Modern Organic Chemistry

Exam

10-04-2017

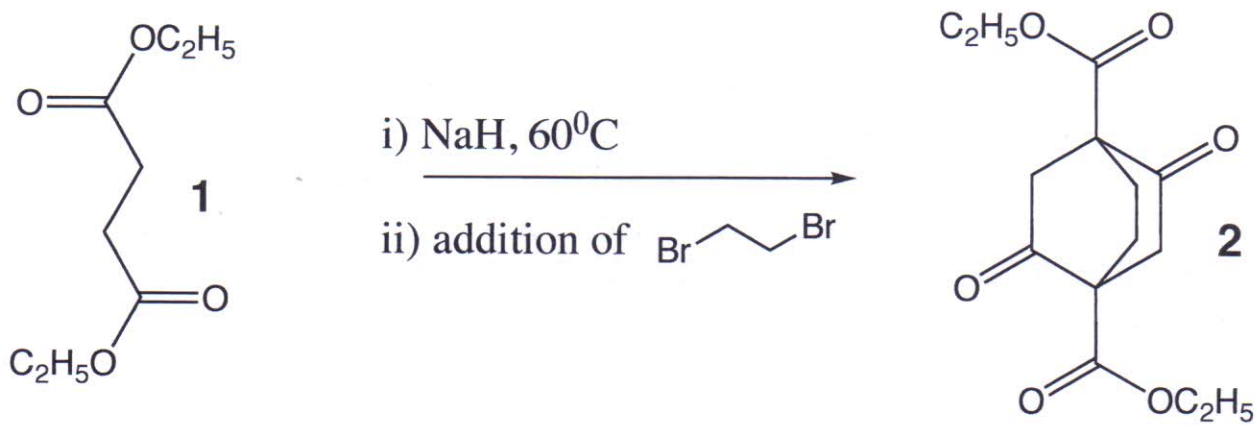
time: 3 hours

Every answer sheet must be provided with page number, your name, and student number

(The maximum points for every question is indicated)

Question 1. *(8 points)*

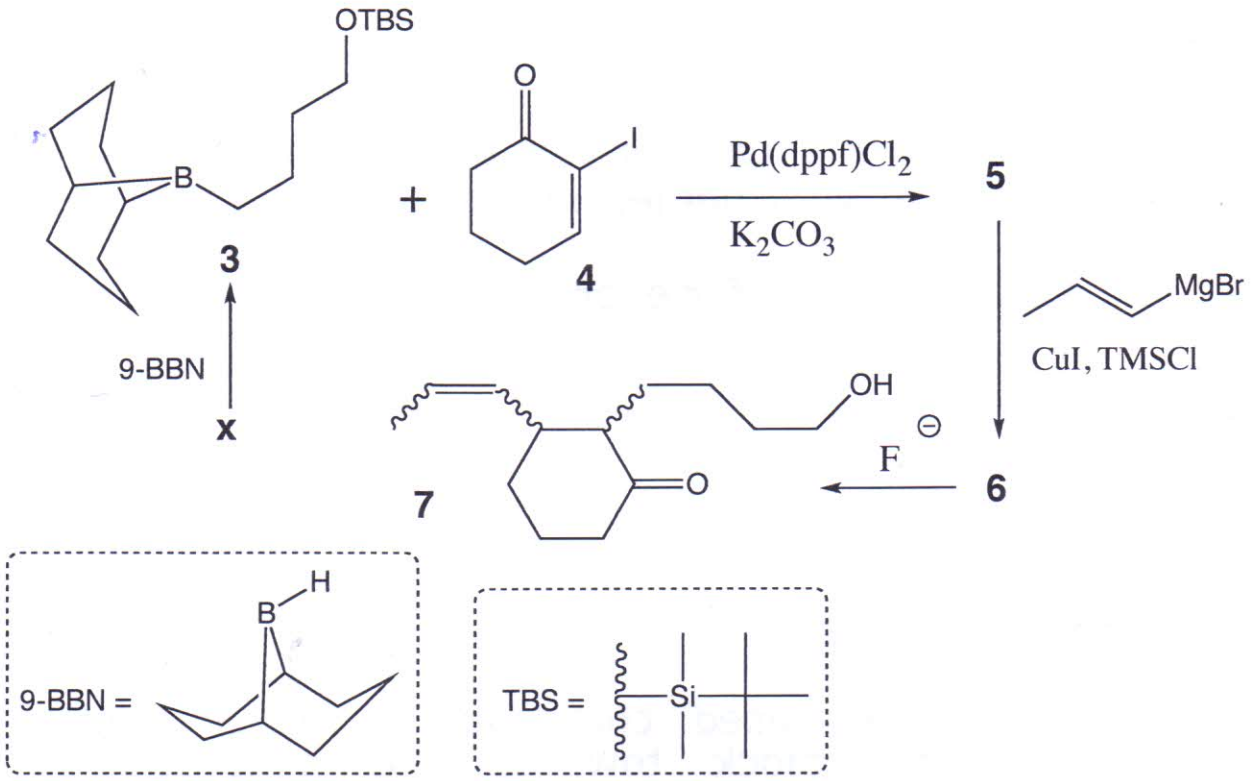
Weiss and Carreira used compound **2** as a readily available building block towards the synthesis of Daphmanidin E.



Provide the mechanism of the reaction of **1→2**.

Question 2. *(14 points)*

In 2010 the group of Nicolaou proved the structure of Vannusal B with the aid of a total synthesis, the first steps of which are shown below.



a) Draw the structure **5**, the product of the palladium mediated (dppf is a ligand) reaction of **3** and **4**. Give the mechanism of this reaction.

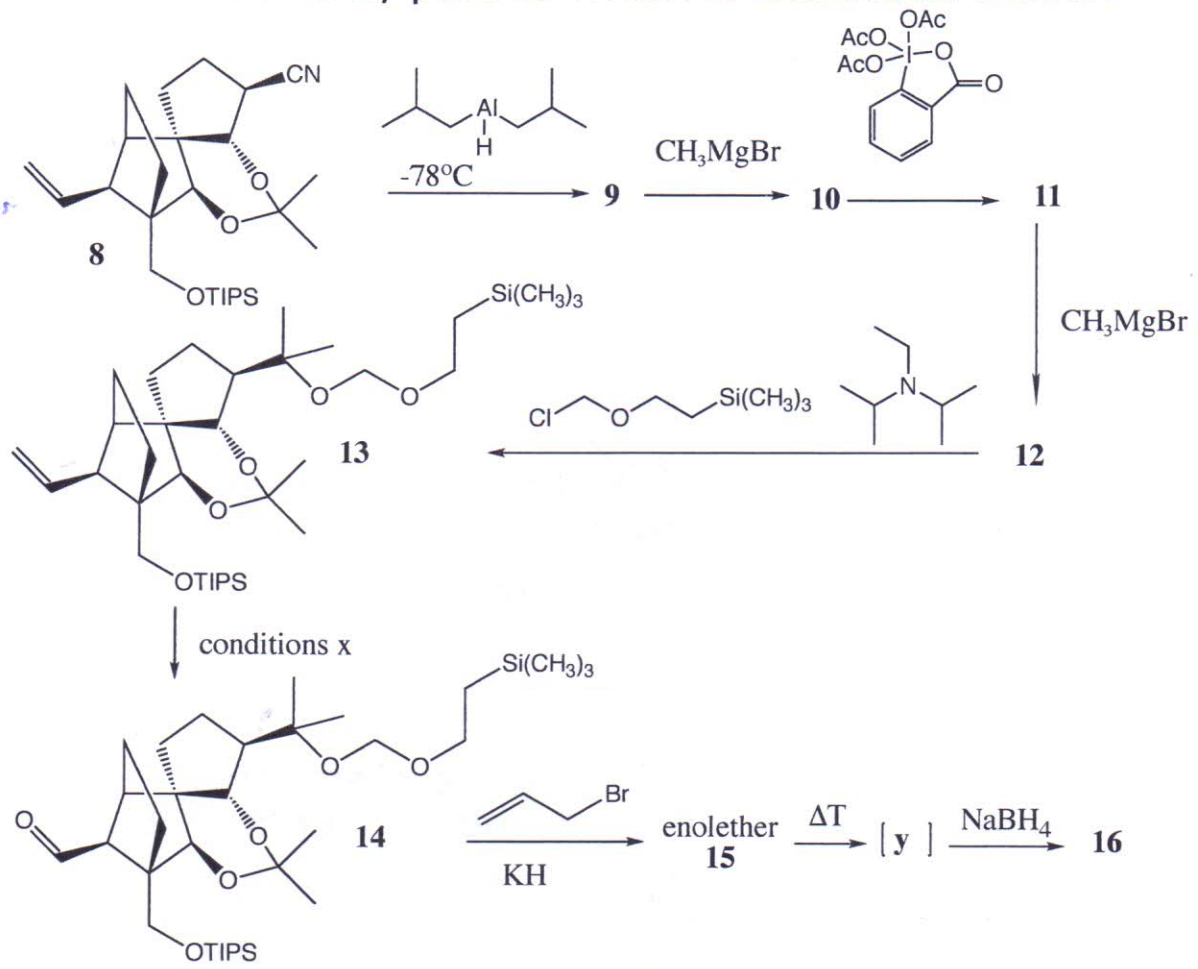
b) Draw the structure of **6** (including relative stereochemistry) and give the mechanism of the corresponding reaction.

Compound **3** can be obtained by reaction of **9-BBN** with compound **x**.

c) Draw the structure of **x** and give the mechanism of the corresponding reaction.

Question 3. *(28 points)*

Nicolaou also presented another synthetic route to both Vannusals A and B, part of which is described below.



Compound **8** was converted in five steps into **13**.

a) Give the structures of the intermediate products **9**, **10**, **11**, **12** and the mechanisms of the reactions.

b) Give the reagent(s) for the conversion of **13** into **14** and the corresponding reaction mechanism(s).

Treatment of **14** with potassium hydride and allyl bromide led to the formation of enolether **15**.

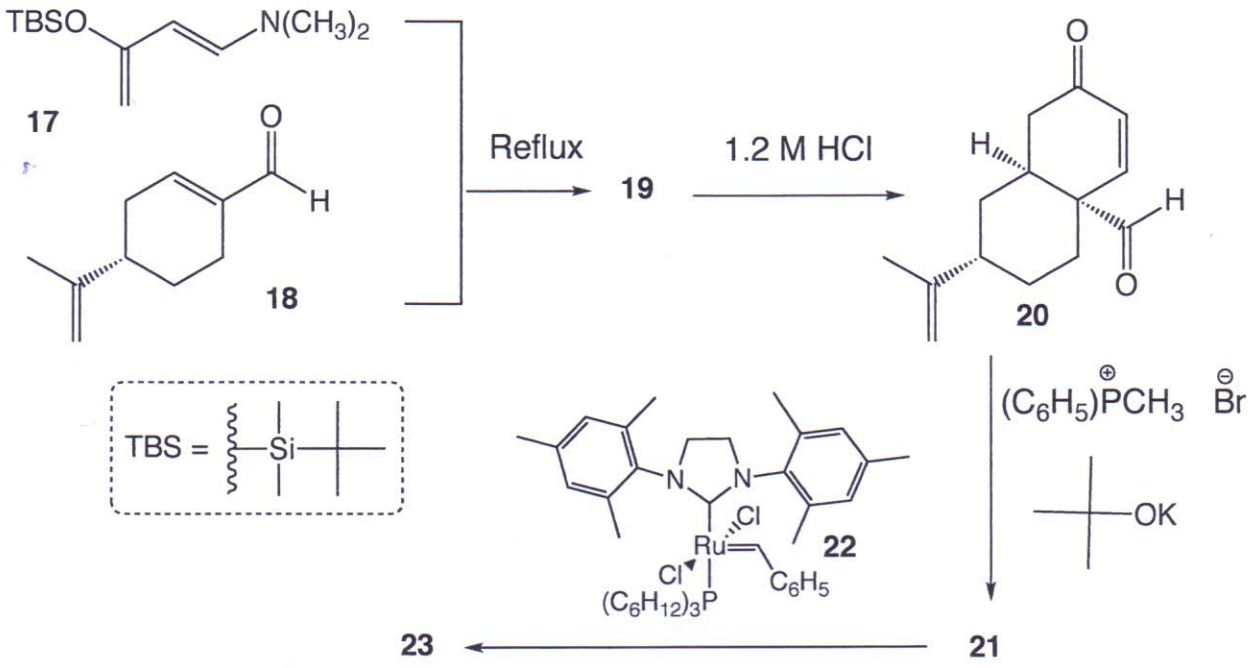
c) Draw the structure of **15** and give the mechanism of the corresponding reaction.

Heating of enolether **15** gave intermediate product **y** that was reduced with sodium borohydride to furnish **16**.

d) Give the structure of **16** and the mechanisms of the corresponding reaction(s).

Question 4. *(20 points)*

In 2009 Tiefenbacher and Mulzer reported the synthesis of the antibiotic Platencin. Some of the reactions are shown below.



a) Draw the structure, including the stereochemistry of **19**. Give the mechanism of the conversion of **17** + **18** into **19** and explain the stereochemistry.

Compound **19** is immediately treated wit acid to give **20**.

b) Give the mechanism of the conversion of **19** into **20**.

Diene **20** is converted into triene **21**.

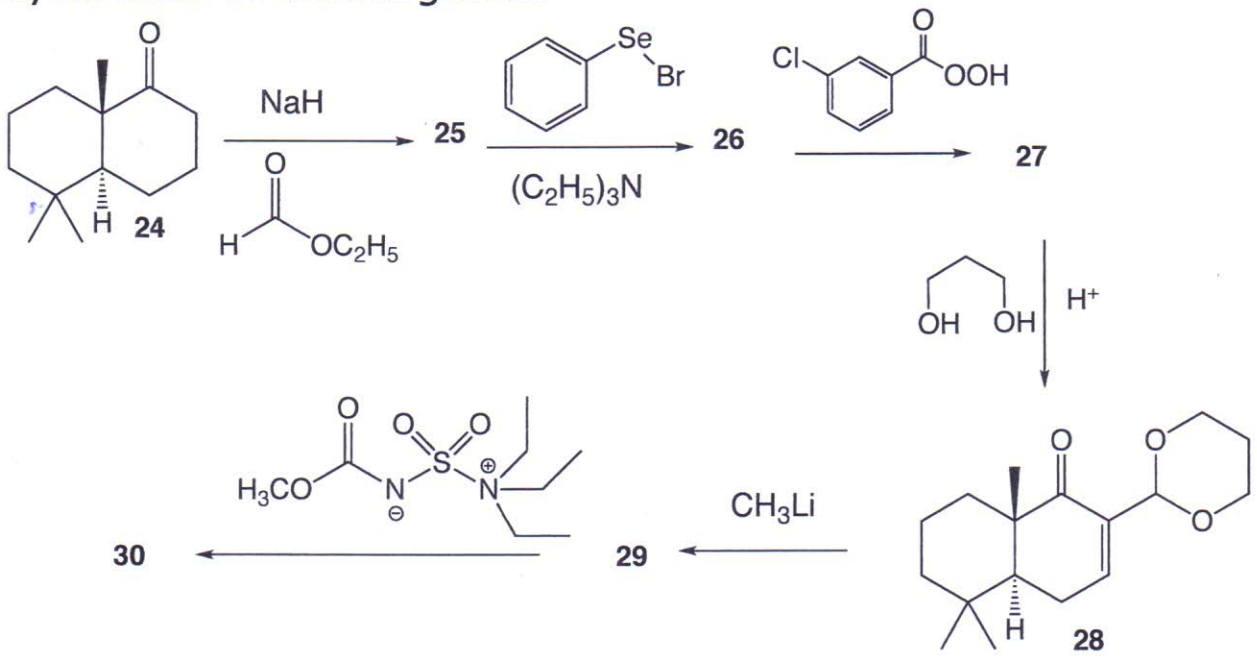
c) Draw the structure of **21**. Give the mechanism of the corresponding conversion.

Compound **21** is treated with catalyst **22** to give **23**.

d) Draw the structure, including the stereochemistry of **23**. Give the mechanism of the corresponding conversion.

Question 5. *(30 points)*

Goldsmith and Kezar reported in 1980 a stereospecific synthesis of Waburganal.



a) Draw the structure of compound **25** and the mechanism of **24 → 25**.

b) Draw the structure of compound **26** and the mechanism of the corresponding reaction.

c) Draw the structure of compound **27** and the mechanism of the corresponding reaction.

d) Give the mechanism of **27 → 28**.

e) Draw the structure of **29** and give the mechanism of the corresponding reaction.

f) Draw the structure of **30** and give the mechanism of the corresponding reaction.