

《有機化學》

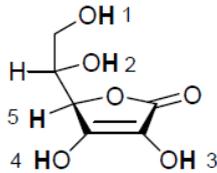
I. Choose one correct answer for the following questions

【單選題】每題 1 分，共計 60 分，答錯 1 題倒扣 0.25 分，倒扣至本大題零分為止，未作答，不給分亦不扣分。

(A)1. Which of the following amines gives the **correct** order of base strengths?

- (A) aliphatic > ammonia > aromatic (B) aliphatic > aromatic > ammonia
(C) aromatic > aliphatic > ammonia (D) aromatic > ammonia > aliphatic
(E) ammonia > aromatic > aliphatic

(D)2. The structural formula for vitamin C is shown below, identified by **H** which is most acidic?



- (A) 1 (B) 2 (C) 3 (D) 4 (E) 5

(D)3. What term describes the structural relationship between (2*R*,3*R*,4*S*)-2,3,4-trichloroheptane and (2*R*,3*R*,4*R*)-2,3,4-trichloroheptane?

- (A) not isomers (B) constitutional isomers
(C) enantiomers (D) diastereomers (E) conformers

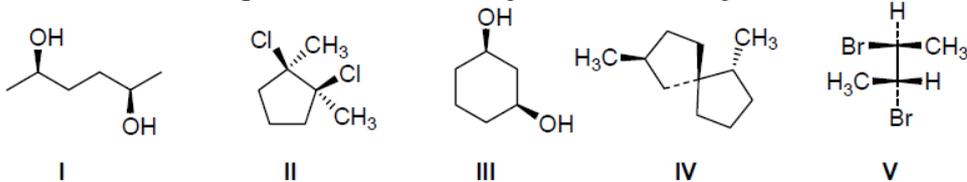
(C)4. Rank the following sets of substituents in order of Cahn-Ingold-Prelog priorities from highest to lowest. Please pick the **wrong** order set.

- (A) -Cl, -S, -P, -H (B) -Br, -OH, -CH₃, -H
(C) -CO₂H, CH₂OH, -CH₂NH₂, -CN (D) -CH₂OH, -CH=CH₂, -CH₂CH₃, -CH₃
(E) -CH₂OCH₃, -CN, -C≡CH, -CH₂CH₃

(A)5. Which of the following pair of structures represent the different enantiomers?

- (A) and (B) and (C) and (D) and (E) none of the above

(D)6. Which of the following structure **does not** represent **meso** compounds?

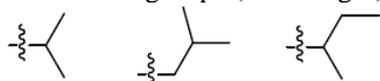


- (A) I (B) II (C) III (D) IV (E) V

(D) 7. Which of the statements below correctly describes an achiral molecule?

- (A) the molecule has a nonsuperimposable mirror image
 (B) the molecule exhibits optical activity when it interacts with plane-polarized light
 (C) the molecule has an enantiomer
 (D) the molecule might be a meso form
 (E) none of the above

(B) 8. Name these groups (left to right)



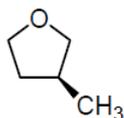
- (A) *sec*-propyl, *sec*-butyl, isobutyl (B) isopropyl, isobutyl, *sec*-butyl
 (C) *sec*-propyl, *tert*-butyl, isobutyl (D) isopropyl, *tert*-butyl, isobutyl
 (E) isopropyl, *tert*-butyl, *sec*-butyl

(A) 9. What compound is formed when 2,2-dimethyloxirane is treated with ethanol containing a trace of HCl?

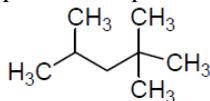
- (A) 2-ethoxy-2-methyl-1-propanol (B) 1-ethoxy-2-methyl-2-propanol
 (C) 2-ethoxy-2-methyl-2-propanol (D) 2-ethoxy-1-butanol
 (E) 1-ethoxy-2-butanol

(C) 10. Which of the following compounds gives a $^1\text{H-NMR}$ spectrum consisting of only two singlets?

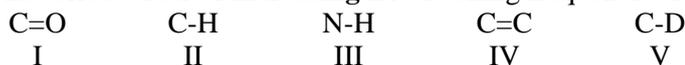
- (A) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ (B) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (C) $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{OCH}_3$ (D) $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{OCH}_3$
 (E) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

(E) 11. How many peaks appear in the proton spin decoupled $^{13}\text{C-NMR}$ spectrum of the compound below?

- (A) 1 (B) 2 (C) 3 (D) 4 (E) 5

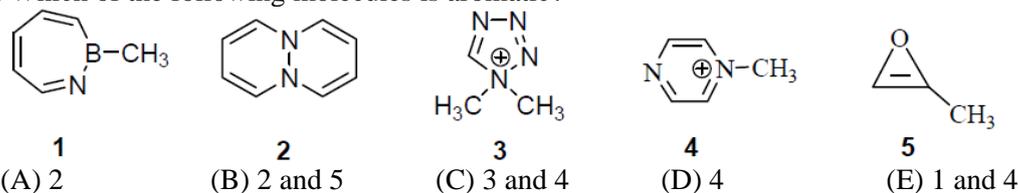
(D) 12. Consider the branched hydrocarbon to the right. Which of the following would **not** be a prominent peak in the mass spectrum of this compound?

- (A) $m/z = 43$ (B) $m/z = 57$ (C) $m/z = 99$ (D) $m/z = 113$
 (E) $m/z = 43$ and $m/z = 99$

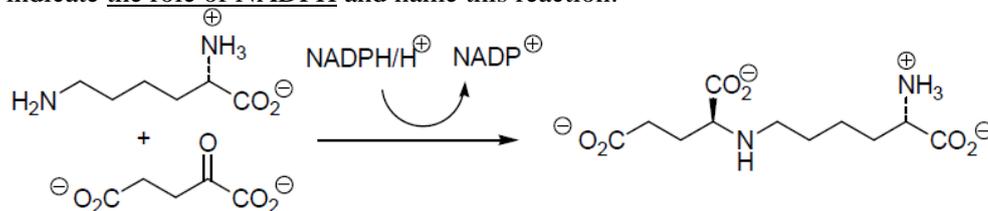
(A) 13. The correct order of **increasing** IR stretching frequencies for the following bonds.

- (A) IV, I, V, II, III (B) IV, III, I, V, II (C) I, IV, II, V, III (D) IV, I, II, III, V
 (E) I, IV, III, II, V

(E) 14. Which of the following molecules is aromatic?

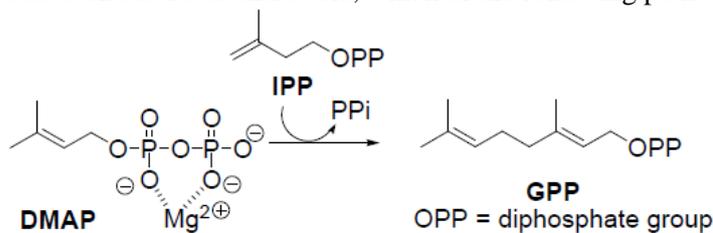


(A) 15. The following reaction presents the first step in the biological degradation of lysine. Please indicate the role of NADPH and name this reaction.



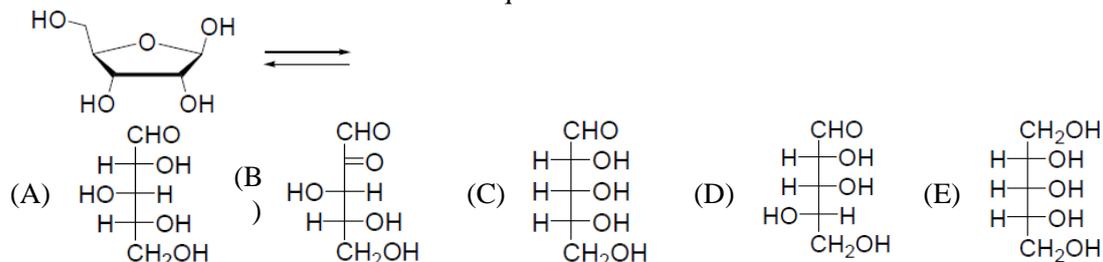
- (A) reducing agent, reductive amination (B) reducing agent, decarboxylation
 (C) hydrogenation agent, Lindlar's reaction (D) oxidized agent, transamination
 (E) oxidized agent, aldol condensation

(A) 16. The exact mechanism of the following reaction is difficult to establish conclusively. However, based on substrate characters, which of the following pathway probably occurs to give GPP?

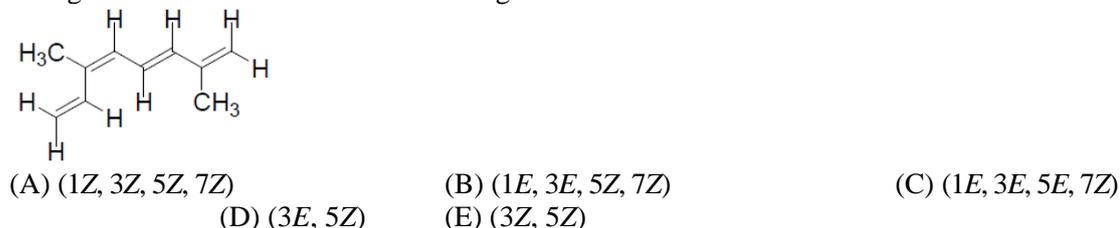


- (A) S_N1-like (B) E2-like (C) E1cB-like (D) E1-like (E) none of the above

(C) 17. Which is the **correct** structure for the equilibrium below?

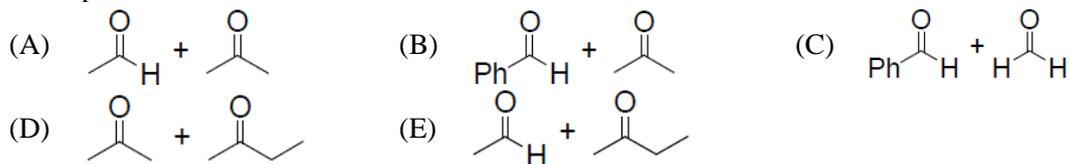


(D) 18. Assign *E/Z* nomenclature to the following alkene.



- (B) 19. Which of the following is least likely to undergo a smooth crossed Claisen condensation with methyl pentanoate?
 (A) $(\text{CH}_3)_3\text{CCO}_2\text{CH}_3$ (B) $\text{PhCH}_2\text{CO}_2\text{CH}_3$ (C) PhCO_2CH_3
 (D) HCO_2CH_3 (E) $(\text{CH}_3\text{O})_2\text{CO}$

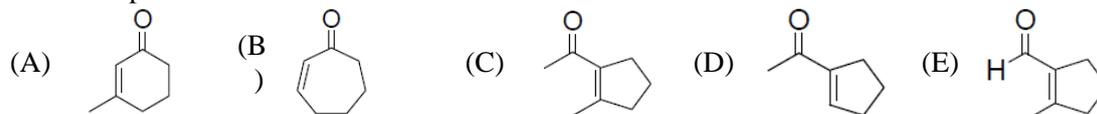
- (B) 20. Which of the following pairs of compounds would be the **most** reasonable choice for an attempt at a "mixed" or "crossed" aldol condensation?



- (C) 21. Which is the only one of these compounds which **cannot** self-condense in the presence of dilute aqueous alkali?

- (A) phenylethanal (B) propanal (C) 2,2-dimethylpropanal
 (D) 2-methylpropanal (E) 3-methylpentanal

- (D) 22. Which of the following compounds would be the major product from aldol condensation of 6-oxoheptanal?



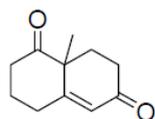
- (A) 23. Which of the following Wittig reagents would be useful for converting $\text{R}_2\text{C}=\text{O}$ into R_2CHCHO after hydrolysis?

- (A) $\text{Ph}_3\text{P}=\text{CHOCH}_3$ (B) $\text{Ph}_3\text{P}=\text{CHCH}_3$ (C) $\text{Ph}_3\text{P}=\text{Cl}_2$
 (D) $\text{Ph}_3\text{P}=\text{CHCH}=\text{CH}_2$ (E) $\text{Ph}_3\text{P}=\text{C}(\text{OCH}_3)_2$

- (C) 24. Reaction of ethylmagnesium bromide with which of the following compounds yields a tertiary alcohol after quenching with aqueous acid?

- (A) H_2CO (B) CH_3CHO (C) $(\text{CH}_3)_2\text{CO}$ (D) ethylene oxide (E) *n*-butyllithium

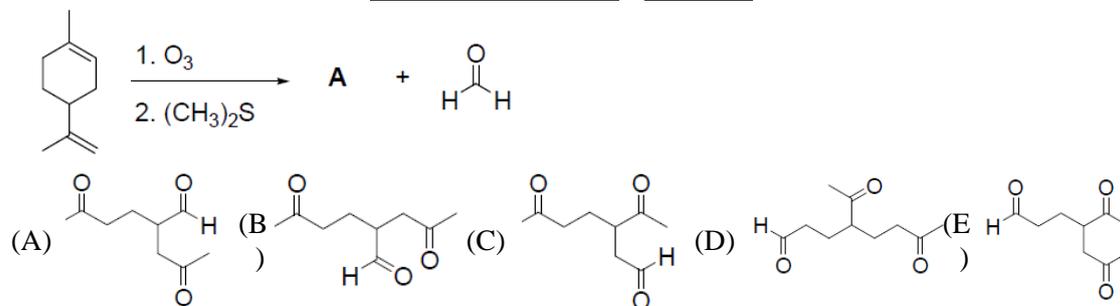
- (B) 25. What starting materials would be suitable for preparing this compound by a combination of Michael and aldol reactions?



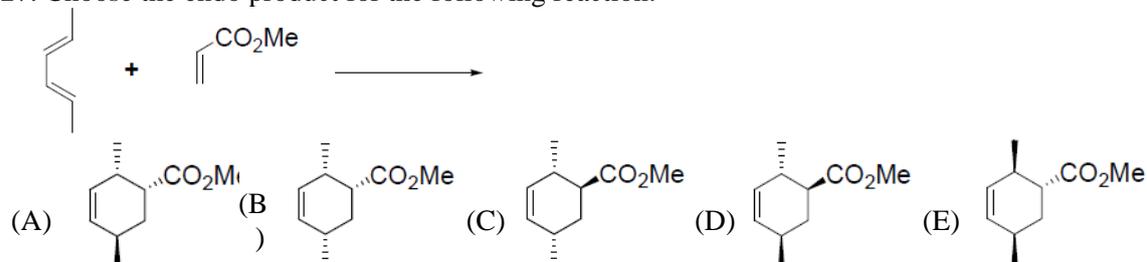
Wieland-Miescher ketone

- (A) 4-methyl-2-cyclohexen-1-one and 3-butenal
 (B) 2-methylcyclohexane-1,3-dione and 3-buten-2-one
 (C) 2-methyl-2-vinyl-3-cyclohexen-1-one and acetaldehyde
 (D) 2-methyl-2-cyclohexen-1-one and 1,4-dichlorobutan-2-one
 (E) 4-methylcyclohexanone and methyl vinyl ketone

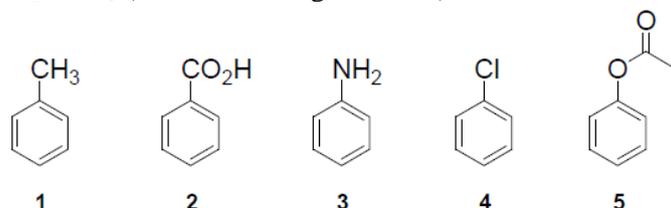
- (C) 26. The ozonolysis of limonene give compound **A** plus formaldehyde. Choose the correct structure for **A**.



(B) 27. Choose the endo product for the following reaction:



(E) 28. Rank the following compounds in order of increasing reactivity towards chlorination with $\text{Cl}_2/\text{AlCl}_3$ (slowest reacting to fastest).



(A) $3 < 4 < 2 < 1 < 5$
 (D) $2 < 4 < 5 < 1 < 3$

(B) $2 < 4 < 1 < 3 < 5$
 (E) $2 < 4 < 1 < 5 < 3$

(C) $4 < 2 < 1 < 3 < 5$

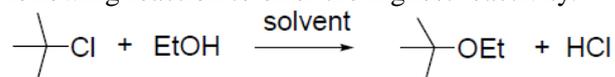
(D) 29. What compound is produced when (*R*)-pentan-2-ol is treated with TsCl followed by NaI ?

(A) sodium (*R*)-pent-3-oxide (B) sodium (*S*)-pent-2-oxide
 (C) (*R*)-2-iodopentane (D) (*S*)-2-iodopentane (E) none of the above

(E) 30. What type of intermediate is present in the $\text{S}_{\text{N}}2$ reaction of cyanide with bromoethane?

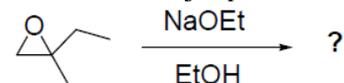
(A) carbocation (B) free radical (C) carbene (D) carbanion
 (E) This reaction has no intermediate

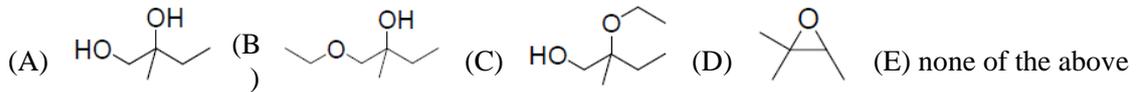
(D) 31. The reaction reactivity was studied in different solvent. Please indicate the **best** solvent for the following reaction to offer the highest reactivity.



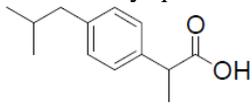
(A) hexane (B) chloroform (C) ethanol (D) water (E) no difference

(B) 32. Predict the major product for the following reaction.



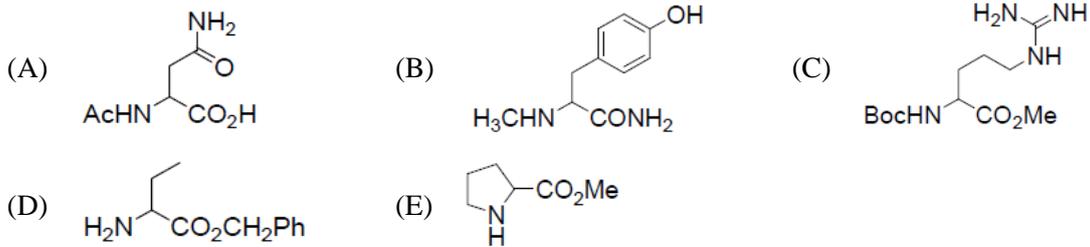


(A) 33. How many sp^3 - and sp^2 -hybridized carbons does the following compound have?



- (A) 6 and 7 (B) 7 and 6 (C) 8 and 4 (D) 4 and 8 (E) none

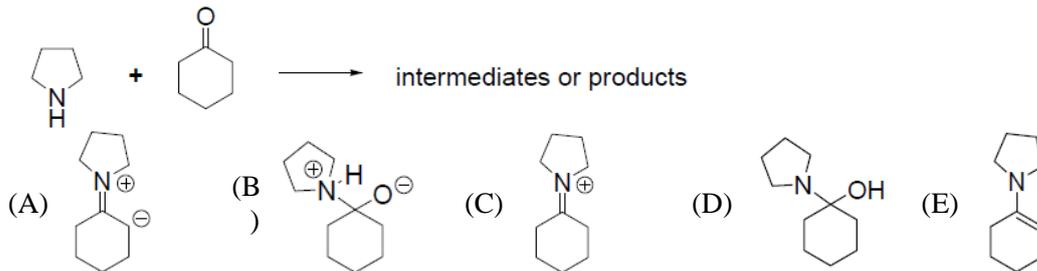
(D) 34. Ninhydrin can rapid react with a certain type of functional group to produce an intense purple color (positive result). Which of the following compound can get positive result after ninhydrin test?



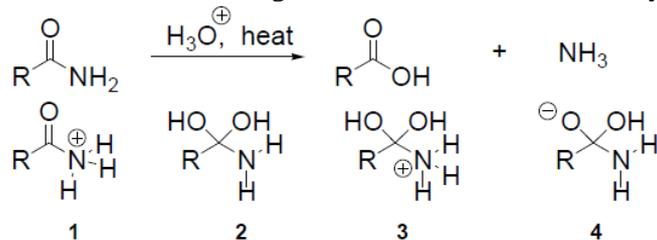
(D) 35. When 2-methylcyclohexanone is treated with catalytic base in excess D_2O , how many deuterium atoms become incorporated in the organic compound?

- (A) 0 (B) 1 (C) 2 (D) 3 (E) 5

(A) 36. Choose the structure that is **not** an intermediate or product of the following reaction.



(E) 37. Which of the following are intermediates in the acid hydrolysis of an amide?

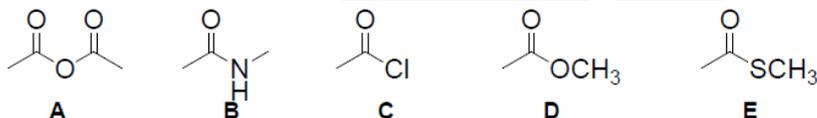


- (A) 4 (B) 1, 2 and 3 (C) 1 (D) 2 (E) 2 and 3

(D) 38. $LiAl[OC(CH_3)_3]_3H$ will reduce an acid chloride to an:

- (A) alcohol (B) alkane (C) acid (D) aldehyde (E) acetal

(B) 39. Rank the following from **highest** to **lowest** reactivity toward reaction with EtOH.



- (A) $A > C > E > D > B$ (B) $C > A > E > D > B$ (C) $E > C > A > D > B$
 (D) $C > A > B > E > D$ (E) $C > A > D > B > E$

(E) 40. In the mechanism for the dehydrohalogenation of 3-chloro-3,7-dimethyloctane, what is the dihedral angle between the hydrogen and chlorine atoms that are eliminated?
 (A) 0 degree (B) 45 degrees (C) 90 degrees (D) 135 degrees (E) 180 degrees

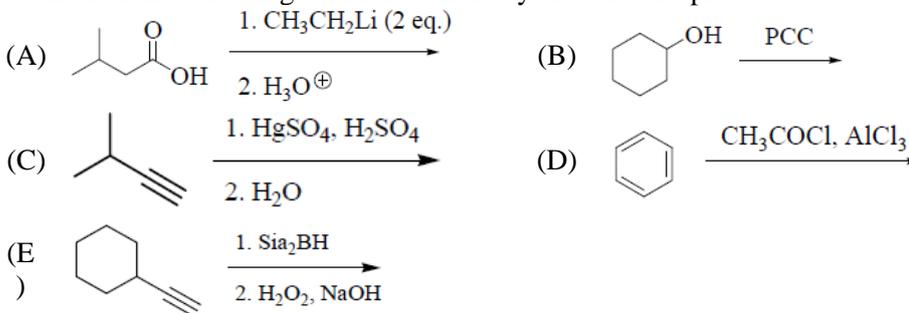
(B) 41. Which reagent is used to accelerate coupling reactions in both laboratory peptide synthesis and laboratory DNA synthesis?

- (A) catalytic H^+ (B) dicyclohexylcarbodiimide (C) sodium hydroxide
 (D) ethyl chloroformate (E) $PhS^- NH_4^+$

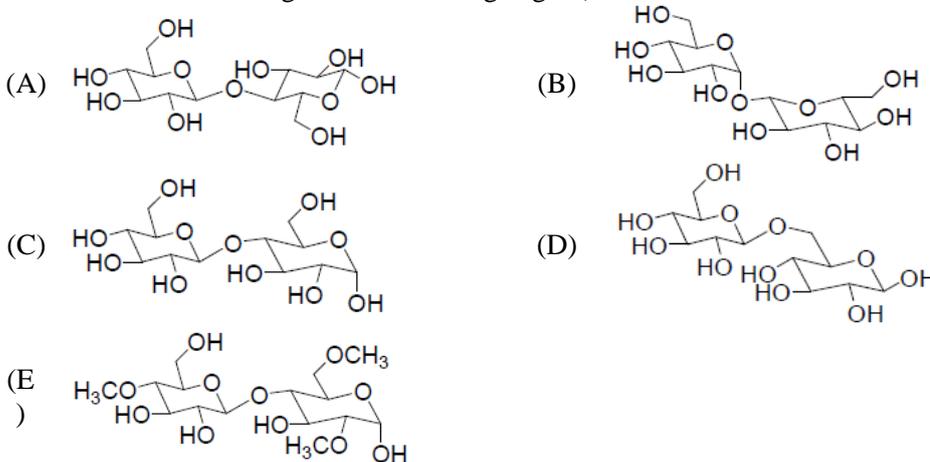
(E) 42. What reagent is used to convert pentanamide to 1-pentanamine?

- (A) $POCl_3$ (B) $CuCN$ (C) $MeMgBr$ (D) $SOCl_2$ (E) $LiAlH_4$

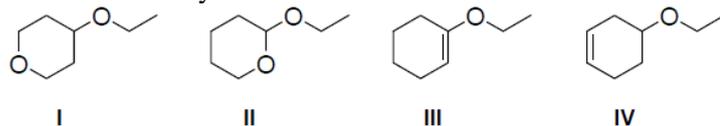
(E) 43. Which of the following reactions will **not** yield a ketone product?



(B) 44. Which of the following is a nonreducing sugar (does **not** react with Tollens' reagent)?

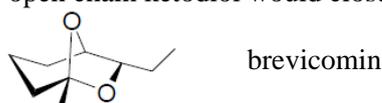


(B) 45. Formulas for four ethyl ethers are drawn below. Which two ethers are cleaved by aqueous acid much more easily than the other two?



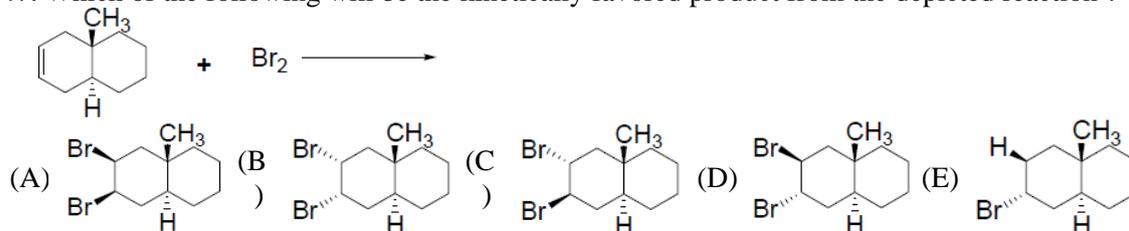
- (A) I and II (B) II and III (C) III and IV (D) I and IV (E) III and IV

(D) 46. The formula of brevicomin, a pheromone of the western pine beetle, is shown below. What open chain ketodiols would close to this bicyclic acetal? (ignore stereoisomer issues)



- (A) 7,8-dihydroxynonan-3-one (B) 6,7-dihydroxynonan-3-one
 (C) 7,8-dihydroxynonan-2-one (D) 6,7-dihydroxynonan-2-one
 (E) 6,7-dihydroxynonan-4-one

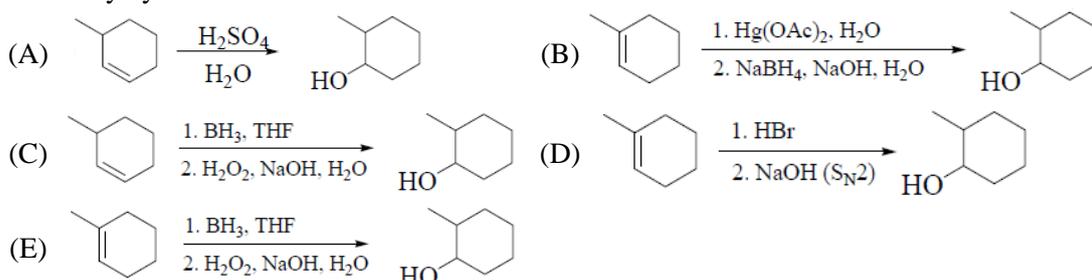
(D) 47. Which of the following will be the kinetically favored product from the depicted reaction?



(B) 48. Which of the following alcohols undergoes dehydration upon heating with concentrated H_2SO_4 **without** carbocation rearrangement?

- (A) 2-methylhexan-3-ol (B) 3-methylpentan-3-ol
 (C) 3,3-dimethylpentan-2-ol (D) 2-methyl-2-phenylpropan-1-ol (E) both A and B

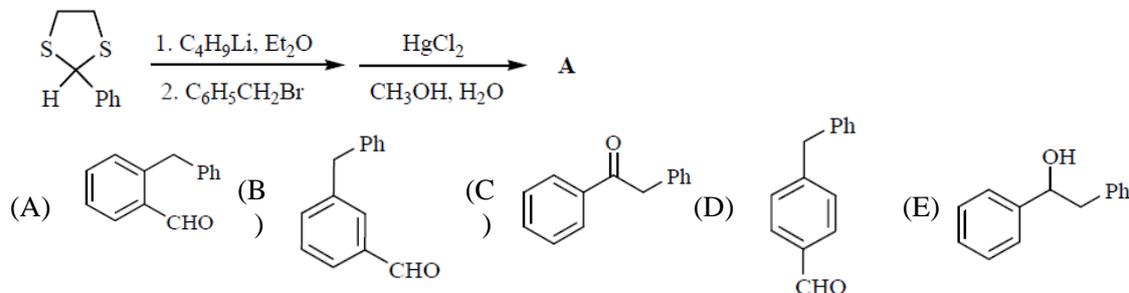
(E) 49. Choose the reaction, or reaction sequence, that best accomplishes the preparation of 2-methylcyclohexanol.



(D) 50. Alkoxymercuration followed by sodium borohydride reduction would be used to produce _____

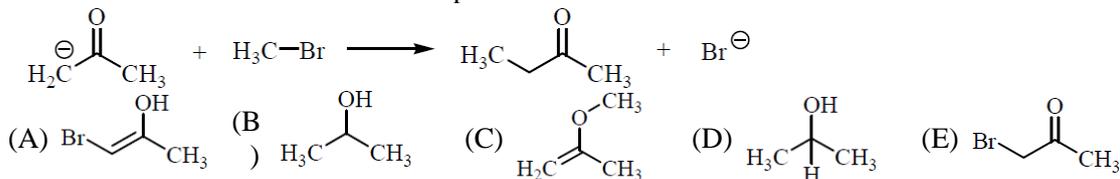
- (A) alcohol from an alkene (B) aldehyde from alcohol
 (C) acid from an alkyne (D) ether from an alkene
 (E) alkene from an aryl halide

(C) 51. What is the structure for **A**?



- (C) 52. Which reagent(s) can be used to convert bromobenzene to benzoic acid?
 (A) 1. NaCN; 2. NaOH, H₂O (B) KMnO₄ (C) 1. Mg; 2. CO₂, then H₃O⁺
 (D) CrO₃, HCl (E) 1. CH₃Br; 2. CrO₃, H₂SO₄.

- (C) 53. In addition to 2-butanone, a second product is formed in the following acid-base reaction. Choose the structure for this second product.

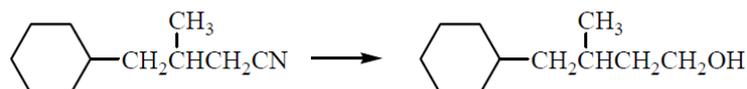


- (A) 54. Which of the base(s) below that **cannot** be used in the following reaction.

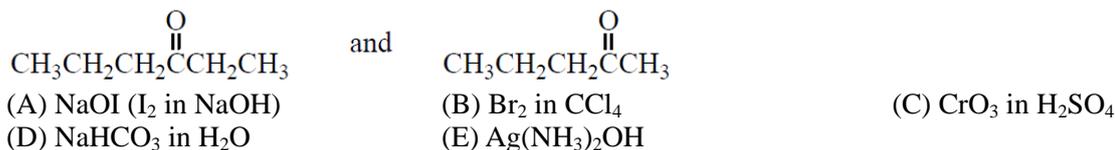


- (A) EtONa (B) NaH (C) BuLi (D) NaNH₂ (E) CH₃MgBr
- (D) 55. What is the major organic product that results when 1-heptyne is treated with 2 equivalents of HBr?
 (A) 2,3-dibromo-1-heptene (B) 2,3-dibromo-2-heptene
 (C) 1,2-dibromoheptane (D) 2,2-dibromoheptane (E) 1,1-dibromoheptane

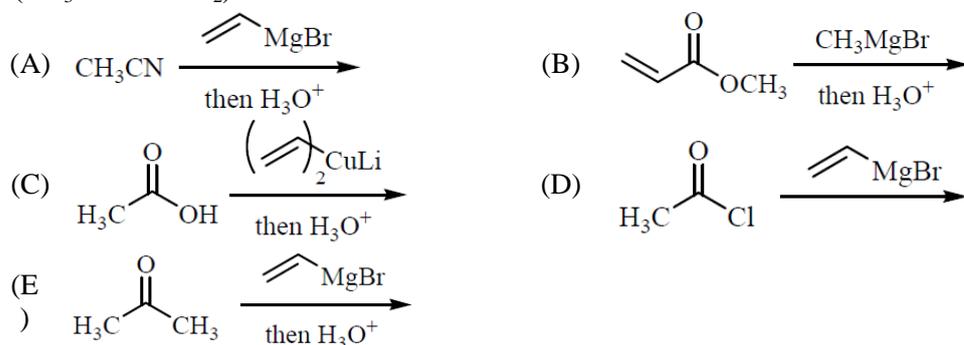
- (A) 56. Which of the following would represent the **correct** reaction conditions for the following conversion?



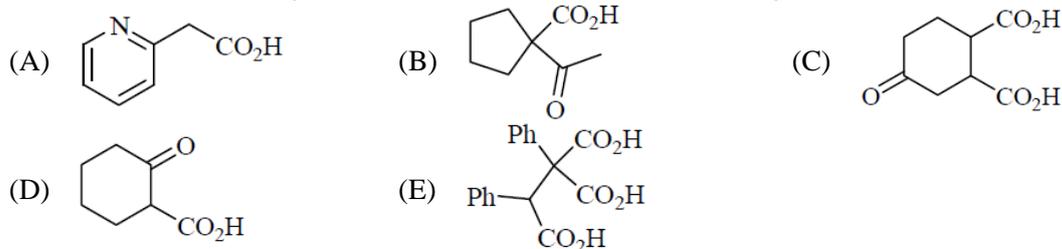
- (A) 1. NaOH, H₂O; 2. LiAlH₄ (B) 1. Mg, ether; 2. CO₂; 3. LiAlH₄
 (C) 1. KMnO₄; 2. LiAlH₄ (D) 1. SOCl₂, benzene; 2. LiAlH₄
 (E) 1. LiAlH₄, H₂O; 2. NaOH, 3-methyl-2-propylpyridine
- (A) 57. Which reagent would best serve as the basis for a simple chemical test to distinguish the two compounds below



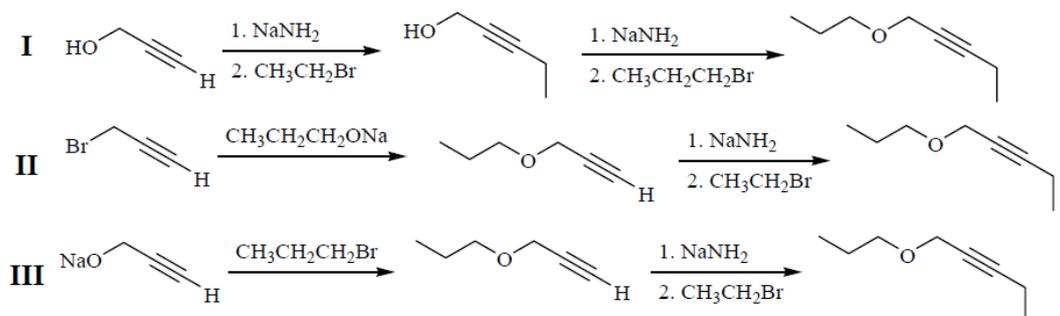
- (A) 58. Which of the following is a suitable method for synthesizing **only** methyl vinyl ketone (CH₃COCH=CH₂)?



(C) 59. Which of the following acids does **not** decarboxylate on heating?



(C) 60. Which of the following schemes will proceed to give the compound indicated as the major product.



(A) I only (B) I and II (C) II and III (D) I and III (E) all of them

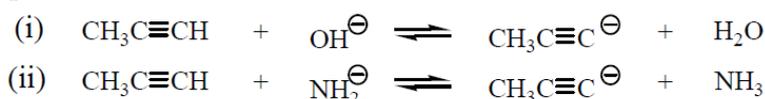
【單選題】每題 2 分，共計 40 分，答錯 1 題倒扣 0.5 分，倒扣至本大題零分為止，未作答，不給分亦不扣分。

(E) 61. Which of the following statement for Diels-Alder reaction is **false**?

- (A) Diels-Alder reaction is a pericyclic process.
 (B) The endo product, rather than exo product, is formed.
 (C) It is a thermal reaction.
 (D) It is a suprafacial [4+2]- π -electron cycloaddition.
 (E) None of the above.

(D) 62. Choose the **incorrect** statement about the following acid/base reactions involving propyne and its anion propynide.

(pKa : H₂O = 16; CH₃C≡CH = 25; NH₃ = 34)



- (A) The equilibrium in (i) lies to the left. (B) The equilibrium in (ii) lies to the right.
 (C) You can prepare propynide salts in NH₃ (D) In reaction (ii) ammonia, NH₃, acts as a base.
 (E) Propyne is a stronger acid than ammonia

(A) 63. Which of the following compound does not contain carbonyl group(s) in its structure?

- (A) dicyclohexylcarbodiimide (B) cycloheptatrienone (C) sulfanilamide
 (D) benzoyl phosphate (E) dimethyl malonate

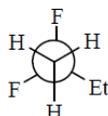
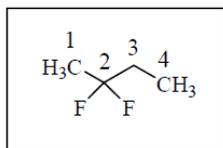
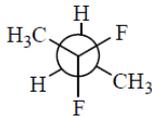
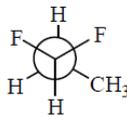
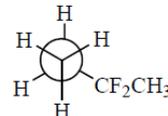
(E) 64. Which compound has the smallest heat of hydrogenation?

- (A) 5-methyl-1,2-hexadiene (B) (*E*)-5-methyl-1,3-hexadiene
 (C) 5-methyl-1,4-hexadiene (D) 2-methyl-1,5-hexadiene

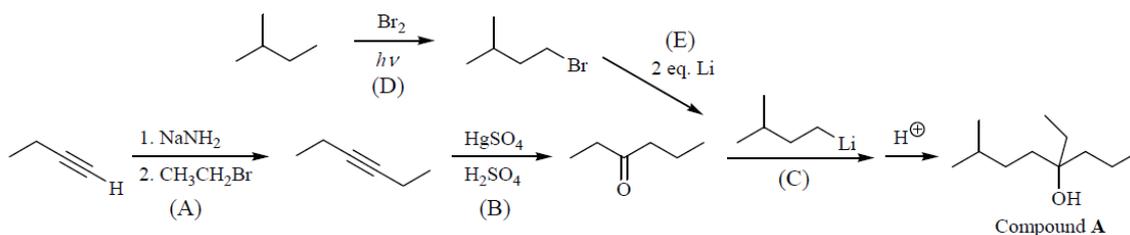
(E) (*E*)-2-methyl-2,4-hexadiene

- (A) 65. The correct priority of functional groups in IUPAC nomenclature is:
 (A) acid > ester > amide > ketone (B) amide > acid > ester > ketone
 (C) amide > ester > acid > ketone (D) ester > amide > ketone > acid
 (E) ketone > acid > ester > amide

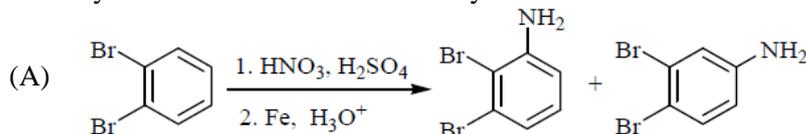
- (C) 66. Structure I-IV may represent a conformation of 2,2-difluorobutane sighting along **any** C-C bond. Please pick up right structures.

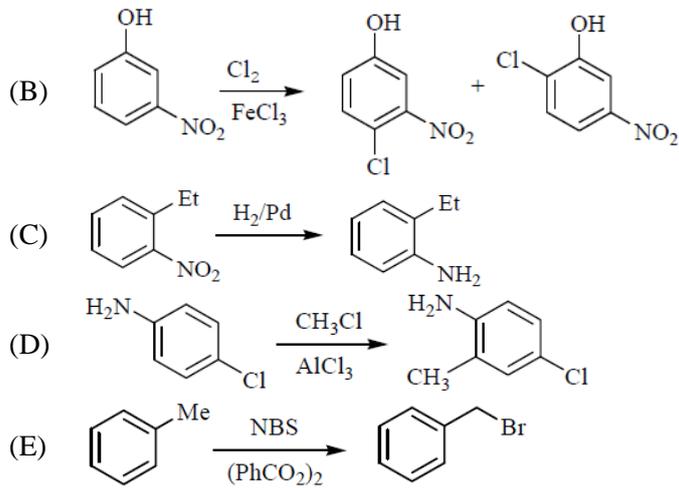
**I****II****III****IV**

- (A) I, II, III (B) II, III, IV (C) I, II, IV (D) all of the above (E) none of the above
- (D) 67. Which of the following reactions of alkenes is **not** stereospecific?
 (A) bromohydrin formation (Br_2 in H_2O) (B) hydrogenation (H_2 , Pd)
 (C) bromination (Br_2) (D) acid-catalyzed hydration (H_2O , H_2SO_4)
 (E) dihydroxylation (OsO_4 , NaHSO_3)
- (D) 68. Which system would give the **largest** ratio of substitution to elimination product(s)?
 (A) cyclohexanol + acid (B) cyclohexyl iodide + *t*-BuOK in *t*-BuOH
 (C) 1-bromobutane + *t*-BuOK in DMSO (D) 1-bromobutane + KI in acetone
 (E) 2-bromobutane + MeONa in DMSO
- (D) 69. Optically pure (*S*)-monosodium glutamate has a specific rotation of $+25^\circ$, what percent of (*R*)-monosodium glutamate in a sample with a specific rotation of -10° ?
 (A) 10% (B) 30% (C) 40% (D) 70% (E) 50%
- (B) 70. What reagents can be used to convert 1-hexyne into 2-hexanone?
 (A) 1. SiAl_2BH ; 2. H_2O_2 , NaOH (B) Hg^{2+} , H_2SO_4 , H_2O (C) 1. O_3 ; 2. $(\text{CH}_3)_2\text{S}$
 (D) 1. CH_3MgBr ; 2. CO_2 (E) 1. H_2 , Ni; 2. $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4
- (D) 71. Below is a propose a synthesis of compound **A**. Which step would **not** work.

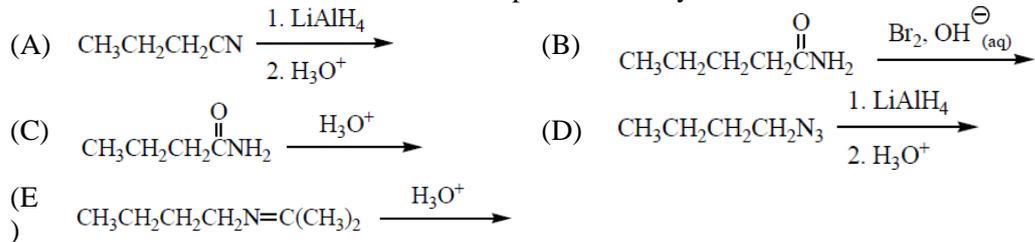


- (D) 72. The syntheses shown here are unlikely to occur as written. What is **wrong** with each?

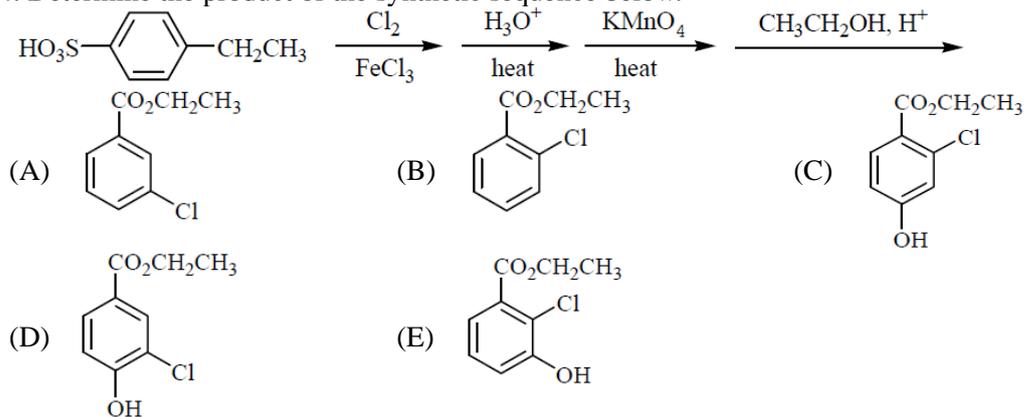




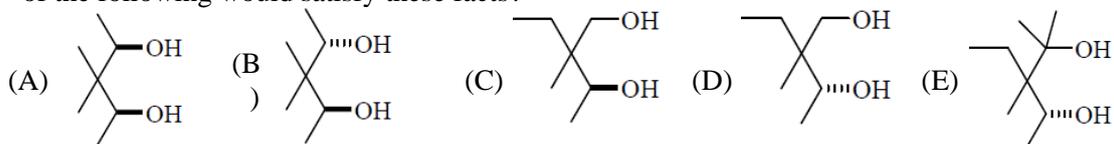
(C) 73. Which of the reactions below would **not** produce *n*-butylamine ?



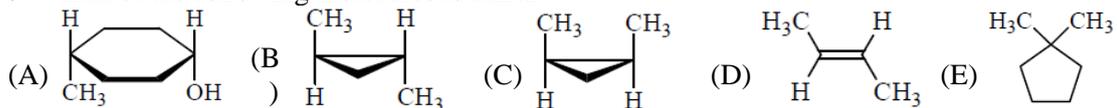
(B) 74. Determine the product of the synthetic sequence below.



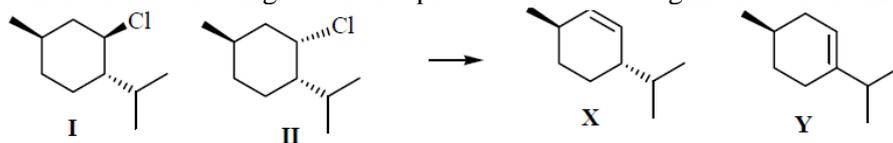
(B) 75. A chiral $\text{C}_7\text{H}_{16}\text{O}_2$ diol is oxidized by PCC in CH_2Cl_2 to an achiral $\text{C}_7\text{H}_{12}\text{O}_2$ compound. Which of the following would satisfy these facts?



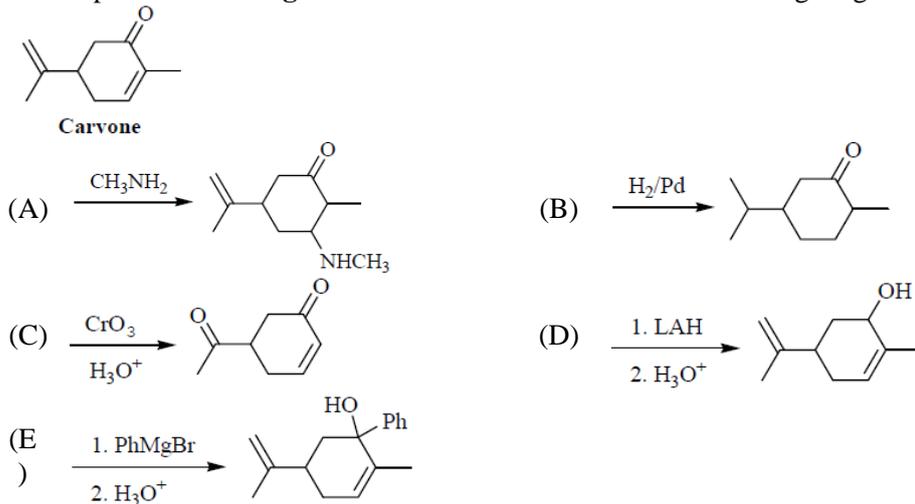
(B) 76. Which of the following molecules is chiral?



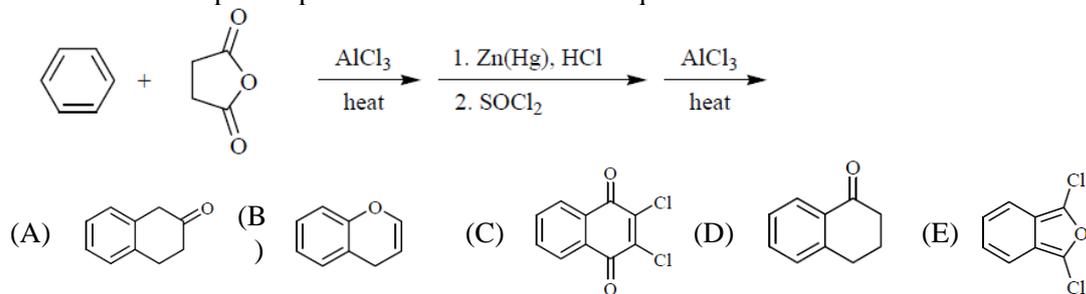
- (A) 77. Stereoisomers **I** and **II** undergo E2 elimination on treatment with sodium ethoxide in ethanol. One isomer reacts 500 times faster than the other. Also, one isomer gives **X** as the only product, whereas the other gives **Y** together with some **X**. Which of the following statements provides the best assignment of **I** and **II**?



- (A) **II** reacts faster and gives both **Y** and **X** (B) **II** reacts faster and gives only **X**
 (C) **I** reacts faster and gives both **Y** and **X** (D) **I** reacts faster and gives only **Y**
 (E) **I** reacts faster and gives only **X**
- (C) 78. What product is **wrong** when carvone is treated with the following reagents?



- (D) 79. What is the expected product from the reaction sequence drawn below?



- (D) 80. Only one of the following amines will lose its nitrogen atom as trimethyl amine by repeated Hofmann elimination reactions (exhaustive methylation followed by heating with AgOH). Identify that amine.

