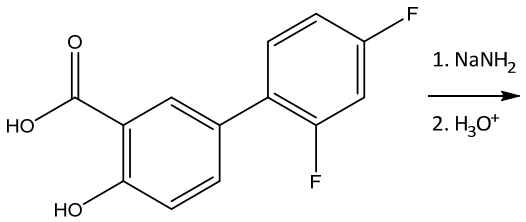
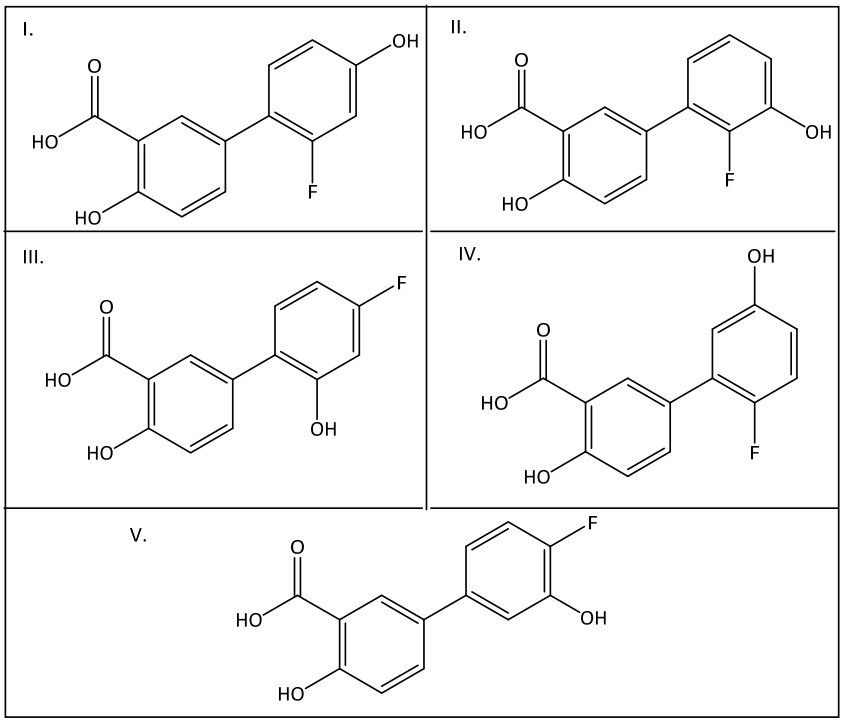
1. The major product(s) in the reaction of diflunisal, an anti-inflammatory drug, with one equivalent of 1. $NaNH_2$ 2. H_3O^+ is (are): A

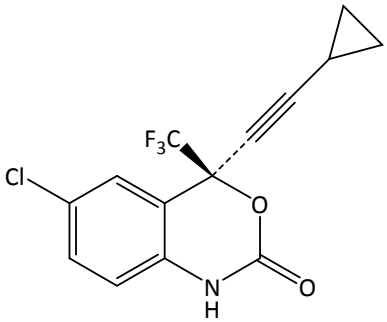


Diflunisal

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

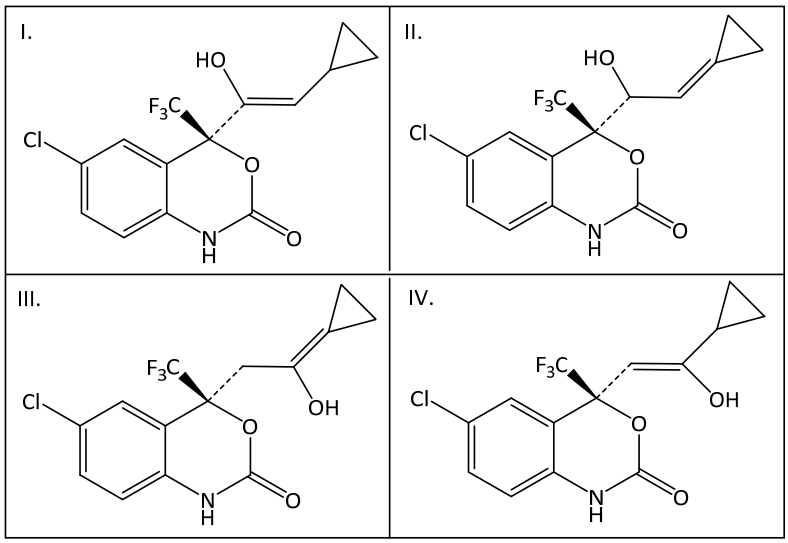


2. Which of the following represents the enol that leads to the major product(s) in the reaction of efavirenz with H_3O^+? C

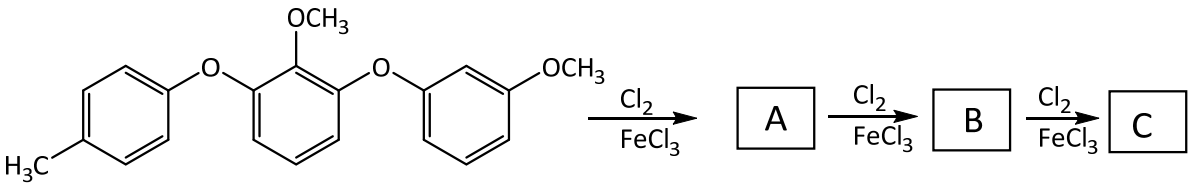


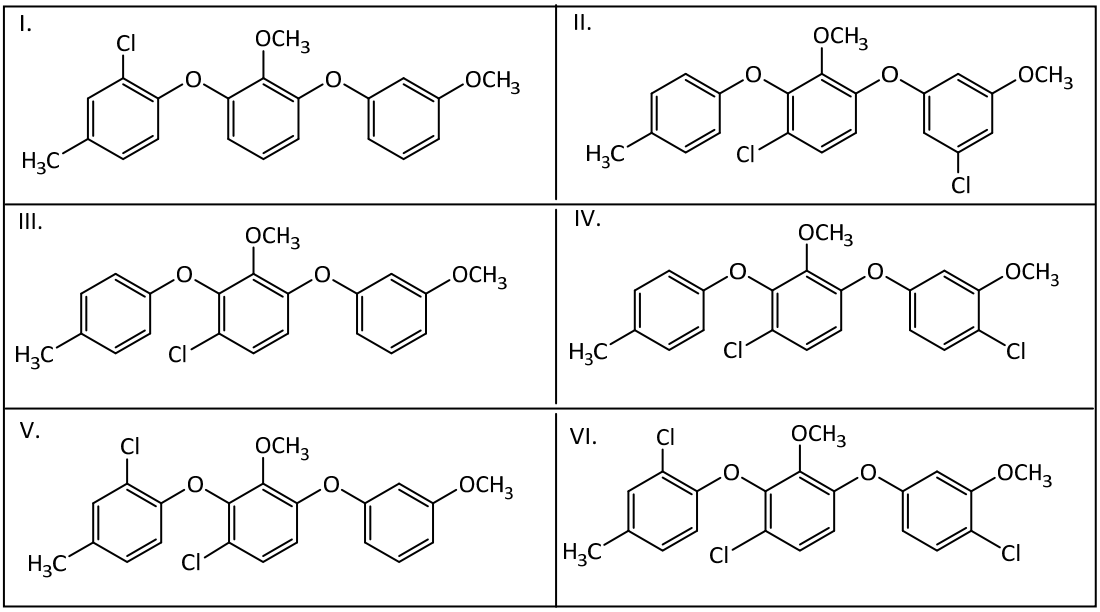
Efavirenz

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



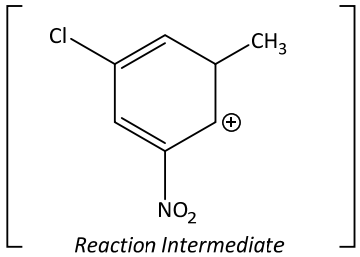
3. Identify compounds A, B and C in the reaction sequence below. For reactions that give mixtures of positional isomers as products, only one of these may be shown. B

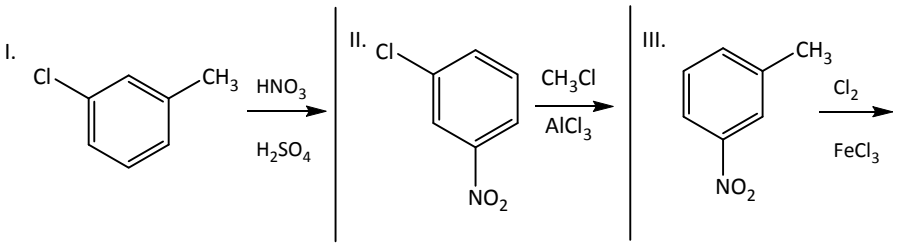




a) A = I; B = V; C = VI
b) A = III; B = IV; C = VI
c) A = III; B = II; C = VI
d) A = III; B = I; C = VI
e) A = I; B = II, C = VI

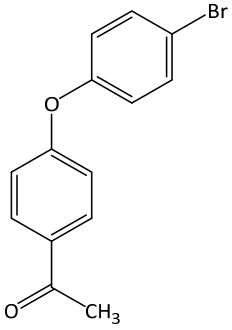
4. The reaction intermediate below will be generated in which of the following reactions? E

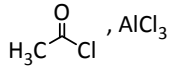
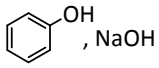


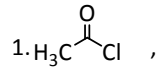
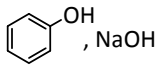


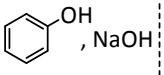
a) I & II
b) II & III
c) I & III
d) II
e) None of these reactions will generate this intermediate.

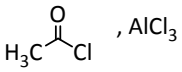
5. Which set of reagents could be used to prepare the compound below using benzene as starting material? Assume other isomers may form in the reaction. D



I. 1. Br_2, $FeBr_3$
2.  , $AlCl_3$
3.  , NaOH
4. Br_2, $FeBr_3$

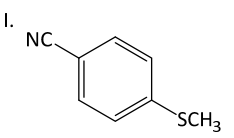
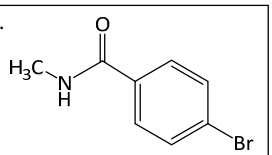
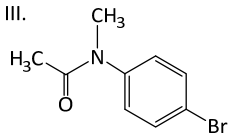
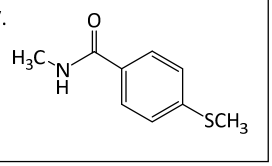
II. 1.  , $AlCl_3$
2. $NaBH_4$, CH_3OH
3. Cl_2, $FeCl_3$
4. PCC, CH_2Cl_2
5.  , NaOH
6. Br_2, $FeBr_3$

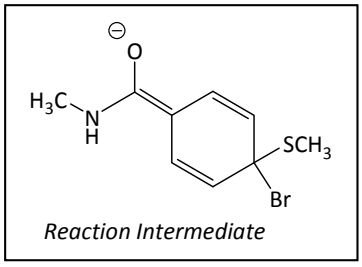
III. 1. CH_3Cl, $AlCl_3$
2. Br_2, $FeBr_3$
3. PCC, CH_2Cl_2
4. Cl_2, $FeCl_3$
5.  , NaOH

IV. 1. Br_2, $FeBr_3$
2. 1. NaH 2. H_3O^+
3.  , $AlCl_3$
4. Br_2, $FeBr_3$
5. NaH, 

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

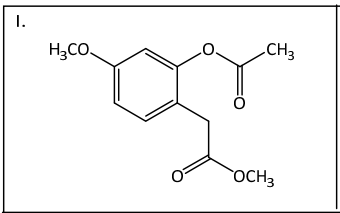
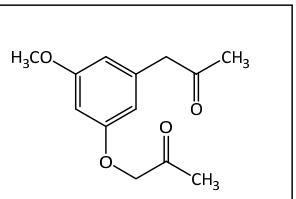
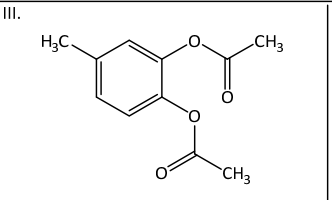
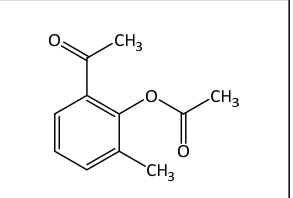
6. Which of the following *<u>starting materials</u>* will give rise to the reaction intermediate below when that starting material is reacted with CH_3S^- Na^+? D

I. 
II. 
III. 
IV. 


Reaction Intermediate

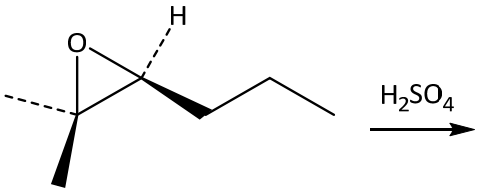
a) III
b) I & IV
c) II & III
d) II
e) IV

7. Rank the relative rate of the electrophilic aromatic substitution reaction (fastest> slowest) for the set of compounds below. C

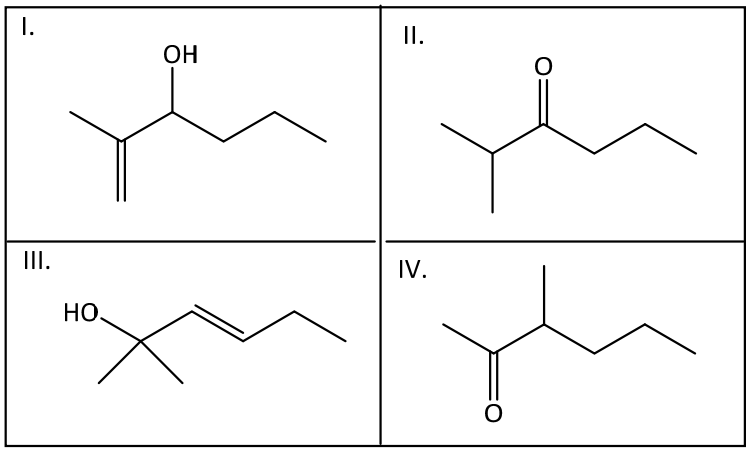
I. 
II. 
III. 
IV. 

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

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



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

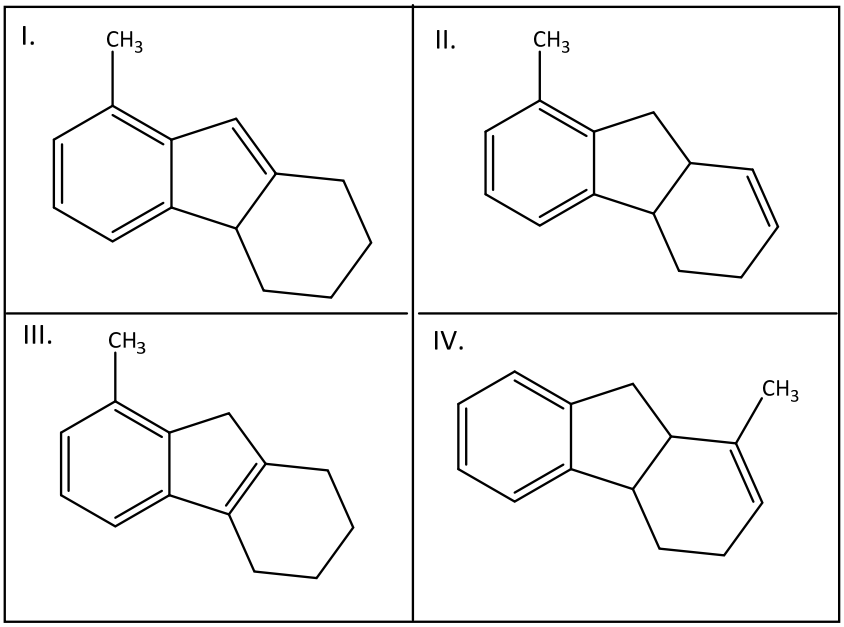


9. Which of the following statements is true when hydride reacts with 3R-3,4-dimethylpentanal from the *re face*? D

I. A mixture of diastereomers are formed as products
II. A racemic mixture is generated.
III. The product contains two chiral centers, both with the R configuration.
IV. The product contains one chiral center with the R configuration.
V. The starting material is prochiral.

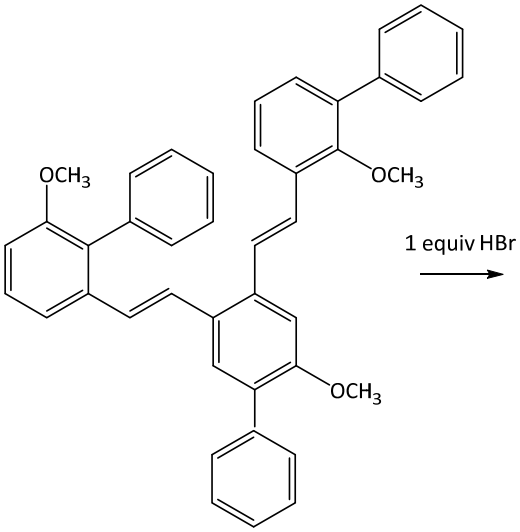
a) I
b) I & III
c) II & III
d) IV
e) IV & V

10. Which of the following starting materials will provide a single product that contains both and aldehyde and ketone upon reaction with 1. O_3, 2. Zn, HCl? A

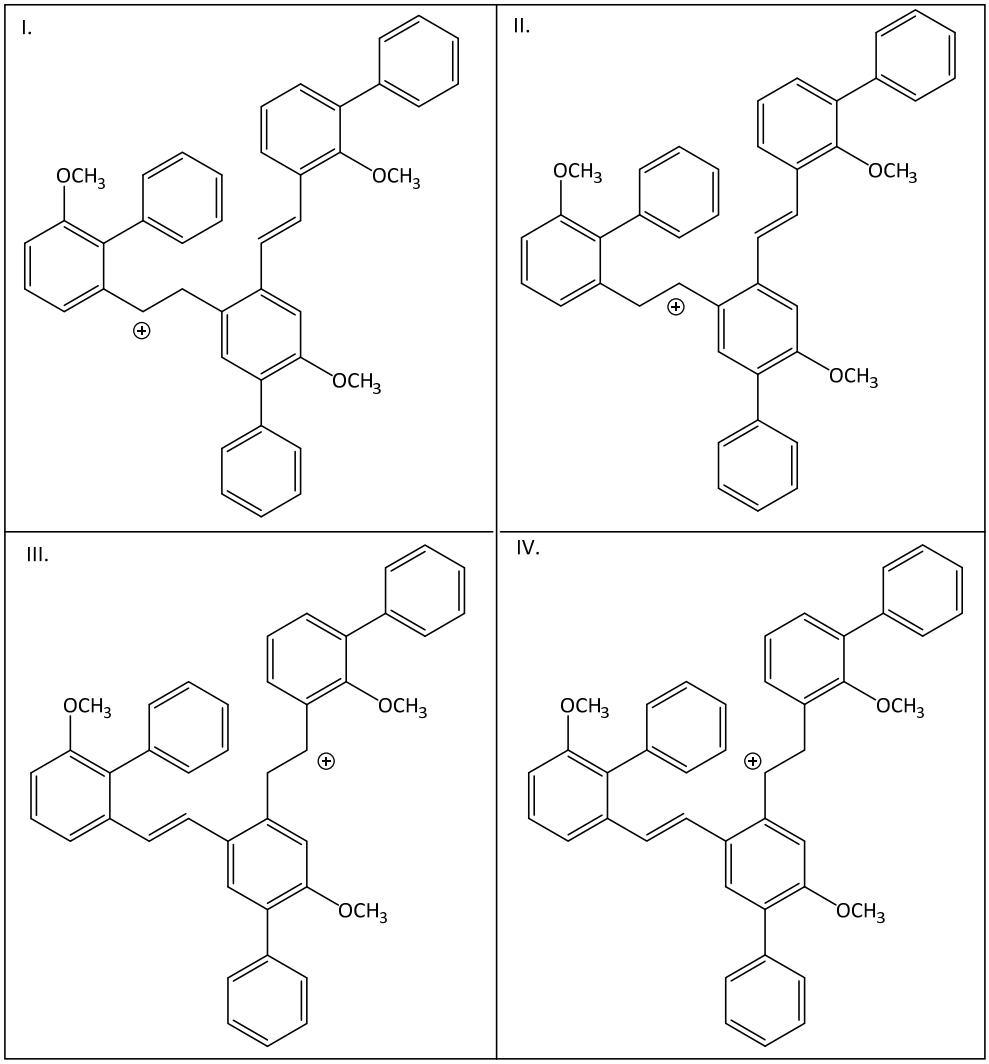


a) I & IV
b) III
c) III & IV
d) I
e) II

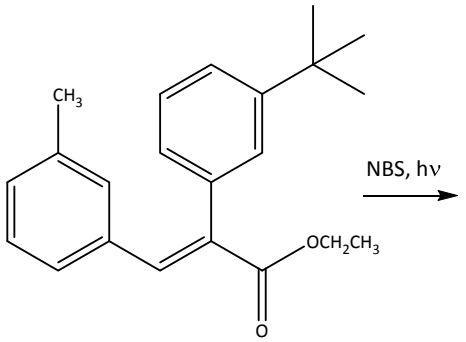
11. Which of the following carbocations will form the ***fastest*** in the reaction below? A



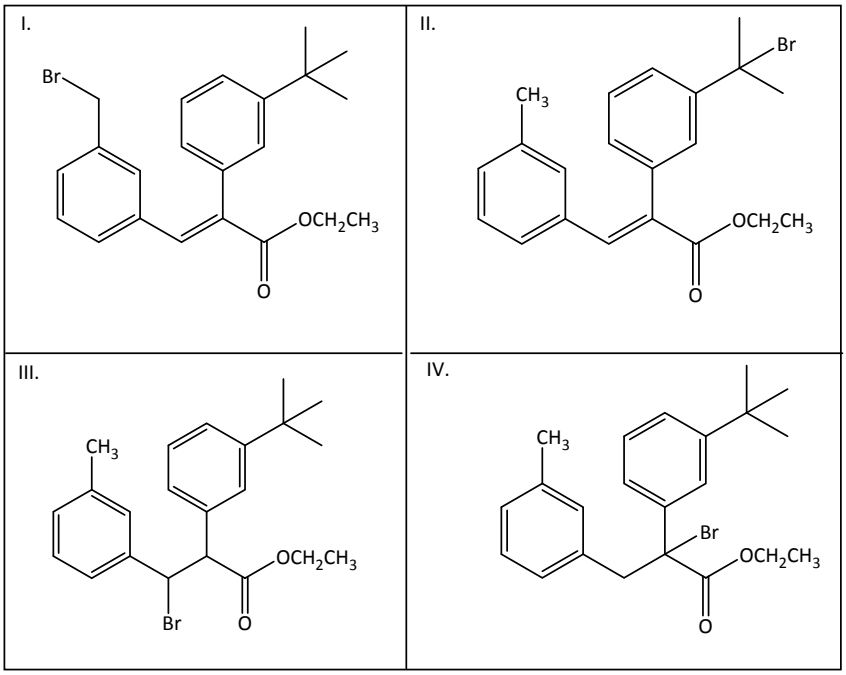
a) II
b) I & II
c) III
d) IV
e) III & IV



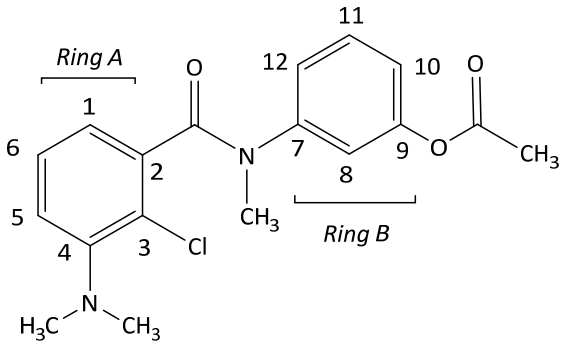
12. The major product(s) of the reaction below is (are): E



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



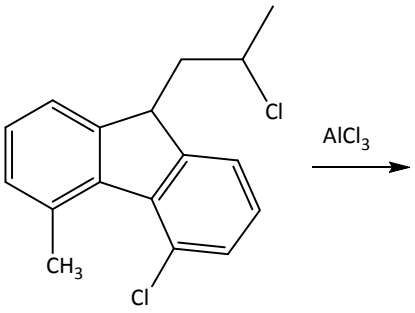
13. Which of the following statements is true regarding the compound below? Do not use sigma values. B



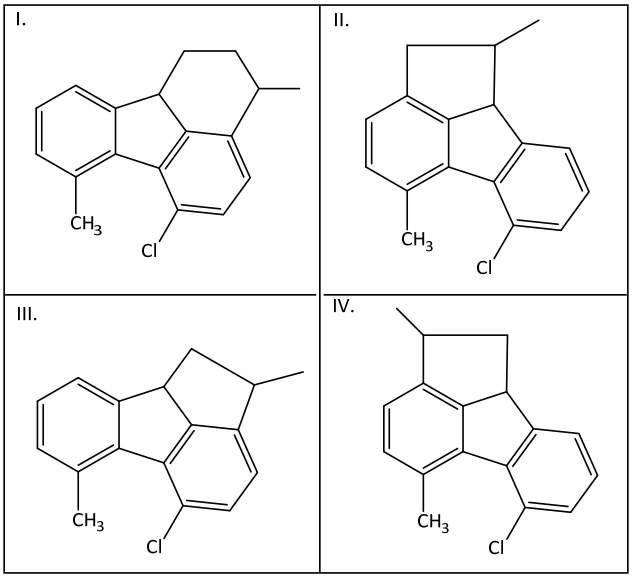
a) I
b) I & II
c) I & III
d) II & IV
e) I & V

I. Ring A contains two EDG by resonance and one EWG by resonance
II. Ring B contains two EWG by induction
III. Ring B contains two EWG by resonance
IV. Ring A contains two EWG by resonance and one EDG by resonance
V. The substituent at C_4 and the substituent at C_7 are both equally EDG by resonance.

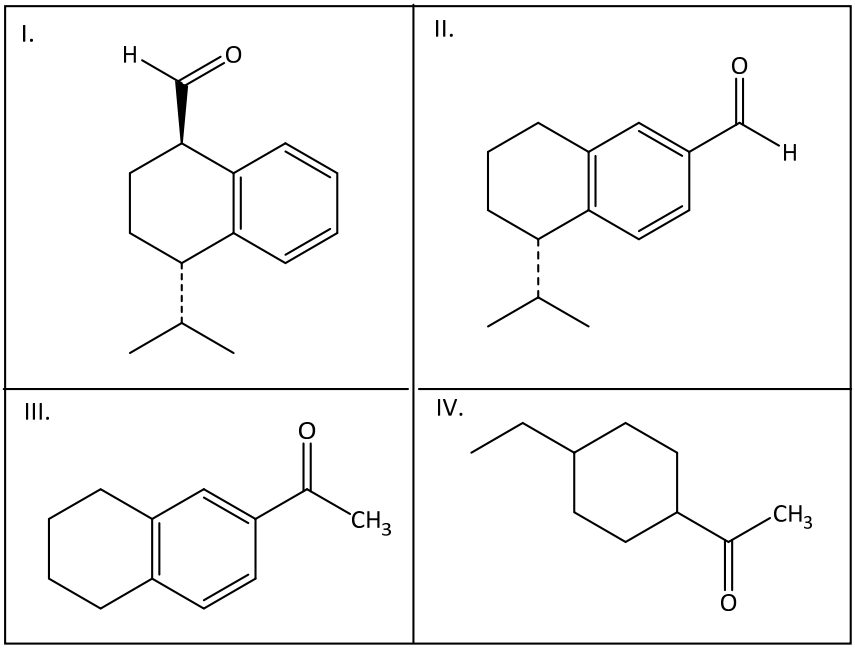
14. The major product(s) of the reaction below is (are): C



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

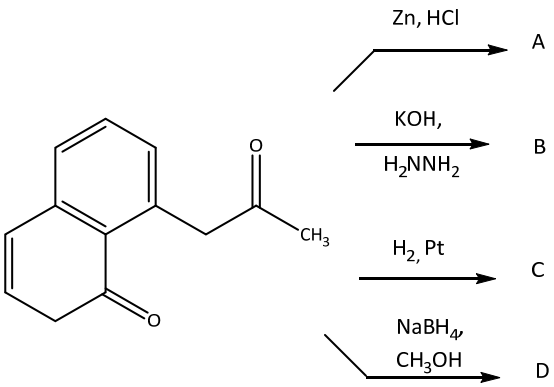


15. Which of the following starting materials is (are) prochiral in the reaction with $NaBH_4$, CH_3OH? E

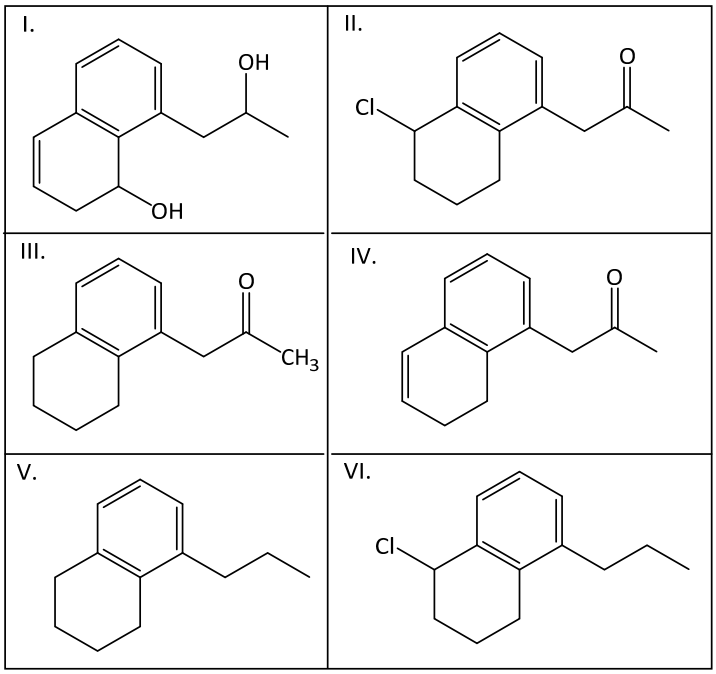


a) I
b) II
c) II & III
d) IV
e) III & IV

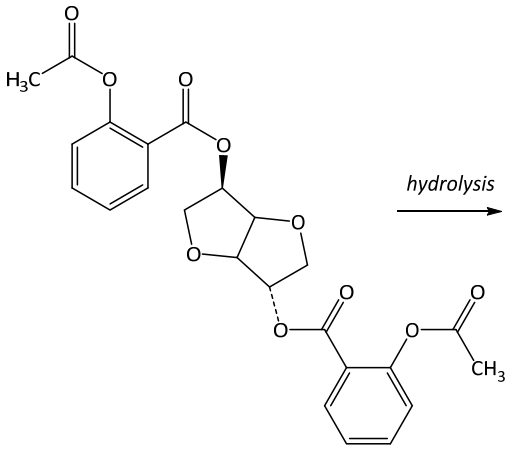
16. Identify the product(s) A, B, C and D that would be generated in each reaction below. Assume excess reagent is available. A



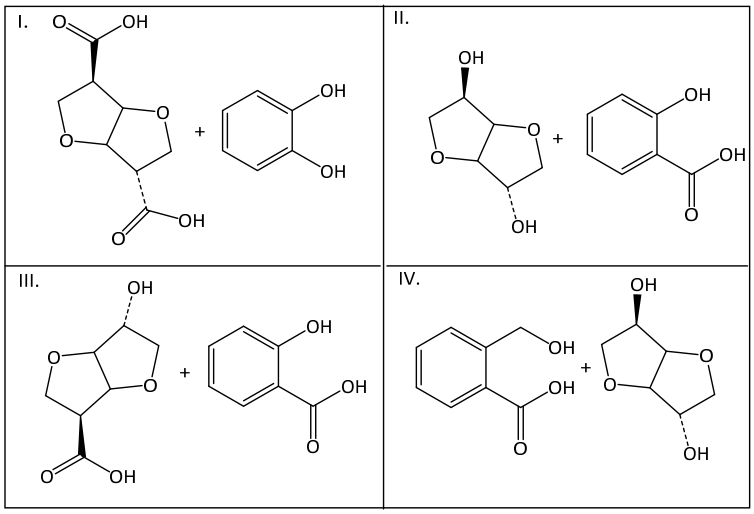
a) A = II; B = IV; C = III; D = I
b) A = VI; B = I; C = V; D = I
c) A = II; B = IV; C = V; D = IV
d) A = VI; B =IV ; C = III; D = V
e) A = II; B = I; C = III; D =V



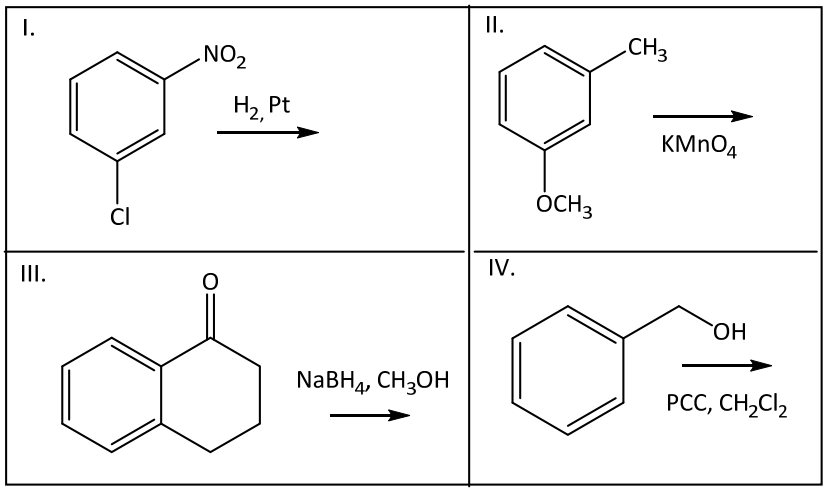
17. Prodrugs are therapeutic agents that are inactive when administered but become activated through metabolism in the body. One mechanism of metabolism used to activate prodrugs is hydrolysis. Prodrugs that contain ester functional groups can be activated when they undergo hydrolysis in the body. Isosorbide diaspirinate is an example of a prodrug that gives two drug products and acetic acid upon *complete* hydrolysis (i.e., all ester groups are hydrolyzed). Identify the two drugs that are generated when isosorbide diaspirinate is activated by hydrolysis. C



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

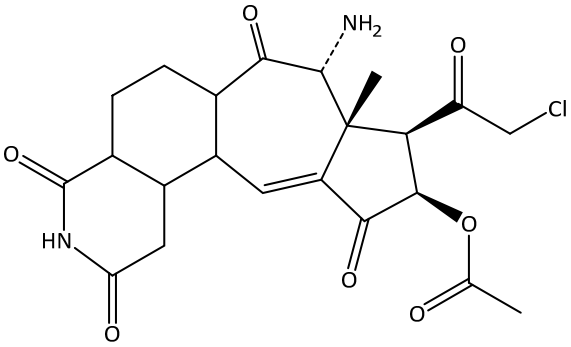


18. For each reaction below, compare the relative reactivity of the starting material in each reaction with the product of the reaction. In which of the following reactions are the *products for each reaction* more reactive in the electrophilic aromatic substitution reaction than the starting material? Assume the EAS reaction will proceed in all cases. D



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

19. Which carbonyl functional groups are present in the structure below? B



I. Aldehyde	IV. Amide	VII. Acid Chloride
II. Ketone	V. Imide	
III. Ester	VI. Anhydride	

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

20. Which of the following statements is true about isomers of fluorobenzaldehyde? B

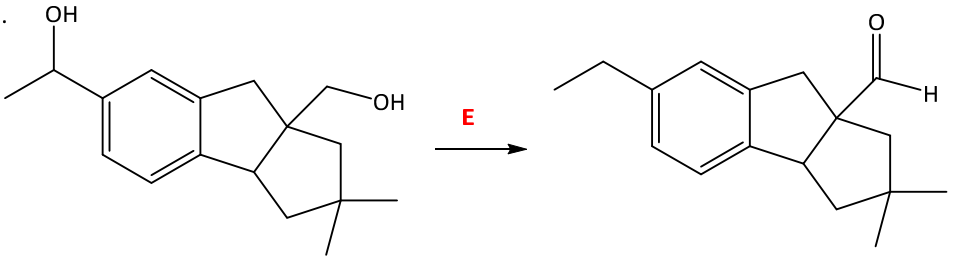
I. In o-fluorobenzaldehyde, the reaction is directed to C_4 upon reaction with HNO_3, H_2SO_4
II. p-Fluorobenzaldehyde reacts with CH_3O^-Na+ to give p-methoxybenzaldehyde as the major product.
III. Reaction of m-fluorobenzaldehyde with Zn, HCl will provide m-fluorotoluene.
IV. Treatment of m-fluorobenzaldehyde with DIBAL will give m-fluorotoluene.

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

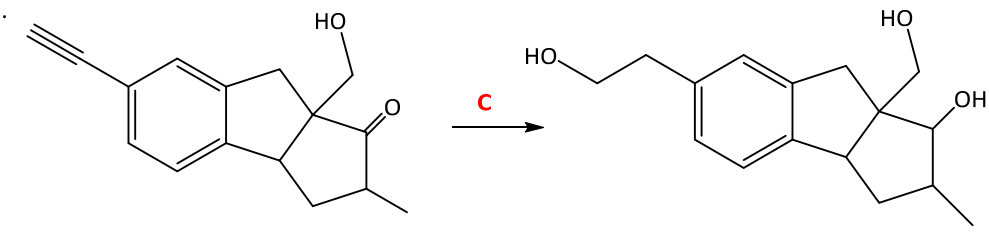
QUESTIONS 21-25: Match one of the five sets of reagents given below (a, b, c, d, e) with the reactions in questions 21-25. Each reagent may be used once, more than once or not at all.

a) 1. H_3O^+ 2. PCC, CH_2Cl_2
b) 1. Et_3N 2. H_2O 3. $NaBH_4$, CH_3OH
c) 1. BH_3 2. H_2O_2, NaOH 3. $NaBH_4$, CH_3OH
d) 1. NBS, hν 2. KOH, H_2NNH2
e) None of these

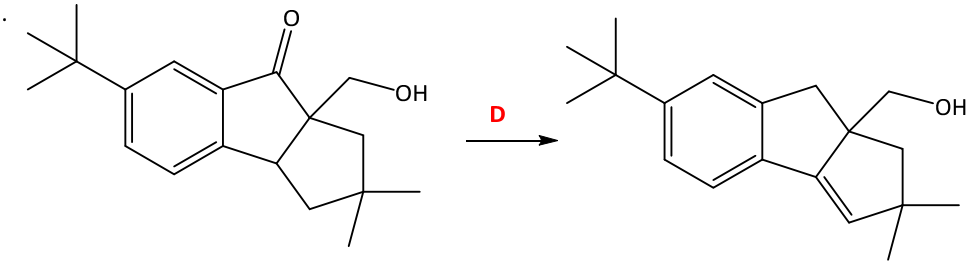
21.



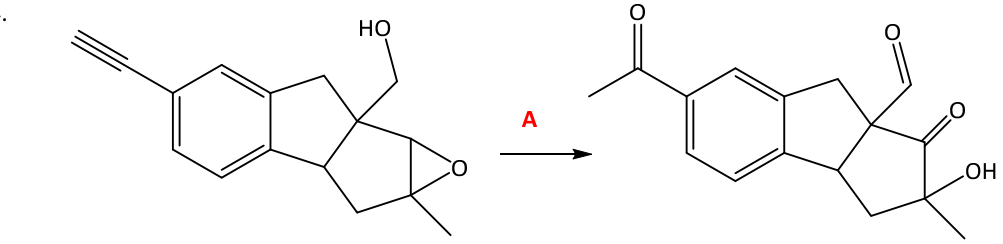
22.



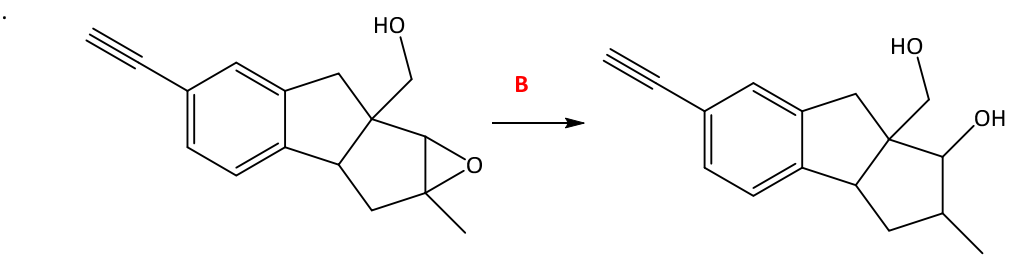
23.



24.



25.



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