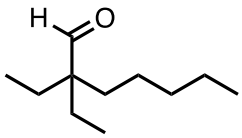
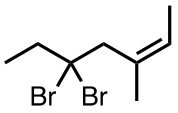
［有機化学基礎］
以下の問（１）～（４）に答えよ．

（１） 化合物 **1** 及び **2** をそれぞれ命名せよ．



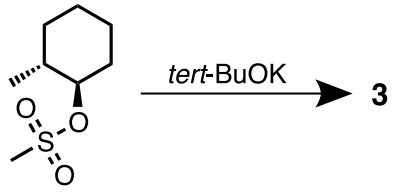
1



2

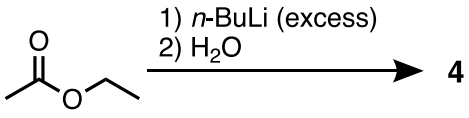
（２） 以下に示す反応(a)～(d)について，主生成物 **3**～**7** の構造式を描け．

(a)



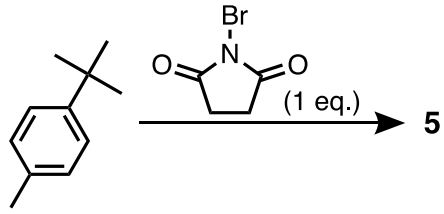
3

(b)



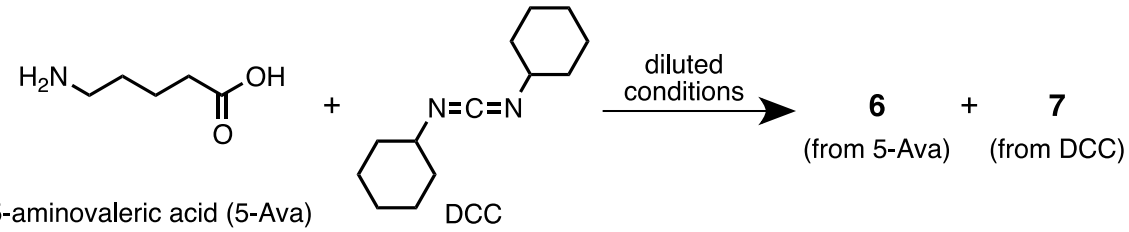
4

(c)



5

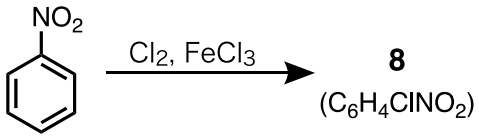
(d)



5-aminovaleric acid (5-Ava)　　DCC

6 (from 5-Ava)　+　**7** (from DCC)

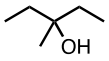
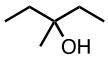
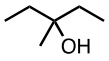
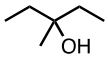
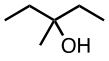
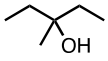
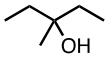
（３） 下記の反応では，化合物 **8** が位置選択的に生成する．この反応機構を電子の移動を表す巻矢印表記法を用いて示せ．また，中間体の共鳴構造式を示した上で，位置選択性が発現する理由を簡潔に説明せよ．



8
($C_6H_4ClNO_2$)

（4） 分子式が C_6H_{12} であるアルケン **9**〜**12** を，反応条件①〜③でそれぞれ反応させたところ，全ての反応において分子式が $C_6H_{14}O$ である生成物が得られた（表１）．^{1}H NMR 測定において，アルケン **9** では二つのカルテットのシグナル間に核オーバーハウザー効果（NOE）が観測されたが，アルケン **10** では二つのカルテットのシグナル間に NOE は観測されなかった．アルケン **11** の ^{1}H NMR スペクトルには，カルテットのシグナルは一つしか観測されなかった．以下の問(e)〜(g)に答えよ．なお，アルケン **9**〜**12** のエナンチオマーは考慮しなくてよい．

表１．アルケン **9**〜**12** を反応条件①〜③で反応させた時の生成物．生成物 **A**〜**E** は互いに異なる．

		反応条件 ① H_2SO_4/H_2O	反応条件 ② 1) $Hg(OAc)_2/H_2O$ 2) $NaBH_4$	反応条件 ③ 1) BH_3 2) $NaOH/H_2O_2$
原料のアルケン	**9**			**B**
	10			**C**
	11			**D**
	12		**A**	**E**

(e) 反応条件①において，アルケン **12** から 3-methyl-3-pentanol が生成する反応機構を電子の移動を表す巻矢印表記法を用いて示せ．

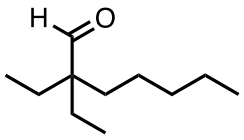
(f) アルケン **9** の構造式を描け．

(g) アルケン **9** を反応条件③で反応させた時に得られた生成物 **B** は，複数の立体異性体の混合物であった．これら全ての立体異性体の構造式を描け．

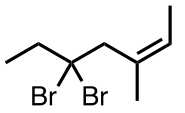
[Organic Chemistry: Basic]

Answer problems (1) through (4).

（1） Provide the names of **1** and **2**.



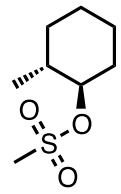
1



2

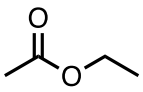
（2） Predict the main products **3**–**7** for the following reactions (a)–(d).

(a)



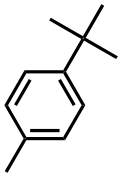
tert-BuOK → **3**

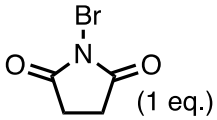
(b)



1) *n*-BuLi (excess)
2) H_2O → **4**

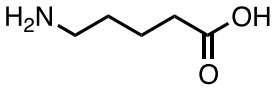
(c)





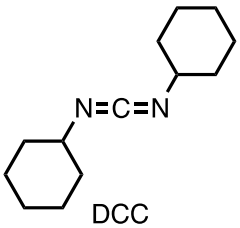
(1 eq.) → **5**

(d)



5-aminovaleric acid (5-Ava)

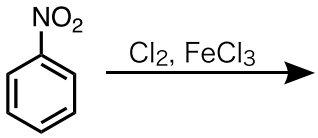
+



DCC

diluted conditions → **6** (from 5-Ava) + **7** (from DCC)

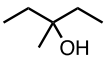
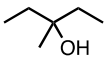
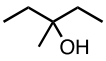
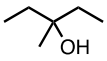
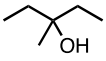
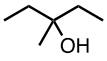
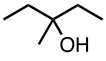
（3） The following reaction affords compound **8** in a regioselective manner. Show the mechanism of this reaction by using the curved arrow formalism. In addition, briefly explain the reason of the regioselectivity by drawing resonance structures of the key intermediate.



Cl_2, $FeCl_3$ → **8** ($C_6H_4ClNO_2$)

（4）Reactions of alkenes **9**–**12** (molecular formula: C_6H_{12}) under the conditions ①–③ gave products with an identical molecular formula of $C_6H_{14}O$ (Table 1). In ^1H NMR spectroscopy, a nuclear Overhauser effect (NOE) between two quartet signals was observed in alkene **9**, whereas no NOE between two quartet signals was observed in alkene **10**. The ^1H NMR spectrum of alkene **11** showed only one quartet signal. Answer the following problems (e)–(g). You do not need to consider enantiomers of alkenes **9**–**12**.

Table 1. Products from alkenes **9**–**12** under the reaction conditions ①–③. Products **A**–**E** are not identical.

alkenes (starting materials)	reaction conditions ① H_2SO_4/H_2O	reaction conditions ② 1) $Hg(OAc)_2/H_2O$ 2) $NaBH_4$	reaction conditions ③ 1) BH_3 2) $NaOH/H_2O_2$
9			**B**
10			**C**
11			**D**
12		**A**	**E**

(e) Show the reaction mechanism from alkene **12** to 3-methyl-3-pentanol under the reaction conditions ① using the curved arrow formalism.

(f) Draw the structure of alkene **9**.

(g) Product **B** from alkene **9** under the reaction conditions ③ was a mixture of stereoisomers. Draw the structures of all the stereoisomers.