

國立清華大學 命題紙

96 學年度__生命科學院、生命科學院醫學生物科技學程__系(所)__乙__組碩士班入學考試

科目__有機化學__ 科目代碼__0302、0506__共__10__頁第__1__頁 *請在【答案卷】內作答

I. Choose one correct answer for each of the following questions.

(36%, 2% each)

- How many chiral carbons are there in an open-chain aldohexose such as glucose?
(A) 2 (B) 3 (C) 4 (D) 5
- Give the products from the reaction of HIO_4 with a ketohexose $\text{HOCH}_2\text{CHOHCHOHCHOHCOCH}_2\text{OH}$
(A) $5\text{HCOOH} + \text{H}_2\text{C}=\text{O}$ (B) $4\text{HCOOH} + \text{H}_2\text{C}=\text{O}$
(C) $3\text{HCOOH} + 3\text{H}_2\text{C}=\text{O}$ (D) $3\text{HCOOH} + 2\text{H}_2\text{C}=\text{O} + \text{CO}_2$
- What is the smallest aldose able to form a cyclic hemiacetal?
(A) triose (B) tetrose (C) pentose (D) hexose
- The specific rotation for α - and β -anomers of glucose is $+112^\circ$ and $+19^\circ$, respectively. For a constant equilibrium mixture with a specific rotation of $+52.7^\circ$, calculate the % composition of each anomer.
(A) α : 45%, β : 55% (B) α : 63.8%, β : 36.2%
(C) α : 36.2%, β : 63.8% (D) α : 55%, β : 45%
- Which of the following amino acids have heterocyclic structures?
I. Lysine II. Histidine III. Proline IV. Tryptophane
(A) II, IV (B) II, III, IV (C) I, II, IV (D) I, II, III
- What is the pI value of Histidine with pK_{a1} , pK_{a2} , pK_{a3} corresponding to 1.82, 6.0, and 9.7, respectively?
(A) 7.59 (B) 3.91 (C) 5.33 (D) 7.82
- Which of the following statements regarding addition and removal of blocking group during peptide synthesis is correct?
(A) The side chain of Ser can be blocked by acetyl group and deprotected by H_2/Pd
(B) The side chain of Lys can be blocked by *p*-toluenesulfonyl group and deprotected by CF_3COOH
(C) The side chain of Glu can be blocked by benzyl ester and deprotected by weak alkali
(D) The side chain of His can be blocked by *N*-benzyl group and deprotected by sodium in liquid ammonia

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8. The artificial sweetener is a synthetic dipeptide AspPhe. How many stereoisomers are possible?
(A) 2 (B) 4 (C) 6 (D) 8
9. Place the following compounds in increasing order of basicity:
I. PhNH₂ II. Piperidine III. Pyridine IV. Pyrrol
(A) I, II, III, IV (B) II, IV, III, I (C) III, II, IV, I (D) IV, I, III, II
10. Which of the following statements is correct?
(A) The dipole moments of phenol and methanol are in opposite directions
(B) *o*-Nitrophenol has higher boiling point than the *m*-isomer
(C) *o*-Hydroxybenzaldehyde has higher boiling point than the *p*-isomer
(D) Phenol has lower boiling point than benzenethiol
11. Place the following compounds in decreasing order of acidity:
I. phenol II. *o*-nitrophenol III. *m*-nitrophenol IV. *p*-nitrophenol
(A) I, II, III, IV (B) II, IV, I, III (C) III, IV, II, I (D) IV, II, III, I
12. Based on the inductive effect, which of the following differences in acidity is correct?
(A) Me₃SiCH₂COOH > Me₃CCH₂COOH (B) ClCH₂COOH > NO₂CH₂COOH
(C) ClCH₂COOH > ClCH₂CH₂COOH (D) Cl₂CHCOOH > Cl₃COCOOH
13. Neutralization of 0.3504 g of an acid requires of 27.24 ml of 0.1500 M NaOH, and the molecular weight is found from mass-spectral data to be 172.1 g/mol. How many ionizable H's are there in the acid?
(A) 1 (B) 2 (C) 3 (D) 4
14. What is the rearrangement of the oxime of propanal in the presence of conc. H₂SO₄ and PCl₅?
(A) PhNHCOPh (B) CH₃CONHCH₃
(C) CH₃CH₂CONH₂ (D) HCONHCH₂CH₃

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15. Which of the following descriptions about solvomercuration-demercuration of an alkene is correct?

- (A) Presence of rearrangement (B) *Anti*-Markovnikov addition
(C) *Syn* addition of $\text{Hg}(\text{COCCF}_3)_2$ (D) *Anti* addition of $\text{R}'\text{-OH}$

16. Which of the following chemical tests can not distinguish between each pair of compounds?

- (A) $(\text{CH}_3)_2\text{CHOH}$ and $(\text{CH}_3)_2\text{CHSH}$; Hg^{2+}
(B) $\text{CH}_3\text{CH}_2\text{SCH}_3$ and $(\text{CH}_3)_2\text{CHSH}$; $\text{NaOH}_{(\text{aq})}$
(C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $(\text{CH}_3)_2\text{CHOH}$; I_2/OH^-
(D) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$; Cr^{3+}

17. Which of the following compounds are aromatic?

- I. cycloheptatrienyl carbocation II. cyclooctatetraene
III. 2,4,6-trinitrotoluene IV. cyclobutadiene
(A) I, III (B) II, IV (C) I, II, III (D) II, III, IV

18. Which of the following molecules are chiral?

- I. 3-methyl-1-pentene II. 2,3-pentadiene III. 2*R*, 5*S*-dimethyloctane IV. Glycine
(A) I, II (B) I, III (C) II, IV (D) I, IV

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II. Provide rational explanations, mechanisms, or calculations for each of the following questions.

(20%, 4% each)

1. A tripeptide **W** is hydrolyzed completely to 2 eq. of Glu and 1 eq. each of Ala and NH_3 . **W** has only 1 free carboxyl group and does not react with 2,4-dinitrofluorobenzene. Ala is released first when **W** is treated with carboxypeptidase. Determine the structure of **W** and briefly explain.
2. Draw a mechanism to explain the isolation of a tetradeuterated product from the reaction of $\text{CH}_3\text{CH}=\text{CHCHO}$ with OD^- in D_2O .
3. Balance the following oxidation reaction (in base) by the ion-electron (half cell) method.
 $\text{PhCH}_2\text{OH} + \text{KMnO}_4 \rightarrow \text{PhCOOH} + \text{MnO}_2 + \text{H}_2\text{O} + \text{OH}^-$
4. The reduction of 4-*t*-butylcyclohexanone with LiAlH_4 gives mainly the *trans* alcohol (90%), but with SiAl_2BH , the product is mainly *cis* alcohol (88%). Draw the structures of the alcohols and explain the different product distributions.
5. Optically active (2*S*,3*R*)-3-bromo-2-butanol (**X**) reacts with KOH and MeOH to give an optically active epoxide (**Y**). **Y** is treated with KOH in H_2O to give 2,3-butanediol (**Z**).
 - (a) Write three-dimensional structures of **X**, **Y**, and **Z**.
 - (b) Does **Z** show optical rotation? Explain.

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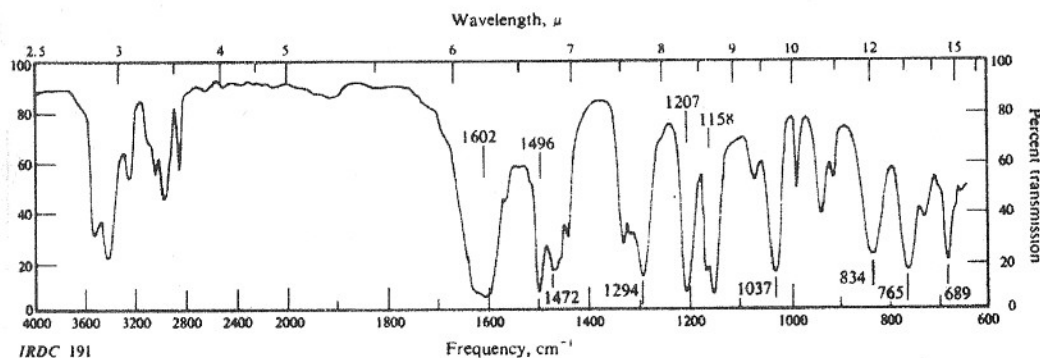
科目__有機化學__ 科目代碼__0302、0506__共 10 頁第 5 頁 *請在【答案卷】內作答

III. Spectroscopy

(20%, 2% each)

Choose one correct answer from each of the following questions.

- Amines P, Q, R, S each have their parent cation peaks at $m/z = 59$. The highest intensity peaks are at $m/z = 44$ for P and Q, 30 for R, and 58 for S. Which one of them contains a tertiary amine?
(A) P (B) Q (C) R (D) S (E) none of them
- The IR spectrum of a dilute solution of *cis*-3-fluorocyclohexanol shows a broader, lower-frequency O-H stretching peak than does the *trans* isomer. Which of the following is the main determining factor?
(A) Van der Waals force (B) dipole-dipole interaction (C) intramolecular hydrogen bond (D) intermolecular hydrogen bond (E) steric hinderance
- The ^{13}C -NMR spectra of *cis*-decalin ($\text{C}_{10}\text{H}_{18}$, consists of two fused cyclohexane rings) can exhibit very different characteristics over a wide temperature range due to the conformational exchange of the molecule. At 90 °C the conformational exchange is very fast. What would you expect to see in the spectrum? The spectrum shows (A) 4 peaks of relative intensities 2:1:1:1 (B) 5 peaks of relative intensities 1:1:1:1:1 (C) 2 peaks of relative intensities 4:1 (D) one peak (E) 3 peaks of relative intensities 2:2:1
- Follow the previous question. What would you expect to see in the ^{13}C -NMR spectrum when the temperature decreases to -50 °C, where the conformational exchange is slow? The spectrum shows (A) 4 peaks of relative intensities 2:1:1:1 (B) 5 peaks of relative intensities 1:1:1:1:1 (C) 2 peaks of relative intensities 4:1 (D) one peak (E) 3 peaks of relative intensities 2:2:1
- Which of the following compounds could give rise to the infrared spectrum shown bellow? (A) acetanilide (B) aniline (C) *N,N*-dimethylformamide (D) *m*-anisidine (E) *n*-butylamine

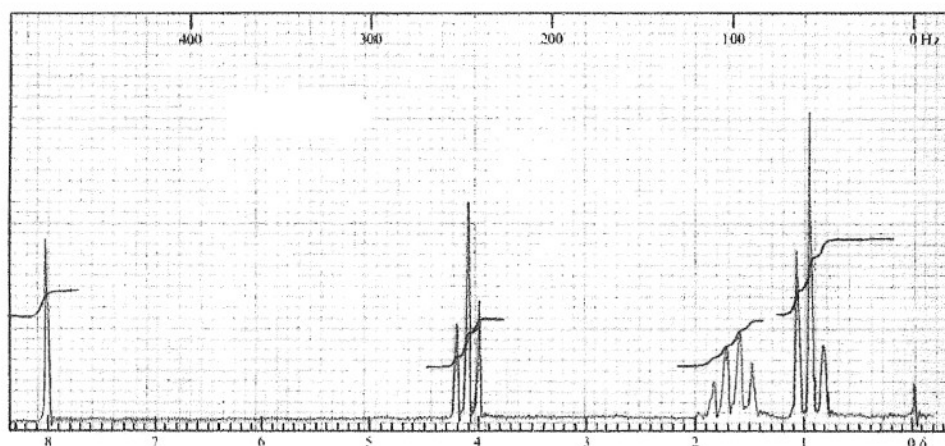


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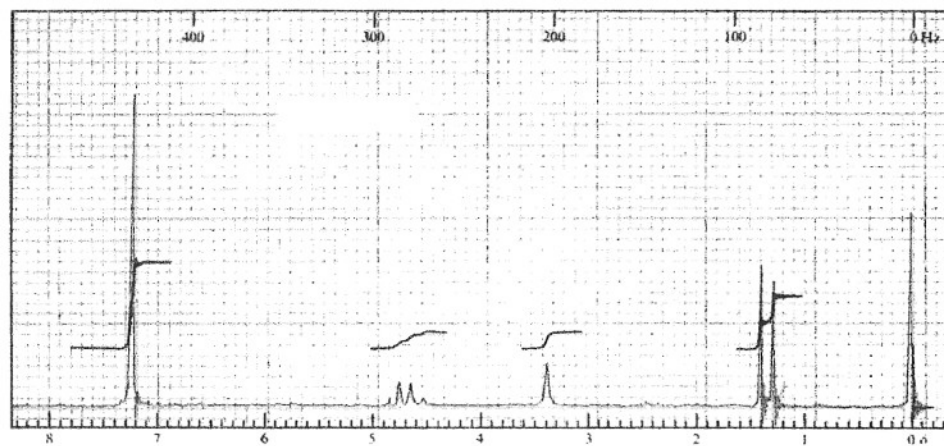
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6. Which of the following compounds is consistent with the ^1H -NMR spectrum shown below? (A) *n*-propyl formate (B) methyl propionate (C) ethyl acetate (D) methacrylic acid (E) ethyl acetate



7. Which of the following compounds is consistent with the ^1H -NMR spectrum shown below? (A) 2,3-xyleneol (B) benzyl methyl ether (C) α -phenylethyl alcohol (D) 3,5-xyleneol (E) β -phenylethyl alcohol



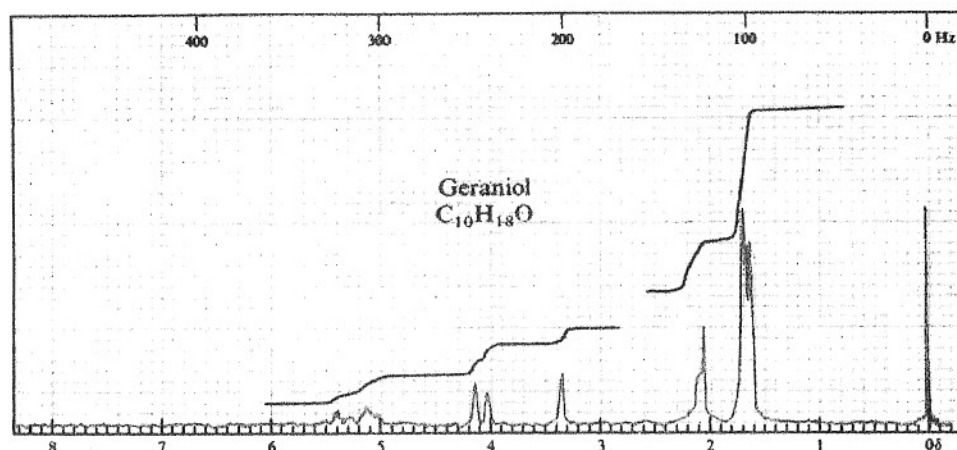
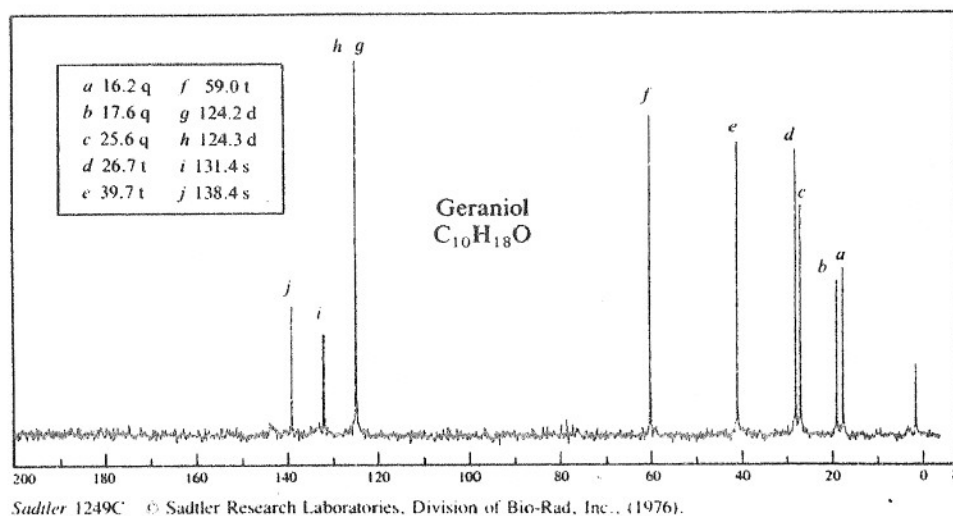
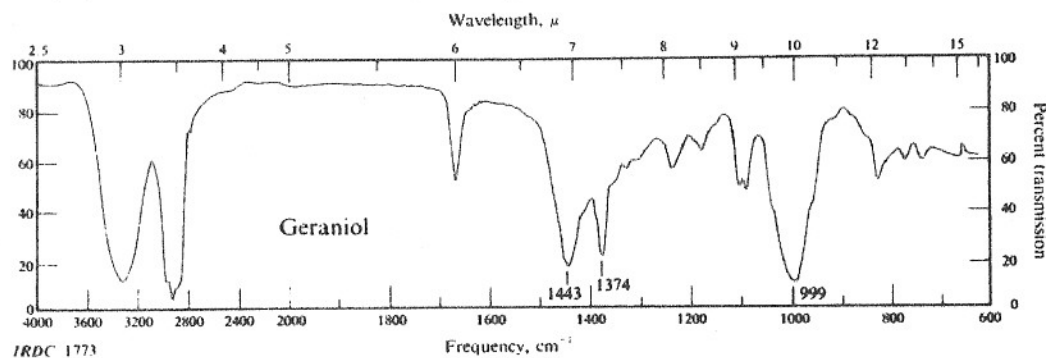
8. Which of the following statements is **wrong**? (A) IR absorption is due to molecular vibration (B) NMR signal is due to the radioactivity of nucleus under the influence of external magnetic field (C) The UV/Visible absorption for organic compounds involves the electronic transition in the π orbitals (D) Mass spectrometry resolves particles according to the charge/mass ratio (E) The bending frequency is often smaller than the stretching frequency of a molecular bond.

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科目__有機化學__ 科目代碼__0302、0506__共 10 頁第 7 頁 *請在【答案卷】內作答

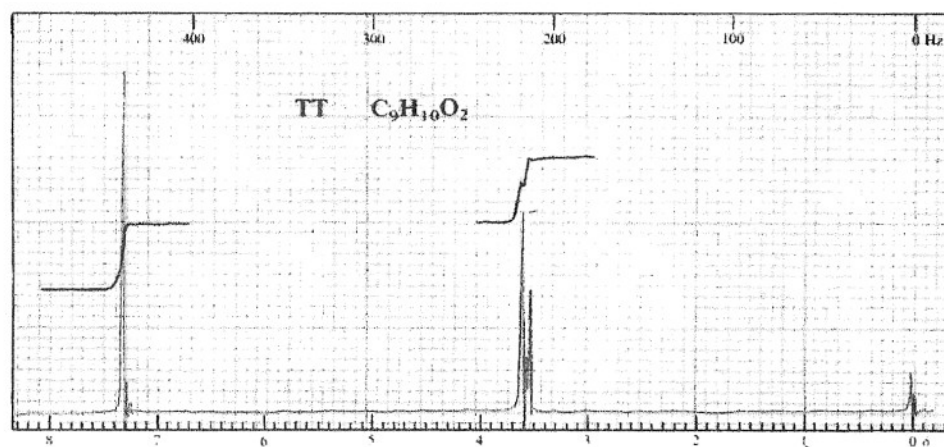
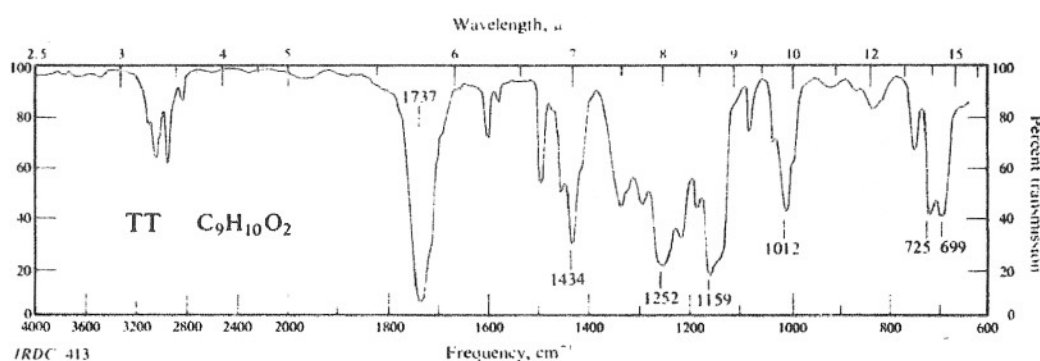
9. Geraniol, $C_{10}H_{18}O$, a terpene found in rose oil, gives the infrared, ^{13}C -NMR and 1H -NMR spectra shown below. Based on the spectra, which of following statements is **wrong**? (A) Geraniol is an aliphatic compound (B) Geraniol is a primary alcohol (C) Geraniol contains only one carbon-carbon double bond (D) Geraniol has three methyl groups (E) There is only one labile proton in Geraniol.



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10. Deduce from the spectra below, the compound TT is (A) Benzyl acetate (B) hydrocinnamic acid $C_6H_5CH_2CH_2COOH$ (C) cyclohexyl acetate (D) methyl phenylacetate (E) none of the above.



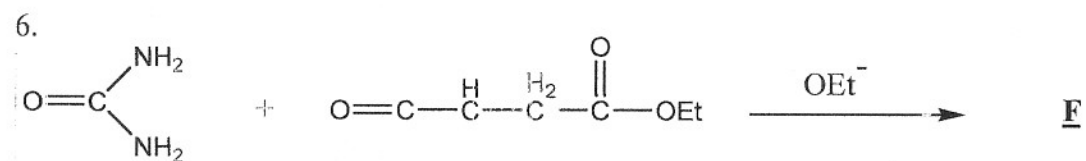
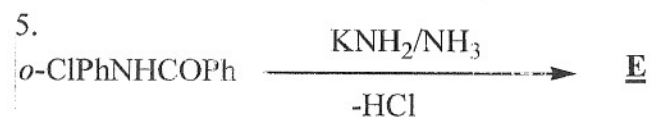
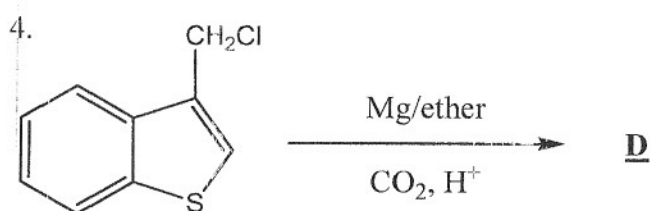
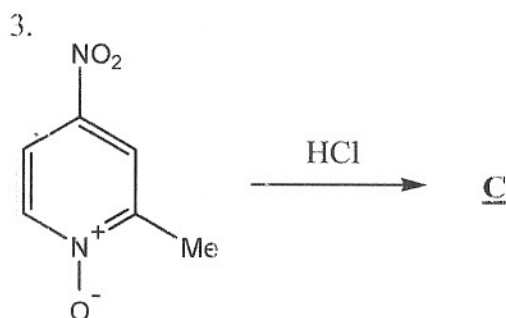
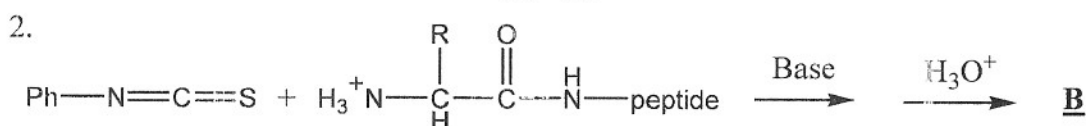
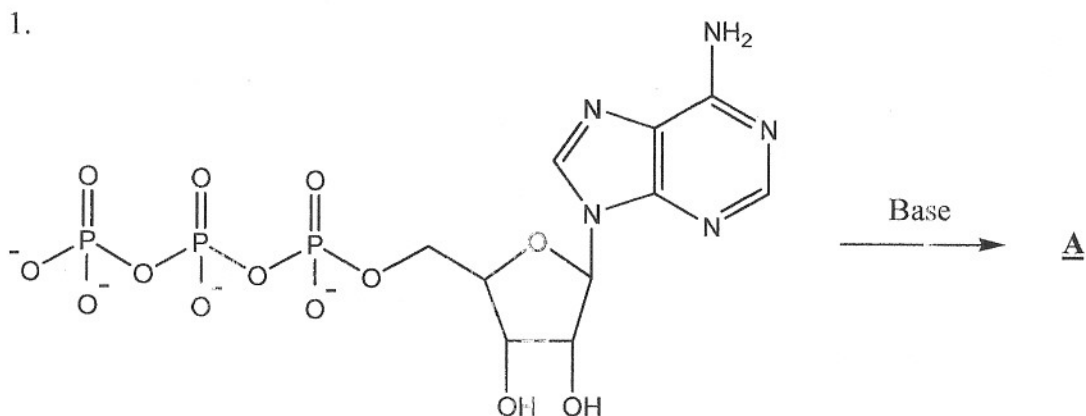
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IV. Predict major product for each of the following reactions.

(24%, 2% each)

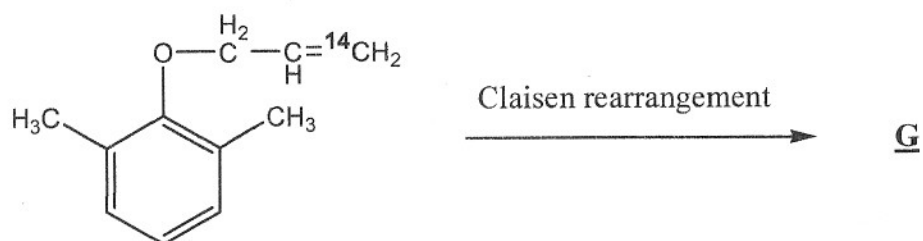


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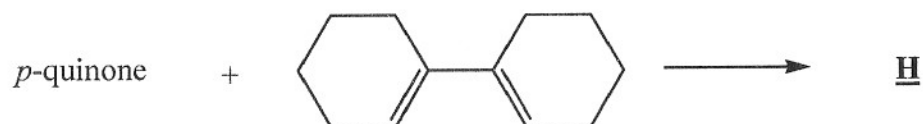
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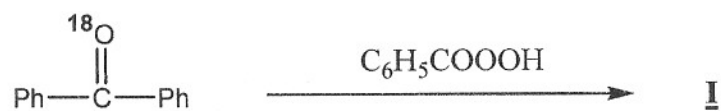
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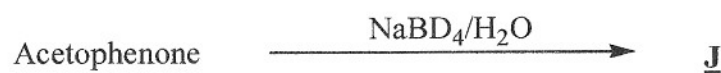
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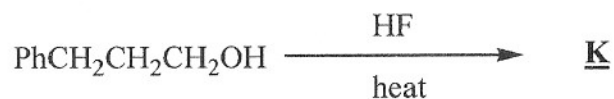
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