



Side 1 (7)

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EXAMINATION IN COURSE TKJ 4180
PHYSICAL ORGANIC CHEMISTRY

LØRDAG 10. DESEMBER 2011,
TIME: KL. 09:00 - 13:00

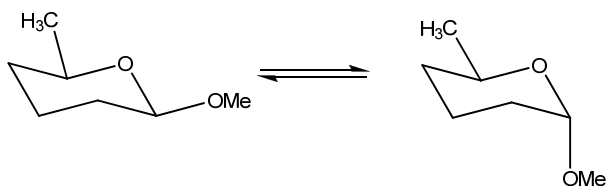
Permitted aids : D
 Approved simple calculator
 Molecular building sets
 Ingen trykte eller håndskrevne hjelpemidler er tillatt

This test consists of seven- 7- pages:

Examination results: 13.01.2012

Exercise 1:

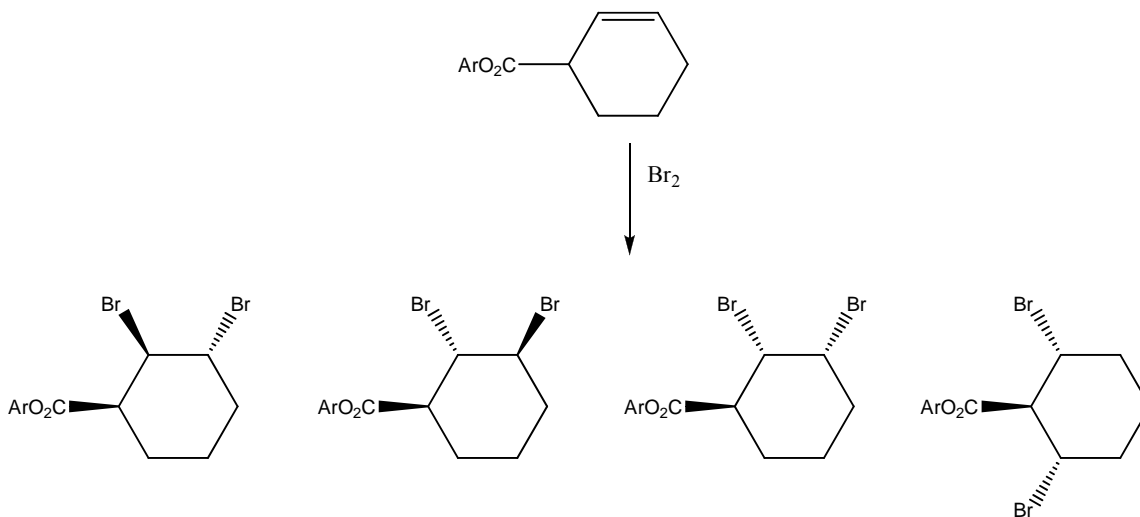
Sepp and co-workers have studied the conformation of 2-oxy-substituted tetrahydropyrans. A representative example is shown below.



- a. Which conformation is the most stable for the compound shown over, explain the reason(s) behind.

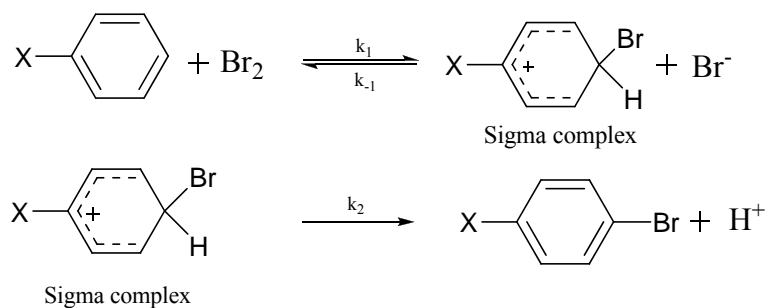
Exercise 2:

- a. The bromination of 3-aryloxycyclohexene gives rise to a mixture of stereoisomers and regioisomeric products. The product composition for Ar= phenyl is shown. Account for both the stereo and regioselectivity outcome for each of these compounds.

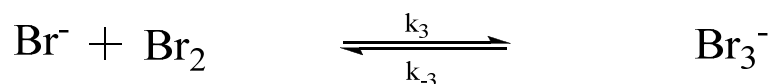


Exercise 3:

- a. The bromination of substituted benzene derivatives shown below is thought to go through an addition-elimination reaction. Assume that the sigma complex is a steady state intermediate. What is the form of the rate expression if the intermediate of the first step goes on to product much faster than it reverts to starting material?



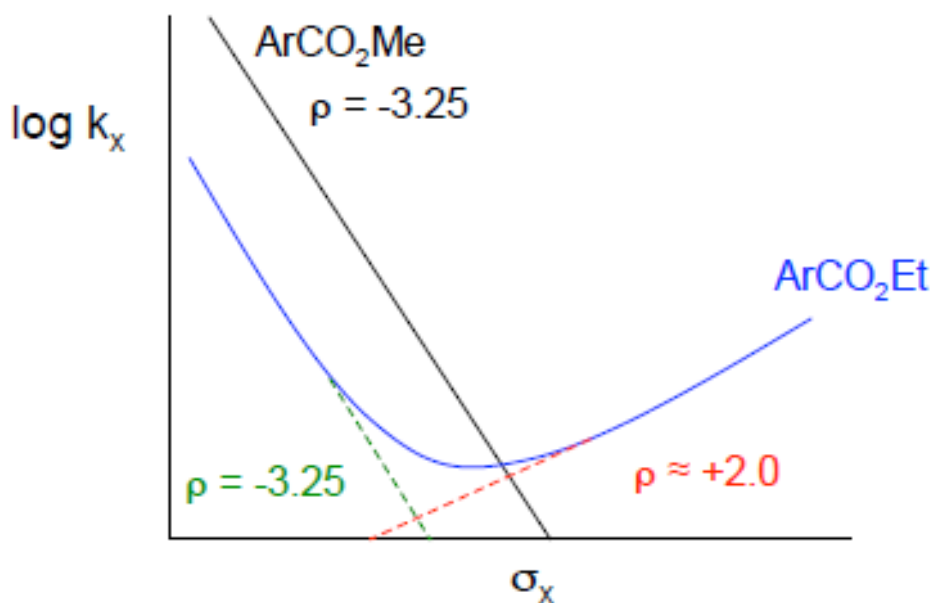
- b. By further investigation of the reaction shown over it was found that there is a rapid equilibrium converting initial Br_2 into unreactive Br_3^- as shown below. What would the the rate expression be if the equilibrium constant for the formation of the tribromide ion is large?



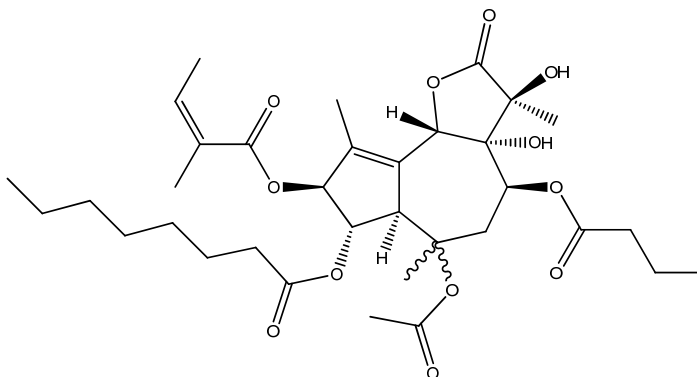
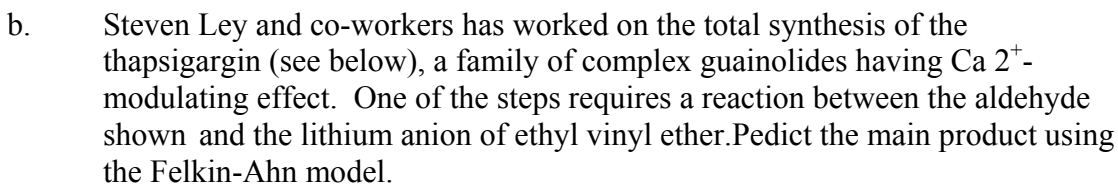
Exercise 4:

The hydrolysis of ArCO_2R ($\text{R}=\text{Me}$ and Et) esters carried out in 99.9 % H_2SO_4 has been plotted in a Hammett plot. The methyl esters shows a linear plot with $\rho=-3.5$. The ethyl ester shows a plot changing from $\rho=-3.5$ to $\rho=2.0$ (left electron donating groups, right electron withdrawing groups)

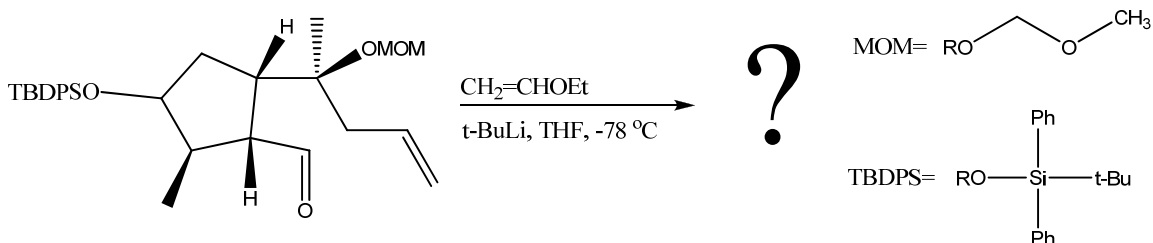
- The plot for the ethyl esters has a break of linearity, what does this type of concave upwards deviations normally indicate?
- What can the rho value (ρ) give information about in a Hammett plot?
- Use the information shown in the Hammett plot to rationalize the mechanism(s) behind hydrolysis of substituted aryl ethyl esters.



a. The Grignard reaction between (S)-2-phenylpropanal and ethylmagnesium bromide is shown below. Predict the stereochemistry of the anticipated main product by using the Cram's rule. Name the main product.

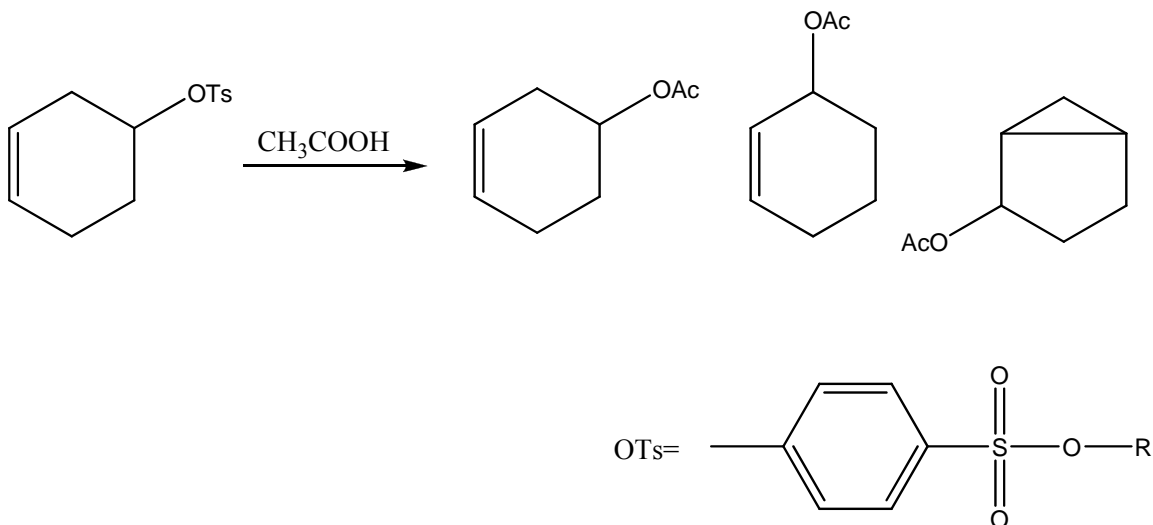


Thapsigargin

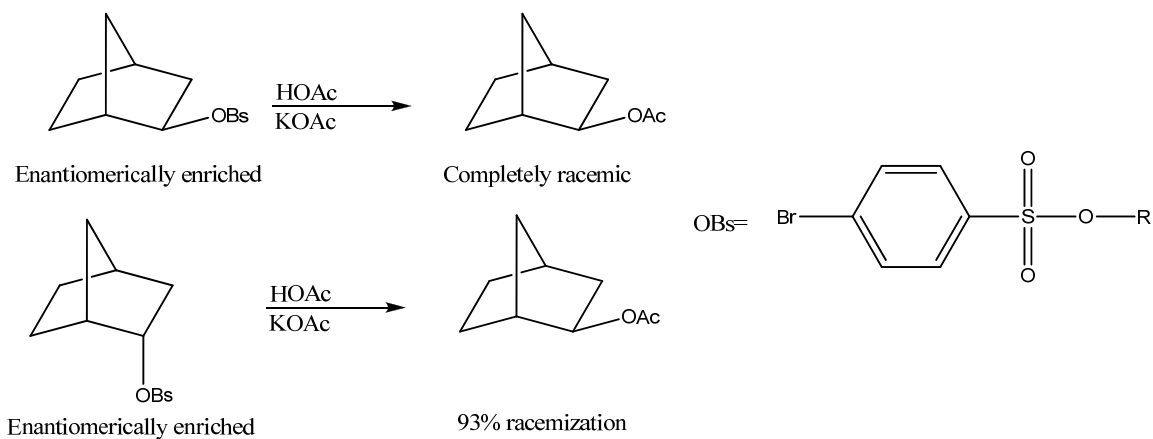


Exercise 6:

- a. The acetolysis of cyclohex-3-enyl 4-methylbenzenesulfonate results in the formation of the three products shown below: Show the mechanism for the formation of these products.

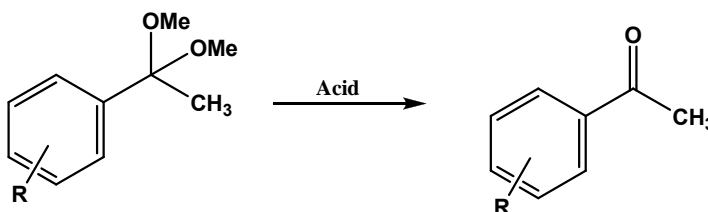


- b. The acetolyses of enantiomerically enriched exo-2-norbornyl brosylate gives rise to completely racemic exo-acetate. Endo-2-norbornyl brosylate gives 93% racemisation. The exo form also reacts 350 times faster than the endo form. Account for both the unusual stereoselectivity and the rate difference.



Exercise 7:

The hydrolysis of several substituted aryl acetals in acidic medium has been investigated and is shown below.



<u>R</u>	<u>σ</u>	<u>Rate</u>
4-Dimethylamino	-0,63	1,47E+05
4-Amino	-0,57	4,91E+04
4-Hydroxy	-0,37	2,83E+04
4-Methoxy	-0,268	9,40E+03
4-Methyl	-0,17	2,09E+03
H	0	9,56E+02
3-Methoxy	0,115	4,53E+02
4-Chloro	0,227	4,07E+02
3-Bromo	0,391	1,56E+02

- Draw a Hammett plot using the substituent constant σ and the rate data. Use the plot to find the slope (rho value).
- Write the mechanism for acid catalyzed hydrolysis of acetals and indicate the rate limiting step. Assume that hydrolysis of the hemiacetals are faster than hydrolysis of the acetals.
- Does the Hammett plot agree with what you have proposed as the rate limiting step in question b?