Institutt for kjemi
NTNU

Contact person:
Associate Professor Odd R. Gautun
Tlf: 73 59 41 01

English

Exam in TKJ4102
Basic Organic Chemistry

Monday 5. December 2011
kl. 09.00 – 13.00

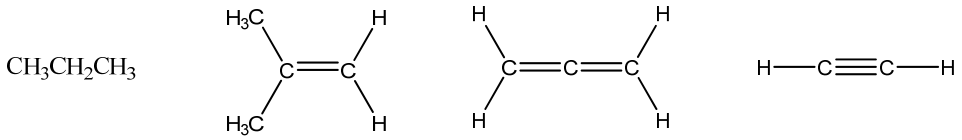
Use of NTNU approved pocket calculator is permitted.
Molecular models and SI is allowed.

No other printed or hand written notes are allowed at the exam.
Electronic devises like MP3 players, iPOD, mobile phone and the like must not be used at any time during the exam.

The result will be available 2. January 2012

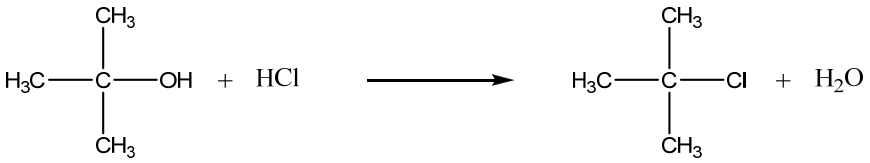
Problem I

a) Describe the kind of hybridization you expect for each carbon atom in the following molecules.



b) What is an electrophile and what is a nucleophile?

c) Draw the mechanism of the reaction shown below



d) What is the difference between a transition state and an intermediate in a reaction? You may use the reaction shown in problem 1c as an example.

e) What does Hammond's postulate say about the structure of a transition state?

Problem II

Tartaric acid [HOOCCH(OH)CH(OH)COOH] was an important compound in the development of the topic stereochemistry. Two naturally occurring crystalline forms of tartaric acid are optically inactive. One of these melts at 206 °C, the other at 140 °C. The form with melting point 206 °C, can be resolved into two optically active forms of tartaric acid with identical melting points (170 °C). One of the optical forms shows $[\alpha]_D = +12$ °, the other form shows $[\alpha]_D = -12$ °. All attempts to resolve the crystalline form with melting point 140 °C into optically active compounds failed.

a) Draw a three dimensional structure of the tartaric acid with the melting point 140 °C.

b) Draw the three dimensional structures possible for the optical active tartaric acids with the melting point 170 °C.

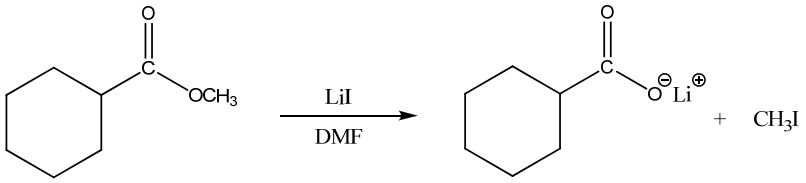
c) Is it possible to determine which configuration that has positive or negative optical rotation by measurements of $[\alpha]_D$?

d) Determine the absolute configurations of all chiral carbon atoms in the structures given in problems a) and b).

e) Describe the construction of the crystalline form with melting point 206 °C.

Problem III

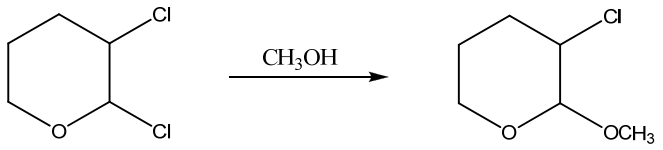
a) Metyl esters (RCO_2CH_3) undergo a cleavage reaction to yield carboxylate ions plus iodomethane upon heating with LiI in dimethylformamide (DMF):



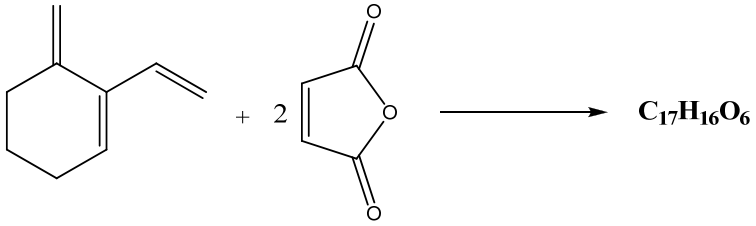
The following evidence has been obtained: (1) The reaction occurs much faster in DMF than in ethanol. (2) The corresponding ethyl ester ($RCO_2CH_2CH_3$) cleaves approximately 10 times slower than the methyl ester. Propose a mechanism for the reaction. What other experimental evidence could you gather to support your hypothesis?

b) 1-Chloro-1,2-diphenylethane can undergo E2 elimination in presence of a strong base to give either *cis*- or *trans*-1,2-diphenylethylene (stilbene). Draw Newman projections of the reactive conformations leading to both possible products, and suggest a reason why the trans alkene is the major product.

c) Draw the mechanism for the reaction given below. Explain why the particular product is the only substitution product in this reaction.



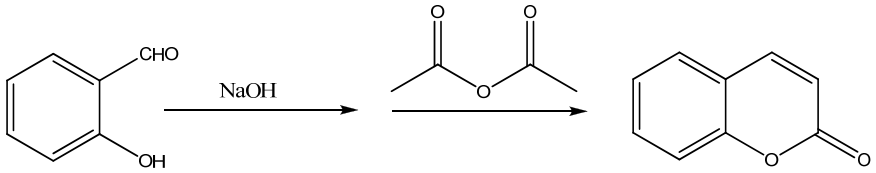
d) The triene shown below reacts with <u>two</u> equivalents of maleic anhydride to yield $C_{17}H_{16}O_6$ as product. Predict a structure for the product.



Problem IV

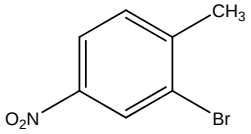
a) Coumarin (**B**) is a bicyclic lactone used in the perfume industry. In 1868 Sir William H. Perkin discovered a synthesis of **B** from 2-hydroxybensaldehyde (**A**, also known as salicylaldehyde). Compound **A** was first treated with NaOH and then with acetic acid anhydride. Draw a detailed mechanism that shows how **B** is formed from **A**.

Tip! Phenols typically have pKa values around 10.



A **B**

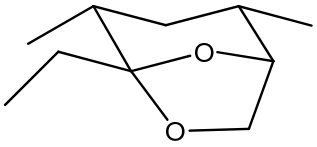
b) Show how compound **C** can be formed from benzene. The synthesis will contain several steps. Draw the mechanism for introduction of the nitro group.



C

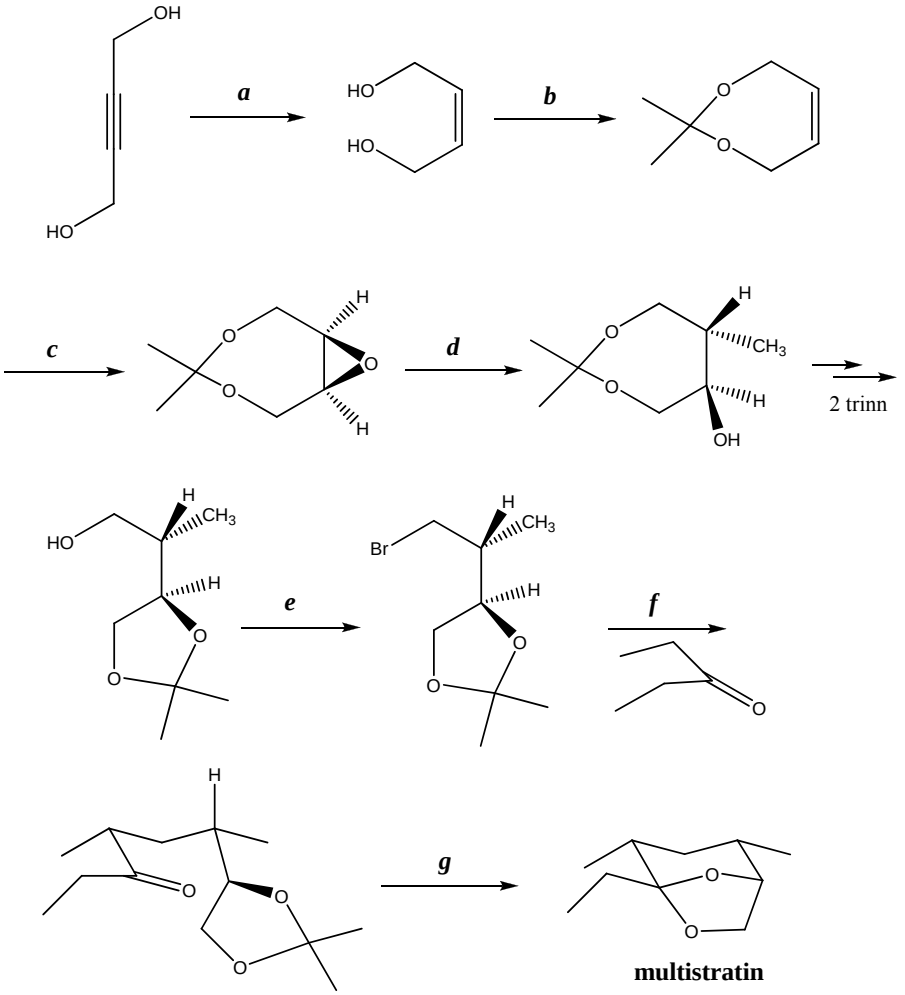
Problem V

Many insects produce volatile, chemical compounds, so called pheromones to communicate with other species. One example is the beetle pheromone multistratin.



multistratin

A total synthesis of multistratin (±) is shown below. Give all necessary reagents to achieve steps (***a*** – ***g***) and the reactions involved. Draw a detailed reaction mechanism for step ***b***.



Good luck!
ORG