編號： 55

國立成功大學 107 學年度碩士班招生考試試題

系　　所：化學系

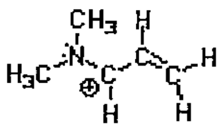
考試科目：有機化學

考試日期：0206，節次：2

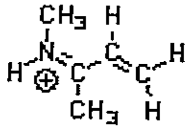
※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Part I Multiple Choice Questions (single choice, 30%, 1.5% each)

1. Structures ________, shown below, are resonance structures, and structure ________ is the major contributor to the overall resonance hybrid.



1



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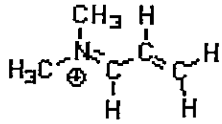

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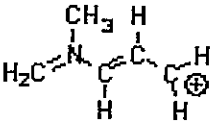

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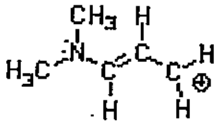

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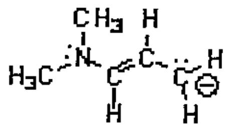
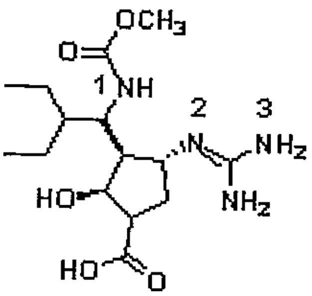


6

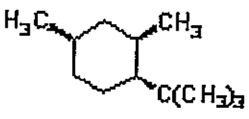
A) 2 & 4; 2　　B) 1, 3 & 5; 3　　C) 4 & 6; 6　　D) 1, 3 & 5; 1　　E) 1, 3, 4 & 5; 3

2. Which sequence ranks the following nitrogen atoms in order of increasing basicity?

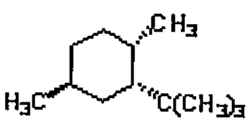


A) 2<3<1　　B) 3<1<2　　C) 1<3<2　　D) 1<2<3

3. With each structure below drawn in its most stable chair conformation, identify the sequence that ranks the structures in order of increasing stability.



1



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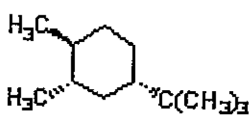
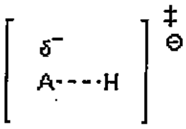


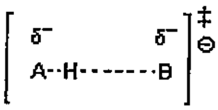
3

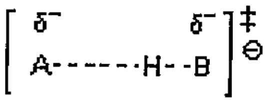
A) 1 < 2 < 3　　B) 2 < 3 < 1　　C) 3 < 1 < 2　　D) 2 < 1 < 3

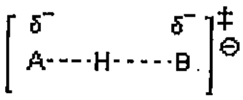
4. Which of the following depictions most closely resembles the structure of the transition state for the following acid-base reaction?

$$\underset{pKa = 9}{H{-}A} + B^- \longrightarrow \underset{pKa = 4}{H{-}B} + A^-$$

A) 

B) 

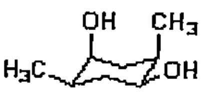
C) 

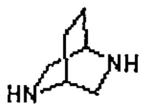
D) 

5. Which of the following alkyl halides would be suitable to use when forming a Grignard reagent?

A) $BrCH_2CH_2CH_2CN$　B) $CH_3COCH_2CH_2Br$　C) $(CH_3)_2NCH_2CH_2Br$
D) $H_2NCH_2CH_2Br$　E) all of the above

6. Which of the following structures are achiral and meso?


1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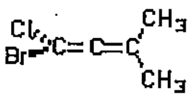
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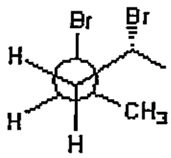
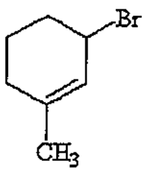
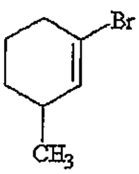
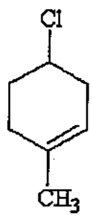

4

A) 1, 2, 3 & 4　B) 1 &2　C) 2 & 3　D) 1 & 4

7. Rank the following molecules in order of increasing relative rate of S_N1 solvolysis with methanol and heat.


1


2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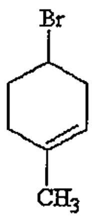
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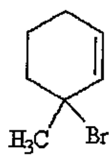

5

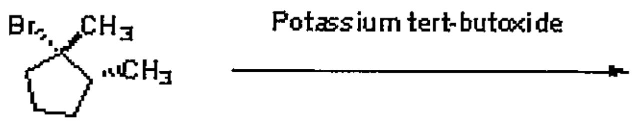
A) 3 < 2 < 4 < 5 < 1　B) 2 < 3 < 4 < 1 < 5　C) 5 < 4 < 3 < 2 < 1
D) 2 < 3 < 4 < 5 < 1　E) 1 < 2 < 5 < 4 < 3

8. Which of the following oxidants will convert a primary alcohol to an aldehyde?

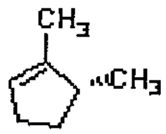
1) sodium dichromate /sulfuric acid　3) pyridinium chlorochromate
2) copper oxide　4) dimethylsulfoxide, oxalyl chloride

A) 3 & 4　B) 2, 3, & 4　C) 3　D) 1, 2, 3, & 4　E) none of the above

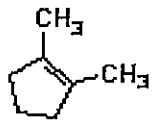
9. Identify the major product of the reaction below.



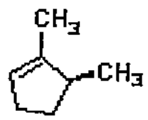
A)



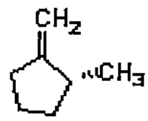
B)



C)



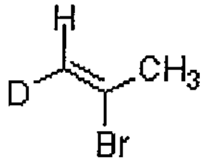
D)



10. When (*R*)-butan-2-ol is treated with TsCl in pyridine, the product formed is:

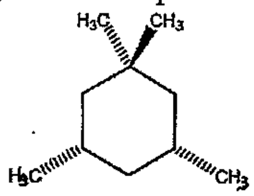
A) a single enantiomer. B) a racemic mixture. C) a mixture of diastereomers.
D) an achial compound. E) none of the above

11. Which bond in the structure below would give rise to the highest absorption frequency in an IR spectrum?



A) sp^2 C-H　　B) sp^3 C-H　　C) C-D　　D) C=C

12. Predict the number of signals expected in the proton spin decoupled and off-resonance decoupled ^{13}C-NMR spectrum, respectively, for the compound show below.



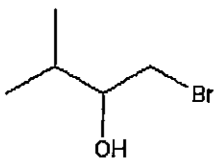
A) 10, 4　　B) 10, 3　　C) 9, 4　　D) 7, 4　　E) 7, 3

13. Deduce the identity of the following compound from the spectral data given.

$C_4H_8O_2$: ^1H NMR, δ 1.23 (3H, triplet), 2.00 (3H, singlet), 4.02 (2H, quartet) (ppm); IR, 2980, 1740 cm^{-1}

A) $CH_3CO_2CH_2CH_3$　　B) $CH_3CH_2CO_2CH_3$　　C) $CH_3CH_2CH_2CO_2H$
D) $CH_3COCH_2OCH_3$

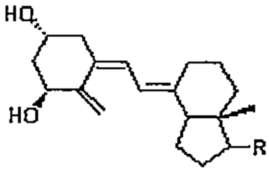
14. How many unique NMR signals (disregard splitting) would be predicted in the ^1H spectrum of the following compound?

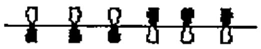
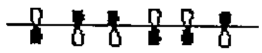
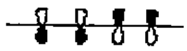


A) 4　　B) 5　　C) 6　　D) 7　　E) 3

15. Treatment of tetrahydrofuran with excess HBr results in the formation of what major organic product?
A) 1-bromobutane　B) 1,2-dibromobutane　C) 1,4-dibromobutane
D) 1-bromopentane　E) 1,5-dibromopentane

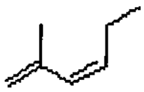
16. Which of the following represents the highest occupied molecular orbital for the conjugated pi system in Vitamin D3?

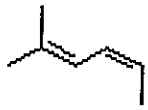


A)  B)  C)  D) 

17. Which sequence correctly ranks the following dienes in order of increasing reactivity in the Diels-Alder reaction?

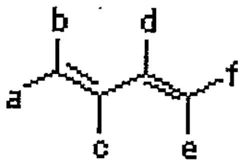

1


2


3

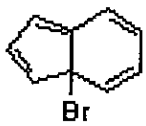
A) 1 < 2 < 3　B) 2 < 3 < 1　C) 3 < 1 < 2　D) 3 < 2 < 1

18. According to the 1,3-butadiene structure below, which positions would be best to place methoxy groups to yield the most reactive dimethoxy-1,3-butadiene isomer in the Diels-Alder reaction?

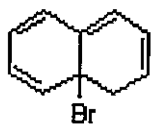


A) c and d　B) a and c　C) b and c　D) a and d　E) a and f

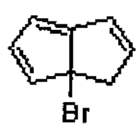
19. Which sequence correctly ranks the following substrates in order of increasing reactivity in an S_N1 reaction?



1



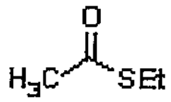
2



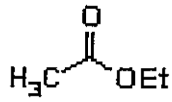
3

A) 1 < 2 < 3　B) 2 < 3 < 1　C) 3 < 1 < 2　D) 1 < 3 < 2

20. Which sequence correctly lists the following structures in order of increasing rate of hydrolysis to a carboxylic acid under basic conditions?



1



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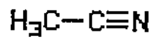
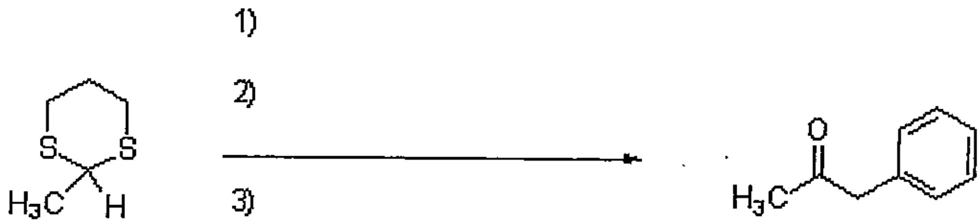


3

A) 1 < 2 < 3　　B) 2 < 3 < 1　　C) 3 < 1 < 2　　D) 3 < 2 < 1　　E) 2 < 1 < 3

Part II. Complete the following reactions by filling in the correct reagents. (16%, 4%each)

1.



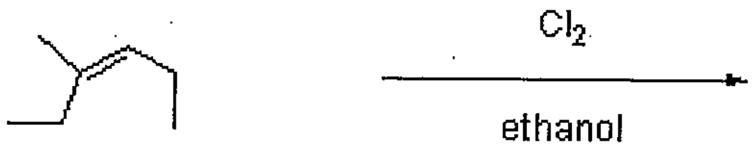
2.

3.

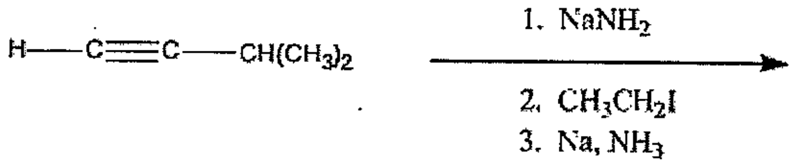
4.

Part III. Provide the major product(s) for the reactions shown below. (If there exists any stereochemistry, be showing it up) (30%, 3% each)

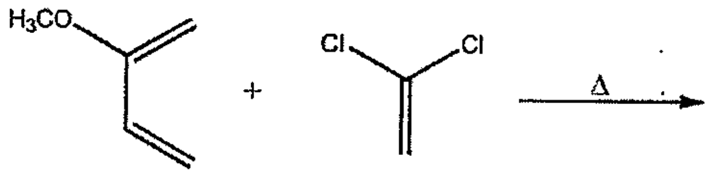
1.



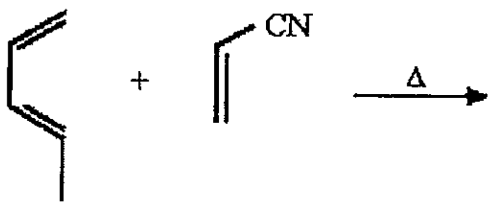
2.



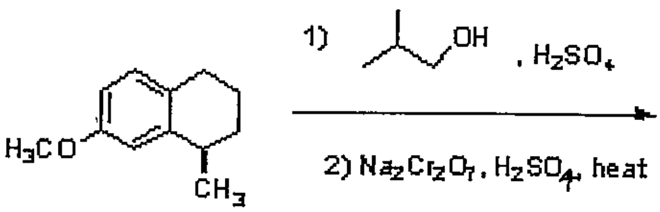
3.



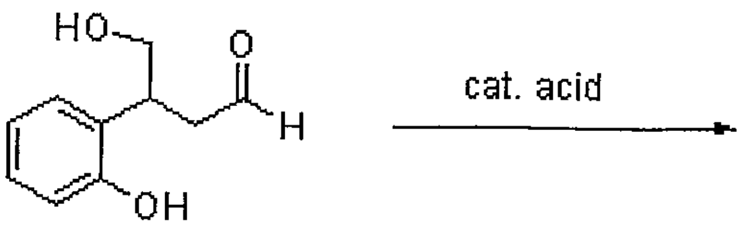
4.



5.



6.



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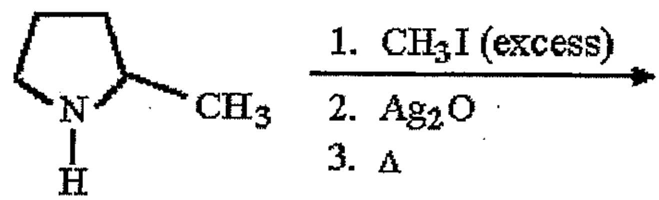

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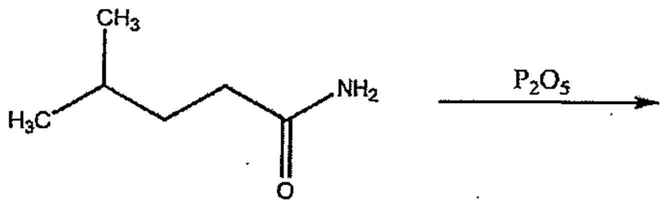

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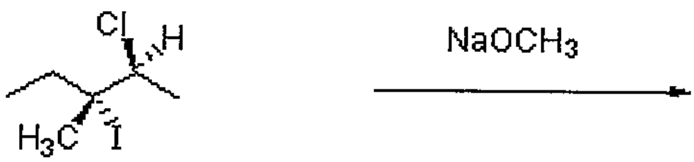
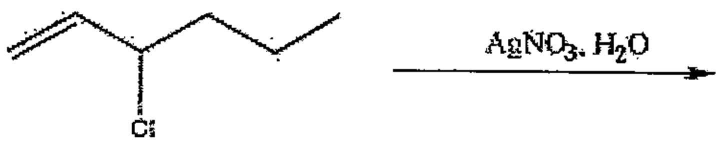
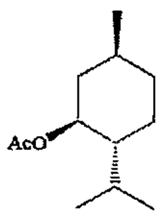


10.

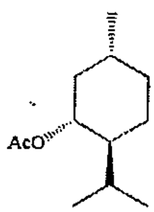


Part IV Answer the following questions

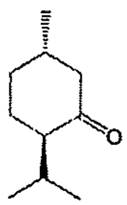
1. (+/-)- Menthyl acetate obtained from peppermint oil was used to prepare (-)-Menthone using enantiomeric hydrolysis to give optically pure (-)-menthol with various bacteria followed by oxidation. Please show how you might achieve this chemically and how to identify that you have obtained the optically pure (-)-Menthone. (8%)



(+)-Menthyl acetate



(-)-Menthyl acetate



(-)-Menthone

2. Benzoic acid can be obtained by hydrolysis of methyl benzoate in NaOH/H_2O solution under reflux. After completion, please show how to work the product out and how to identify that the target compound has been obtained (6%)

3. Give the structure for the molecule with the following spectra: MS, M(164) 100%, M+1 (165) 12.21%, M+2 (166) 0.945%. The molecular ion is rather weak, but there are prominent daughter ions at *m/z* 146 and *m/z* 77. IR: 3050, 3000 – 3860, 1460 cm^{-1}. ^{1}H-NMR: 7.54 – 7.38 (broad s, 5H), 3.65 (s, 1H; diminished when treated with D_2O), 1.77 (q, 4H), 0.90 (t, 6H) ppm. ^{13}C-NMR: 128.8, 128.1, 126.0, 144.4, 78.6, 34.2, 7.8 ppm. Account for your answer. (10%)