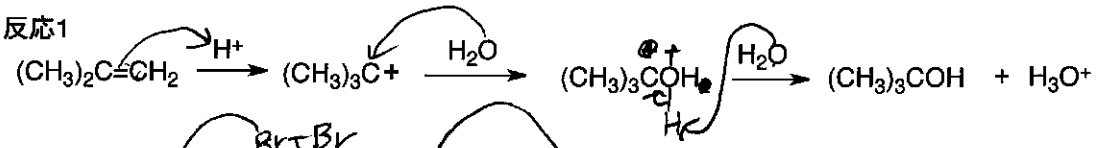
基礎有機化学 課題 解答例

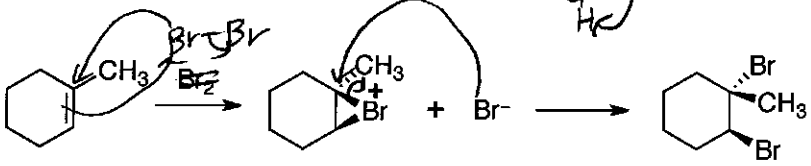
2017.6.6

反応 1〜6 の各段階における電子の移動を曲がった矢印を使って示せ。

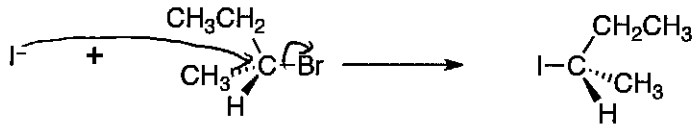
反応1



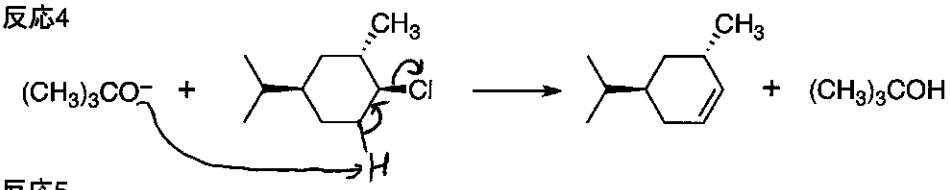
反応2



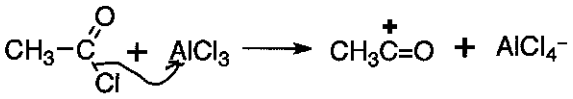
反応3

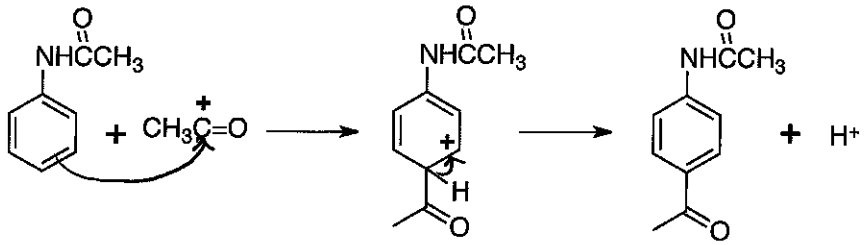


反応4

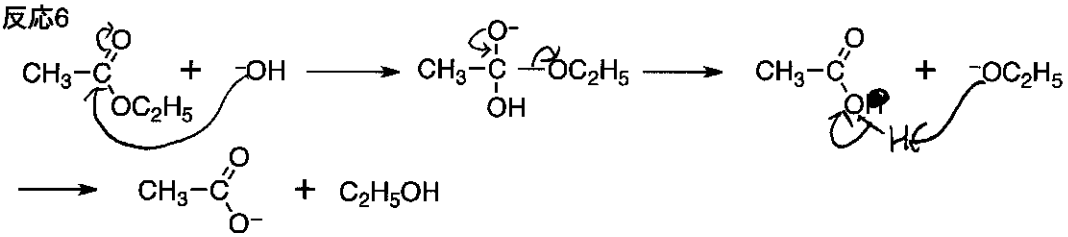


反応5



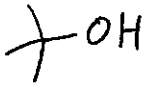
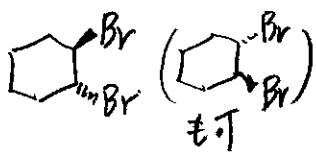


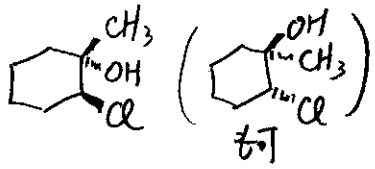
反応6

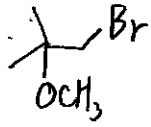


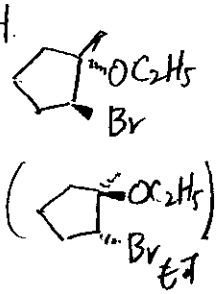
課題解答例 (6/27)

問題1

A. $CH_3CH(Br)CH_3$　B.  　C. $CH_3CH(OCH_3)CH_3$　D. 

E. $CH_3CH(OH)CH_2Cl$　F. 

G. 

H. 

問題2

(1). $CH_3\overset{+}{C}HCH_2CH_3$ (A)　(2). B. $CH_3CH_2CH(Br)CH_2CH_3$　C. $CH_3CH_2CH(Br)CH_3$

(3). $CH_3CH(OH)CH_2CH_3$　$[H_2O] > [Br^-]$

問題3.

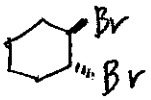
(考え方) すべての共鳴寄与体を描いて、安定性を考える. (オクテット則. 電気陰性度 超共役)

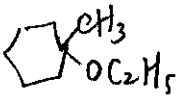
問題4

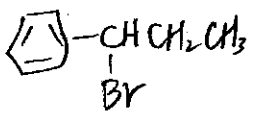
(1) 反応1 $(CH_3)_2C{=}CH_2 \xrightarrow{H^+} (CH_3)_3\overset{+}{C} \xrightarrow{H_2O} (CH_3)_3C\overset{+}{O}H \overset{-H^+}{\rightarrow} (CH_3)_3COH + H^+$

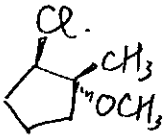
反応2 $CH_3CH{=}CHCH_3 \xrightarrow{Cl\text{-}Cl} CH_3\overset{+}{C}H{-}CHCH_3 + Cl^- \rightarrow CH_3CH(Cl)CHCH_3$

(2) 超共役で説明する　(3) オクテット則を満たす

(4) ① A 

B 

C 

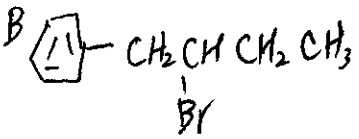
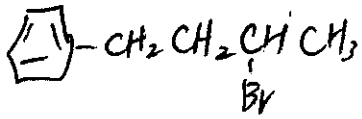
D 

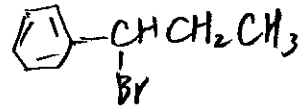
③ 正電荷の非局在化を考える.　④ $[CH_3OH] \gg [Cl^-]$

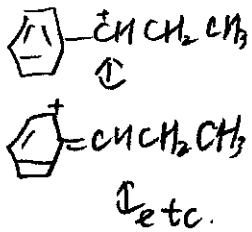
② 

結合の生成と開裂が同時
Br は立体障害の小さな反対側から近づく.
(Br の)

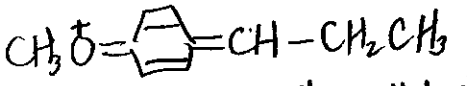
問題5.

(1) A.B  

C. 

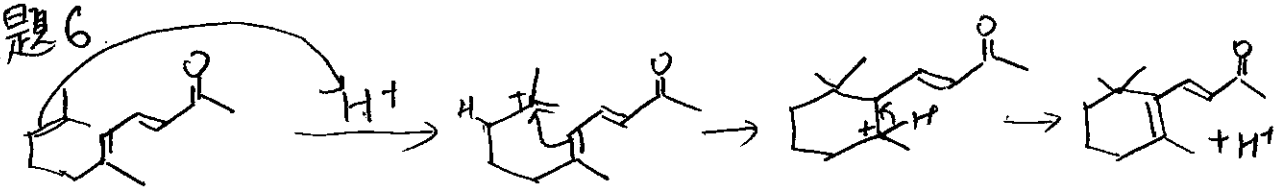
(2) A, B：中間体のカルボカチオンは共に第二級　C. 

(3) 速く進行する



オクテット則を満たす共鳴寄与体が余分に描ける

問題6

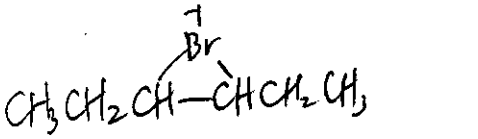


問題7

A. $CH_3CH_2CH(Cl)CHCH_2CH_3$ (Br)

B. $CH_3CH_2CH(OH)CHCH_2CH_3$ (Br)

C. $CH_3CH_2CH(OC_2H_5)CHCH_2CH_3$ (Br)

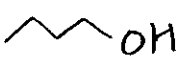
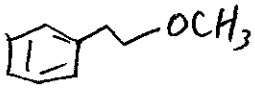


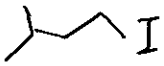
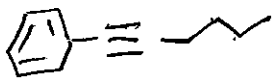
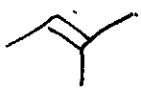
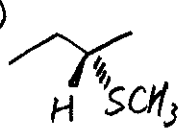
$[Cl^-] \gg [Br^-]$

$[H_2O] \gg [Br^-]$

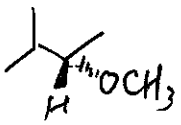
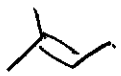
$[C_2H_5OH] \gg [Br^-]$

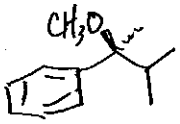
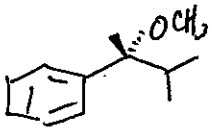
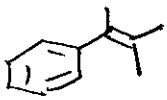
課題解答例(7/4)

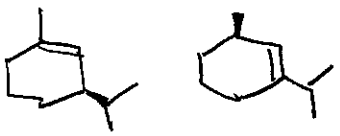
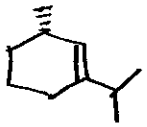
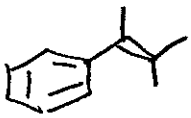
問題1. (1)  (2)  (3) 

(4)  (5)  (6)  (7) 

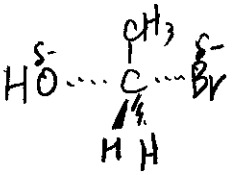
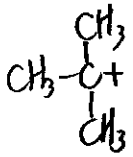
(9) 
主生成物

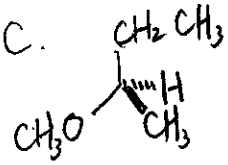
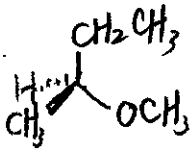
(8) 
S_N2 
E2

(10) 
S_N1 

E1.

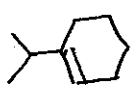
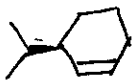
(11)  (12)  (13) 

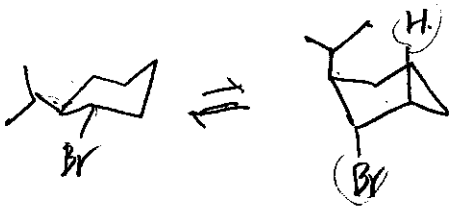
問題2.

(1) A.  B. 

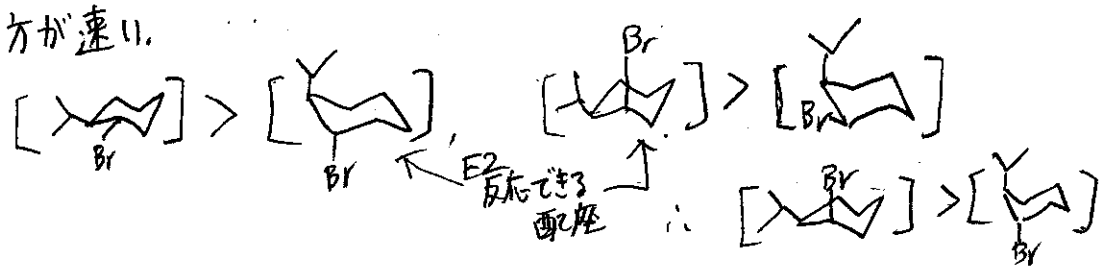
(2) C.  D. 

問題3.

(1) A.  B 

(2) 
アンチペリ平面上にある水素原子は一つだけ.

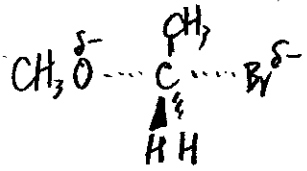
(3) 上の方が速い.

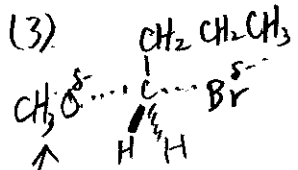


問題4

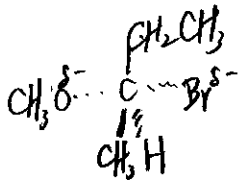
(1) $CH_3O^- + CH_3CH_2{-}Br \longrightarrow CH_3CH_2OCH_3 + Br^-$

$(CH_3)_2CH{-}Cl \rightarrow (CH_3)_2\overset{+}{C}H \xrightarrow{CH_3OH} (CH_3)_2CH\overset{+}{O}(H)CH_3 \rightarrow (CH_3)_2CHOCH_3 + H^+$

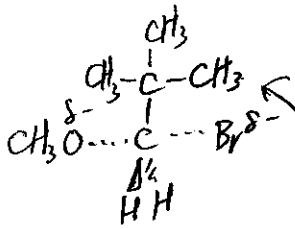
(2) 

(3) 

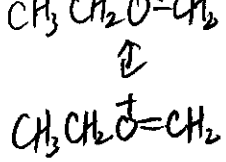
CH_3O^- である必要はない．Nu^-, OH^- でも良い



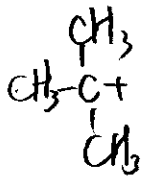
置換基が多いので
立体障害が大きく不安定化

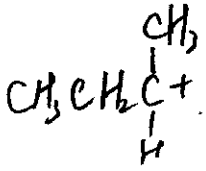


(大きい)
置換基がかさ高いので
反応点上の置換基が
1つでも，3つの中では
もっとも不安定

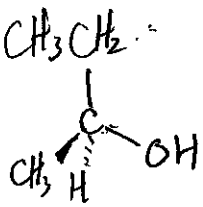
(4) 

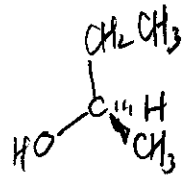
オクテット則を
満たす共鳴寄与体
が描ける





起来段できる結合の数

(5) ① A. 

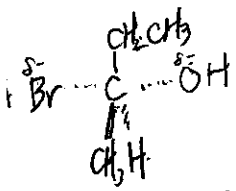
B 

A, B 逆も可

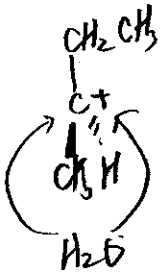
C. $CH_3CH_2CH_2CH_2I$

問題訂正 誤 $CH_3CH_2CHCH_2Cl$ ↓ 正 $CH_3CH_2CH_2CH_2Cl$

D $CH_3C{\equiv}CCH_2CH_3$

② 

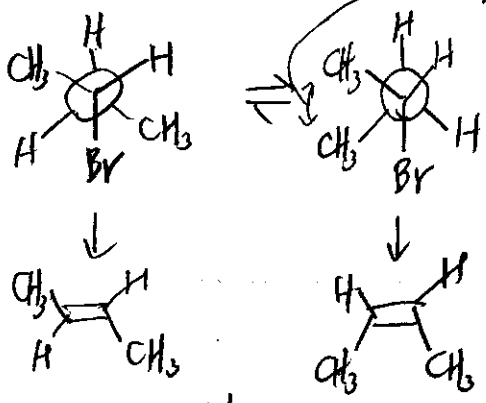
脱離基の切断と形成が同時
脱離する Br^- と逆方向から ^-OH
が攻撃する方が立体障害が小さく
遷移状態が安定化

③ 

カルボカチオンは平面なので
H_2O はどちら側からも
等しく攻撃可能

問題5.

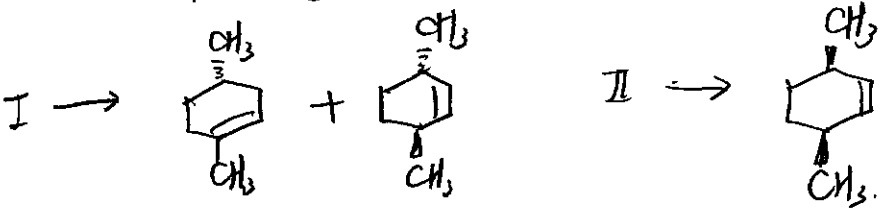
(2) トランス体



メチル基同士が近く 立体障害大 → より不安定

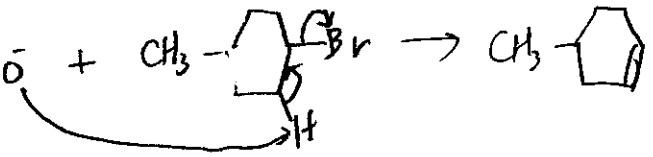
(1) $C_2H_5O^- + CH_3CH(Br)CH(H)CH_3 \rightarrow CH_3CH{=}CHCH_3 + C_2H_5OH + Br^-$

(3)



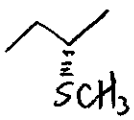
問題6.

(1) E2.

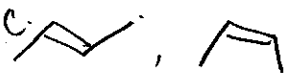


(2). (3) 省略

(4) ① A.



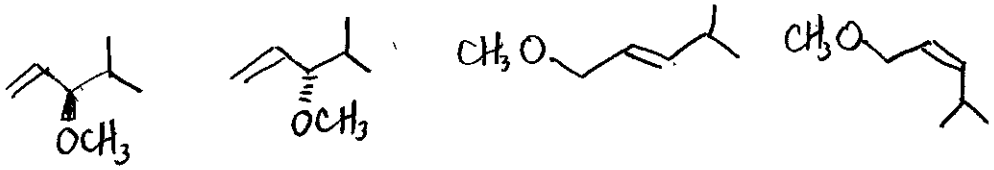
B, C.



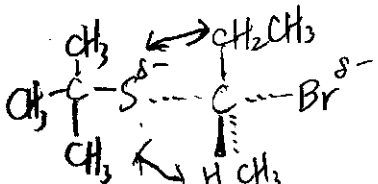
D. $CH_3CH_2CH_2CN$

E. $CH_3C{\equiv}CCH_2CH_2CH_3$

F~I

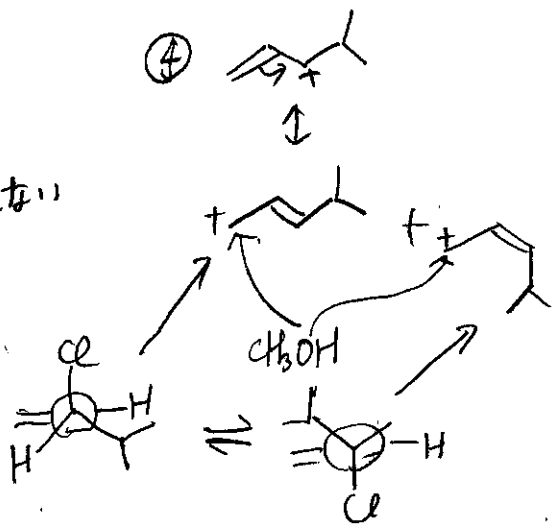


③



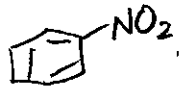
立体障害大 → S_N2 反応が起こさない

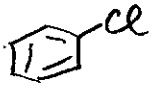
④

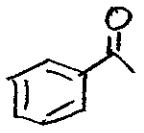


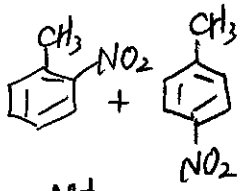
課題解答例 (7/11)

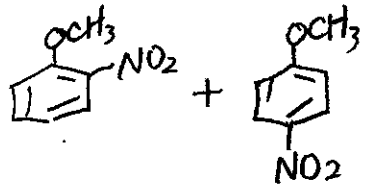
問題1

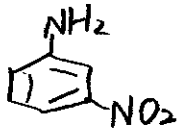
A 

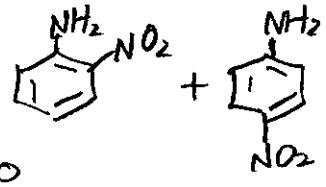
B 

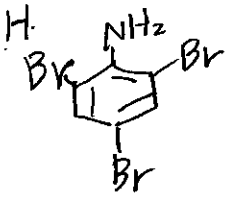
C 

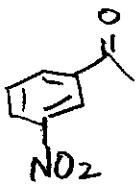
D 

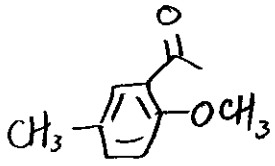
E 

F 

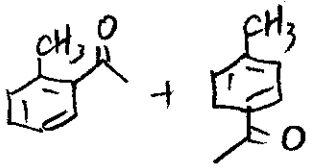
G 

H 

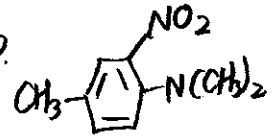
I 

J 

問題2

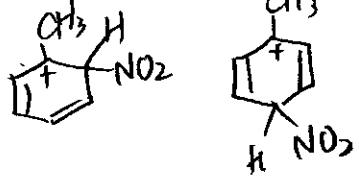
(1) A, B 

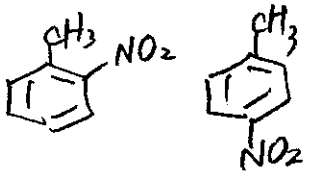
C 

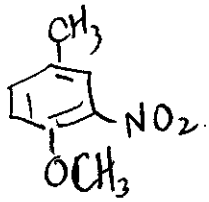
D 

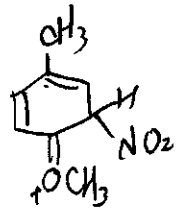
(2) 省略

問題3

(1) A, B 

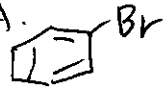
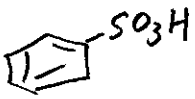
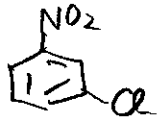
C, D 

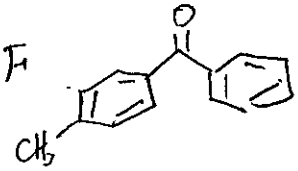
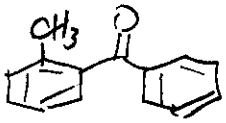
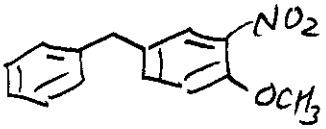
(2) 



オクテット則を満たす
共鳴寄与体が余分に描ける

問題4.

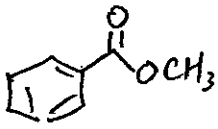
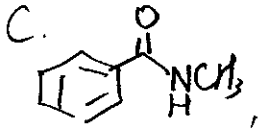
(1) A  B  C  D 

E, F   G 

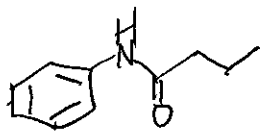
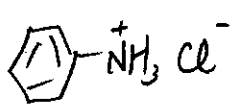
(2) 略. 中間体の安定性(共鳴寄与体数, オクテット則, 超共役, 正電荷)を比較する.

課題解答例(7/18)

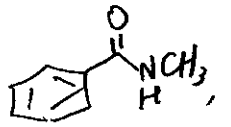
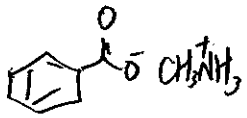
問題1. (1)

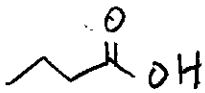
A. CH_3COOH　B.  　C.  　D $CH_3\overset{+}{N}H_3\ Cl^-$

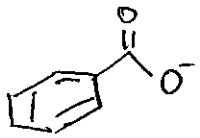
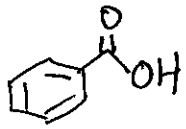
C, D. 逆でも可

E.  　F  　G CH_3COOH

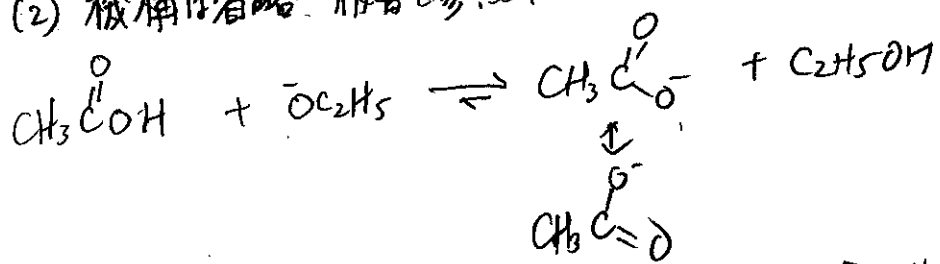
E, F 逆も可

H, I CH_3COCH_3, CH_3COOH　J, K  , 

L. CH_3COOCH_3　M. 

N  　O CH_3OH　P 

問題 (1), (2) 機構は省略. 板書を参照.



負電荷が非局在化し、$^-OC_2H_5$ より安定化