Organic Chemistry 2
Examination January 13 2014, 9.00-12.00 h

This exam consists of 6 questions.
- Read the questions carefully!
- For each question the maximum score is given (total 60 points)
- Draw clear structures and write in a clear manner
- On each piece of paper write your name and student number

Enjoy and good luck!

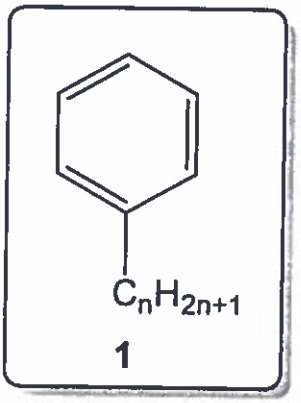
Question 1 (8 points)

Treatment of *benzene* with an *alkyl* chloride (*R*-Cl) in the presence of $AlCl_3$ (*Friedel-Crafts* alkylation) gives access to alkylated benzene derivatives.

Despite its utility, *Friedel-Crafts* alkylation has several limitations especially for the synthesis of 'simple' *n*-alkylated benzenes, *viz.* benzene functionalized with one extended (*anti*-periplanar) *n*-alkyl chain (see **1**).

a. Explain in detail (*Hint:* take into account the complete reaction mechanism for *Friedel-Crafts* alkylation using, for example, *n*-butyl chloride). **(4 points)**

b. Propose another synthetic approach to access *pure* *n*-alkylated benzenes. **(4 points)**



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Question 2 (12 points)

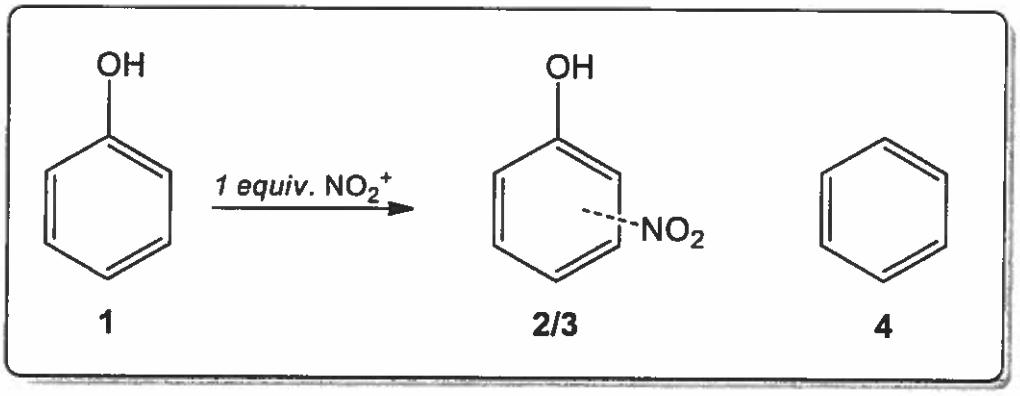
Treatment of *phenol* (**1**) with *1 equiv.* of the *electrophile* NO_2^+ generated *in situ* by reaction of *1 equiv.* of *conc.* nitric acid (HNO_3) and *1 equiv.* of *conc.* sulfuric acid (H_2SO_4) gives only <u>two</u> (**2** and **3**) out of <u>three</u> possible products. The products **2** and **3** are formed in a *1:1* molar ratio.

a. Provide the <u>complete</u> reaction mechanism for the *in situ* formation of the electrophile NO_2^+ by reaction of *1 equiv.* of *conc.* nitric acid (HNO_3) and *1 equiv.* of *conc.* sulfuric acid (H_2SO_4). **(2 point)**

b. Provide structures for the <u>two</u> products **2** and **3** that are formed upon treatment of *phenol* (**1**) with *1 equiv.* of the *electrophile* NO_2^+. **(4 points)**

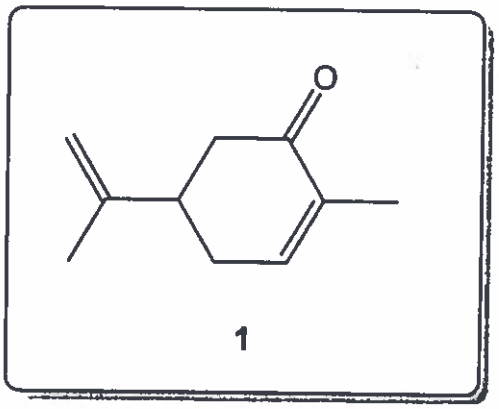
c. Explain in detail (<u>complete</u> reaction mechanism) why only <u>two</u> (**2** and **3**) out of <u>three</u> possible products are formed. **(4 points)**

d. *Phenol* (**1**) is *ca.* 1000 times <u>more</u> reactive than *benzene* (**4**) under the applied reaction conditions. Explain in detail. **(2 points)**



Question 3. (10 points)

Carvone (**1**) is the major constituent of spearmint oil. What product(s) would you expect to find from reaction of *carvone* (**1**) with the following reagents?:



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a. $LiAlH_4$, then H_3O^+ **(2 points)**

b. C_6H_5MgBr, then H_3O^+ **(2 points)**

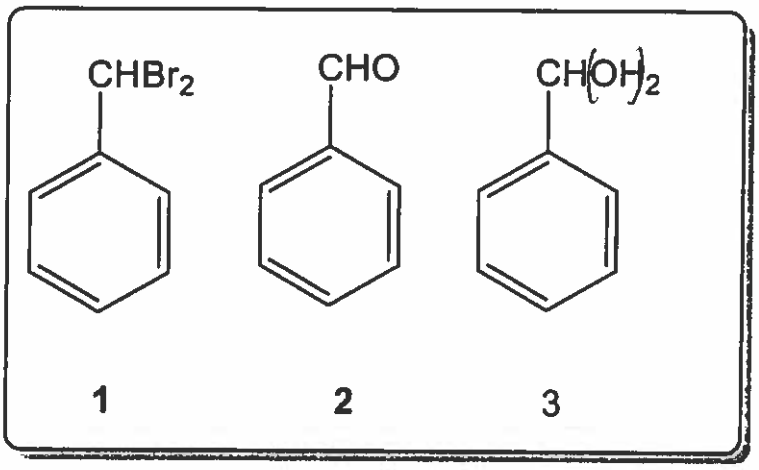
c. CH_3NH_2 **(2 points)**

d. $(C_6H_5)_3P^+\text{-}^-CHCH_3$ **(2 points)**

e. H_2, Pd/C **(2 points)**

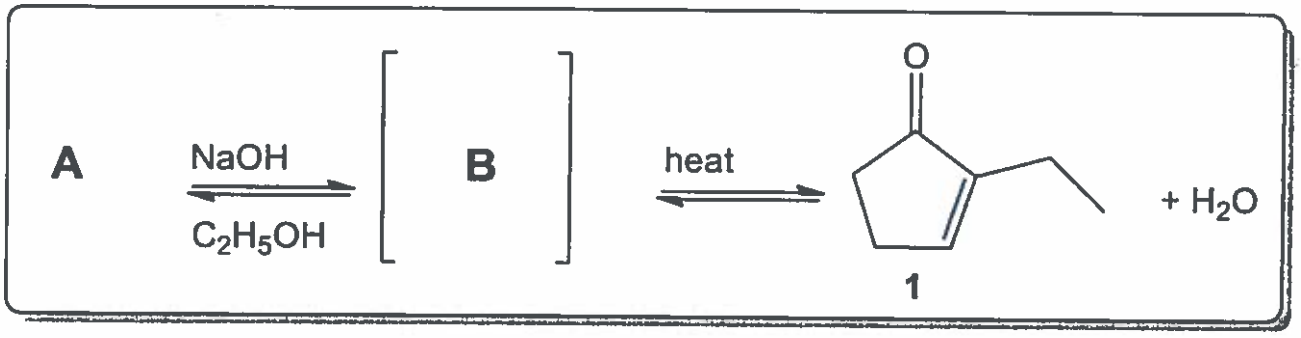
Question 4 (8 points)

The S_N2 reaction of *dibromomethylbenzene* ($C_6H_5CHBr_2$ (**1**)) with a solution containing at least *2 equiv.* Na^+ ^-OH yields *benzaldehyde* (**2**) instead of *dihydroxymethylbenzene* ($C_6H_5CH(OH)_2$ (**3**)). Explain in detail (complete reaction mechanism).



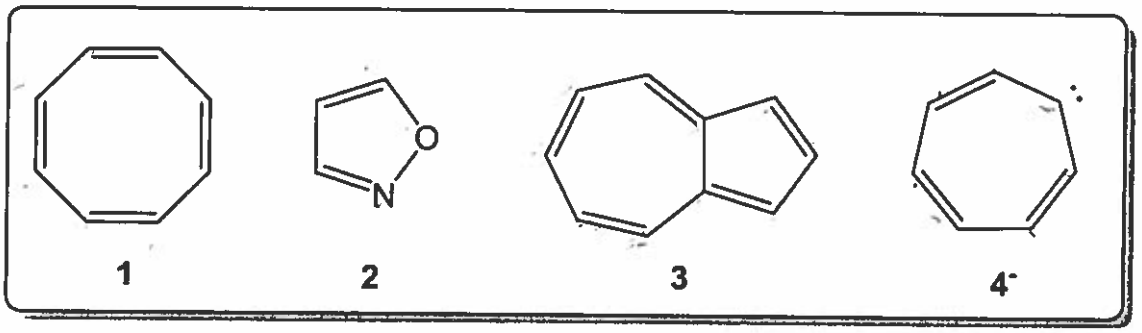
Question 5 (8 points)

The *cyclopentenone* derivative **1** can be synthesized by an *intramolecular* aldol condensation reaction. What *reactant* **A** was used for the preparation of **1**? Also give the structure of the *primary condensation product* **B** obtained after treatment of **A** with NaOH in C_2H_5OH. What happens during heat treatment of **B**? Explain in detail (complete reaction mechanism).



Question 6 (14 points)

a. Explain in detail whether the conjugated compounds **1**, **2**, **3** and **4**$^-$ are either aromatic or anti-aromatic. (*Hint:* apply the Hückel rule). **(8 points)**



b. *Cyclopropanone* (**5**) is highly reactive because of its large amount of angle strain. In contrast, *methylcyclopropenone* (**6**), although more strained than *cyclopropanone* (**5**), is stable. Compound **6** can even be distilled. Explain in detail. (*Hint:* take the polarity of the carbonyl (C=O) group into account). **(6 points)**