國立成功大學
111學年度碩士班招生考試試題

編　號：45

系　所：化學系

科　目：有機化學

日　期：0220

節　次：第 2 節

備　註：不可使用計算機

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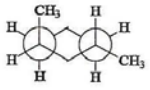
※ 考生請注意：本試題不可使用計算機。 請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

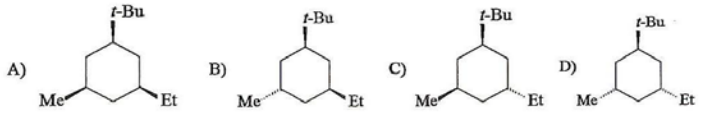
Part I. Multiple choice (single answer, 36%, 2%each)

1. The following structure is:



A) *cis*-1,3-dimethylcyclohexane B) *trans*-1,3-dimethylcyclohexane
C) *cis*-1,4-dimethylcyclohexane D) *trans*-1,4-dimethylcyclohexane

2. Which isomer of 1-*tert*-butyl-3-ethyl-5-methylcyclohexane below is thermodynamically the most stable?



A) A　　B) B　　C) C　　D) D

3. Chlorination of pentane gives a mixture of isomers having the molecular formula $C_5H_{11}Cl$. The percentage of 1-chloropentane is 22%. Assuming the secondary hydrogens in pentane are equally reactive to monochlorination, what is the percentage of 3-chloropentane in the mixture?

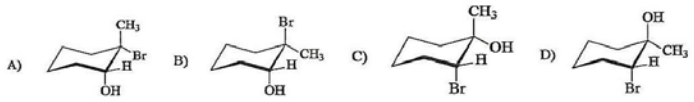
A) 48%　　B) 26%　　C) 22%　　D) 14%

4. Studies indicate that the methyl radical is trigonal planar. Based on this, which of the following best describes the methyl radical?

I. The carbon is sp^2 hybridized and the unpaired electron occupies an sp^2 orbital.
II. The carbon is sp^2 hybridized and the unpaired electron occupies a 2p orbital.
III. The carbon is sp^3 hybridized and the unpaired electron occupies an sp^3 orbital.
IV The carbon is sp^3 hybridized and the unpaired electron occupies a 2p orbital.

A) I　　B) II　　C) III　　D) IV

5. Addition of hypobromous acid, HOBr, to 1-methylcyclohexene gives:



A) A　　B)　　C) C　　D) D

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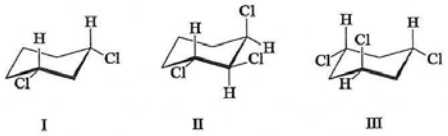
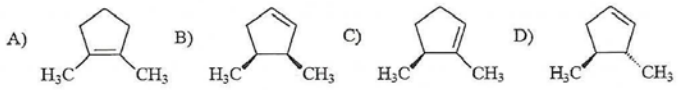
6. Which of the following molecules are chiral?



I　　II　　III

A) only II　　B) only III　　C) II and III　　D) I, II, and III

7. Compound X (C_7H_{12}) is optically active. Hydrogenation of compound X gives two isomeric 1,2-dimethylcyclopentanes, one is optically active and the other is optically inactive. Of the following compounds, which is the only one that fits the data?



A) A　　B) B　　C) C　　D) D

8. Consider the reaction of each of the following with 1-bromopentane. Which one would have the highest elimination/substitution ratio?

A) $NaOCH_2CH_3$, ethanol, 55°C　　B) NaSH, ethanol-water, 25°C
C) $KOC(CH_3)_3$, $(CH_3)_3COH$, 55°C　　D) KCN, DMSO, 40°C

9. Which of the following ions has a ground state which is predicted to be a diradical by simple molecular orbital theory?

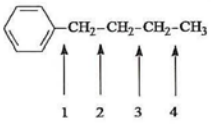
A) A　　B) B　　C) C　　D) D

10. Rank the following compounds in order of decreasing reactivity to aromatic electrophilic bromination.

I. benzene　　II. toluene　　III. benzoic acid　　IV. Phenol

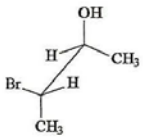
A) IV > II > I > III　　B) IV > III > II > I　　C) II > I > IV > III　　D) II > III > IV > I

11. Which C-C bond would most likely break and give fragments in the mass spectrum of butyl benzene?



A) 1　　B) 2　　C) 3　　D) 4

12. Which of the following epoxides is formed when KOH is added to the optically active halohydrin shown below?



A) *trans*-(2S,3S)-2,3-dimethyloxirane　B) *trans*-(2R,3R)-2,3-dimethyloxirane
C) 2,2-dimethyloxirane　D) *meso*-2,3-dimethyloxirane

13. Which one of the following reagents adds a methyl group by conjugate (1,4-addition) addition to an α,β-unsaturated ketone or aldehyde?

A) $LiCu(CH_3)_2$　B) CH_3MgBr　C) $Hg(O_2CCH_3)_2$　D) CH_3Li

14. Rank the following in order of decreasing rate of hydrolysis.

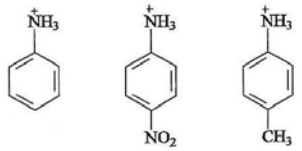
I. acetyl chloride　II. acetic anhydride
III. ethyl acetate　IV. Acetamide

A) I > II > III > IV　B) IV > III > II > I　C) I > III > II > IV
D) II > III > IV > I

15. Which of the following works best as a base to quantitatively convert ethyl acetate, $CH_3CO_2CH_2CH_3$, to its enolate?

A) NaOH　B) $KOC(CH_3)_3$　C) CH_3Li　D) $[(CH_3)_2CH]_2NLi$

16. Rank the following three compounds in order of decreasing acidity.



I　II　III

A) II > III > I　B) II > I > III　C) III > I > II　D) III > II > I

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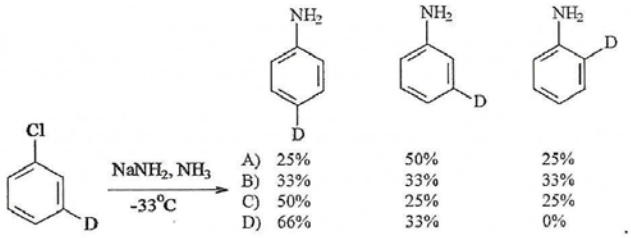
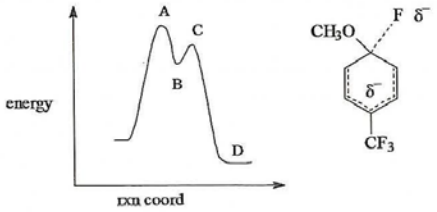
17. Which of the following best estimates the percentages of the three isomeric deuterated anilines from the reaction shown below?



A)	25%	50%	25%
B)	33%	33%	33%
C)	50%	25%	25%
D)	66%	33%	0%

A) A　　B) B　　C) C　　D) D

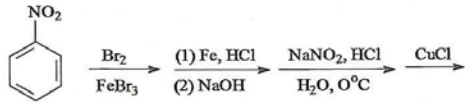
18. Which position on the potential energy diagram corresponds to the species shown for the reaction of *para*-fluoro (trifluoromethyl) benzene with sodium methoxide?



A) A　　B) B　　C) C　　D) D

Part II. Give the (major) product for each of the following reactions. (27%, 3% each)

1.



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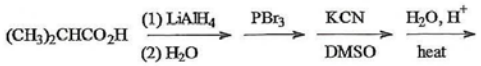

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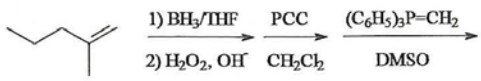

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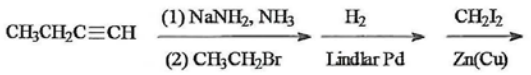

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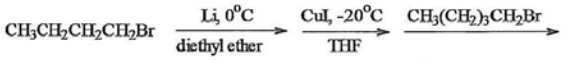

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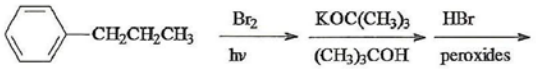

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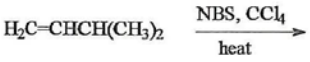

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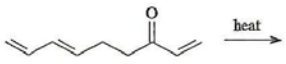

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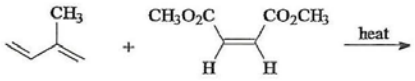
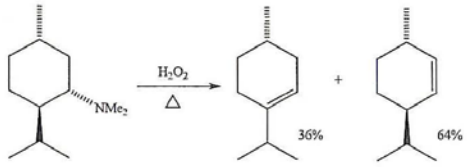
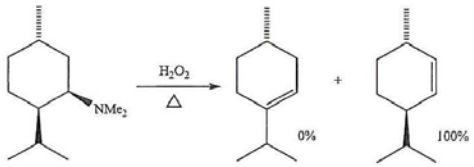


Part III. Please answer the following questions. (37%)

1. The kinetic study showed that the hydrolysis of acetamide was a third-order kinetics with the rate expression of $k[CH_3CONH_2][HO^-]^2$. Please write the reaction mechanism and decide the rate determine step. (8%)

2. Please explain the following observations (8%)





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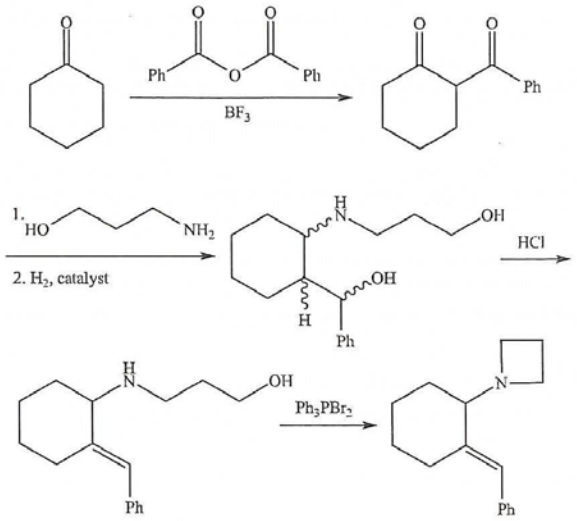
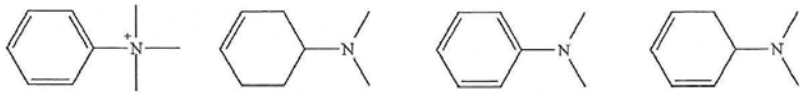
3. This is a synthesis of the racemic drug tazadolene. If the enantiomers of the drug are to be evaluated for biological activity, they must be separated. At which stage would you like to resolve the enantiomers. Why? And how would you do it? (8%)



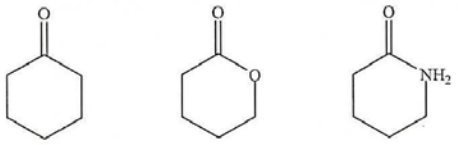
4. Please answer the following questions. (13%)

i. Which occurs at a larger wavenumber: the C¬N stretch of an amine or the C¬N stretch of an amide? Account for your answer. (4%)

ii. Rank the compounds in order of decreasing λ_{max}: (3%)



iii. Rank the following compounds from highest wavenumber to lowest wavenumber for their C=O absorption bands: (3%)



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iv. What type of the protons are for the indicated hydrogens in the following compound's and how many signals would you expect for its ^{1}H-NMR spectrum? (3%)