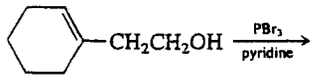
編號： 56　系所：化學系　　科目：有機化學

本試題是否可以使用計算機：☐可使用 ，☑不可使用 （請命題老師勾選）

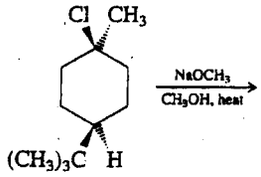
請將答案寫在答案紙上並清楚地註明題號。

1. Show the principal product for the following reactions. (3% each)

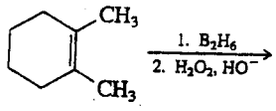
a).



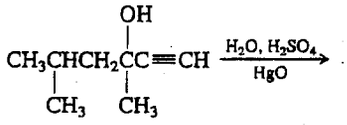
b).



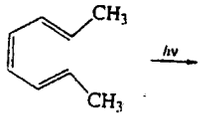
c).



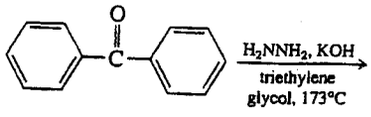
d).



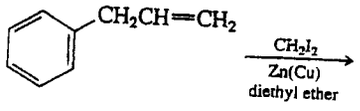
e).



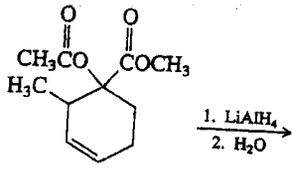
f).



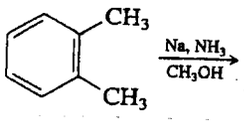
g).



h).



i).



（背面仍有題目，請繼續作答）

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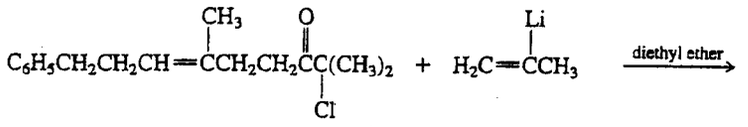
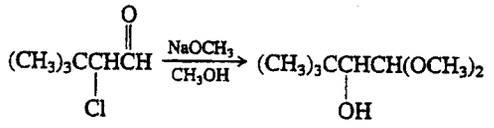
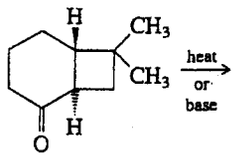
j).



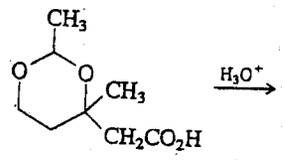
k).



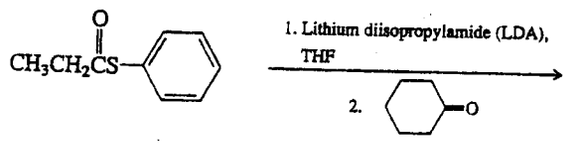
l).



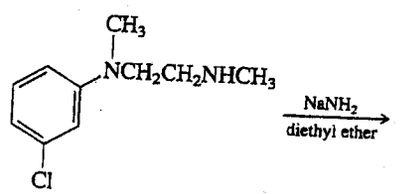
m).



n).



o).

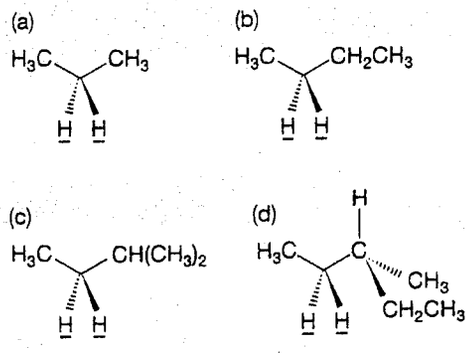


2. Spectral data for isomeric compounds A and B are summarized below. Assign structures for compounds A and B, and explain your reasoning. (10%)

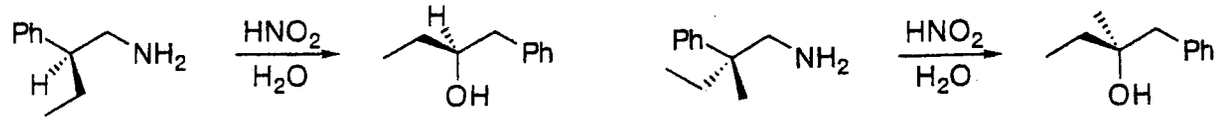
Compound A
Mass spectrum: *m/z* = 148 (molecular ion, 7%), 106 (8%), 105 (100%), 77 (29%), 51 (8%)
IR (neat): 1675 (s), 1220 (s), 980 (s), and 702 (s) cm^{-1}
1H-NMR ($CDCl_3$): δ 1.20 (d, J = 7 Hz, 6H) ; 3.53 (septet, J = 7 Hz, 1H)
7.20 – 7.60 (m, 3H) ; 7.80 – 8.08 (m, 2H)

Compound B
IR (neat): 1705 (s), 738 (m), and 698 (s) cm^{-1}
1H-NMR ($CDCl_3$): δ 0.95 (t, J = 7 Hz, 3H) ; 2.35 (q, J = 7 Hz, 2H)
3.60 (s, 2H) ; 7.20 (s, 5H)

3. Are the underlined hydrogens in the following molecules homotopic, enantiotopic, or diastereotopic? Account for your answer. (8%)

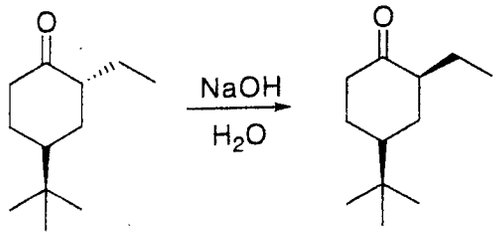


4. The optical pure amine A reacts with HNO_2/H_2O to give alcohol B in which the stereogenic center is 77% inverted. However, when the optically pure amine C is subjected to the same conditions, almost complete racemization of the product alcohol is observed. Explain (8%)

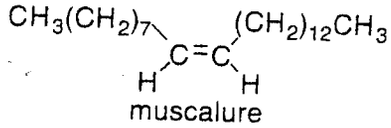


A　　B　　C　　D

5. Provide a mechanistic rationale for the formation of *cis*-4-*tert*-butyl-2-ethyl-cyclohexane from its *trans* isomer in the following reaction. (5%)



6. Propose an efficient synthesis for the following compound, a sex pheromone of common housefly, from a suitable alkyne and any other necessary starting materials. (6%)



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（背面仍有題目，請繼續作答）

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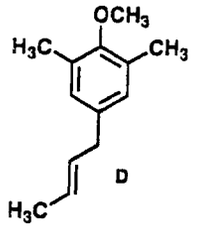
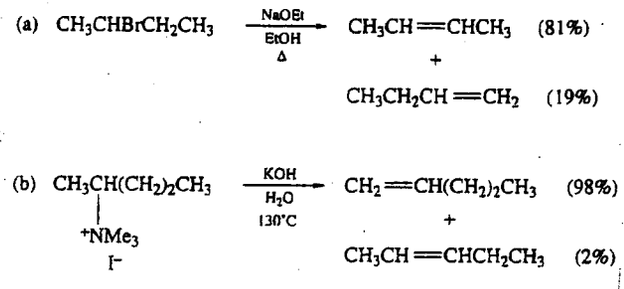
7. Propose a synthesis of D from 2,6-dimethylphenol, iodomethane, and *trans*-1-bromo-2-butene. Use any inorganic reagents (e.g. acids, based, Lewis acids. etc.) necessary, but no other carbon-containing compounds. Show arrow-pushing mechanism for each step. (8%)



8. Both the following two reactions are regioselective but neither is regiospecific. Explain the regioselectivity difference between these two reactions. (6%)



9. Heat of combustion can be used to analyze the total strain energy of cycloalkane. It was found that the heat of combustion for a methylene (CH_2) group in strain-free straight-chain alkane, $(CH_2)_\infty$, is 157.44 kcal/mol and that for cyclobutane is 656.07 kcal/mol. What is the strain energy per CH_2 for cyclobutane. (4%)