13.1
 b) A = 7.2 B = 13.1 C = 10
 c) A = 10 B = 7.2 C = 13.1
 d) A = 10 B = 13.1 C = 7.2
 e) A = 13.1 B = 10 C = 7.2

19. Which of the following statements is true as they relate to the reaction sequence outlined below? **B**



- a) H_A = pro-R H_B = pro-S H_C = pro-R H_D is pro-S
 b) H_A = pro-S H_B = pro-R H_C = pro-S H_D is pro-R
 c) H_A = pro-R H_B = pro-S H_C = pro-S H_D is pro-R
 d) H_A = pro-S H_B = pro-R H_C = pro-R H_D is pro-S
 e) H_A, H_B, H_C and H_D are not prochiral.

20. Identify the product(s) A, B and C that would be generated in each reaction below. Assume excess reagent is available. **C**

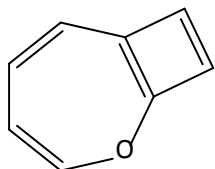


- a) A = I B = II C = III
 b) A = IV B = I C = III
 c) A = IV B = I C = II
 d) A = I B = I C = II
 e) A = IV B = I C = I

21. The major product(s) in the reaction of meta-fluorophenol with 1) NaNH_2 and 2) H_2O is (are): **E**

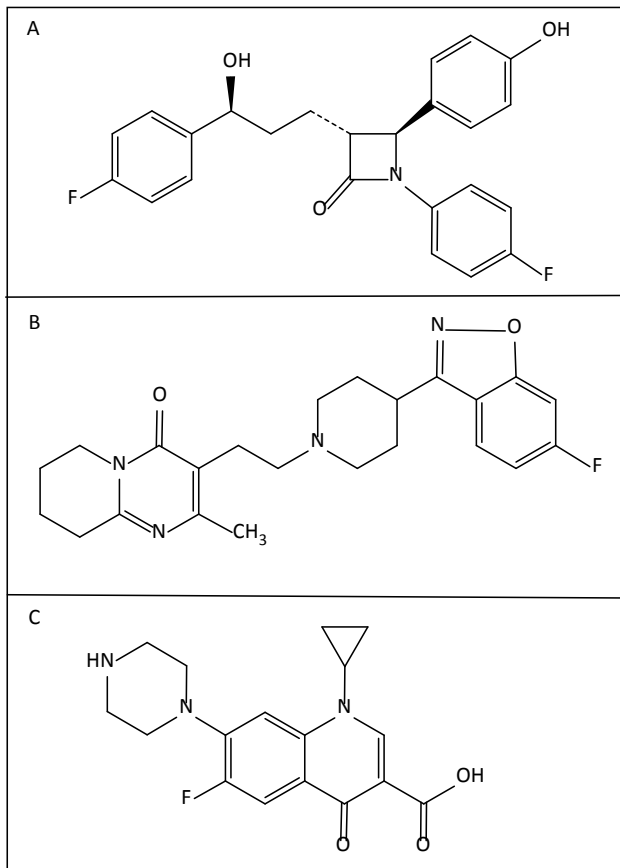
- | | |
|-------------------------|----------------|
| I. para-aminophenol | a) I & III |
| II. meta-aminophenol | b) IV only |
| III. ortho-aminophenol | c) I, II & III |
| IV. meta-methoxyaniline | d) IV & V |
| V. ortho-methoxyaniline | e) II only |

22. Which of the following statements is true for the bicyclic compound below? **E**



- | | |
|--|--|
| | I. The four-membered ring alone is aromatic |
| | II. The seven membered ring alone is aromatic. |
| | III. The nine membered ring is aromatic |
| | IV. The four membered ring is planar. |
- a) I only
b) I & II
c) II only
d) III only
e) III & IV

23. Match each compound (A-C) with its reaction chemistry in electrophilic aromatic substitutions (EAS) nucleophilic aromatic substitutions (NAS) and Benzyne reaction. **E**

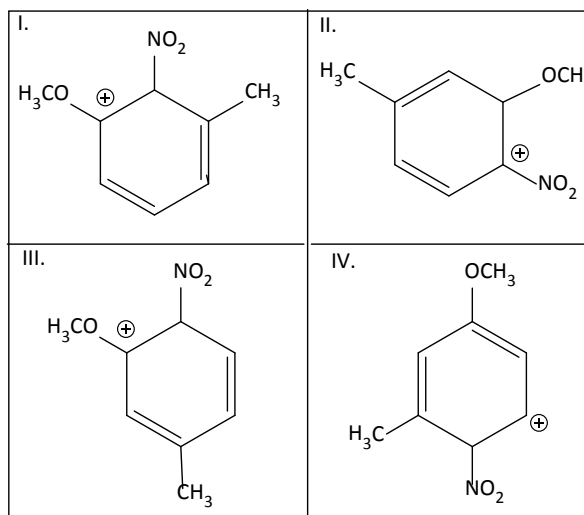


- | |
|---|
| I. Reacts in EAS |
| II. Reacts in NAS |
| III. Reacts in Benzyne |
| IV. Does not react in EAS, NAS or Benzyne |

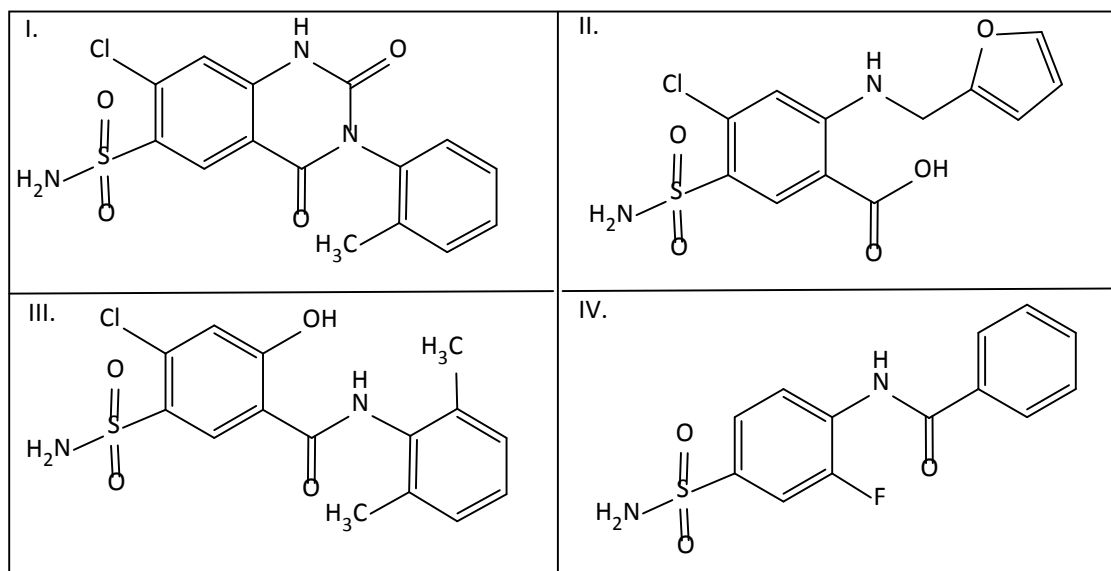
- | | | |
|-------------------|----------------|-------------|
| a) A = I, II, III | B = I, II, III | C = II, III |
| b) A = I, II | B = II, III | C = II, III |
| c) A = II, III | B = I, II, III | C = IV |
| d) A = I | B = II, III | C = IV |
| e) A = I, III | B = I, II, III | C = III |

24. A reaction intermediate that leads to a major product in the reaction of meta-methylanisole with HNO_3 , H_2SO_4 is (are): **D**

- | |
|--|
| <p>a) I & III
b) I & II
c) I, III & IV
d) III & IV
e) III only</p> |
|--|



25. Rank the sulfonamides below from strongest acid to weakest acid (strongest > weakest). **A**



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

Substituent	Abbreviation	σ meta	σ para
acetamido-	AcNH-	0.21	-0.02
acetoxy-	AcO-	0.39	-0.01
acetyl-	Ac-	0.38	0.50
acetylenyl-	$\text{—C}\equiv\text{CH}$	0.08	0.11
alkenyl-	$\text{—CH}_2=\text{CH}_2$	0.05	-0.02
amino-	NH ₂ -	-0.16	-0.66
bromo-	Br-	0.39	0.23
tert-butyl-	(CH ₃) ₃ C-	-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 ₃ C-	0.43	0.54
trimethylamino-	(CH ₃) ₃ N ⁺ -	0.88	0.82

Table 1: σ values for Various Substituents