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1. a) Why does compound A boil at a much lower temperature than compound B? (2 %)

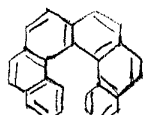


- b) Most simple aldehydes and ketones exist primarily in their keto forms. However, 2,4-pentanedione exists as 80% enol form. Explain. (2 %)

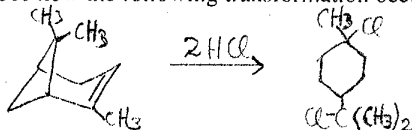
- c) Azulene is a polar compound. Why? (2 %)



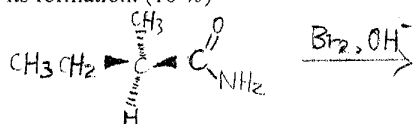
- d) Hexahelicene can exist as a pair of enantiomers. Suggest why? (2 %)



- e) See how the following transformation occurs. (2 %)



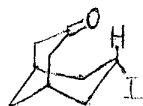
2. Preparation of amine containing a bulky tertiary alkyl group is difficult, but can be achieved through Hofmann rearrangement. Write the major product of the following reaction and the mechanism for its formation. (10 %)



3. When 1,2-diols are heated in acidic solution, a rearrangement called pinacol rearrangement occurs. The following conversion is one example of such a reaction. Suggest a mechanism for this. (5 %)



4. When the following iodoketone was treated with KOH in  $\text{CH}_3\text{OH}$ , compound A ( $\text{C}_{10}\text{H}_{16}\text{O}_2$ ) was obtained in 92% yield. What is the structure of compound A?



參考用

(1)

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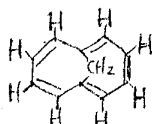
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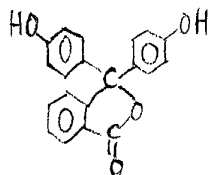
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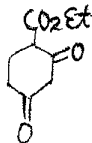
5. In the  $^1\text{H}$  NMR spectrum of 1,6-methanol[10]annulene, the ring protons absorb at low field ( $\delta$  6.8-7.5 ppm), while the  $-\text{CH}_2-$  protons absorb far upfield ( $\delta$   $-0.5$  ppm). Explain. (5 %)



6. Phenolphthalein is a well-known titration indicator. In acidic solution, it is a colorless lactone. At pH greater than 8.3, it give rise to the red color. In strongly alkaline solution, it becomes colorless again. Explain. (5 %)

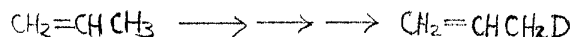


7. Prepare the following compound by the Michael addition and Dieckman condensation. (5 %)

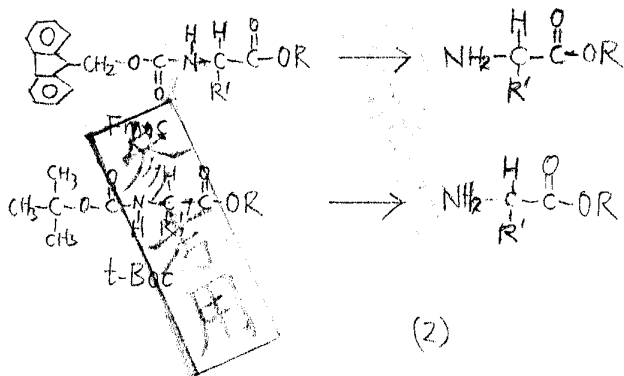


8.  $\Phi-\text{CH}=\text{CHCH}_2\text{CH}_3$  can be prepared from  $\Phi-\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ , triphenyl phosphine ( $\text{C}_6\text{H}_5$ ) $_3\text{P}$  and butyl-lithium. Write its synthesis from these reagents in proper order. (5 %)

9. How can one prepare 3-deuterioisopropene from a non-deuterioisopropene through the  $\text{D}_2\text{O}$ , Mg, and N-bromo-succinimide reagents (note that these reagents are not listed in sequential order)? (5 %)



10. In solid phase peptide synthesis, the N-terminal amino group can be either protected by a Fmoc- or a tBoc-group as shown below. Predict which protection group is removed by TFA ( $\text{CF}_3\text{COOH}$ ), which by weak base piperidine and their respective mechanism<sup>s</sup>. (10 %)



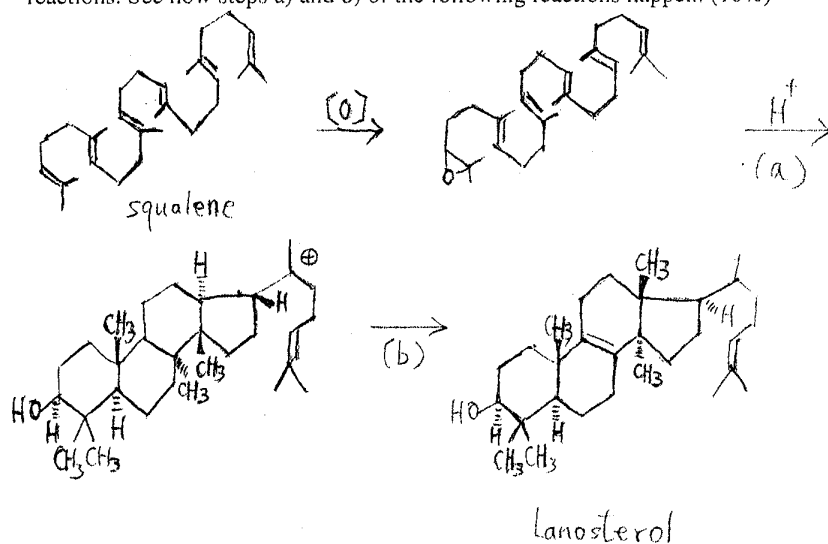
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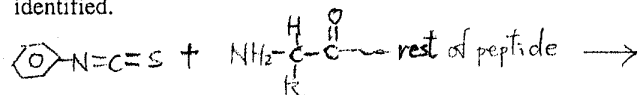
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11. Lanosterol, the important cholesterol precursor, is covered from squalene by the following reactions. See how steps a) and b) of the following reactions happen. (10%)



12. a) A peptide sequence can be determined by stepwise treating the peptide with Edman reagent (phenyl isothiocyanate) that results in cleavage of the N-terminal amino acid from the peptide and in the formation of a phenylthiohydantoin (PTH), a derivative of an amino acid that can be identified.



Write the structure of the product PTH. (5%)

- b) Another reagent useful for determining the N-terminal residue is the Sanger reagent, 1-fluoro-2,4-dinitrobenzene, which reacts readily with the N-terminal amino acid of a peptide. What kind of reaction is this? (5%)

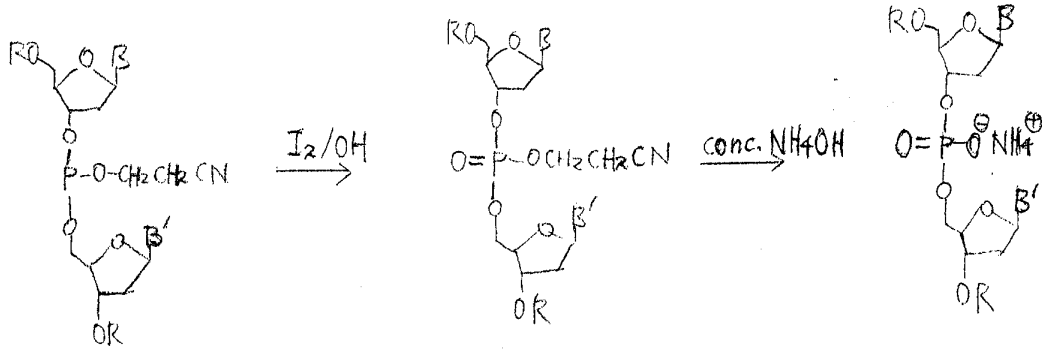


(3)

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13. The facile chemical synthesis of DNA molecules is a cornerstone of modern molecular biology. Describe why the following reactions can occur readily. (10%)



14. A buffer solution can be prepared by mixing an acid with its salt in appropriate ratio through the following equation:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Derive such an equation. (5%)

