科目：有機化學(1002)

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清華大學化學系
清華大學材料科學工程學系（丙組）

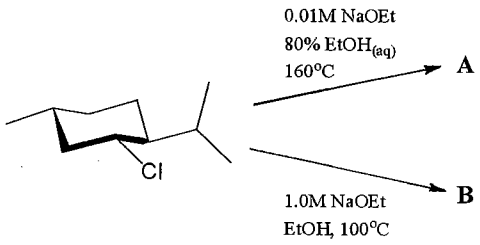
一、選擇題 (請選擇一個最適當的答案; 每題 2 分；沒有倒扣; 題目中的 "~" 符號表示 "近似於")

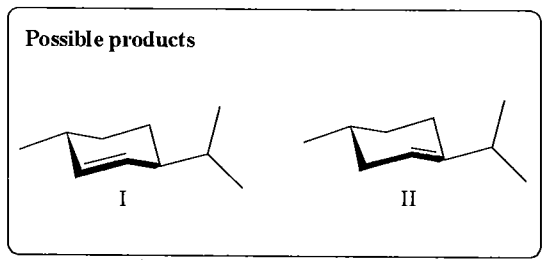
1). The correct ranking for the relative stability of the listed carbocations is:

I ; II ; III ; IV ; V

(A) I > II > III > IV > V
(B) I < II < III < IV < V
(C) I > II ~ IV ~ V > III
(D) I > II > IV ~ V > III
(E) I ~ IV ~ V > II > III

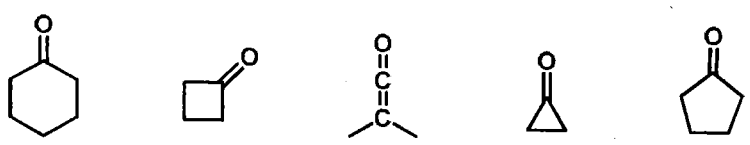
2). For the following reaction, choose the correct combination of products:





(A) **A**: I + II; **B**: II only
(B) **A**: I + II; **B**: I only
(C) **A**: I only; **B**: II only
(D) **A**: II only; **B**: I + II
(E) All the listed products are incorrect

3). Which is the correct theoretical ranking of the C=O stretching vibration energy (in cm^{-1}) for the following compounds:



(a) **(b)** **(c)** **(d)** **(e)**

(A) (b) > (a) > (c) >(e) > (d)
(B) (a) > (b) > (c) > (d) > (e)
(C) (c) > (d) > (b) > (e) > (a)
(D) (b) > (d) > (c) > (a) > (e)
(E) (a) > (e) > (b) > (d) > (c)

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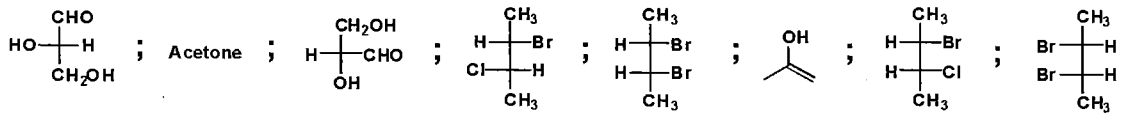
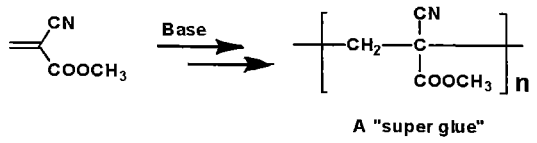
4). For the listed compounds, select the correct statement(s):



(A) All the listed compounds are optically active.
(B) **D** and **G** are diastereomers; **A** and **C** are tautomers.
(C) The mixture of equal amount of **E** and **H** is a racemate.
(D) **A** and **C** are enantiomers; **B** and **F** are tautomers.
(E) **B** and **F** are tautomers and **F** is the dominant isomer at room temperature.

5). Classify the reaction below:



(A) Elimination;
(B) Rearrangement;
(C) Substitution;
(D) Anionic polymerization;
(E) None of the above.

6). What is the product of the following reaction?

(A) *meso*-1,2-Dihydroxyl-1,2-diphenylethane
(B) (*E*)-1-Bromo-1,2-diphenylethylene
(C) *cis*-Dibromoethylene
(D) *trans*-Diphenylethylene
(E) (*Z*)-1-Bromo-1,2-diphenylethylene

注意：背面有試題

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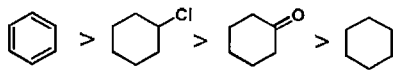
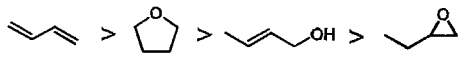
7). Which of the following represents the correct ranking of decreasing oxidation level ? (high oxidation level > low oxidation level)

(A) $CH_3CN > CH_3CH_2NH_2 > H_2NCH_2CH_2NH_2$

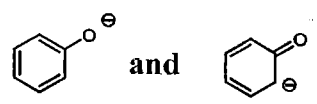
(B) 

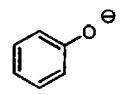
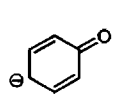
(C) 

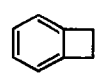
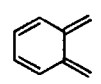
(D) $CH_3CH_2CH_2NH_2 > CH_3CH_2CH_2Br > BrCH_2CH_2CH_2Cl > CH_3\overset{O}{\overset{\|}{C}}CH_2Cl$

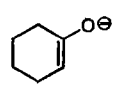
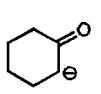
(E) $CH_3CH_2CH_2COOH > CH_3CH_2CH_2CHO > CH_3CH_2CH{=}CH_2 > CH_3CH_2CH_2CH_3$

8). Which of the following pairs of structures do not represent resonance forms?

(A)  **and**

(B)  **and** 

(C)  **and** 

(D)  **and** 

(E) **All of the above**

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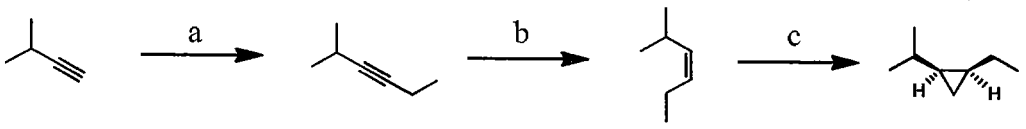
9). What are the reagents a-c in the following scheme?



(A) a: $NaNH_2$, NH_3, then CH_3CH_2Br
b: H_2, Lindlar catalyst
c: CH_2I_2, Zn(Cu)

(B) a: KOH, EtOH, then CH_3CH_2Br
b: H_2, Pd(C)
c: *meta*-Chloroperoxybenzoic acid (MCPBA)

(C) a: Li, liquid NH_3
b: $KMnO_4$, H_3O^+
c: NBS, CCl_4

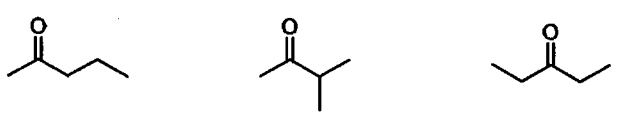
(D) a: $Hg(OAc)_2$, H_2O, then $NaBH_4$
b: MCPBA
c: H_2, Lindlar catalyst

(E) a: $NaNH_2$, NH_3, then $CH_3CH_2CH_2Br$
b: H_2, Pd(C)
c: KOH, $CHCl_3$

10). A ketone sample ($M^+ = 86$) shows the following fragmentation signals in its mass spectrum:

$m/z = 71$ and $m/z = 43$

Identify the possible structure(s) that represent this sample from the following compounds and select the correct statement.



a　　b　　c

(A) All of them are possible to be the unknown compound.
(B) a only.
(C) b and c.
(D) a and b.
(E) None of them is possible to be the unknown compound.

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11). If a nucleus is strongly shielded:

(A) The effective field is smaller than the applied field, and the absorption is shifted downfield.
(B) The effective field is larger than the applied field, and the absorption is shifted upfield.
(C) The effective field is smaller than the applied field, and the absorption is shifted upfield.
(D) The effective field is larger than the applied field, and the absorption is shifted downfield.
(E) The effective field is equal to the applied field.

12). The protons on carbon 3 (3 號碳上的氫) of (*R*)-2-bromobutane are:

(A) homotopic; (B) enantiotopic; (C) diastereotopic; (D) unrelated; (E) none of the above

13). IR spectroscopy is especially useful for:

(A) determining an alkyne is a terminal alkyne or an internal alkyne.
(B) predicting the type of carbonyl group that is presented in a compound.
(C) deciding if a double bond (C=C) is monosubstituted or disubstituted.
(D) predicting whether the phenyl ring is presented or not.
(E) All of these situations.

14). Which of the following is both a good nucleophile and a good leaving group?

(A) OH^-; (B) CN^-; (C) Cl^-; (D) I^-; (E) None of the listed species.

15). Which of the following is true for S_N1 reactions:

(A) The rate varies with the concentration of nucleophile
(B) The rate varies with the type of nucleophile
(C) The rate is increased by use of a polar solvent
(D) The nucleophile is involved in the rate-determining step
(E) All of theses statements are true

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16). What is the degree of unsaturation of a compound whose molecular formula is $C_{11}H_{13}N$?

(A) 3; (B) 4; (C) 5; (D) 6; (E) 7

17). Which of the following compound contains primary, secondary, tertiary and quaternary carbons?

(A) 2,2,4-trimethylhexane; (B) ethylcyclohexane; (C) 2-methyl-4-ethylclcohexane; (D) 2,2,-dimethylcyclohexane; (E) 3-bromocyclohexanone.

18). How many isomers of the formula $C_4H_8Br_2$ are there?

(A) 4; (B) 6; (C) 8; (D) 9; (E) No isomers

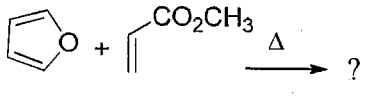
19). According to Cahn-Ingold-Prelog sequence rule, which of the following group is of lower priority then a vinyl group?

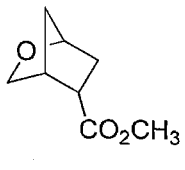
(A) an isopropyl group; (B) $-CH=C(CH_3)_2$; (C) $-C\equiv CH$; (D) a *t*-butyl group; (E) None of them.

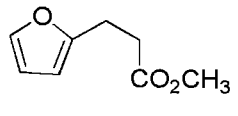
20). Which of the following reactions probably has the greatest entropy increase?

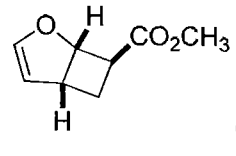
(A) Addition reaction; (B) Elimination; (C) Substitution reaction; (D) Rearrangement; (E) All of them.

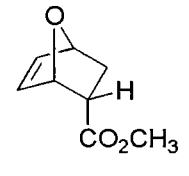
21). What is the major product of the following reaction?

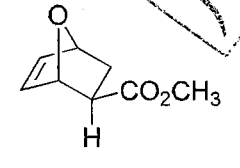


(A) 

(B) 

(C) 

(D) 

(E) 

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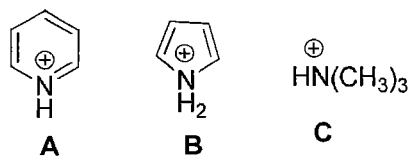
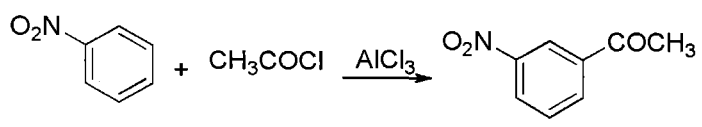
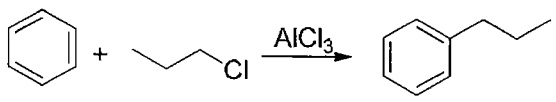
22). Rank the following compounds in order of **increasing** p*K*a (from the lowest to highest p*K*a).

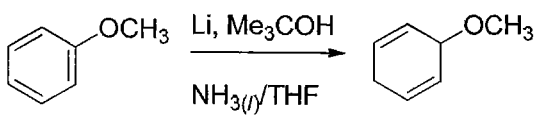


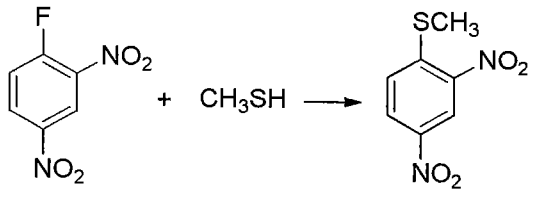
(A) A<B<C (B) B<A<C (C) A<C<B (D) C<B<A (E) B<C<A

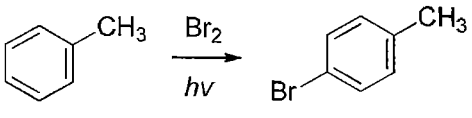
23). Which of the following reaction can proceed smoothly as predicted?

(A) 

(B) 

(C) 

(D) 

(E) 

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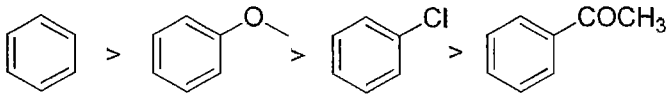
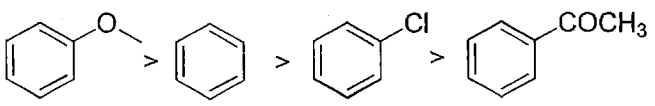
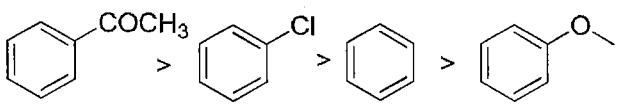
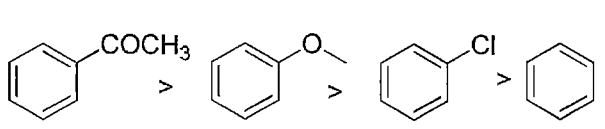
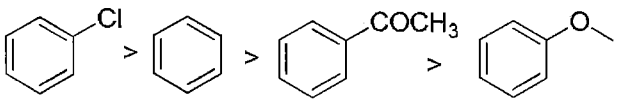
24). Arrange the following compounds in order of **decreasing** reactivity to *electrophilic aromatic substitution*.

(A) 

(B) 

(C) 

(D) 

(E) 

25). The ^{1}H NMR spectrum of an unknown compound contains a doublet at 9.9 ppm. Which of the following could be this unknown?

(A) $(CH_3)_3CCHO$
(B) $CH_3CH_2CH_2CO_2H$
(C) $(CH_3)_2CHCHO$
(D) CH_3COCH_2Ph
(E) PhCHO

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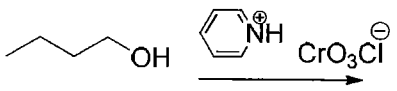
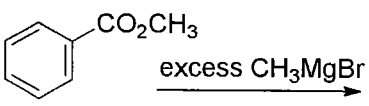
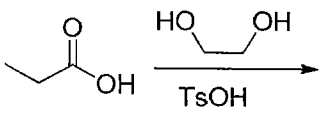
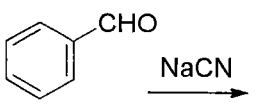
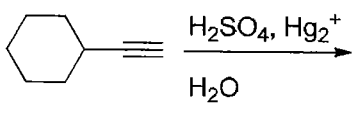
26). Which of the following reactions will give a ketone as a product?

(A) 

(B) 

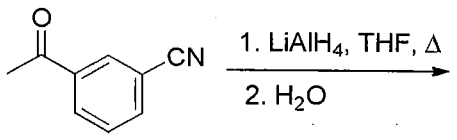
(C) 

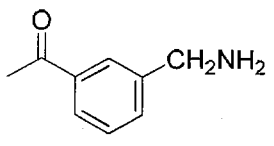
(D) 

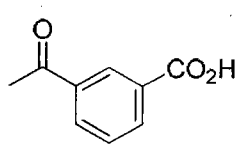
(E) 

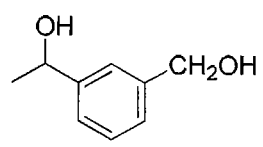
參考用

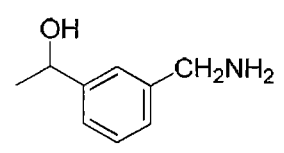
27). What is the product of the following reaction:

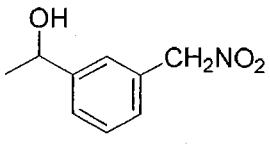


(A) 

(B) 

(C) 

(D) 

(E) 

注意：背面有試題

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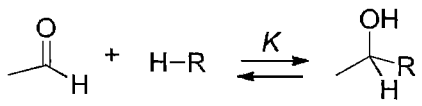
28). For the following reversible reaction, which has the largest equilibrium constant (*K*)?



(A) R = CN
(B) R = Br
(C) R = OCH_3
(D) R = OH
(E) R = NO_2

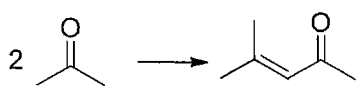
29). Which of the following amines could be formed by reduction of an amide?
1) benzylamine　2) 2-butanamine　3) aniline　4) triethylamine

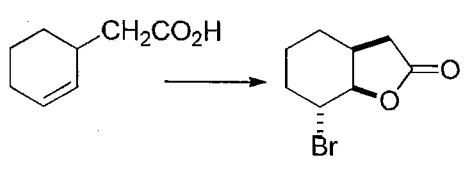
(A) 1 only
(B) 1 and 4
(C) 2 and 3
(D) 3 and 4
(E) 1, 3 and 4

30). Which of the following methods of preparation of amines can be used to prepare primary, secondary, and tertiary amines?

(A) reduction of a nitrile
(B) Gabriel synthesis from an alkyl halide
(C) Hofman rearrangement of an amide
(D) reductive amination of a ketone
(E) reduction of an alkyl azide

31). Which of the following reactions does *not* involve a reducing or oxidizing agent?

(A) 

(B) 

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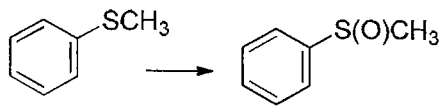
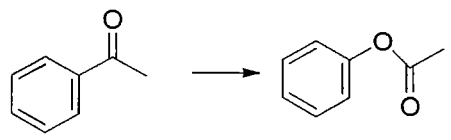
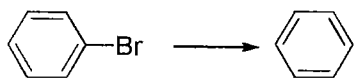
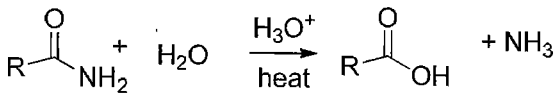
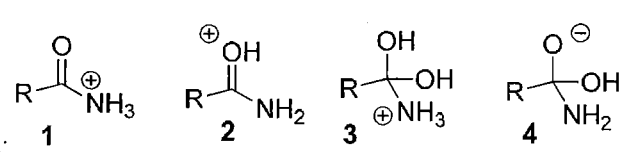
(C) 

(D) 

(E) 

32). Which of the following are the intermediates in the acid hydrolysis of an amide?



Intermediates: 

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

33). Which of the following will take place via nucleophilic acyl substitution?

(A) thioester producing an acid chloride
(B) ester producing an acid anhydride
(C) amide producing an ester
(D) acid anhydride producing an acid chloride
(E) ester producing an amide

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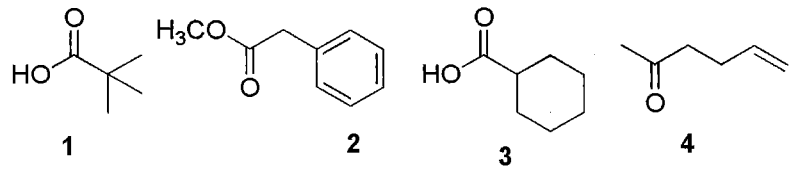
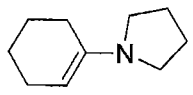
34). Which of the following structures could be constructed by way of a malonate ester alkylation?



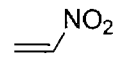
1　　2　　3　　4

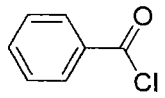
(A) 1 only
(B) 1 and 3
(C) 1 and 2
(D) 3 and 4
(E) 1, 2 and 3

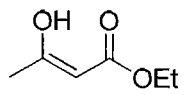
35). Which of the following is the *best* Michael acceptor?

(A) 

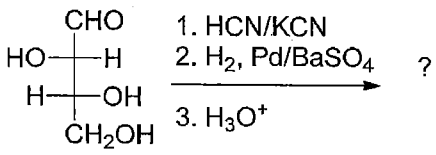
(B) 

(C) 

(D) 

(E) 

36). What is/are the major products of the following reaction?



(A) D-xylose and D-lyxose
(B) L-ribose
(C) D-glucose and D-galactose
(D) L-fructose and D-arabinose
(E) L-xylose and D-xylose

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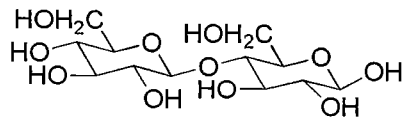
37). What kind of linkage is shown in the following disaccharide?

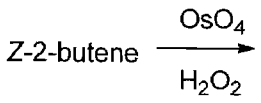


(A) β-1,4' glucosidic linkage
(B) α-1,4' glucosidic linkage
(C) β -1,6' glucosidic linkage
(D) α-1,6' glucosidic linkage
(E) γ-1,6' glucosidic linkage

38). Which of the following amino acids does not have an aromatic group within its side chain?

(A) tryptophan
(B) tyrosine
(C) histidine
(D) phenylalanine
(E) glutamine

39). Which statement is correct for the product obtained from the following reaction?



(A) 1,2-butandiol
(B) a 1:1 mixture of enantiomeric epoxides
(C) a meso diol
(D) a 1:1 mixture of enantiomeric diols
(E) butan-2-ol

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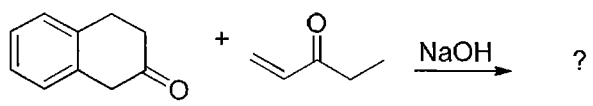
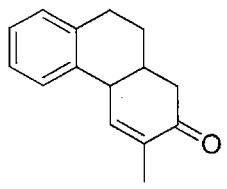
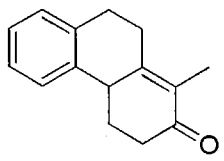
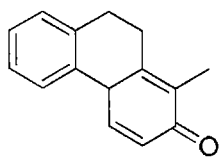
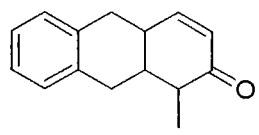
40). What is the product for the following reaction?

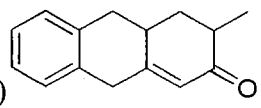


(A) 

(B) 

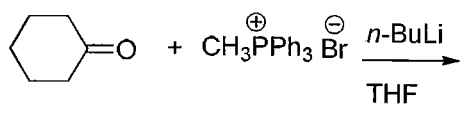
(C) 

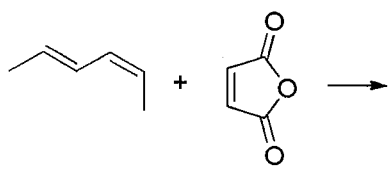
(D) 

(E) 

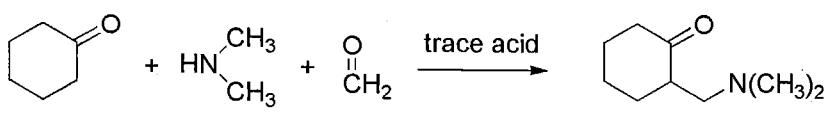
二、非選擇題 (共 20 分)

1) Provide the product for the following reactions. 提供下列反應的產物結構 (4 分)

(a) 

(b) 

2) Provide a reaction mechanism for the following reaction. 提供下列反應之機構 (6 分)



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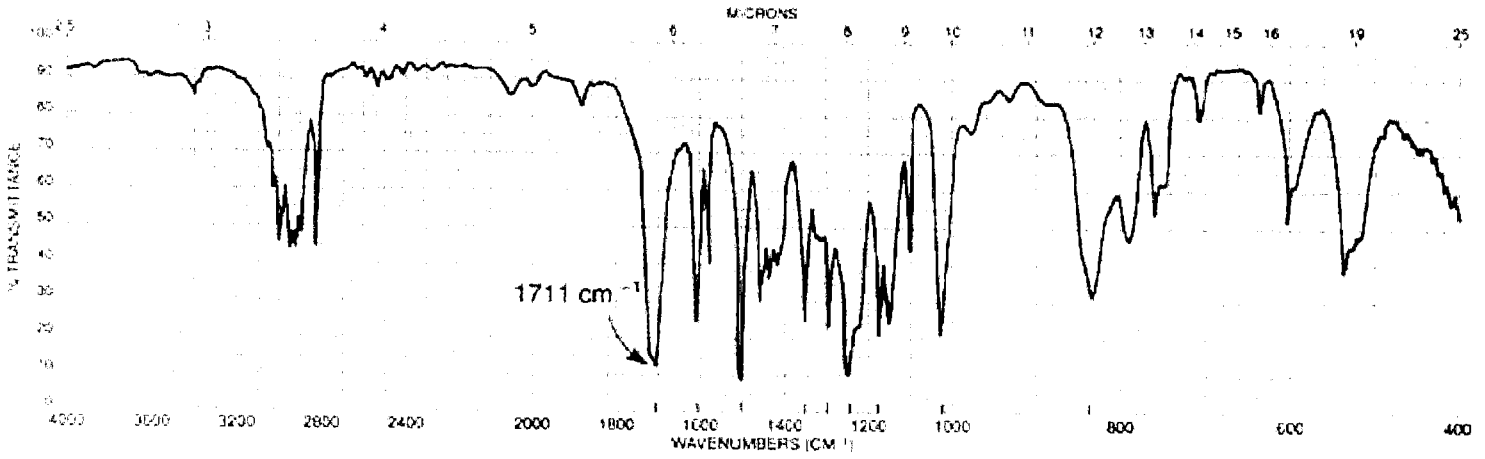
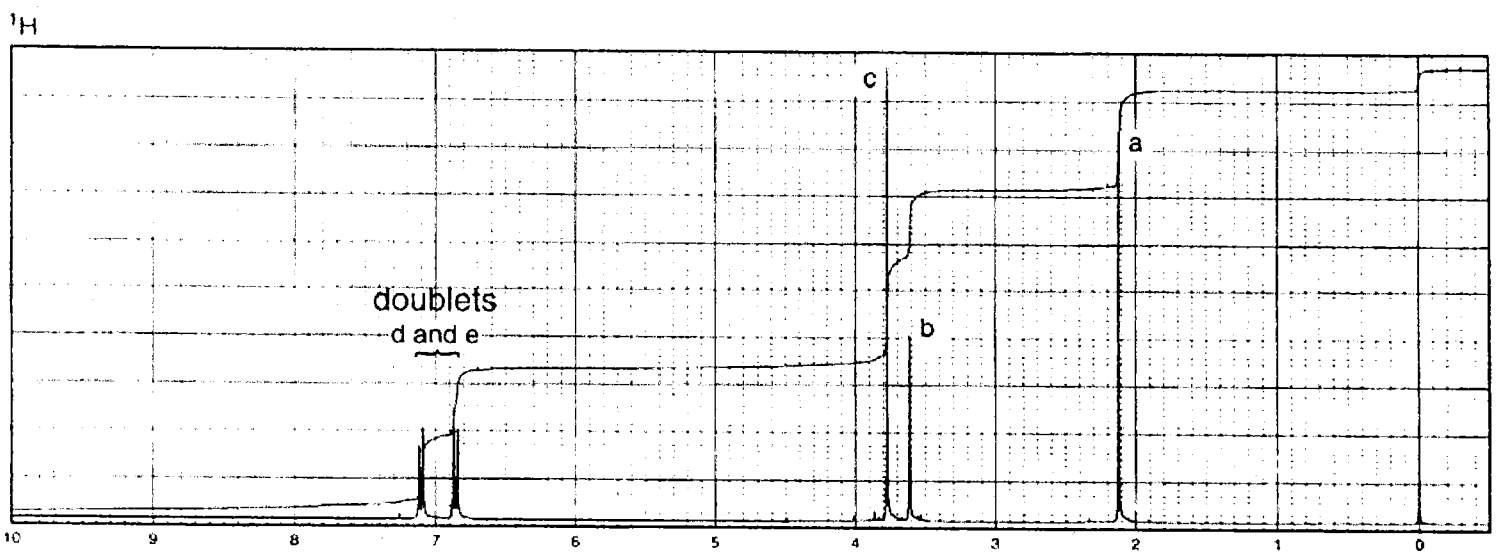
3) Determine the structure of a compound with the formula $C_{10}H_{12}O_2$ from the following spectra and the tabulated data.
(10 分; 沒有部份給分!)





Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50	Negative	No peak
55	Positive	No peak
114	Positive	Positive
126	No peak	No peak
130	Positive	Positive
159	No peak	No peak
207	No peak	No peak