

CHEMISTRY 212

Final

17 June 1999

2 Hours

Family Name: _____

First Name: _____

ID Number: _____

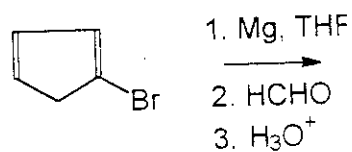
Section: _____

Section A [50 marks]

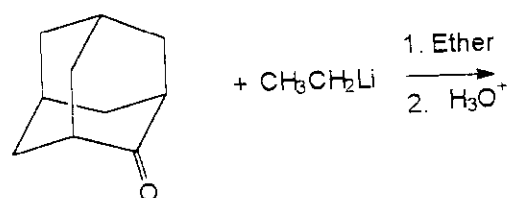
Question 1. [10 marks]

Predict the principal organic product of each of the following reactions. Specify the stereochemistry where appropriate.

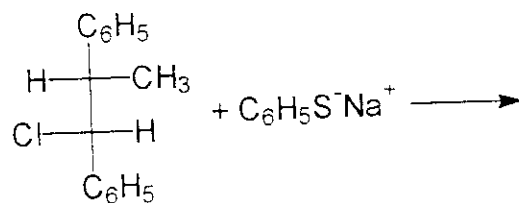
1.



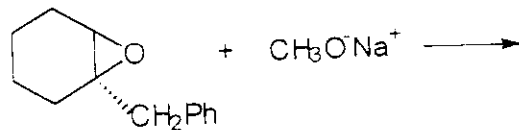
2.



3.



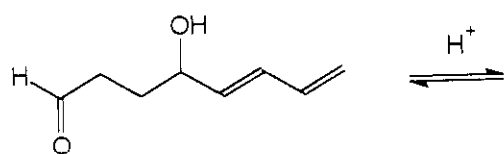
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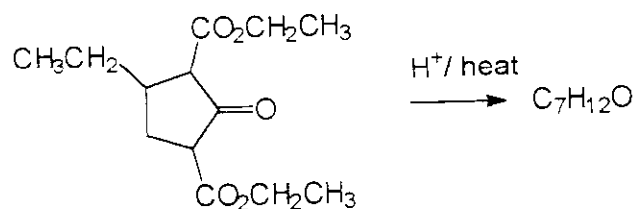
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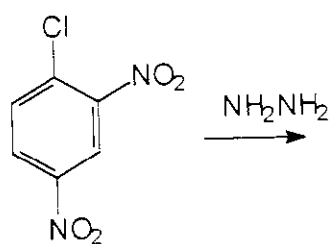
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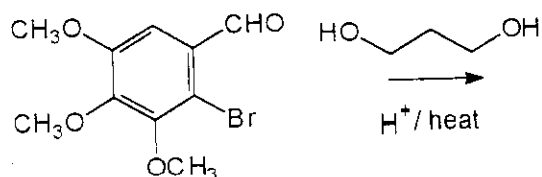
7.



8.



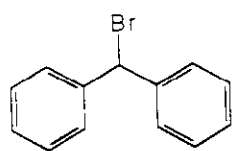
9.



Question 2 [15 marks]

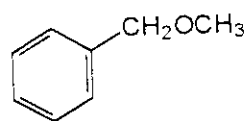
Using any organic or inorganic reagent, suggest efficient synthesis of each of the following:

1.

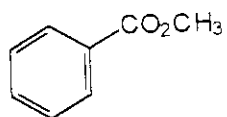


From Bromobenzene

2.



From



3.

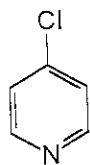
PhCOPh From Benzylalcohol and Bromobenzene

4.

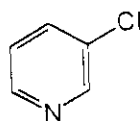
1-Bromo-2-fluoro-3,5-dimethylbenzene From m-Xylene

Question 3 [3 marks]

Offer an explanation for the observation that 4-chloropyridine is more reactive towards nucleophiles than 3-chloropyridine



4-Chloropyridine



3-Chloropyridine

Question 4 [12 marks]

Propane was reacted with chlorine (2 moles) under conditions that favoured free-radical substitution. Four dichloropropanes were isolated. The nmr of these compounds are given. Deduce the structures of the dichloropropanes. Briefly explain your answers.

Structure A

δ 2.4, singlet, 6H

Structure B

δ 1.2, triplet, 3H
 δ 5.8, triplet, 1H
 δ 1.9, quintet, 2H

Structure C

δ 1.4, doublet, 3H
 δ 4.3, sextet, 1H
 δ 3.8 doublets, 2H

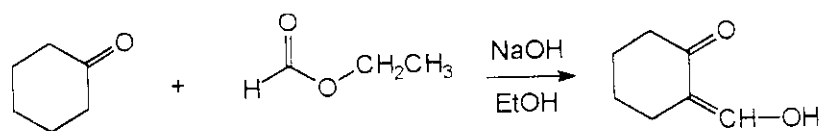
Structure D

δ 2.2, quintet, 2H
 δ 3.7, triplet, 4H

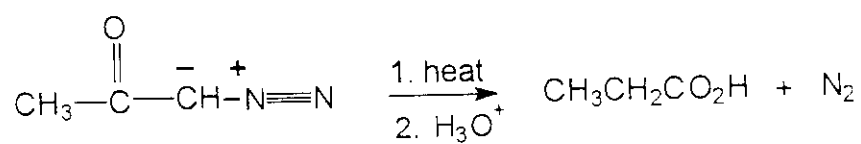
Question 5 [10 marks]

Suggest plausible mechanisms that would justify the formation of the indicated products:

1.



2.



Hint: Similar to the Hoffman degradation of amides

Section B [50 marks]

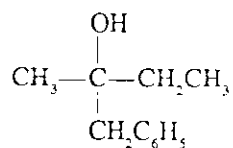
Answer by putting the correct letter next to the question i.e. A, B

No marks will be given if your answer contains two letters.

If none of the answers is correct i.e. A, B, C, D, then answer by adding E as your answer.

1. Which of the following compounds would have an off-resonance decoupled ^{13}C NMR spectrum that shows two quartets, a triplet, and a doublet?
- a. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ c. $\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_3)_3$
b. $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)_2$ d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
2. How many ^1H NMR signals will 2-chloro-3-methyl-2-butene exhibit?
- a. one b. two c. three d. four
3. Which compound ($\text{C}_6\text{H}_{12}\text{O}_2$) shows two singlets at 1.3 and 2.1 ppm with a corresponding relative integration ratio of 3:1 in ^1H NMR?
- a. $\text{CH}_3\text{OCC}(\text{CH}_3)_3$ c. $(\text{CH}_3\text{O})_2\text{C}=\text{C}(\text{OCH}_3)_2$
b. $\text{CH}_3\text{COOC}(\text{CH}_3)_3$ d. $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$
4. Which of the following compounds has an odd P^\oplus ?
- CH_3NH_2 BrCH_2CH_3 CH_3N CH_3NHNH_2
A **B** **C** **D**
- a. A b. A and C c. all but B d. all of the above

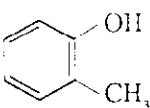
5. Give the best route for the synthesis of this alcohol:



- a. $\text{C}_2\text{H}_5\text{COOCH}_3 + \text{C}_6\text{H}_5\text{MgBr} \longrightarrow$
b. $\text{C}_2\text{H}_5\text{COCH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{MgBr} \longrightarrow$
c. $\text{CH}_3\text{COCH}_2\text{C}_6\text{H}_5 + \text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} \longrightarrow$
d. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{MgBr} + \text{C}_6\text{H}_5\text{CHO} \longrightarrow$

6. The product(s) of the reaction of 2-methyl-1,2-pentanediol with HIO_4 is (are)
- a. $\text{CH}_3(\text{CH}_2)_2\text{COCH}_3 + \text{HCHO}$ c. $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{COOH}$
b. $\text{CH}_3(\text{CH}_2)_2\text{COOH} + \text{HCOOH}$ d. $\text{CH}_3(\text{CH}_2)_2\text{COCH}_3 + \text{HCOOH}$

7. Which of the following compounds would yield a ketone when reacted with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$?

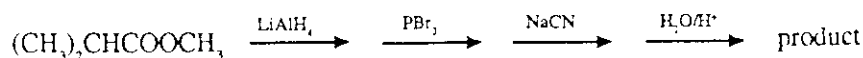
- a.  b. $(\text{CH}_3)_2\text{C}(\text{OH})\text{H}$
c. $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_3$
d. $(\text{CH}_3)_3\text{CCH}_2\text{OH}$
e. $\text{CH}_3\text{OCH}_2\text{CH}_3$

8. Which of the following diols would not react with HIO_4 ?
- a. 2,3-hexanediol c. *cis*-1,2-cyclohexanediol
b. *trans*-1,2-cyclohexanediol d. 2,4-pentanediol
9. The reaction of propylene oxide with *excess* concentrated HCl yields
- a. 1-chloro-2-propanol c. 1,2-dichloropropane
b. 2-chloro-1-propanol d. 1-chloro-1-propane

10. Which of the following is hydrolyzed the slowest by base?

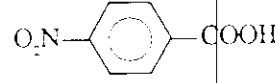
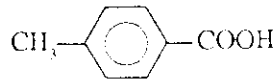
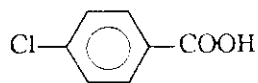
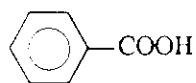
- a. $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$ c. $\text{CH}_3\text{CH}_2\text{CONH}_2$
 b. $\text{CH}_3\text{CH}_2\text{COCl}$ d. $\text{CH}_3\text{CH}_2\text{COOCH}_3$

11. What is the product in this sequence?



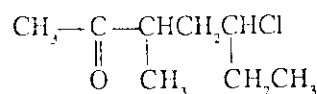
- a. $(\text{CH}_3)_2\text{CHCONH}_2$ c. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$
 b. $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$ d. $(\text{CH}_3)_2\text{CHCH}_2\text{COO}^-\text{NH}_4^+$

12. What is the correct descending order in acid strength of the following compounds?



- a. $\text{A} > \text{D} > \text{C} > \text{B}$ c. $\text{C} > \text{D} > \text{A} > \text{B}$
 b. $\text{B} > \text{A} > \text{D} > \text{C}$ d. $\text{D} > \text{B} > \text{A} > \text{C}$

13. The IUPAC name of the compound below is



- a. 1-chloro-1,3-dimethyl-4-pentanone c. 5-chloro-3,5-dimethyl-2-hexanone
 b. 5-chloro-3-methyl-2-heptanone d. 3-chloro-5-methyl-6-heptanone

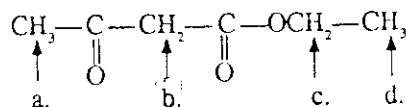
14. What is the four-membered intermediate in the Wittig reaction called?

- a. betaine b. oxaphosphetane c. ylide d. phosphonium ion

15. During the first step of the base-catalyzed (OH^-) aldol condensation,

- a. the carbonyl is protonated. c. the HO^- ion abstracts an α -hydrogen to form an enolate.
 b. the HO^- ion attacks the carbonyl group. d. the carbonyl gets ionized.

16. Which are the most acidic hydrogens in the compound below?



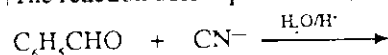
17. Decarboxylation is common in _____.

- a. β -oxoketones c. β -oxoarenes
 b. β -ketocarboxylic acids d. β -hydroxyketones

18. At room temperature in the liquid phase $\text{CH}_3\text{COCH}_2\text{COOCH}_3$ is at equilibrium with _____.

- a. $\text{H}_2\text{C}=\text{C}(\text{OH})\text{CH}_2\text{COOCH}_3$ c. $\text{CH}_3\text{COCH}=\text{C}(\text{OH})\text{OCH}_3$
 b. $\text{CH}_3\text{C}(\text{OH})=\text{CHCOOCH}_3$ d. $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})=\text{CH}_2$

19. The reaction below produces a(n) _____.



- a. optically active compound c. *meso* compound
 b. racemic pair d. a pair of diastereomers

20. Which is the weakest base?

- a. *N*-methylaniline b. benzylamine c. aniline d. cyclohexylamine

21. Which compound will not react with $\text{C}_6\text{H}_5\text{N}=\text{N}^+\text{Cl}^-$ to yield an azo dye?

- a. phenol b. benzene c. *N,N*-dimethylaniline d. 2-naphthol

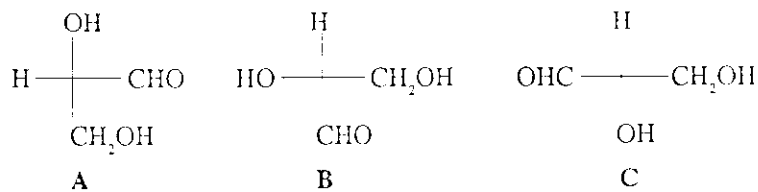
22. Which method would produce N-methylbenzylamine?

- a. $C_6H_5CH_2Cl + NH_2OH/HCl$, followed by H_2/Pt
- b. $C_6H_5CHO + CH_3NH_2$, followed by H_2/Ni
- c. $C_6H_5COCH_3 + NH_3/H^+$, followed by H_2/Ni
- d. $C_6H_6 + (CH_3CO)_2O/H^+$, followed by NH_2OH/HCl

23. Exhaustive methylation and Ag_2O treatment of methyl (2-methylcyclohexyl) amine yields _____-methylcyclohexene.

- a. 1
- b. 2
- c. 3
- d. 4

24. Which projection(s) correspond(s) to D-glyceraldehyde?



- a. A
- b. B
- c. C
- d. A and B

25. The fact that sucrose is a nonreducing sugar, proves that the _____ unit of sucrose is linked to the _____ unit via a _____ linkage.

- a. glucose, fructose, C_5 to C_6
- b. glucose, fructose, C_1 to C_2
- c. fructose, glucose, C_1 to C_2
- d. fructose, glucose, C_3 to C_6