國立清華大學 105 學年度碩士班考試入學試題

系所班組別：生醫工程與環境科學系乙組（環境與分子科學組）

考試科目（代碼）：有機化學 (2204)

　*請在【答案卷】作答

一、單選題（每題 2.5 分共 50 分）

1. Which of the following compounds has the most negative heat of hydrogenation?

(A) 1,4-hexadiene (B) 1,5-hexadiene (C) 1,2-hexadiene (D) 1,3- hexadiene (E) hex-1-ene

2. Which compounds is the most stable?

(A) 1,4-pentadiene (B) trans-1,3-pentadiene (C) trans-1,4-pentadiene (D) cis-1,4-pentadiene

3. The Diels-Alder reaction is a concerted reaction; this means:

(A) A mixture of endo and exo products is formed.

(B) All bond making and bond breaking occurs simultaneously.

(C) The products contain rings.

(D) The reaction follows Markovnikov's rule.

(E) The reaction is highly endothermic.

4. Which of the statements below correctly describes an achiral molecular?

(A) The molecule has a non-superimposable 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 meso form

5. The reaction conditions to carry out the production of cyclopentene using bromocycylpentane as the starting material would be:

(A) KOH, CH_3CH_3OH

(B) H_2SO_4, THF

(C) H_2O_2, OH^-

(D) $Hg(OAc)_2$, H_2O

6. Which is the reaction major product when benzene reacts with propene in the presence of HF?

(A) propylbenzene (B) iso propylbenzene (C) 3- propylbenzene (D)1- propylbenzene

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7. When pyridine is treated with a mixture of nitric and sulfuric acids, the major product is:

(A) 2-nitropyridine (B) 3- nitropyridine (C) 4- nitropyridine (D) 3-aminopyridine (E) 4-aminopyridine

8. What is the major product which results when tetrahydrofuran is reacted with excess HBr?

(A) 1,2-dibromobutane (B) 1,3-dibromobutane (C) 1,4-dibromobutane

(D) 4-bromobutan-ol (E) 3-bromobutan-1-ol

9. Which of the following compound is the least reactive toward 1-propanol in Nucleophilic Acyl Substitution?

(A) acetyl bromide (B) acetamide (C) acetic anhydride (D) ethyl acetate

10. A molecule has three degrees of unsaturation. In this molecule there would be

(A) three rings

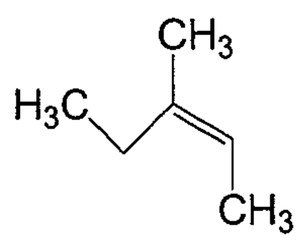
(B) three double bonds

(C) two rings and one double bond

(D) one ring and two double bonds

(E) any of the above

11. What is the IUPAC name of the following compound?



(A) (E)-3-methylpent-3-ene

(B) (Z)-3-methylpent-3-ene

(C) (E)-3-methylpent-2-ene

(D) (Z)-3-methylpent-2-ene

12. Which of the following amines is most basic?

(A) aniline (B) N-ethylaniline (C) N,N-diethylaniline (D) piperidine

(E) pyrrole

13. Which reagent would convert cyclohexene into a *cis*-glycol?

(A) cold dilute potassium permanganate

(B) hydrogen peroxide and aqueous acetic acid

(C) ozone and moist zinc dust

(D) periodic acid　(E)sodium tert-butoxide in chloroform

14. Please indicate which type of compounds are not derivatives of the nucleophilic acyl substitution reactions.

(A) Ester

(B) Amindes

(C) Acid anhydrides

(D) Amines

15. Which of the following compounds is a suitable base to prepare ester enolate of ethyl acetate?

(A) Lithium diisopropylamide

(B) Pyridine

(C) Diisopropyl amine

(D) Pyrrolidine

16. Which of following addition reactions of alkenes occur specifically in an anti- fashion:

(A) Dihydroxylation using OsO_4, H_2O_2

(B) Addition of Br_2

(C) Hydroboration-oxidation

(D) Hydrogenation using H_2-Pt

17. The conversion of 2-pentanone to butanoic acid is best accomplished with:

(A) I_2, NaOH

(B) $NaBH_4$

(C) CrO_3

(D) Ag_2O

18. A molecule has three degrees of unsaturation. In this molecule there would be

(A) three rings

(B) three double bonds

(C) two rings and one double bond

(D) one ring and two double bonds

(E) any of the above

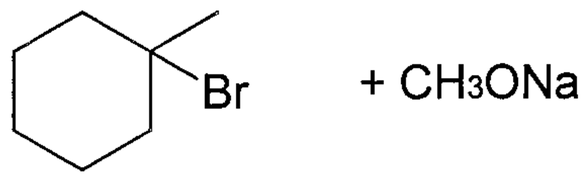
19. How many different form(s) for 1,3-dichloroallene and the relationship is

(A) 1 form only　(B) 2 forms and there are enantiomeric forms

(C) 2 forms and there are diastereomeric forms

(D) 3 forms and there are enantiomeric forms

20. For the reaction shown below, the major product is formed by



(A) a S_N1 reaction　(B) a S_N2 reaction　(C) a E1 reaction　(D) a E2 reaction

二、 問答題（每題 2.5 分共 50 分）

1. Arrange the following acids in order of decreasing acidity (1 being the most acidic, 6 being the least acidic).

H_2SO_4:

CH_3CO_2H:

H_3O^+:

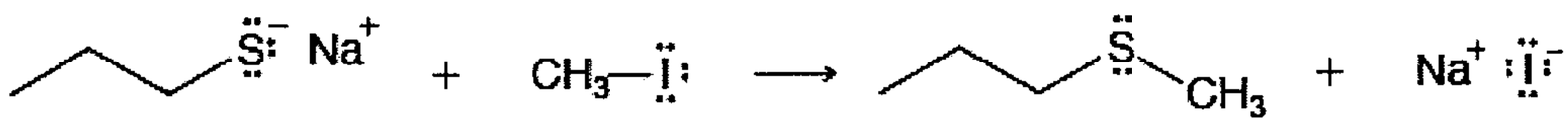
$CH_3NH_3^+$:

NH_3:

CH_3CH_3:

2. Drawing Curved Arrows to Show Mechanisms

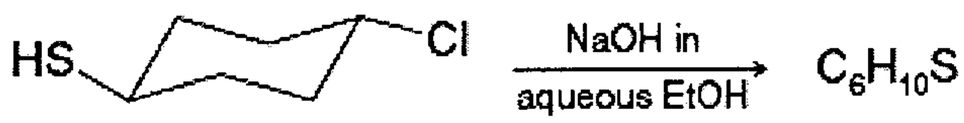
Draw the curved arrows necessary to show the mechanism for the following transformation. Show all lone pairs, formal charges and cations when drawing the mechanism.



3. Draw a dash-wedge structure for *(S,trans)*-5-fluoro-2,2-dimethylhex-3-ene.

4. Draw a dash-wedge structure for *(3R,6R)*-3-bromo-6-methylcyclohex-1-ene.

5. Predict the structure of the product of this reaction:



The product has no infrared absorption in the 1620-1680 cm^{-1} region.

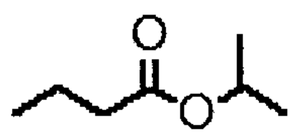
6. Typically alkyl chlorides are slow in S_N2 reactions with sodium methoxide in methanol, however the rate of the reaction can be greatly increased with a small addition of NaI. Explain.

7. Propose a two-step synthetic strategy for the synthesis of 2-methylhexane from 5-methyl-2-hexanol.

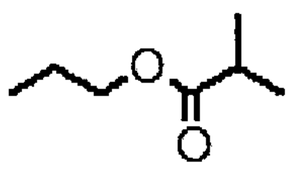
8. Write the structural formula for the product that forms when 1-methylcyclopentene reacts with HBr.
Note: All structures should be drawn with no bonds between carbon and hydrogen.

9. Compound T (C_5H_8O) has a strong IR absorption band at 1745 cm^{-1}. The broad-band proton decoupled ^{13}C spectrum of T shows three signals at δ 220 (C), 23 (CH_2), and 38 (CH_2). Propose a structure for T.

10. Briefly explain how you might distinguish between the following substances by comparing their ^{1}H-NMR spectra:

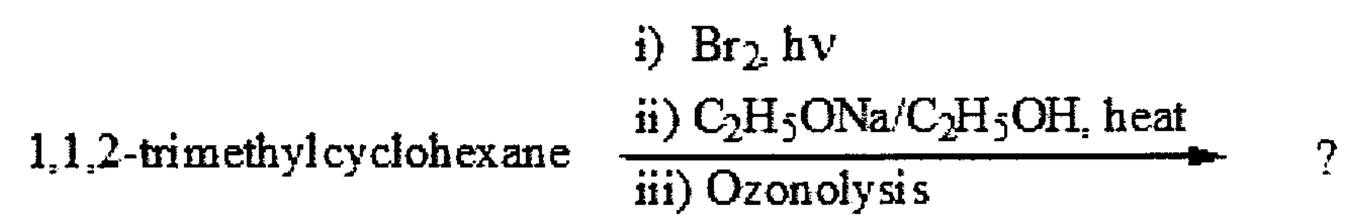


I



II

11. Complete the following reaction sequence: indicate regiochemical/stereochemical details as relevant.



12. Draw the structure of the product that would be formed when cyclopentanol reacts with hydrogen bromide.

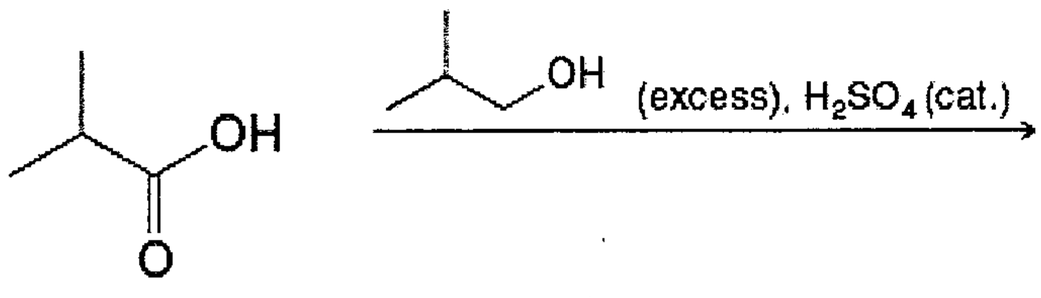
13. What major product(s) would you expect to obtain when succinic anhydride reacts with the following reagent?

Note: All structures should be drawn with no bonds to hydrogen atoms.

(a) NH_3 (excess) (draw the counterion)

14. Write structural formula for the major organic product(s) of the following reaction.

Note: All structures should be drawn with no bonds to hydrogen atoms.



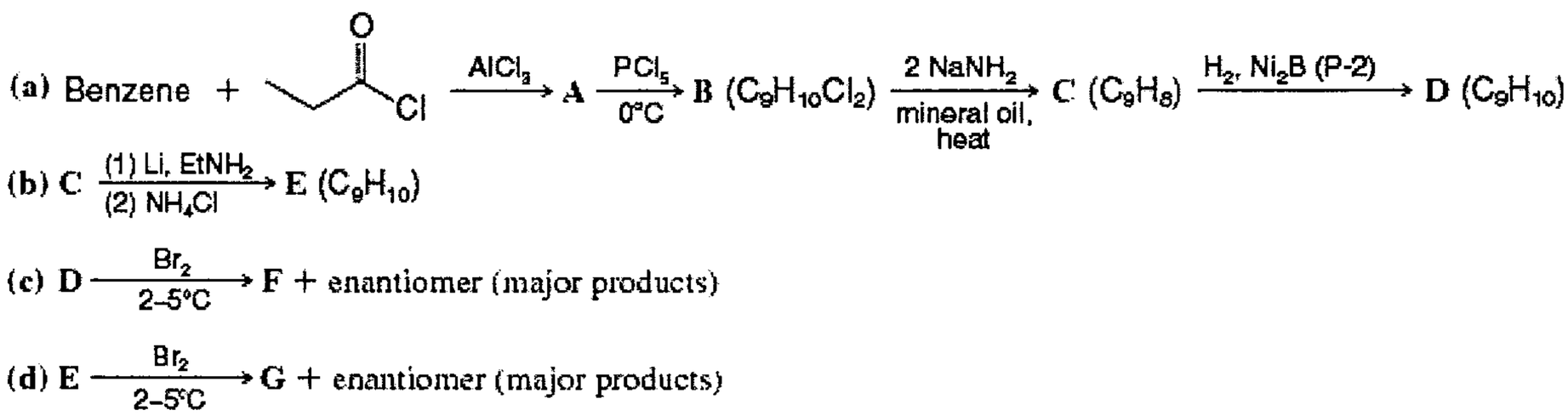
15. Draw the structure corresponding to the following name: 3-nitro-4-iodoanisole.

16. Draw the structure of the product likely to be obtained from the reaction between acetoacetic ester, bromobenzene and 2 molar equivalents of sodium amide in liquid ammonia. Briefly explain your rationale.

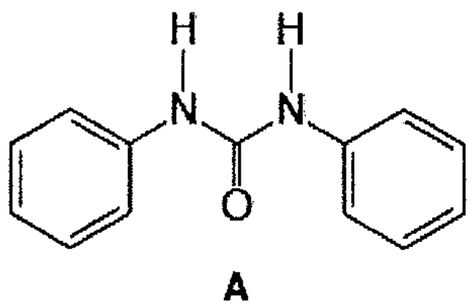
17. Explain briefly why cyclopentadiene readily reacts with strong bases.

18. Draw the major product (or products) that would be obtained when nitrobenzene reacts with Cl_2 and $FeCl_3$. If two structures exist, draw them both.

19. Consider the reactions below and draw the structure (including stereochemistry where applicable) for compound C:



20. When N,N'-9-diphenylurea (A) is reacted with tosyl chloride in pyridine, it yields product B. The spectral data for B include:



A

The spectral data for B include:
MS (*m/z*): 194 (M^+)
IR (cm^{-1}): 3060, 2130, 1590, 1490, 760, 700
^{1}H NMR (δ): only 6.9–7.4 (m)
^{13}C NMR (δ): 122 (CH), 127 (CH), 130 (CH), 149 (C), and 163 (C)

Draw structure B: