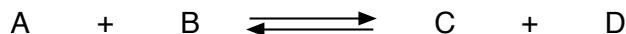


Organic Chemistry

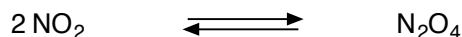
Exercise 6

1. How is the equilibrium constant of the following reaction defined?



What is the exact relation of the equilibrium constant and the standard Gibbs free energy?

2. Give the Gibbs Helmholtz equation. What does the reaction enthalpy “describe” (illustratively), and what is the reaction entropy related to? Describe the temperature dependence of a reaction using the Gibbs Helmholtz equation.
3. Transfer: Is a reaction in which one molecule decomposes into two molecules ($A \rightarrow 2 B$) endotrophic or exotrophic? The decomposition reaction is endothermic. What is the consequence of decreasing the temperature at which the reaction is conducted?
4. Transfer: Consider the equilibrium of the following dimerization reaction:



NO_2 is a brown gas, whereas N_2O_4 is colorless. The Gibbs free energy of the dimerization reaction (left to right) is $\Delta G = -5.13 \text{ kJ/mol}$ at a temperature of 23°C and $\Delta G = 8.41 \text{ kJ/mol}$ at a temperature of 100°C .

- a) What would you expect to observe in terms of color upon heating a sealed flask from room temperature to 100°C ?
- b) A sealed flask with a volume of $V = 1 \text{ L}$ is filled with 0.26 mol of pure NO_2 . After a while the equilibrium is reached and a measurement shows that 0.08 mol N_2O_4 is present. Determine the equilibrium constant.
5. Describe what is the difference between reaction thermodynamics and reaction kinetics!

Reading Suggestions:

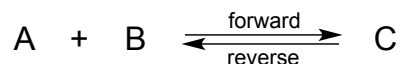
Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 304–334.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**, pp. 105-114.

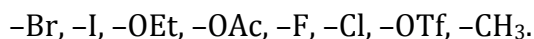
Organic Chemistry

Exercise 7

1. What is the rate law of the following forward and reverse reactions? For both the forward and reverse reaction, please indicate the molecularity and reaction order.



2. Considering the reaction above, draw a reaction profile that illustrates the thermodynamics as well as the kinetics. The forward reaction is endergonic. What is the result of an increase of the activation barrier? Moreover, derive the relationship between the rate constants k_f , k_r and the equilibrium constant K in thermodynamic equilibrium.
3. Draw the reaction scheme (including intermediate) and the reaction profile of a nucleophilic substitution via the S_N1 mechanism from the starting material *benzyl iodide* or and *sodium ethanolate* to the product *benzyl ethyl ether* via a reactive intermediate.
- Mark the two transition states T1 and T2. Indicate the Gibbs' free reaction energy, and the activation energies (Gibbs free energies of activation) for the two steps. Which step is rate-determining? What is the overall reaction order of this reaction (and explain why)?
 - Explain in detail (using chemical structures) how the phenyl residue influences the stability of the intermediate cation in the nucleophilic substitution reaction above? What is the coordination geometry of the carbocation intermediate according to VSEPR theory?
4. What makes a leaving group "good"? How can you roughly estimate/measure leaving group quality? What are the approximate limits for good, moderate, and poor leaving groups? Give two examples of each.
5. Sort the following leaving groups in the order of decreasing leaving group quality:



Reading Suggestions:

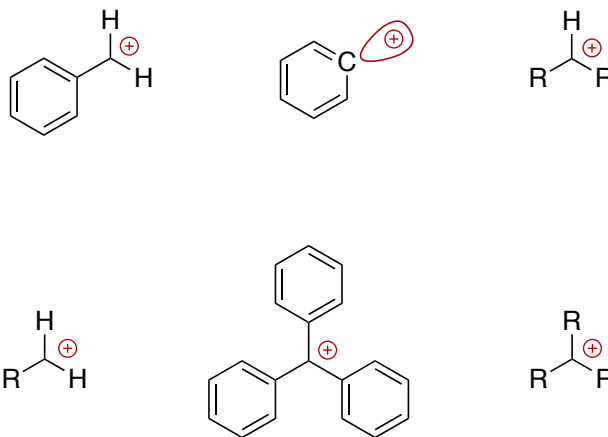
Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 407–441.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**, pp. 105-114.

Organic Chemistry

Exercise 8

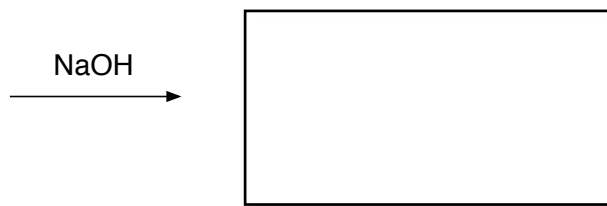
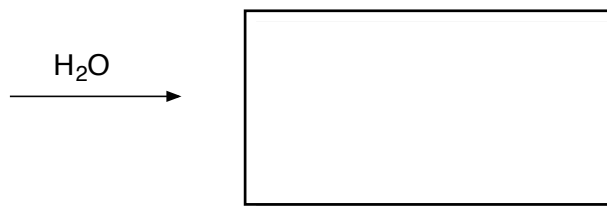
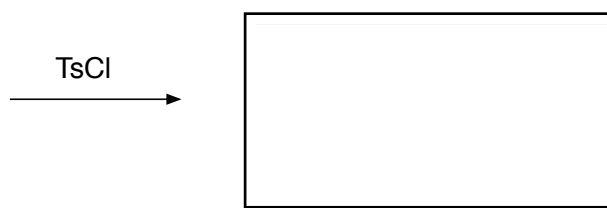
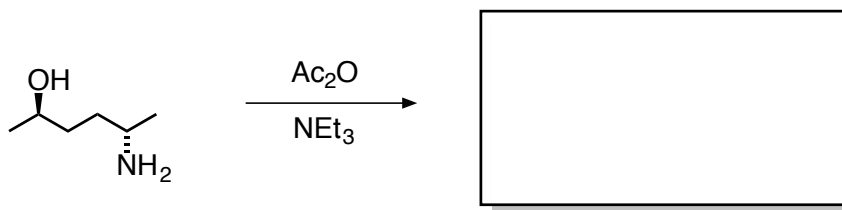
1. Define substitution, addition, and elimination reactions (scheme or words)!
2. Sort the following carbocations in the order of decreasing stabilization (R = alkyl):



3. Draw the reaction scheme and the reaction profile of a nucleophilic substitution via the S_N2 mechanism from the starting material (*R*)-2-iodopentane and sodium phenolate to the corresponding product.
 - a. Give the full IUPAC name of the product. What is the overall reaction order of this reaction (and explain why)?
 - b. According to which mechanism will the substitution reaction proceed when (*R*)-2-iodo-3,3-dimethylpentane is used as the starting material? What is the product of the reaction?
4. Transfer: In practical terms, the S_N1 and S_N2 mechanism are idealizations; real substitution reactions are “somewhere in between”. Nevertheless, try to make an educated guess which one of the following reactions is more S_N1 -type or more S_N2 -type and give a very short explanation (keywords):



5. *Transfer:* Complete the following reaction sequence. Comment on the purpose of the overall reaction sequence. For each step indicate the attack of the electron pairs on the electrophilic center.



Reading Suggestions:

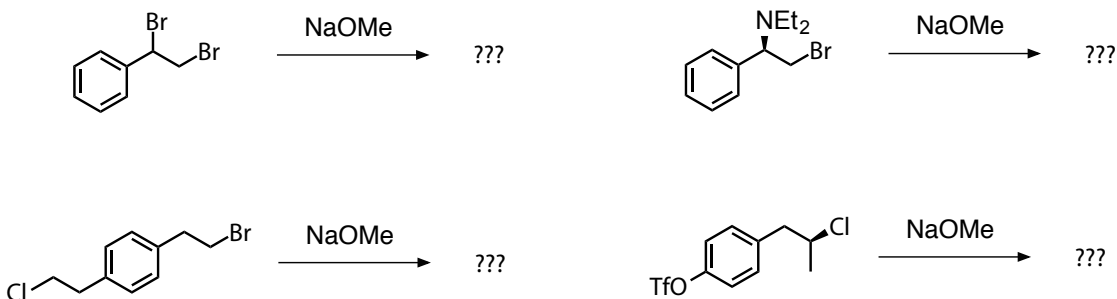
Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 407–441 and 279–301.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**, pp. 105-114.

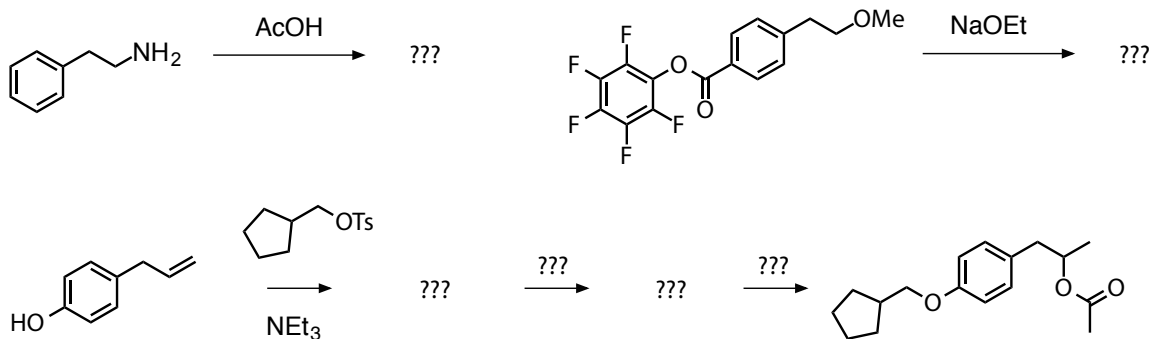
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Exercise 9

1. Give the major product of the following reactions and give a very short explanation (keywords):



2. Formulate the mechanism and the energy profile of the reaction of NaOMe with propanoic acid chloride. What is the name of this mechanism? What is the molecularity of this reaction in the rate-determining step? Why is this reaction different from a comparable S_N2 reaction (e.g., of NaOMe with 1-butylchloride)?
3. *Transfer*: Give the major product or intermediates of the following reactions and give a very short explanation (keywords):



4. Formulate the complete reaction mechanisms for the tosylation of *S*-2-pentanol and for the acetylation of 3-pentanamine!
5. Draw the reaction scheme and the energy profile of the electrophilic addition of HBr to 1-phenyl-1-propene! Explain the Markovnikov rule for the *regioselectivity* of this reaction, using the energy profile of the two possible reaction pathways!

Reading Suggestions:

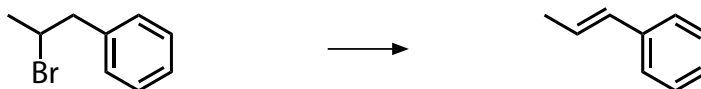
Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 407–441, 279–301, and 503–520.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**: pp. 609–618, 305–312, and 217–232.

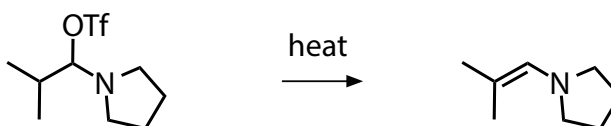
Organic Chemistry

Exercise 10

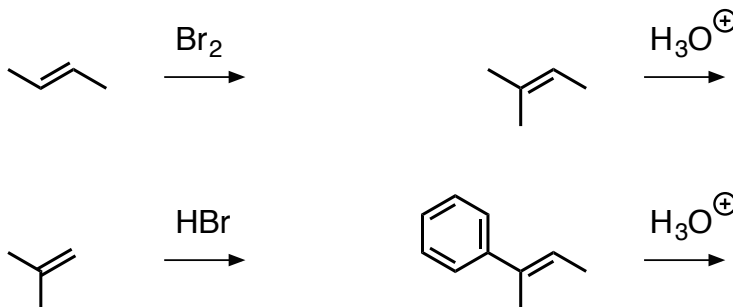
1. The following chemical transformation of 2-bromo-1-phenylpropane to (*E*)-1-phenylprop-1-ene is an elimination reaction. These β -hydrogen eliminations can proceed via three different mechanisms. Please provide the chemical drawings including intermediates and transition states for all three mechanisms.



2. Transfer: Provide a detailed mechanism (including relevant resonance structures) for the following elimination reaction and explain according to what mechanism it proceeds. Give at least three reasons for your decision.



3. Draw the main product(s) of the following electrophilic additions, including all stereoisomers, but without drawing identical molecules. Give the IUPAC names for all the products obtained in the reactions.



4. Transfer: Give the intermediate and product of the following reaction sequence and give a very short explanation (keywords):



Reading Suggestions:

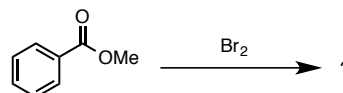
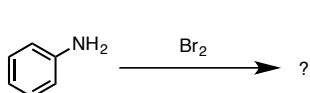
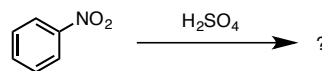
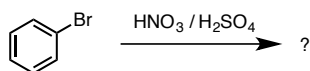
Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 477–501, 503–520.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**: pp. 619–621, 217–232.

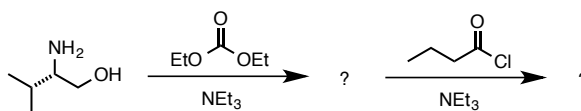
Organic Chemistry

Exercise 11

1. Give the energy profile of an electrophilic aromatic substitution reaction including drawings of the structures of all intermediates and name them. Which one is the rate-determining step?
2. Draw the main product(s) of the following electrophilic aromatic substitution reactions and support your results on the basis of relevant resonance structures.



3. Formulate the net reaction for the Friedel-Crafts acylation of methyl benzoate (phenylformic acid methyl ester) with propanoyl chloride and AlCl_3 as the catalyst.
4. *Transfer:* Give the intermediate and product of the following reaction sequence and provide a detailed reaction mechanism (for each step indicate the attack of the electron pairs on the electrophilic center). Hint: primary amines are more nucleophilic than alcohols, but secondary amines are less nucleophilic than alcohols.



5. The solvents dichloromethane (CH_2Cl_2), trichloromethane (chloroform, CHCl_3) and tetrachloromethane (CCl_4) are obtained by chlorination of methane.
 - a) Give a detailed reaction mechanism for the formation of tetrachloromethane.
 - b) How could you separate a mixture of dichloromethane, trichloromethane and tetrachloromethane?
 - c) Which reaction conditions would favor the formation of tetrachloromethane?

Reading Suggestions:

Clayden, Greeves, Warren, Wothers, *Oxford University Press*, **2001**, pp. 547-576, 1021-1050.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**: pp. 277-295, 303-322.