

岡山大学大学院自然科学研究科
博士前期課程
物質生命工学専攻
物質応用化学系

平成18年度入学学力試験問題
専門科目 有機化学

(注意)

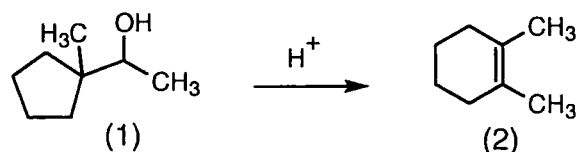
- 各解答用紙の全てに受験番号と氏名を記入のこと。

問題 1 .

(50点)

次の問に答えよ。

- 1) VSEPR理論を基にして二酸化イオウのLewis構造式を立体構造がわかる様を書け。また、二酸化イオウと二硫化炭素ではどちらが双極子モーメントが大きいか。
- 2) (1*S*,2*R*)-1-chloro-1-phenyl-2-propanol の安定な立体配座を、C₁-C₂結合軸を通して、C₁側から見た Newman 投影式を書け。
- 3) 化合物 (1) を酸触媒下に加熱すると1,2-dimethylcyclohexene (2) が生成した。この反応の反応機構を書け。また、この転位反応の駆動力は何か簡潔に述べよ。



- 4) マレイン酸 (*cis*-HO₂CCH=CHCO₂H)の p*K*₁は1.9, p*K*₂は 6.1であり、フマル酸 (*trans*- HO₂CCH=CHCO₂H)の p*K*₁は3.0, p*K*₂は4.4である。これらのp*K*_aのデータは二塩基酸である マレイン酸 は第一段解離ではフマル酸より強酸であるが、第二段解離ではその逆で、より弱酸となることを示している。その理由を簡潔に示せ。
- 5) 次の英文の[]に適切な英単語を入れよ。ただし、複数個の英単語が入る場合もある。
 - 5-1) Hydroboration of 1-methylcyclopentene (**A**) followed by treatment of alkaline hydrogen peroxide provides (1*R*,2*R*)-2-methylcyclopentanol (**B**) and its [a]. The stereochemistry between hydroxy and methyl groups of the alcohol (**B**) is *trans*. The fact indicates the hydroboration proceeds *via* [b]-addition.
 - 5-2) Oxidation of (**A**) with KMnO₄ in a cold alkaline aqueous solution provides a diol in which the stereochemistry of two hydroxy groups is [c].
 - 5-3) Judging from the p*K*_a of ethane, ethene, ethyne, ethanol, acetylacetone, and phenol = 50, 44, 35, 16, 10, and 9, respectively, it is understandable that *n*-butyl lithium can abstract any protons, in principle, of ethene, ethyne, acetylacetone, and phenol. Therefore, sodium ethoxide can effectively abstract proton of [d].
 - 5-4) Basicity of aniline is [e] than that of ethylamine due to [f] of the unshared electrons on nitrogen atom of aniline into benzene ring.

問題 2 .

(50点)

次の英文を読んで問に答えよ。

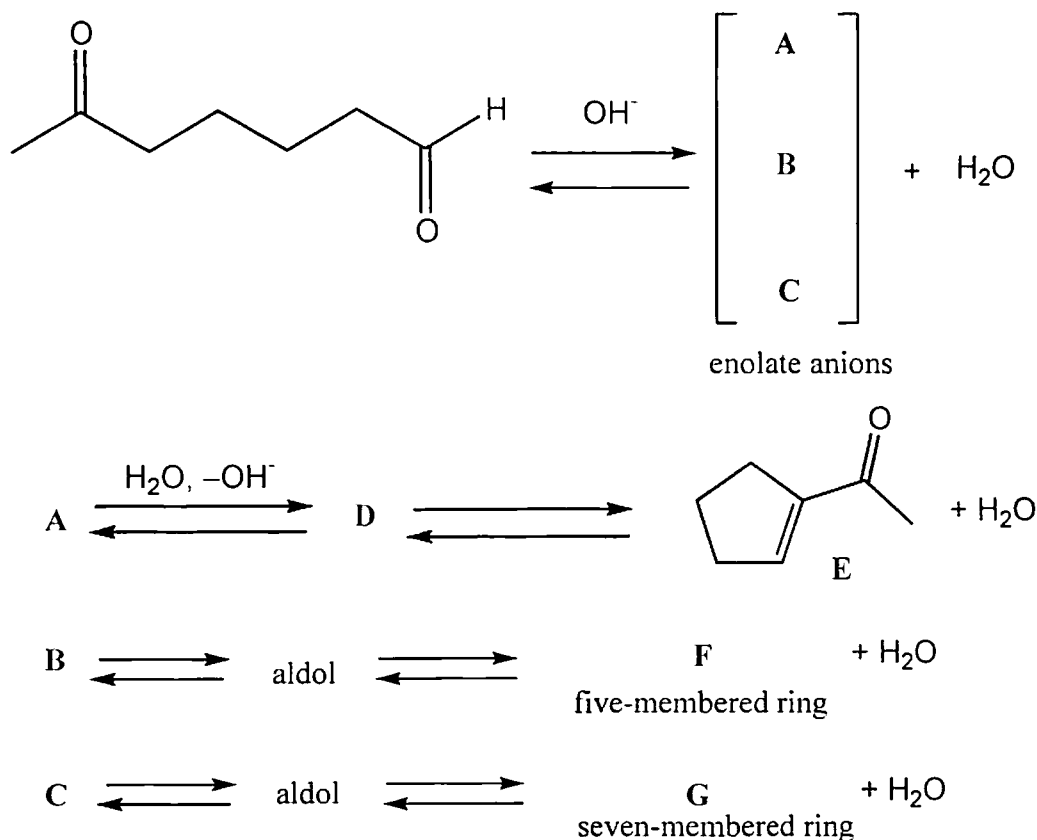
- 1) Reduction of (3*R*,4*S*)-4-isopropyl-3-methylcyclohexanone (**A**) with LiAlH_4 provided a mixture of alcohols (**B**, thermodynamically more stable) and (**C**, thermodynamically less stable), in which **B** was a major product. Write the structure and IUPAC name of the thermodynamically less stable isomer (**C**) to indicate the proper stereochemistry.
- 2) Both tosylates of alcohols (**B**) and (**C**) were subjected to the *t*-BuOK-promoted elimination reaction in *t*-butyl alcohol. Suggest which tosylate reacts faster and write structures of the products produced from the more reactive tosylate.
- 3) The tosylate of alcohol (**B**) reacted with sodium acetate in polar aprotic solvents such as DMF. Provide the structure of the product.
- 4) S_N1 reaction of the tosylate of alcohol (**B**) in acetic acid gave a (1:1) mixture of (1*S*) and (1*R*)-acetoxy-derivatives. Suggest whether the mixture is optically active or not, and give a brief explanation.
- 5) (*S*)-2-Ethylcyclopentanone reacted with phenyl Grignard reagent in ether, affording two alcohols. Write the structures of the products in the Grignard reaction and show a stereochemical relation between the two alcohols.
- 6) Both alcohols produced in the above Grignard reaction were acid-sensitive and underwent facile dehydration under acidic conditions. Write the structure of the major product.
- 7) Radical chlorination of (*R*)-2-phenylbutane (**D**) yielded several monochlorides.
 - 7-1) Which hydrogen in (**D**) is most reactive in this radical chlorination?
 - 7-2) Assuming all of the intermediate carbon radicals are planar, write a structure of an optically inactive monochloride.

問題 3.

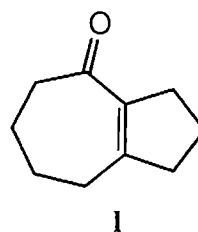
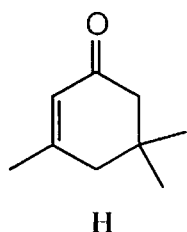
(50点)

以下の英文を読んで 1)~4) に答えよ。

The intramolecular aldol condensation offers a convenient way to synthesize molecules with five- and six-membered rings and sometimes even larger rings. For example, the following keto-aldehyde cyclizes to yield 1-cyclopentenyl methyl ketone E. This reaction almost certainly involves the formation of at least three different enolates A, B, and C. However, only enolate A gives the cyclized product E through the corresponding aldol D. Assuming that the aldol cyclization occurs in all instances, two other products F and G with five- and seven-membered rings might have been formed, respectively.

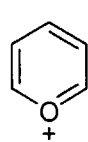


- 1) Write the structures of A, B, C, D, F, and G.
- 2) Explain why only the enolate A undergoes cyclization exclusively to afford E.
- 3) What experimental conditions would favor the intramolecular cyclization over the intermolecular condensation.
- 4) What carbonyl compound would you use in an aldol condensation to prepare each of the following?

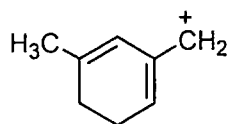


問題 4.

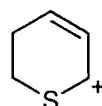
問1. 以下の化合物 A-D の共鳴構造式を記せ。また、それぞれの内で、最も重要な（寄与の大きい）共鳴構造式を選び、円で囲め。



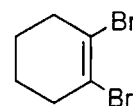
A



B

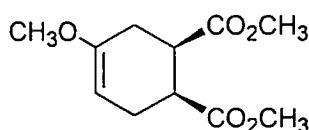


C

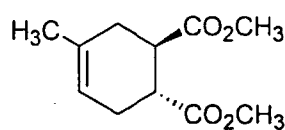


D

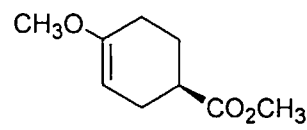
問2. Diels-Alder反応で、以下の化合物を合成するために必要な化合物の構造式を記せ。どの生成物が同一条件下で最も速やかに生成するか、生成物 (E-G) の記号で答えよ。



E

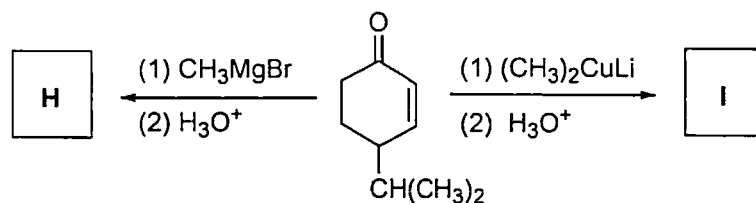


F

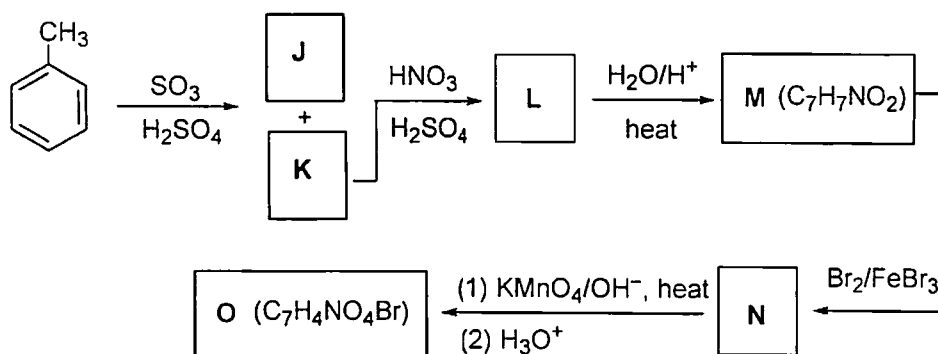


G

問3. 以下の反応における主生成物 H および I を記せ。I は立体化学も含めて記せ。



問4. 以下の反応経路で生成する主生成物 J-O の構造式を記せ。図中の J と K は構造異性体であり、化合物 K は、 ^1H NMR スペクトルにおいて芳香族水素領域に、それぞれ 2H 分の積分強度をもつ 2 種類の二重線を示した。



IR スペクトル: $3400\text{--}2500, 1700\text{ cm}^{-1}$