

國立臺北科技大學九十八學年度碩士班招生考試

系所組別：3711 3712 3713 有機高分子研究所甲組

第一節 有機化學 試題

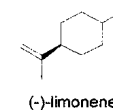
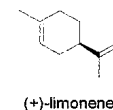
第一頁 共二頁

注意事項：

1. 本試題共 10 題，配分共 100 分。
2. 請標明大題、子題編號作答，不必抄題。
3. 全部答案均須在答案卷之答案欄內作答，否則不予計分。

1. An aryl halide such as chlorobenzene can undergo a nucleophilic substitution reaction in the presence of a very strong base such as NH_2^- . There are two surprising aspects to this reaction: the aryl halide does not have to contain an electron-withdrawing group, and the incoming substituent does not always end up on the carbon vacated by the leaving group. For example, when chlorobenzene—with the carbon to which the chlorine is attached isotopically labeled with ^{14}C —is reacted with amide ion in liquid ammonia, aniline is obtained as the product. Half of the product has the amino group attached to the isotopically labeled carbon as expected, but the other half has the amino group attached to the carbon adjacent to the labeled carbon.
 - (a) Write the mechanism for this reaction. (10 分)
 - (b) What products will be obtained when chlorobenzene is replaced by *o*-bromotoluene (without ^{14}C labeling) in this reaction? (5 分)
2. A carbene is an unusual carbon-containing species: it has a carbon with a lone pair of electrons and an empty orbital. The empty orbital makes the carbene highly reactive. The simplest carbene, methylene, is generated by heating diazomethane. What product will you obtain when diazomethane and ethene are heated together? (5 分)
3. The first organometallic compounds used in coupling reactions were Gilman reagents. They are prepared by the reaction of an organolithium compound with cuprous iodide in diethyl ether or THF. Gilman reagents can be used to prepare compounds that cannot be prepared by using nucleophilic substitution reactions and replace halogens in compounds that contain other functional groups. Using butyllithium as a representative, write the equation for the preparation of Gilman reagent. (5 分)

4. Although chloro and bromo substituents can be placed directly on a benzene ring by halogenation, the Sandmeyer reaction can be a useful alternative. For example, if you wanted to make *para*-chloroethylbenzene, the chlorination of ethylbenzene leads to a mixture of *ortho* and *para* isomers. If, however, you started with *para*-ethylaniline and used a Sandmeyer reaction for chlorination, only the desired *para* product would be formed. Write the equations to show that how *para*-chloroethylbenzene is prepared from *para*-ethylaniline by Sandmeyer reaction? (10 分)
5. When an alkene is treated with ozone at low temperatures, the double bond breaks and the carbons that were doubly bonded to each other are now doubly bonded to oxygens instead. This oxidation reaction is known as ozonolysis. What products will you obtain when 3-methyl-3-hexene is treated by ozonolysis? (5 分)
6. Limonene exists as two different stereoisomers. The *R* enantiomer is found in oranges and the *S* enantiomer is found in lemons. Which of the following molecules is found in oranges? (5 分)



7. If a compound has two functional groups that will react with a given reagent and you want only one of them to react, it is necessary to protect the other functional group from the reagent. A group that protects a functional group from a synthetic operation that it would not otherwise survive is called a protecting group.
 - (a) Which compound can be used to protect a keto group? (5 分)
 - (b) Which compound can be used to protect an alcohol? (5 分)
8. A compound does not have to be a hydrocarbon to be aromatic. Many heterocyclic compounds are aromatic. A heterocyclic compound is a cyclic compound in which one or more of the ring atoms is an atom other than carbon. Please draw the structures for five heterocyclic aromatic compounds and give their English names. (10 分)

注意：背面尚有試題

9. Typical bases such as sodium hydroxide or an alkoxide ion cannot be used to form enolates for alkylation because at equilibrium a large quantity of the hydroxide or alkoxide base is still present. These strongly nucleophilic bases give side reactions with the alkyl halide or tosylate. Lithium diisopropylamide (LDA) avoids these side reactions. Because it is a much stronger base, LDA converts the ketone entirely to its enolate. All the LDA is consumed in forming the enolate, leaving the enolate to react without interference from the LDA. Also, LDA is a very bulky base and thus a poor nucleophile, so it generally does not react with the alkyl halide or tosylate.

(a) Write an equation to show how would you prepare LDA? (5 分)

(b) Predict the product when acetone is treated with LDA then reacts with allyl bromide. (5 分)

10. 請簡答下列問題。(每題 5 分，共 25 分)

(a) A tetrahedral amine with three different substituents is nonsuperimposable on its mirror image. In most cases, we cannot resolve such an amine into two enantiomers. Why?

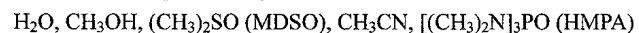
(b) The addition of a phosphorus-stabilized carbanion (ylide) to a ketone or aldehyde produces an alkene. What is the name of this reaction?

(c) Which of the following compounds proceeds Mclafferty rearrangement?



(d) Lindlar's catalyst is a poisoned metal catalyst, composed of powdered barium sulfate coated with catalytic metal, poisoned with quinoline. What is the catalytic metal in Lindlar's catalyst?

(e) Which of the following solvents gives the fastest $\text{S}_{\text{N}}1$ reaction rate?



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