# Answers to Puzzles of Chapter 19
# Enolate Ions and Related Compounds

19.1

```
                                         H  O          O  H
                                         |  ‖  -    -  ‖  |
the basicity of the conjugate bases:   —C-C-N— < —C-C-N—
                                         |          |
```

Although resonance stabilizes both bases, the <u>base e's</u> are stabler on the more EN N. Therefore, an H on the amide N is more acidic than an H on the amide α C.

19.2 (a)

```
                                     O         O
                                     ‖         ‖
basicity of the conjugate bases:  ⁻:CH2-COH > CH3C-O:⁻
```

The <u>base e's</u> are stabler on the more EN O than on the C, so the H on the O is more acidic.

(b)

```
                                     O            O⁻          O           O
                                  ..  ‖            |           ‖         ..  ‖
basicity of the conjugate bases: CH3CHCH <—> CH3CH=CH < CH3CH2C:⁻ < CH2CH2CH
                                                              δ+
```

In the 1st base, resonance stabilizes the <u>base e's</u>. In the 2nd, the δ+ due to the EN O stabilizes the adjacent <u>base e's</u>. So the ranking of acidity:

```
     O
     ‖
CH3CH2CH
 3   1  2
```

(c)

```
                                     O          O
                                     ‖          ‖ ..
basicity of the conjugate bases:  ⁻:CH2-CNH2 > CH3C-NH
```

The <u>base e's</u> are stabler on the more EN N than on the C, so the H's on the N are more acidic.

(d)

```
                                     O         O
                                     ‖         ‖ ..
basicity of the conjugate bases:  ⁻:O-CNH2 < HOC-NH
```

The <u>base e's</u> are stabler on the more EN O than on the N, so the H's on the O are more acidic.

(e)

```
                              O    O:⁻          O    O              O:⁻  O
                              ‖    |            ‖ .. ‖              |    ‖
basicity of conjugate bases: MeC-CH=COMe <—> MeC-CH-COMe <—> MeC=CH-COMe <
                                  O   O             O:⁻ O            O   O
                                  ‖   ‖             |   ‖            ‖   ‖ ..
                           ⁻:CH2-CCH2COMe <—> CH2=CCH2COMe   <   MeCCH2COCH2
```

In the 1st base, extra resonance stabilizes the <u>base e's</u>. So the ranking of acidity:

```
   O    O
   ‖    ‖
CH3CCH2COCH3
 2    1    3
```

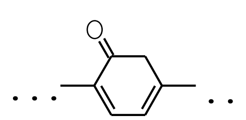
(f)

```
                                      O             O:⁻           O
                                  ..  ‖             |           ..  ‖
basicity of the conjugate bases: CH3CH-NO⁻ <—> CH3CH=NO⁻  <  CH2CH2NO⁻
                                       +             +             +
```

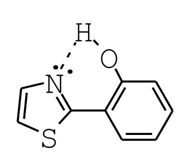
In the 1st base, resonance stabilizes the <u>base e's</u>. So the ranking of acidity:

```
CH3CH2NO2
 2   1
```

19.3 (a) All the rings can be aromatic (b)



(c) In the enol the ring is aromatic & there is an intramolecular H "bond":



19.4

(a) $CH_3CH_2C(=O)-CHBrCH_3$ (b)  (c) $CH_3C(=O)-CHIC(=O)CH_3$

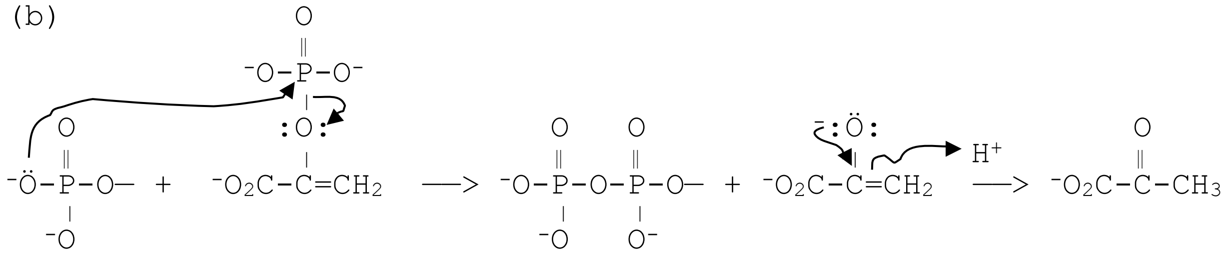
19.5

(a) $CH_3C(=O)-\bar{C}H_2$ (b) major product: $CH_3C(=O)CH_2-CH_2CH_3$, minor: $CH_3C(OCH_2CH_3)=CH_2$

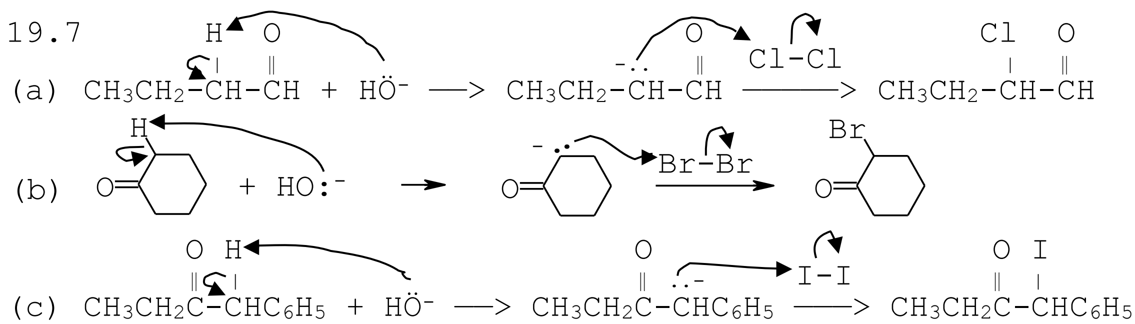
(c) By H "bonding" with the enolate O, the protic solvent, $Me_3COH$, stabilizes the enolate O. By not H bonding to the enolate O, the aprotic solvent, DMSO, leaves the enolate O freer to react.

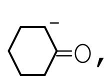
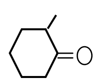
19.6 (a) $^-O_2C-C(O^-)=CH_2$

(b)



19.7

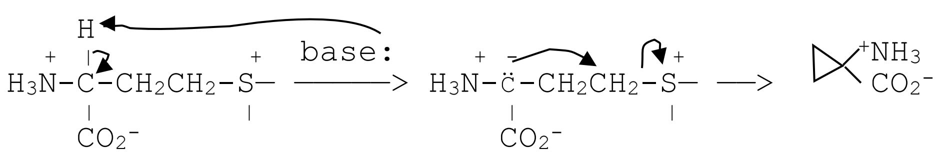


19.8 (a) **A** ≡ , **B** ≡ 

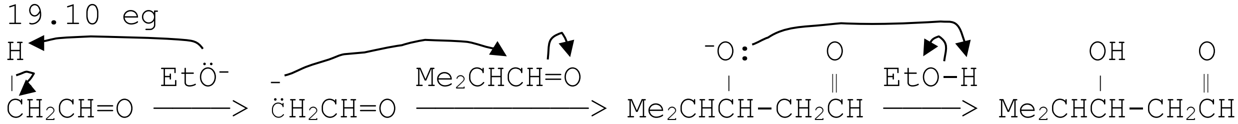
(b) **C** ≡ $Me_3CO^-$, **D** ≡ $CH_3\bar{C}HCO_2CH_2CH_3$, **E** ≡ $Br-CH_2CH=CH_2$

(c) **F** = $Me_3CO^-$, **G** ≡ $CH_3I$, **H** ≡ $Me_3CO^-$, **I** ≡ $CH_3Cl$

(d) **J** ≡ $Br-CH_2CH_2CH_2C(=O)CH_3$

19.9 

19.10 eg



19.11

(a) **A** ≡ $Me\overset{Me}{C}H\overset{OH}{C}H-\underset{Me}{\overset{Me}{C}}-\overset{O}{\overset{\|}{C}}H$  (b) **B** ≡ $Et\overset{O}{\overset{\|}{C}}\underset{Me}{C}H-\overset{OH}{C}HCMe_3$;  **C** ≡ $Et\overset{O}{\overset{\|}{C}}\underset{Me}{C}=CHCMe_3$

(c) **D** ≡ $Ph-\overset{O}{\overset{\|}{C}}H$;  **E** ≡ $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$;  **F** ≡ $Ph-CH=\overset{Me}{C}-\overset{O}{\overset{\|}{C}}CH_2CH_3$

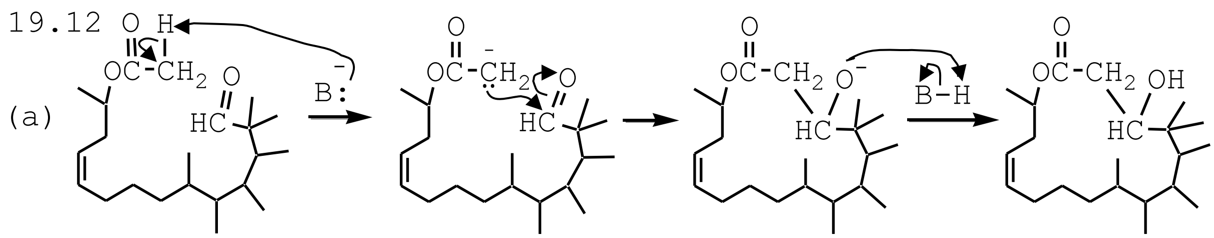
(d) **G** ≡ $H\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$;  **H** ≡ $H\overset{O}{\overset{\|}{C}}\underset{CH_2CH_3}{C}H-\overset{OH}{C}HCH_2CH_2CH_3$

(e) **I** ≡ $CH_3CH_2\overset{OH}{C}H-\underset{CH_3}{C}H\overset{O}{\overset{\|}{C}}H$;  **J** ≡ $CH_3CH_2\overset{OH}{C}H-CH_2CO_2CH_2CH_3$

(f) **K** ≡ $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

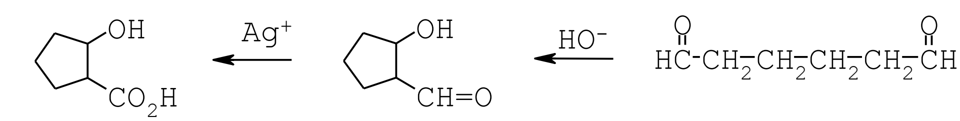
(g) **L** ≡ $H_2C=O$;  **M** ≡ $CH_3\overset{O}{\overset{\|}{C}}CH_3$;  **N** ≡ $\overset{OH}{C}H_2-CH_2\overset{O}{\overset{\|}{C}}CH_3$;  **O** ≡ HCl or $SOCl_2$

19.12 (a)

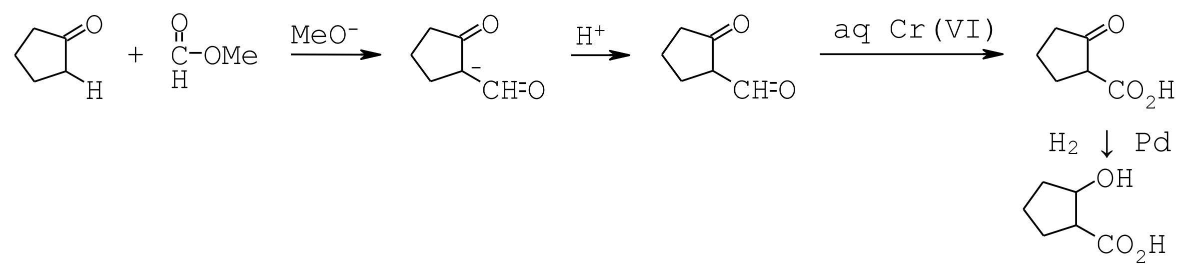


(b) It is intramolecular with a larger, more favorable ΔS.

19.13 (a)



(b)



19.14

(a) **A** ≡ $CH_3\overset{O}{\overset{\|}{C}}-\overset{-}{C}HCO_2CH_3$;  **B** ≡ $CH_3\overset{O}{\overset{\|}{C}}-CH_2CO_2CH_3$

(b) **C** ≡ $C_6H_5CH_2CO_2CH_2CH_3$;  **D** ≡ $(CH_3)_3CO^-$

(c) **E** ≡ $(CH_3)_3CO^-$;  **F** ≡ $\square-\overset{O}{\overset{\|}{C}}-\overset{Me}{C}H-\overset{O}{\overset{\|}{C}}CH_2CH_3$

(d) **G** ≡ $Me_3CO^-$;  **H** ≡ $H^+$;  **I** ≡ $Et\overset{O}{\overset{\|}{C}}-\overset{Me}{C}HCO_2Et$;  **J** ≡ $Me_2CH\overset{O}{\overset{\|}{C}}-\overset{Me}{C}HCO_2Et$

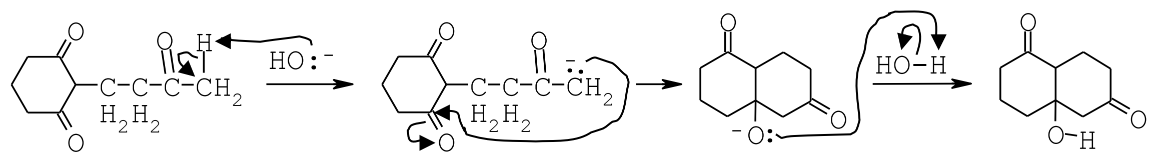
(e) **K** ≡ $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CO_2CH_3$; **L** = $Me_3CO^-$

(f) **M** ≡ $EtO_2CH$; **N** ≡ $Me\overset{O}{\overset{\|}{C}}Me$; **O** ≡ $Me_3CO^-$

(g) **P** ≡ $C_6H_5CO_2Me$; **Q** ≡ $EtCO_2Me$; **R** ≡ $Me_3CO^-$; **S** ≡ $C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Me}{\overset{|}{C}}HCO_2Me$;

**T** ≡ $H^+$, $H_2O$; **U** ≡ $C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Me}{\overset{|}{C}}HCO_2H$; **V** ≡ $MeNH_2$, $H^+$

19.15



19.16

(a) $Me\overset{O}{\overset{\|}{C}}-CH_2CO_2Me + Me_3CO^- \longrightarrow Me\overset{O}{\overset{\|}{C}}-\overset{-}{C}HCO_2Me \xrightarrow{EtBr} Me\overset{O}{\overset{\|}{C}}-\overset{Et}{\overset{|}{C}}HCO_2Me$

$\downarrow H_3O^+$

$Me\overset{O}{\overset{\|}{C}}-CH_2Et \xleftarrow{\Delta,\ -CO_2} Me\overset{O}{\overset{\|}{C}}-\overset{Et}{\overset{|}{C}}HCO_2H$

(b) $Me_2CH\overset{O}{\overset{\|}{C}}-\overset{Me}{\overset{|}{C}}H-CO_2Me + Me_3CO^- \longrightarrow Me_2CH\overset{O}{\overset{\|}{C}}-\underset{-}{\overset{Me}{\overset{|}{C}}}-CO_2Me$

$\downarrow MeBr$

$Me_2CH\overset{O}{\overset{\|}{C}}-CHMe_2 \xleftarrow{\Delta,\ -CO_2} Me_2CH\overset{O}{\overset{\|}{C}}-\underset{\underset{Me}{|}}{\overset{Me}{\overset{|}{C}}}-CO_2H \xleftarrow{H_3O^+} Me_2CH\overset{O}{\overset{\|}{C}}-\underset{\underset{Me}{|}}{\overset{Me}{\overset{|}{C}}}-CO_2Me$

(c) $MeO_2CCH_2CO_2Me \xrightarrow{MeO^-} MeO_2C\overset{-}{C}HCO_2Me \xrightarrow{Me_2CHBr} MeO_2C\overset{Me_2CH}{\overset{|}{C}}HCO_2Me$

$\downarrow H_3O^+$

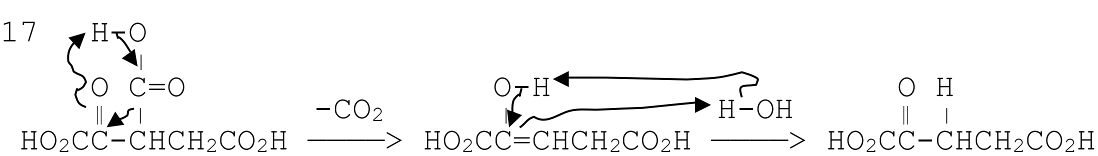
$CO_2 + HO_2CCH_2CHMe_2 \xleftarrow{\Delta} HO_2C\overset{Me_2CH}{\overset{|}{C}}HCO_2H$

(d) $MeO_2C\overset{Me}{\overset{|}{C}}HCO_2Me \xrightarrow{MeO^-} MeO_2C\underset{-}{\overset{Me}{\overset{|}{C}}}CO_2Me \xrightarrow{EtCl} MeO_2C\underset{\underset{Et}{|}}{\overset{Me}{\overset{|}{C}}}CO_2Me$

$\downarrow H_3O^+$

$HO_2C\overset{Me}{\overset{|}{C}}HEt \xleftarrow{\Delta} HO_2C\underset{\underset{Et}{|}}{\overset{Me}{\overset{|}{C}}}CO_2H$

19.17



```
19.18  O                          O              O     O            O     O
       ‖         base:            ‖  ..          ‖     ‖            ‖     ‖
    —SC-CH2-H  ———————>  —SC-CH2  ———————>  —SC-CH2-C-O⁻  ——>  —SCCH2-C-OH
                             -     O=C=O                  H+
```

```
19.23                                                     OH
                                                          |
(a)  CH3CH=CH-OH; keto is stabler   (b)  CH3CH=CCH2CH3; keto
        OH  O
        |   ‖
(c)  CH3C=CHCCH3; enol   (d)  C6H5—OH; enol
```

```
                                          - +  ..-      δ- δ+  ..-
19.25 (a) basicity of conjugate bases:    O2N-CH2  <   N≡C-CH2
```

because the + of the $O_2N$ stabilizes <u>base e’s</u> more than the δ+ on the N≡C does.

```
(b)  CH3CH2
        |
     CH3CHNO2
```

```
19.26        O              :O⁻                 O
             ‖               |                  ‖
 HÖ⁻ + I3C-C—  ——>  I3C-C—  ——>  I3C⁻ + HO-C—
                        |
                        OH
```

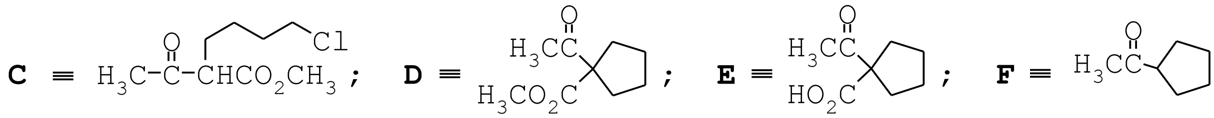
```
19.27  Cl O           Et O           O Me O          OH
        | ‖            | ‖           ‖ |  ‖           |
(a)  CH3CHCEt   (b) CH3CHCEt   (c) PhC-CH-CEt   (e) EtCEt
                                                      |
                                                      Me

                                      ┌─┐
           O           OH            O O        HO Me O
        -  ‖           |              \ /        |  |  ‖
(f) CH3CHCEt   (g) EtCHEt   (h) EtCEt   (i) H2C-CH-CEt

      NMe          Me O
       ‖            | ‖
 (j) EtCEt   (k) H2C=C-CEt   (m) no reaction
```

```
               Br O          OH          HO Me O              OH
                | ‖           |           |  | ‖               |
19.28 (a) CH3CHCH   (c) EtCHMe   (d) EtCH-CHCH   (e) CH3CH2CH2

           O        MeO OMe        HO Me O
           ‖          \ /           |  | ‖
(f) CH3CI2CH   (g) EtCH     (h) EtCH-CHCH

    H3CN             Me O
      ‖               | ‖
(i) EtCH   (j) EtCH=C-CH   (l) EtCO2H
```

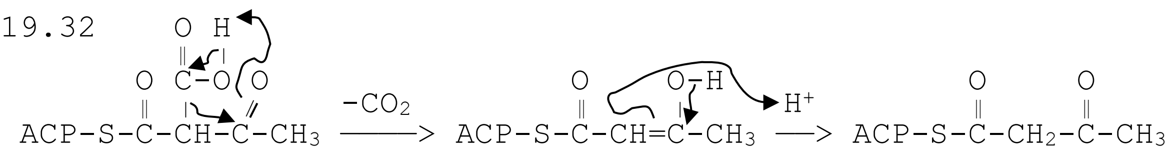
```
              Me               O Me             OH          OH
               |               ‖ |               |           |
19.29 (a) CH3CHCO2Me   (b) EtC-CHCO2Me   (c) EtCMe2   (d) EtCH2

                          HO CH3            CH3
                           |  |              |
(e) EtCO2CH2CH3   (f) H2C-CHCO2Me   (g) H2C=CCO2Me   (h) no reaction
```

```
        H-O  OH O             :O⁻ OH O          O         OH O         OH O
         |    |  ‖      -H+    |   |  ‖         ‖          |  ‖          |  ‖
19.30  —CH-CH-C—   ———>  —CH-CH-C—  ——>  —CH  +  ⁻:CH-C—  ——>  CH2-C—
```

19.31 **A** ≡ $CH_3\overset{O}{\overset{\|}{C}}\text{-}CH_2CO_2CH_3$; **B** ≡ $CH_3\overset{O}{\overset{\|}{C}}\text{-}\overset{-}{C}HCO_2CH_3$;



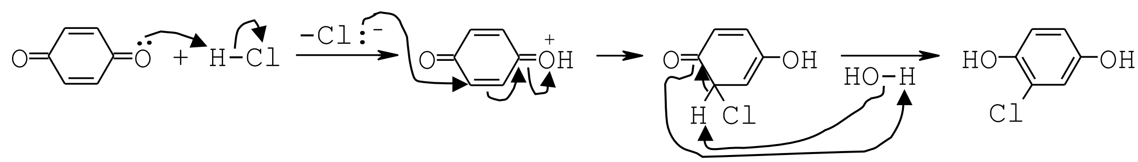
19.32



19.35 (b), (c), (d), (e)

19.36 (c), (d)

19.38

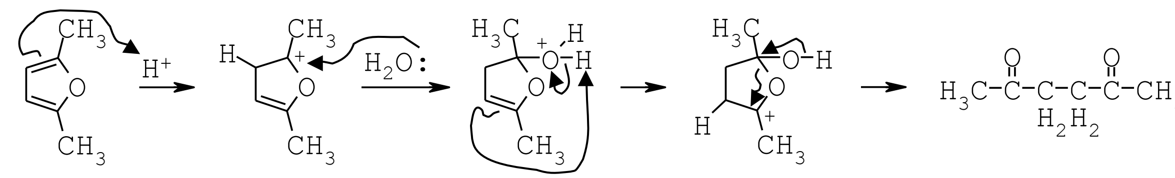


19.39

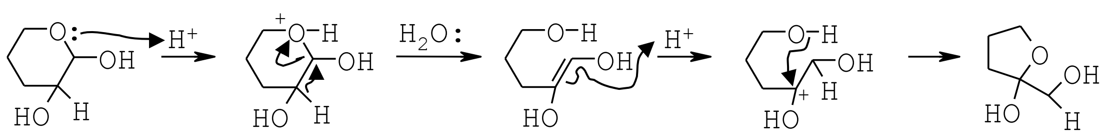
(a) $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

(b) C<u>H</u>$_3$: δ 2.2; C<u>H</u>$_2$: δ 2.7; <u>C</u>=O: δ 206; <u>C</u>H$_2$: δ 37; <u>C</u>H$_3$: δ 30

(c)



19.40

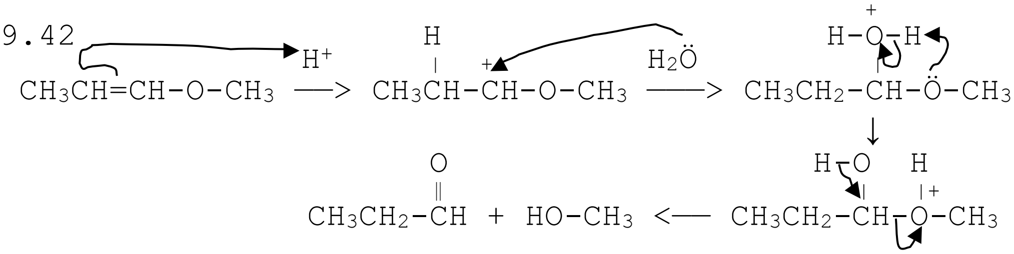


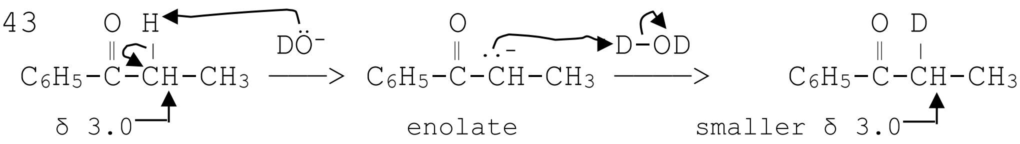
19.41

in acidity: $CH_3CH_2CH_3$ < $CH_3\text{-}C{\equiv}C\underline{H}$ < $H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$ < $CH_3\text{-}\overset{O\text{-}\underline{H}}{\overset{|}{C}H}\text{-}CH_3$

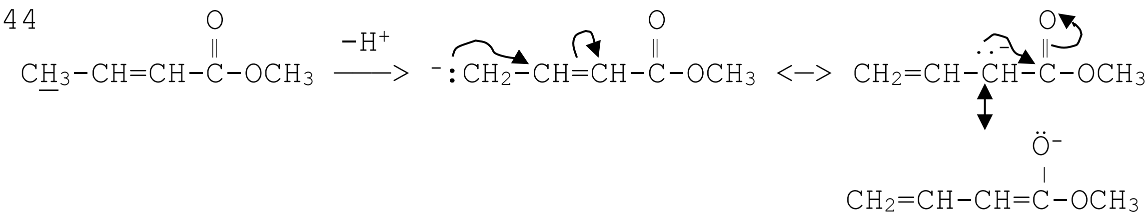
$K_a$: $10^{-50}$ $10^{-25}$ $10^{-20}$ $10^{-16}$

19.42



19.43 

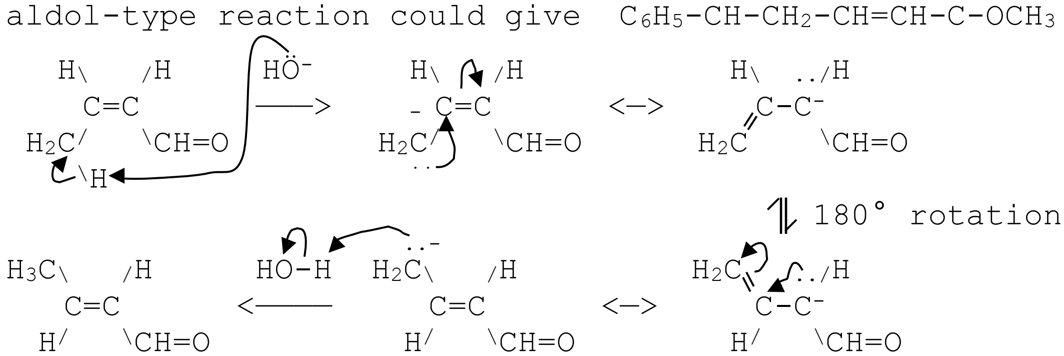

19.44

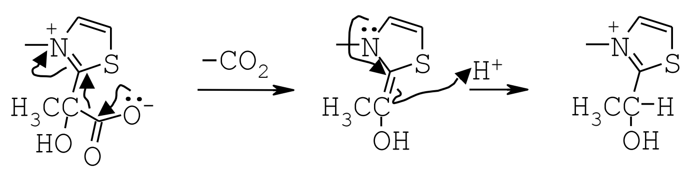
(a) 

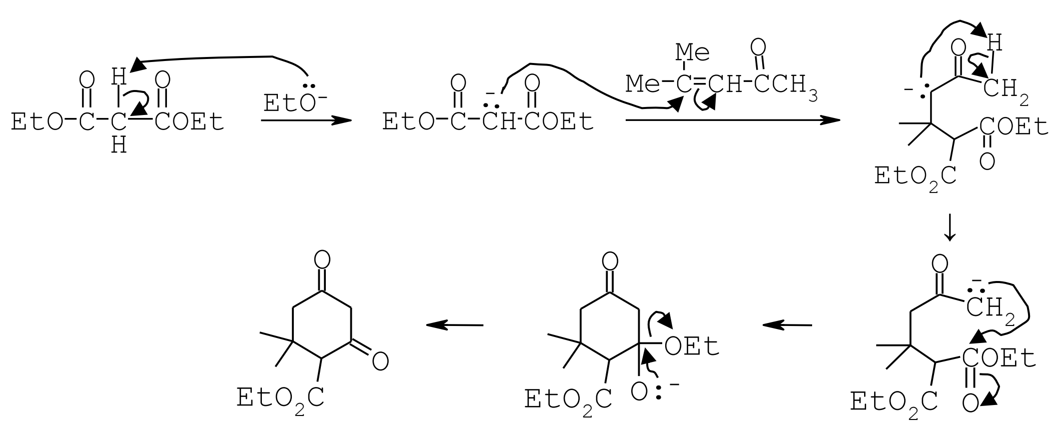

The underlined H's are most acidic because resonance stabilizes their conjugate base e’s.

(b)

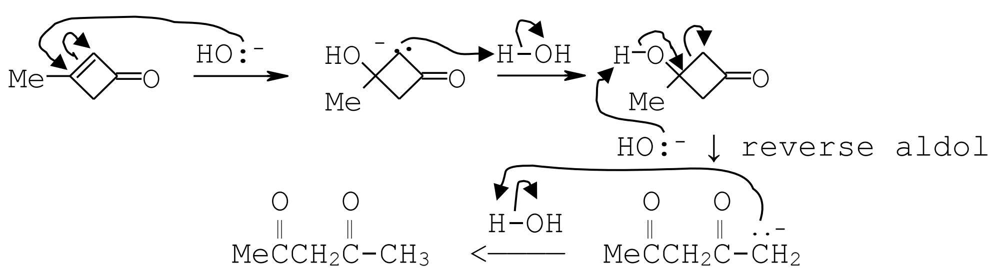
An aldol-type reaction could give $C_6H_5-CH(OH)-CH_2-CH=CH-C(=O)-OCH_3$

(c) 


19.45 


19.46 (a) 


(b) part (a) product + $H_3O^+$ + Δ ⟶ EtOH + $CO_2$ + new product

19.47 

19.49

a. $$\underset{\text{OH}}{\text{PhCH}}\text{-CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3 \xleftarrow{\text{Aldol}} \text{Me}_3\text{CO}^- + \text{Ph}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{H} + \text{CH}_3\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3$$

$$\text{Me}_3\text{COH} \xrightarrow{\text{Na}} \text{Me}_3\text{CO}^- \qquad \text{PhCH}_2\text{OH} \xrightarrow{\text{anhyd Cr(VI)}} \text{PhCHO} \qquad \text{CH}_3\overset{\text{OH}}{\overset{|}{\text{C}}}\text{HCH}_3 \xrightarrow{\text{any Cr(VI)}} \text{CH}_3\text{COCH}_3$$

b. $$\text{PhCH}_2\text{CH}_2\text{-}\overset{\text{Ph}}{\overset{|}{\text{C}}}\text{HCO}_2\text{Et} \xleftarrow{\text{Zn, HCl}} \text{PhCH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{Ph}}{\overset{|}{\text{C}}}\text{HCO}_2\text{Et} \xleftarrow{\text{H}^+} \text{PhCH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{Ph}}{\overset{|}{\underset{-}{\text{C}}}}\text{-CO}_2\text{Et}$$

$$\uparrow \text{ Claisen, EtO}^-$$

$$2\ \text{PhCH}_2\text{CO}_2\text{H} \xrightarrow{\text{SOCl}_2} 2\ \text{PhCH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{Cl} \xrightarrow{\text{EtOH}} 2\ \text{PhCH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OEt}$$

$$2\ \text{PhCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{aq Cr(VI)}} 2\ \text{PhCH}_2\text{CO}_2\text{H}$$

c. $$\text{CH}_3\text{CH}_2\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{H-}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{HCO}_2\text{H} \xleftarrow{\text{HCl}} \text{CH}_3\text{CH}_2\overset{\text{OH}}{\overset{|}{\text{C}}}\text{H-}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{HCO}_2\text{H} \xleftarrow{\text{Ag}^+} \text{CH}_3\text{CH}_2\overset{\text{OH}}{\overset{|}{\text{C}}}\text{H-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{H-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{H}$$

$$\text{Me}_3\text{CO}^- \uparrow \text{ Aldol}$$

$$2\ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{anhyd Cr(VI)}} 2\ \text{CH}_3\text{CH}_2\text{CH=O}$$

(d) $$\text{CH}_3\text{CH}_2\text{CH}_2\text{-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{HCH}_2\text{OH} \xleftarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{HCH}_2\text{O}^- \xleftarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{HCO}_2\text{H}$$

$$\text{Zn} \uparrow \text{HCl}$$

$$\xrightarrow{\text{as above}} 2\ \text{CH}_3\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{H} \xrightarrow[\text{Aldol}]{\text{Me}_3\text{CO}^-} \text{CH}_3\text{CH}_2\overset{\text{HO}}{\overset{|}{\text{C}}}\text{H-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{H}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{H} \xrightarrow{\text{aq Cr(VI)}} \text{CH}_3\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{Me}}{\overset{|}{\text{C}}}\text{HCO}_2\text{H}$$

5/09