國立中山大學100學年度碩士班招生考試試題

科目：有機化學【材光系碩士班甲組】

1. 選擇題 (單選, total 40%, each 2%)

1) ( ) How many sets of equivalent hydrogen atoms are there for 2-propanol?
a) 2 b) 3 c) 4 d) 8.

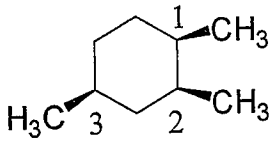
2) ( ) Which of the following molecules would you expect to be nonpolar?
I. CH_2Cl_2 II.. CO_2 III.. CCl_4 IV. CH_3OCH_3
a) I and II b) I and III c) I and IV d) II and III.

3) ( ) In which of the following bond dipole, the oxygen is located on the positive end? a) O-N, b) O-S, c) O-F, d) O-H.

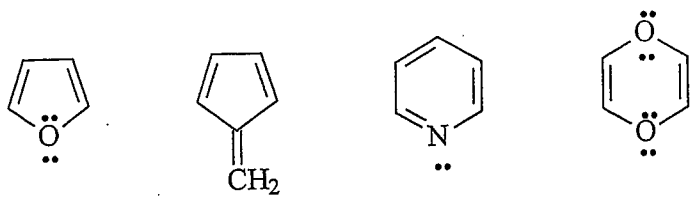
4) ( ) which one of the following is chiral? a) 1,1-Dibromo-1-chloropropane, b) 1,1-Dibromo-3-chloropropane, c) 1,3-Dibromo-1-chloropropane, d) 1,3-Dibromo-2-chloropropane

5) ( ) Which is the electrophile responsible for the nitration of benzene?
a) HNO_3 b) $\overset{\oplus}{N}O_2$ c) $\overset{\oplus}{N}O_3$ d) $\overset{\oplus}{N}O$

6) ( ) The most stable conformation of the compound below (all methyl groups are *cis* to each other) has a) All methyl groups axial, b) All methyl groups equatorial, c) Equatorial methyl groups at C-1 and C-2, d) Equatorial methyl groups at C-2 and C-4.



7) ( ) Which structures are aromatic? a) II and III, b) III and IV, c) I and III, d) II and IV.



I II III IV

8) ( ) Which compound has a sharp IR absorption at 1710 cm^{-1} and a broad band at 3300 cm^{-1}?

a) $CH_3\overset{\overset{O}{\|}}{C}OH$ b) CH_3CH_2OH c) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ d) CH_3OCH_3

9) ( ) Which region in the IR spectrum could be used to distinguish between benzene and cyclohexane?
a) 3000 cm^{-1} b) 1600 cm^{-1} c) 1680-1750 cm^{-1} d) 3200-3600 cm^{-1}

10) ( ) Which of the following statements concerning the effect of a trifluoromethyl group, CF_3, on an electrophilic aromatic substitution is true?
I. The CF_3 group will activate the ring; II. The CF_3 group will deactivate the ring;
III. The CF_3 group will be a *meta* director; IV. The CF_3 group will be an *ortho*, *para* director.
a) I and III b) I and IV c) II and III d) II and IV.

11) ( ) The separation of a racemic mixture into the pure enantiomers is termed
a) Racemization, b) Isomerization, c) Resolution, d) Equilibrium.

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12) ( ) Which of the following statements pertaining to an SN2 reaction are true?

I. The rate of reaction is independent of the concentration of the nucleophile.

II. The nucleophile attacks carbon on the side to the molecule opposite the group being displaced.

III The reaction proceeds with simultaneous bond formation and bond rupture.

IV Partial racemization of an optically active substrate results.

a) I and IV b) I, III and IV c) II and III d) All

13) ( ) All the following groups are activating *ortho, para* directors when attached to a benzene ring except a) $-OCH_3$ b) $-NHC(=O)CH_3$ c) $-Cl$ d) $-N(CH_3)_2$.

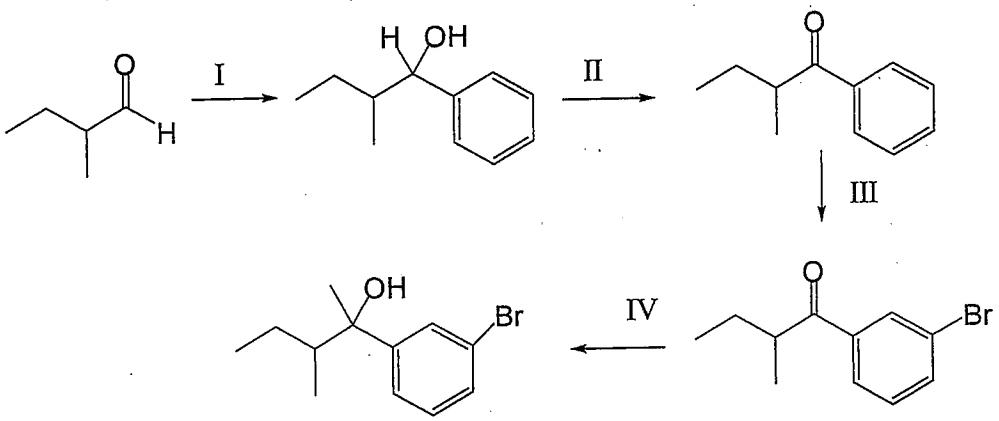
14) ( ) 2,3-pentdiene, $CH_3CH=CH=CHCH_3$, is a) A planar substance, b) A conjugated diene, c) An allene, d) A substance capable of *cis-trans* isomerism.

15) ( ) Which alkyne yields butanoic acid ($CH_3CH_2CH_2CO_2H$) as the only organic product on treatment with ozone followed by hydrolysis? a) 1-Butyne b) 4-Octyne c) 1-Pentyne d) 2-Hexyne.

16) ( ) Which is not a step in the mechanism of a chain growth (addition) polymerization?

a) Initiation b) Propagation c) Proliferation d) Termination.

(Questions 17) - 20)) There are four reagents I ~ IV required to perform the reaction scheme below



a) Periodinane; b) PhMgBr; c) CH_3OH/H^+; d) NaOH, heat; e) $LiAlH_4$ in ether, then H_3O^+; f) $Br_2/FeBr_3$

17) ( ) Chose the right reagents I from the above reagent lists from a) to f).

18) ( ) Chose the right reagents II from the above reagent lists from a) to f).

19) ( ) Chose the right reagents III from the above reagent lists from a) to f).

20) ( ) Chose the right reagents IV from the above reagent lists from a) to f).

2. (Total: 30%) Most of organic reactions are initialized by the nucleophilic attack of electron-rich (nucleophiles) to electron-poor (electrophiles) groups. The initial nucelophilic attacks are then followed by various bond-forming and bond-breaking steps to result in the final reaction products. Typical example can be illustrated by that under attacks of versatile nucleophilic reagents, simple alkyl and aryl halides result in different substitution and/or elimination products dependent on the experimental conditions. Inter-conversions of carobonyl compounds under the attacks of different nucleophilic reagents can be also regarded as the nucleophilic substitution reactions. The following statements in a) ~ d) relate to different previous experimental results concerning the reactions between nucleophiles and electrophiles. Explain it.

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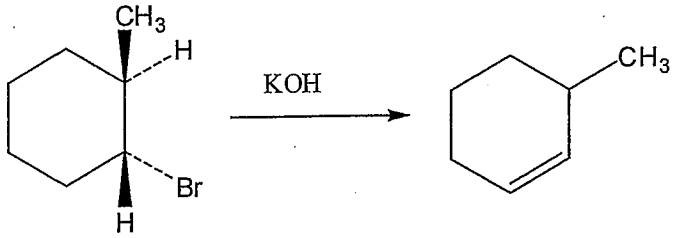
a) (6 %) Sodium ethoxide (CH_3CH_2ONa) reacted with methyl bromide with a SN2 substitution mechanism. However, no reaction would occur when sodium ethoxide reacted with phenyl bromide (C_6H_5-Br). Explain it.

b) (9 %) *trans*-1-Bromo-2-methylcyclohexane yields the non-Zaitsev elimination product 3-methylcyclohexene on treatment with KOH. Explain why E2 reaction proceeds to give the specific product below?



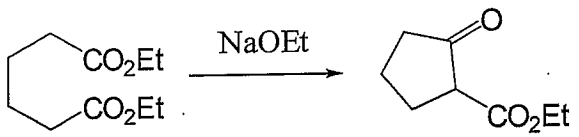
trans-1-Bromo-2-methylcyclohexane 3-methylcyclohexene

c) (9%) Interconversions of carboxylic acid derivatives by nucleophiles undergoes with the reactivity sequence of acid chloride (R-CO-Cl) > acid anhydride (RC(=O)OC(=O)R') > ester (RCOOR') > amide (RCONR'R"). Explain it.

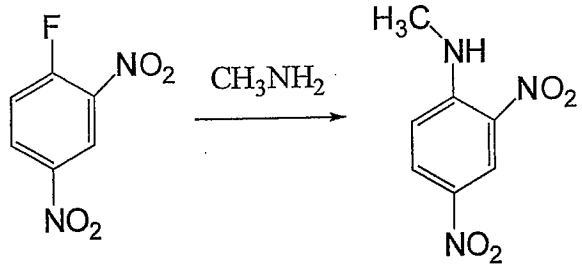
d) (6 %) Methyl trifluoroacetate, $CF_3CO_2CH_3$, is more reactive than methyl acetate, $CH_3CO_2CH_3$, in nucleophilic acyl substitution reactions. Explain it.

3. Write detailed mechanistic steps for the following transformations? (Total: 30 %, each 5 %)

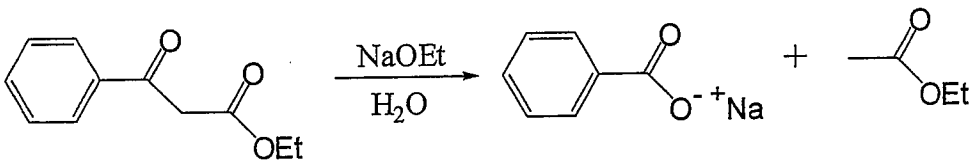
a) (5 %)



b) (5 %)



c) (5 %)



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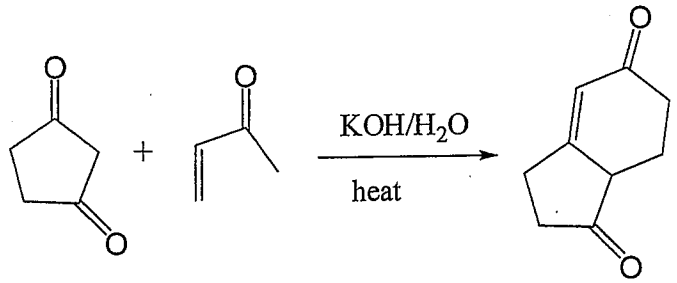
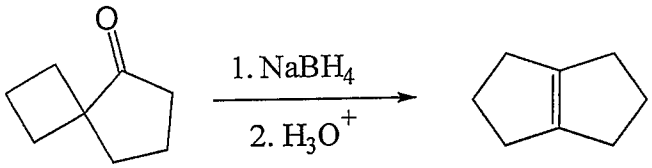
d) (5 %)



e) (5 %)



f) (5 %)