## **Solutions to problems - Set 11: Rearrangements**

## Problem 1

Complete the following transformations and explain by giving detailed mechanisms.

### **Problem 2**

Find the structure of products after treating the following compounds at high temperature.

a) 
$$\xrightarrow{350\,^{\circ}\text{C}}$$
 ? d)  $\xrightarrow{60\,^{\circ}\text{C}}$  ?   
b)  $\xrightarrow{\text{H}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{98\,^{\circ}\text{C}}$  ?  $\xrightarrow{\text{CO}_2\text{Me}}$  ?  $\xrightarrow{\text{CO}_2\text{Me}}$  ?

## Solution

b) 
$$H \downarrow 5$$
  $1 \downarrow 5$   $1 \downarrow 6$   $1 \downarrow 6$   $1 \downarrow 7$   $1$ 

releasing 3-membered ring strain is driving force, reaction runs smoothly at lower temp.

c) 
$$\frac{195 \, ^{\circ}\text{C}}{\text{Claisen}} = \frac{60 \, ^{\circ}\text{C}}{\text{Cope}} = \frac{60 \, ^{\circ}\text{C}}{\text{Cope}}$$

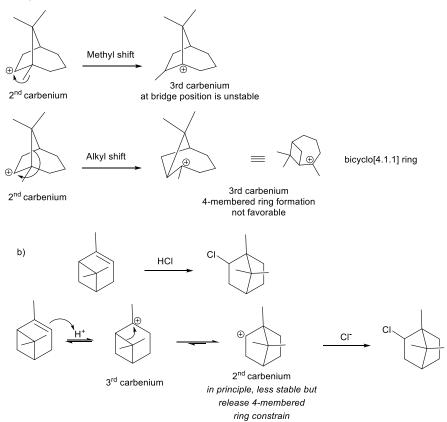
e) 
$$CO_2Me$$
  $CO_2Me$   $CO_2Me$ 

## **Problem 3**

Propose mechanisms for the following transformations.

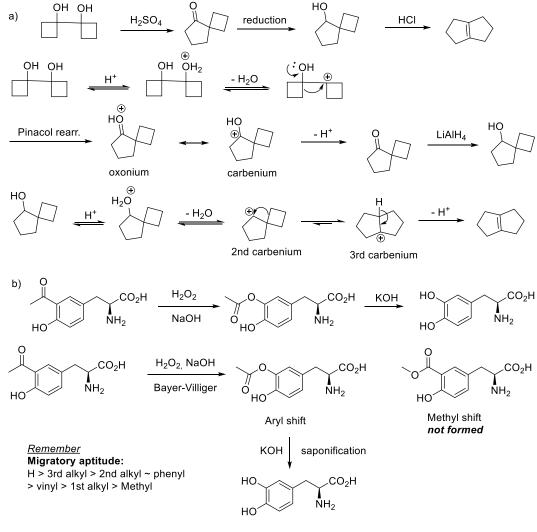
a) 
$$H^{+}$$
  $H^{+}$   $H$ 

#### Other posibilities



## **Problem 4**

Complete the following transformations and explain by giving detailed mechanisms.



Mechanism of Bayer-Villiger:

c) 
$$\frac{1. \text{ KOH}}{2. \text{ SOCl}_2}$$
  $\frac{1. \text{ KOH}}{3. \text{ CH}_2 \text{N}_2}$   $\frac{\text{PhCO}_2 \text{Ag}}{\text{H}_2 \text{O/THF}}$   $\frac{\text{CO}_2 \text{H}}{\text{H}_2 \text{O/THF}}$   $\frac{\text{CO}_2 \text{H}}{\text{CI}}$   $\frac$ 

(The Wolff rearrangement = Arndt Eistert Homologation)

## **Problem 5**

Find the structure of products for each of the following reactions.

a) 
$$CF_3SO_2CI, Et_3N$$
 ?

 $N-OH$   $DCM$  ?

b)  $M-CPBA$  ?

c)  $N_2$   $N_3$   $N_4$   $N_4$   $N_5$   $N_5$ 

a) 
$$CF_3SO_2CI, Et_3N$$
 $CF_3SO_2CI, Et_3N$ 
 $CF_3SO_3$ 
 $CF_3SO_2CI, Et_3N$ 
 $CF_3SO_2CI$ 

tertiary alkyl shift more favorable

primary alkyl shift less favorable not formed

Notes: There is retention of configuration of alkyl group which is shifted

tertiary carbenium te stabilized by 2 phenyl groups very stable

tertiary carbenium

less stable

not formed