## 北京师大二附中PGA高中课程班2021－2022学年度高三年级 有机化学 第二学期期末测试题 <br> 考试时间： 120 分钟 试卷总分： 100 分

原班级：姓名： $\qquad$学号： $\qquad$

Attention！All writing in this box will NOT be graded！

## Chem 12 (2022 Spring)

## Final Exam

Time Allowed: 120 min Total Score: 100

## Instructions

- You have 120 minutes to complete this exam. Any submission after the 120 -minute mark is not accepted, so please submit your exam before this point, even if you are not done.
- This is a closed-book exam. You are not allowed to check your notes, the workbook, the previous quizzes, and any documents that may be related to today's exam. You may not use any electronic devices or collaborate or consult with any other person.
- This exam includes three parts: multiple-choice questions, fill-in-blank and short answer questions, and free-response questions. The score points allocated for each part are shown in the part directions. Use them as indicators to manage your time to answer questions.
- All pages of the exam must be turned in.
- Be NEAT! Non-legible structure drawings and writings will not be graded.


## Good luck!!!

Name: $\qquad$

Class: $\qquad$

Student ID: $\qquad$

| Part I Score | Part II Score | Part III Score | Total Score |
| :---: | :---: | :---: | :---: |
|  |  |  |  |

## Part I: Multiple-Choice Questions (20\%)

## Directions

- There are 20 questions.
- Each question is worth 1 point.
- There are 20 points in total.
- Write your answer in the box below. Answers that are written before the question number/after the question will not be graded!

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  |  |
| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|  |  |  |  |  |  |  |  |  |  |

1. $(1 \mathrm{pt})$ Choose the correct common name for the following benzene derivative.

A. toluene
B. anisole
C. aniline
D. styrene
2. ( 1 pt ) What is the descriptor of the asterisk(*) marked position?

A. ipso
B. ortho
C. meta
D. para
3. $(1 \mathrm{pt}) 15$-crown- 5 (drawn below) can best solvate:

A. $\mathrm{Li}^{+}$
B. $\mathrm{Na}^{+}$
C. $\mathrm{K}^{+}$
D. $\mathrm{Rb}^{+}$
4. ( 1 pt ) Identify the oxidation state of the asterisk(*) marked carbon.

A. -1
B. 0
C. +2
D. +3
5. ( $1 \mathrm{pt)}$ metal-catalyzed reduction prefers to reduce $\qquad$ double bond, while hydride reduction only reduces $\qquad$ double bond.
A. polar, polar
B. non-polar, non-polar
C. polar, non-polar
D. non-polar, polar
6. ( 1 pt ) In an IR spectrum, a peak at wavenumber $1700 \mathrm{~cm}^{-1}$ most likely indicates that there is a:
A. hydroxyl group ( $\mathrm{R}-\mathrm{OH}$ )
B. amino group $\left(\mathrm{R}-\mathrm{NH}_{2}\right)$
C. carboxyl group ( $\mathrm{R}_{\mathrm{OH}}^{\mathrm{O}}$ )
D. carbonyl group ( $\mathrm{R}_{\mathrm{R}}^{\mathrm{O}} \mathrm{O}_{\mathrm{R}}$ )
7. ( 1 pt ) In mass spectrometry, ketones and aldehydes will undergo McLafferty rearrangement to give an alkene fragment. Based on this information, choose the characteristic peak for ketones and aldehydes:
A. $\mathrm{M}-18$
B. $M-x$, where $x=$ even number
C. $M-x$, where $x=$ odd number
D. $M+1$
8. (1 pt) Which of the following radicals is the most stable:
A.

C.

D.

9. ( 1 pt ) Which of the following species is an ortho-para director:
A.

B.

C.

D.

10. (1 pt) What is EArS stands for:
A. aromatic elimination-addition reaction
B. electron-donating substitution reaction
C. nucleophilic aromatic substitution reaction
D. electrophilic aromatic substitution reaction
11. (1 pt) Identify the major product of the following reaction:

A.

B.
C.

D.

12. ( 1 pt ) Identify the major product of the following reaction:

A.

B.

C.

D.

13. ( 1 pt ) Identify the major product of the following reaction:

A.

B.

C.

D.

14. (1 pt) Identify the major product of the following reaction:

A.

B.

C.

D.

15. ( 1 pt ) Identify the major product of the following reaction:

A.

B.

C.

D.

16. (1 pt) Identify the suitable reagent(s) used for the following transformation:

A. dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$
B. fuming $\mathrm{H}_{2} \mathrm{SO}_{4}$
C. $\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{HNO}_{3}$
D. $\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{AlCl}_{3}$
17. ( 1 pt ) Identify the suitable reagents and condition used for the following transformation:

A.
B.

C. 1)
2) $\mathrm{Zn}(\mathrm{Hg}), \mathrm{HCl}$, heat
D. 1)

3) $\mathrm{Zn}(\mathrm{Hg}), \mathrm{HCl}$, heat
18. ( 1 pt ) Identify the suitable reagents used for the following transformation:

A. 1) EtMgBr
2) $\mathrm{H}_{2} \mathrm{O}_{2}, \mathrm{NaOH}$
B. 1) EtMgBr
3) $\mathrm{H}_{3} \mathrm{O}^{+}$
C. 1) EtMgBr
4) NaOH
5) PCC
D. 1) EtMgBr
6) $\mathrm{H}_{2} \mathrm{O}$
7) $\mathrm{Na}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}, \mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{H}_{2} \mathrm{O}$
19. ( 1 pt ) Identify the suitable reagent and condition used for the following transformation:

A. xs. $\mathrm{Br}_{2}$, heat
B. xs. HBr, heat
C. xs. $\mathrm{HBrO}_{3}$, heat
D. xs. $\mathrm{HBrO}_{4}$, heat
20. ( 1 pt ) Identify the suitable reagents and condition used for the following transformation:

A. 1) $\mathrm{NaOH}, 70^{\circ} \mathrm{C}$
2) $\mathrm{H}_{3} \mathrm{O}^{+}$
B. 1) $\mathrm{NaNH}_{2}, \mathrm{NH}_{3}(l)$
3) $\mathrm{H}_{3} \mathrm{O}^{+}$
C. 1) $\mathrm{NaOH}, 350^{\circ} \mathrm{C}$
4) $\mathrm{H}_{3} \mathrm{O}^{+}$
D. 1) $\mathrm{NaNH}_{2}, \mathrm{NH}_{3}(l), 350^{\circ} \mathrm{C}$
5) $\mathrm{H}_{3} \mathrm{O}^{+}$

## Part II: Fill-in-Blank and Short Answer Questions (25\%)

## Directions

- There are 11 questions. 21-28 are fill-in-blank questions; 29-31 are short answer questions.
- For the fill-in-blank questions, one space (the blank that needs you to fill) is worth 1 point.
- For the short answer questions, the point worth is indicated at the beginning of each of the questions.
- There are 25 points in total.
- Write your answer on the line in each of the questions.

21. ( 1 pt ) $\qquad$ groups, such as the trimethylsilyl group, can be used to circumvent the problem of Grignard incompatibility and can be easily removed after the desired Grignard reaction has been performed.
22. ( 1 pt ) PCC can be used to convert a primary alcohol into an $\qquad$ .
23. (1 pt) The intensity of an IR signal is dependent on the $\qquad$ of the bond giving rise to the signal.
24. ( 2 pts ) Electron impact ionization (EI) involves bombarding the compound with high energy
$\qquad$ , generating a radical cation that is symbolized by $(M)^{+\bullet}$ and is called the
$\qquad$ ion, or the parent ion.
25. ( 2 pts ) A signal at $\mathrm{M}-15$ indicates the loss of a $\qquad$ group; a signal at M-29 indicates the loss of an $\qquad$ group.
26. ( 2 pts ) When two protons are interchangeable by rotational symmetry, the protons are said to be $\qquad$ ; when two protons are interchangeable by reflectional symmetry, the protons are said to be $\qquad$ .
27. ( 2 pts ) The left side of an NMR spectrum is described as $\qquad$ field, and the right side is described as $\qquad$ field.
28. ( 1 pt ) The stability of benzene can be explained with MO theory. The six $\pi$ electrons all occupy
$\qquad$ MOs.
29. (3 pts) Describe the criteria for aromaticity (your answer should include the condition of being aromatic, antiaromatic, and nonaromatic).
$\qquad$
$\qquad$
$\qquad$
$\qquad$
30. (4 pts) Using the Hooke's law to describe the factors that affect the wavenumber of different bonds.
31. (6 pts) Explain the anisotropic effect in benzene.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

## Part III: Free-Response Questions (55\%)

## Directions

- There are 5 questions.
- The point worth is indicated at the beginning of each of the questions.
- There are 55 points in total.
- Only answers located within or very close to the answer boxes (or located at the question required places) will be graded.

32. ( 18 pts ) Diols are compounds with two hydroxyl groups.
(a) (4 pts) Name the following diols.


$\square$
(b) ( 5 pts ) Different diols can be prepared via different methods. Some of the methods are classical in synthetic chemistry, such as the synthesis of 1,2-diol and 1,6-diol.
(i) (2 pts) Identify the reagents used in converting cyclohexene to hexane-1,6-diol.
(ii) (3 pts) Starting with an appropriate epoxide, propose a mechanism of preparing a 2,3-dimethylbutane-2,3-diol
 (also known as pinacol).
(c) (4 pts) An alternative method of preparing pinacol involves the use of Grignard reagent. Identify the reagents, and propose a plausible mechanism for the conversion shown below.

(d) (5 pts) Pinacol rearrangement is a very useful reaction in preparing spiro compounds. It follows the reaction pattern shown below. Propose a mechanism for the following transformation. (Hint: consider the resonance effect - a carbocation is resonance stabilized when it is adjacent to an oxygen atom, and such a carbocation is even more stable than a tertiary carbocation.)

33. ( 6 pts ) The Grignard reagent is one of the earliest organometallic reagents invented by chemists. In the transformation shown below, Identify the reagents, and draw all intermediates associated with each step of the reaction (Hint: you may take care of the acidic functional groups - Grignard reagent is incompatible with them!).

34. (8 pts) A new compound was synthesized, and the relevant spectroscopic data are obtained.

- The mass spectrum indicates that the molecular formula is $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}$
- The infrared spectrum is:

- The proton NMR spectrum is:

(a) (2 pts) From the infrared spectrum, circle the functional groups that are definitely present:

$$
\mathrm{O}-\mathrm{H} \quad \mathrm{C}=\mathrm{O} \quad \mathrm{C}=\mathrm{C} \quad \mathrm{C} \equiv \mathrm{~N}
$$

(b) (2 pts) From the infrared spectrum, circle the functional groups that are definitely absent:

| $\mathrm{O}-\mathrm{H}$ | $\mathrm{C}=\mathrm{O} \quad \mathrm{C}=\mathrm{C} \quad \mathrm{C}=\mathrm{N}$ |
| :--- | :--- | :--- |

(c) (4 pts) Deduce the structure of this compound. A detailed reasoning process can help you earn parts of points.
35. ( 6 pts ) Aromaticity is one of the most interesting properties in chemistry.
(a) (4 pts) Using Frost circles to determine whether the following compounds are aromatic, antiaromatic, or nonaromatic.


$\square$

Cyclic compounds containing heteroatoms (such as $\mathrm{S}, \mathrm{N}$, or O ) are called heterocycles. Below are two examples of nitrogen-containing heterocycles.

pyridine

pyrrole

Both of these compounds are aromatic, but for very different reasons.

Pyridine exhibits a continuous system of overlapping $p$ orbitals and therefore satisfies one of the criteria for aromaticity. The nitrogen atom in pyridine is $s p^{2}$ hybridized, and the lone pair on the nitrogen atom occupies an $s p^{2}$-hybridized orbital, which is pointing away from the ring. This lone pair is not part of the conjugated system and therefore is not included when we count the number of $\pi$ electrons. In this case, there are six $\pi$ electrons, so the compound is aromatic.

In pyrrole, once again, the nitrogen atom is $s p^{2}$ hybridized, but in this case, the lone pair occupies a $p$ orbital. In order for the pyrrole ring to achieve a continuous system of overlapping $p$ orbitals, the lone pair of the nitrogen atom must occupy a $p$ orbital. With six $\pi$ electrons (four from the $\pi$ bonds and two from the lone pair), this compound is aromatic. In this case, the lone pair is crucial in establishing aromaticity.
(b) (2 pts) Histamine is another example of heterocyclic compound. It is responsible for many physiological responses and is known to mediate the onset of allergic reactions. Determine whether the ring in histamine is aromatic; if so, determine which lone pair(s) participate in aromaticity.

36. ( 17 pts ) Different substituents perform a vital role in the reactivity of benzene rings.
(a) (3 pts) Explain why nitro group is a deactivator.
(b) (4 pts) Explain why amino group is an ortho-para director (Hint: your answer should include multiple resonance structures.)
(c) (10 pts) Starting with benzene and using any other reagents of your choice, design a synthesis for each of the following compounds. You must draw mechanisms for each step to receive the full score.


