Modern Organic Chemistry

14-06-2013

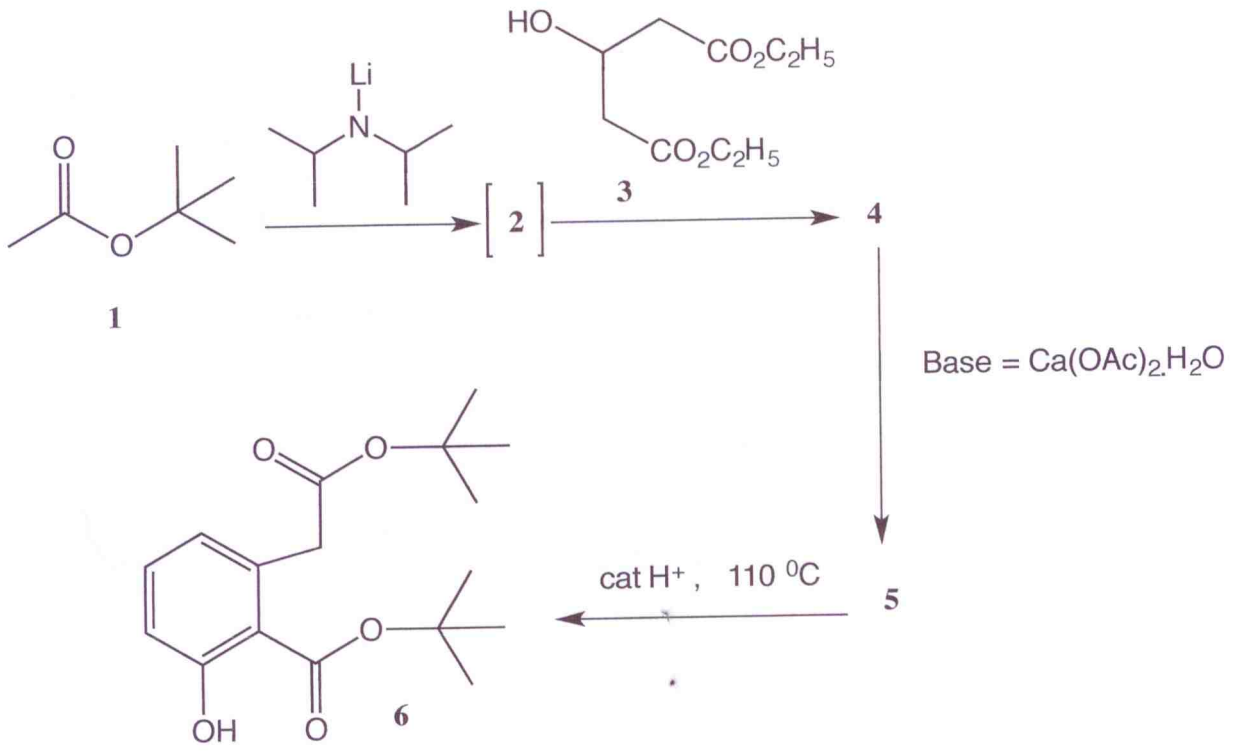
Time: 3 hours

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

(The maximum points for every question is indicated)

Question 1. *(16 points)*

Part of the synthetic route to rac-γ-Indomycinone is shown in the scheme (Eur. J. Org. Chem. 2011, 2223).

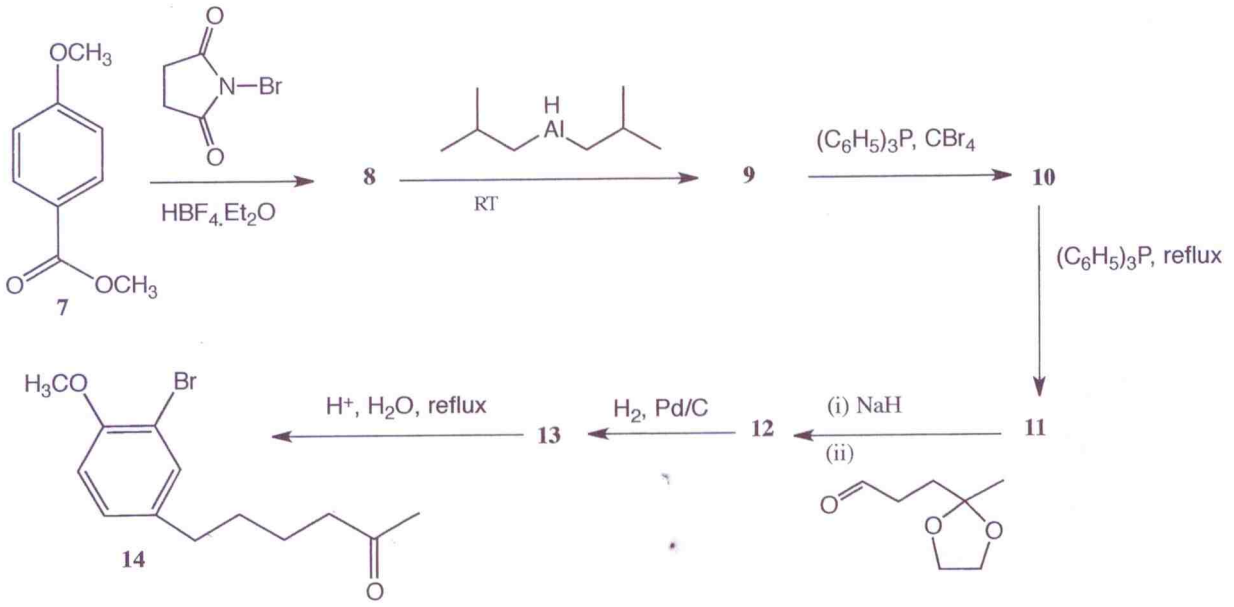


To a solution of an excess of intermediate **2**, obtained by treatment of *tert*-Butyl acetate (**1**) with one equivalent of LDA, is added compound **3**. After work-up product **4** cyclizes upon treatment with base to give **5**. Finally heating of **5** under reflux in the presence of a catalytic amount of acid gives **6**.

a) Provide the structure of the (not isolated) intermediate **2** and the mechanism of the corresponding reaction.
b) Provide the structure of compound **4**, and the mechanism of the conversion of **2** + **3**→**4**.
c) Provide the structure of compound **5**, and the mechanism of the conversion of **4** → **5**.
d) Provide the mechanism of the conversion of **5** → **6**.

Question 2. *(18 points)*

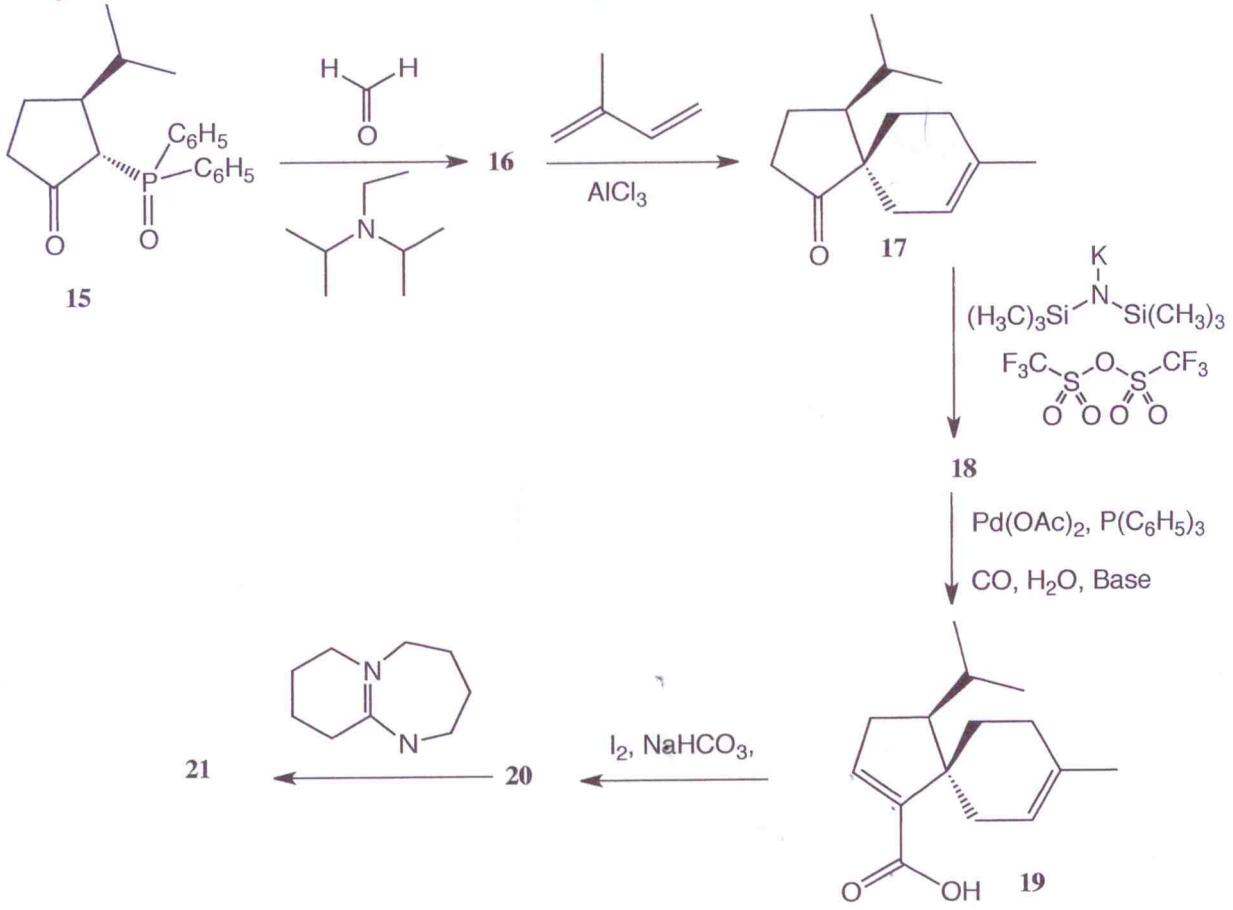
Part of the synthetic route to acerogenins and centrolobol is depicted in the scheme (Tetrahedron 69 (2013) 2807).



a) Provide the structure of compound **8**, and the mechanism of the corresponding reaction.
b) Provide the structure of compound **9**, and the mechanism of the corresponding reaction.
c) Provide the structure of compound **10**, and the mechanism of the corresponding reaction.
d) Provide the structure of compound **11**, and the mechanism of the corresponding reaction.
e) Provide the structure of compound **12**, and the mechanism of the corresponding reaction.
f) Provide the structure of the compound **13**. Provide the mechanism of the conversion of **13 → 14**.

Question 3. *(25 points)*

Part of the synthetic route to (+)-Colletoic Acid is depicted in the scheme (Org. Lett., 15, 2013, 1004).



a) Provide the structure of compound **16**, and the mechanism of the corresponding reaction.
b) Provide the mechanism of the conversion of **16** into **17**.
c) Provide the structure of compound **18**, and the mechanism of the corresponding reaction.
d) Provide the mechanism of the conversion of **18** → **19**.
d) Provide the structure of compound **20** (including the stereochemistry) and the mechanism of the corresponding reaction.
e) Provide the structure of compound **21**, and the mechanism of the corresponding reaction.