

中央大學八十九學年度碩士班研究生入學試題

化學學系 不分組

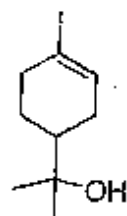
科目:

有機與無機化學

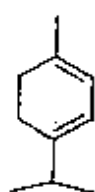
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簡答題 (5% for each)

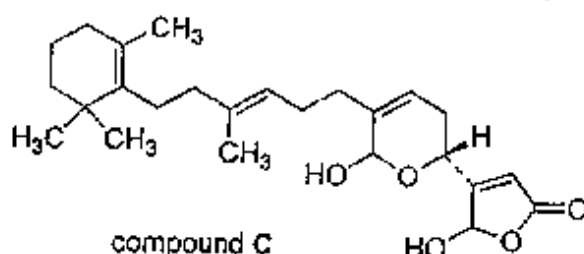
1. When 1-butene react with HBr, either the Markovnikov or the anti-Markovnikov product can be the major product depending on the reaction conditions. What are the conditions that will lead to these two different products.
2. Do you agree with the following statement? "Strongly electron-withdrawing substituents on benzene rings are *meta* directing because they deactivate the meta positions less than they deactivate the *ortho* and *para* positions." Explain your answer.
3. Alkanoyl halides, amides, esters, and anhydrides are four common derivatives of carboxylic acids, and have different reactivities. Rank them in order of decreasing reactivities toward nucleophilic addition-elimination reactions and explain your answer.
4. In a S_N2 reaction, the statement: "a stronger base is usually a better nucleophile than a weaker base" is not always true. Give a pair of nucleophiles, in which the weaker base is a better nucleophile than the stronger one.
5. Give an example for the Wittig reaction by using benzyl bromide as one of the substrates.
6. Give an example for the Diels-Alder reaction by using anthracene as one of the substrates.
7. Explain why phenol has a lower pK_a than ethanol.
8. Draw the structure of *cis*-1-*tert*-butyl-4-methylcyclohexane. (make sure your bond angles are making sense)
9. The major product of the acid-catalyzed dehydration of α -terpineol (compound A) is α -terpinene (compound B). Propose a reasonable mechanism for the transformation.
10. In NMR experiments, deuterated solvents such as $CDCl_3$ are generally used. (a) What is the function of deuterated solvent? In addition, Manoalide (compound C) was isolated from a sponge in 1977. (b) Which carbon in Manoalide will give the largest chemical shift in its ^{13}C NMR spectrum? (draw the structure in your answer sheet first and then mark it)



compound A



compound B



compound C

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11. Determine the point groups of the following orbitals, including the signs on the orbital lobes: (a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (9 %)
12. Except in cases where ligand geometry requires it, square-planar geometry occurs in d^7 , d^8 , and d^9 ions with strong field, π -acceptor ligands. Explain why these restrictions apply. (9 %)
13. The azide ion, N_3^- , is linear, with equal N-N bond distances. (8 %)
- (a) Describe the π -molecular orbitals of azide.
- (b) Describe, in HOMO-LUMO terms, the reaction between azide and H^+ , to form hydrazoic acid, HN_3 .
14. When *cis*- OsO_2F_4 is dissolved in SbF_5 , a cation X^+ is formed. The ^{19}F -NMR spectrum of this cation showed two resonances, a doublet and a triplet having relative intensities of 2 : 1. What is the most likely structure of this ion X^+ ? What is its point group? (8 %)
15. B_2O_3 is acidic, Al_2O_3 is amphoteric, and Sc_2O_3 is basic. Why? (8 %)
16. The high-spin d^4 complex $[Cr(H_2O)_6]^{2+}$ is labile, but the low-spin d^4 complex $[Cr(CN)_6]^{4-}$ is inert. Explain. (8 %)