Loughborough
University

# Structure and Reactivity 2

21CMB106

Semester 2 2021-2022 Online Long-window Exam paper

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This is an online long-window examination, meaning you have **23 hours** in which to complete and submit this paper. How you manage your time within the 23-hour window is up to you, but we expect you should only need to spend approximately **2 hours** working on it. If you have extra time or rest breaks as part of a Reasonable Adjustment, you will need to add this to the amount of time you are expected to spend on the paper.

**It is your responsibility to submit your work by the deadline for this examination. You must make sure you leave yourself enough time to do so.**

**It is also your responsibility to check that you have submitted the correct file.**

Exam Help

If you are experiencing difficulties in accessing or uploading files during the exam period, you should contact the Exam Helpline. For urgent queries please call **01509 222900**.

For other queries email examhelp@lboro.ac.uk

You may use a calculator and molecular model kits for this exam.

Where a question involves drawing molecular reaction schemes or mechanisms, you should include a commentary explaining each step of the transformation. Diagrams *must* be hand drawn. When photographing your answers for upload, please check that all parts of your answer are clearly visible and legible in the recorded version.

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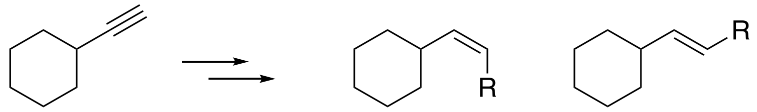
1. Answer **ALL** parts

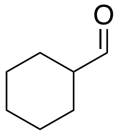
a) The *cis* and *trans* alkenes **2** and **3** (shown overleaf) can be prepared from alkyne **1**. With your choice of R group, describe synthetic routes to both compounds **2** and **3**. Your routes should include all reagents and conditions, and mechanistic details. [10 marks]

*continued…*



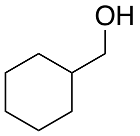
**1** **2** **3**

b) The same two alkenes **2** and **3** can also be prepared from the aldehyde **4**. Again, with your choice of R group, describe synthetic routes to each compound including reagents and conditions. You should pay particular attention to the reaction intermediates, and how these relate to the particular isomers formed. [12 marks]



**4**

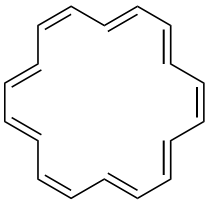
c) The aldehyde **4** above can be formed from the corresponding alcohol **5**. Give *two* different sets of reactions conditions that can perform this reaction. You should give full mechanisms in your answer. [8 marks]



**5**

2. Answer **ALL** parts

a) (i) Apply Hückel's rule to [18]-annulene, shown below, and discuss whether the molecule can be considered aromatic. Account for the $^1$H chemical shifts of the compound listed below.



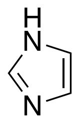
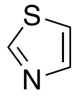
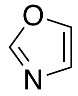
$\delta_H$ 8.9 (12H, m), -1.8 (6H, m)

[18]-annulene

[4 marks]

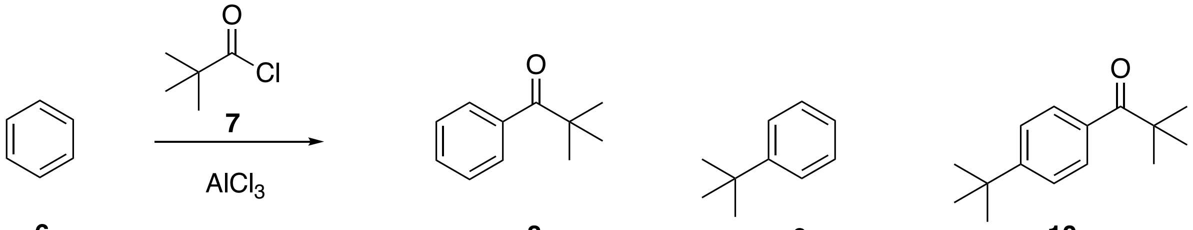
*continued…*

(ii) Account for the decrease in basicity shown for the following three azoles by drawing resonance structures (the p$K_a$ values given refer to the acidity of the *protonated* forms of the molecules).

| | imidazole | thiazole | oxazole |
|---|---|---|---|
| |  |  |  |
| p$K_a$ | 7.1 | 2.5 | 0.8 |

[6 marks]

b) When benzene **6** is treated with 2,2-dimethylpropanoyl (pivaloyl) chloride **7** in the presence of aluminium chloride, the expected Friedel-Crafts acylation product **8** is only formed in low yield. The major product is ketone **10**, formed along with a small amount of *t*-butylbenzene **9**. Discuss the course of this reaction, and account mechanistically for the three products formed. Comment on the relative rates of the different reaction pathways occurring.



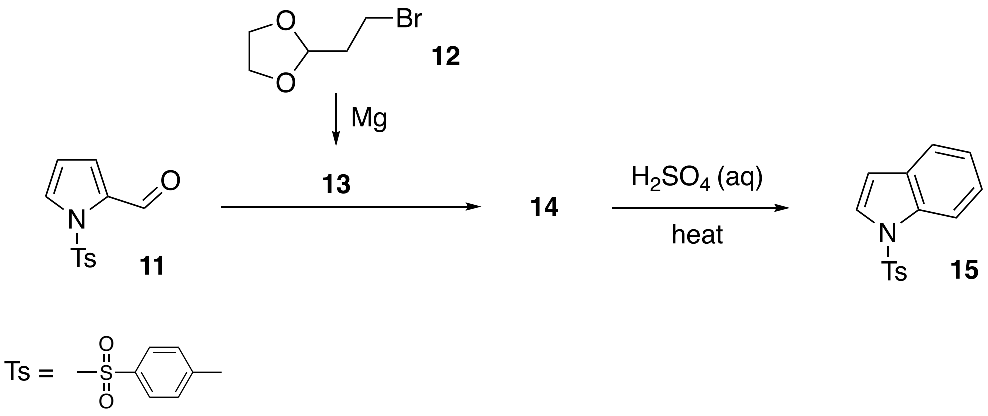
6 8 9 10

minor minor major

[10 marks]

c) A synthesis of *N*-tosyl indole **15** starting from the pyrrole-2-carboxaldehyde **11** and acetal containing alkyl bromide **12** is shown overleaf. Identify intermediate **13** formed on treating the alkyl bromide **12** with magnesium. Explain how **13** then reacts with pyrrole **11** and identify compound **14** formed after aqueous work-up. Show how **14** is finally converted into indole **15** on treatment with acid (hint: the acetal group in **12** is a protected form of an aldehyde). Give mechanisms for each step of the transformation.

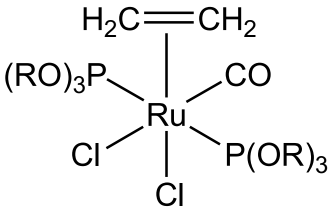
*continued…*



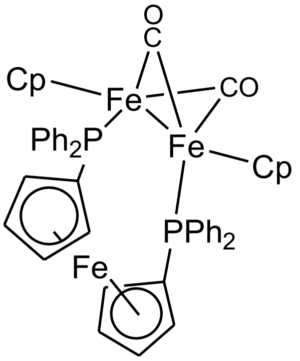
[10 marks]

3. Answer **ALL** parts

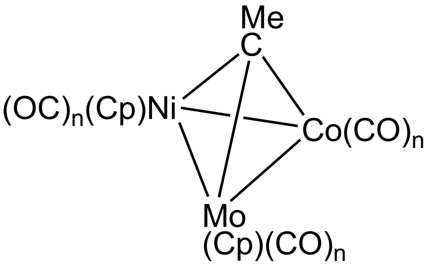
a) Give electron counts for the following organometallic compounds **16** and **17**. Show clearly how you deduce your answer in each case. [4 marks]



**16**



**17**



**18**

b) Calculate the number (n) of terminal CO ligands at the Co, Mo and Ni metal centres in **18**. Assume each metal centre obeys the eighteen electron rule, the bridging CMe ligand is a 1e donor and the Cp ligand is $\eta^5$ bound. [3 marks]

c) Explain the meaning of the term **sandwich compound** using **17** as a suitable example. [1 mark]

*continued…*

d) State reagents you would use to prepare a sample of the $P(OR)_3$ ligand (shown in compound **16**, chose an R group of your preference) and the diphosphine in **17**. Discuss briefly any important experimental reaction conditions, including stoichiometry, that apply to both these reactions.

[6 marks]

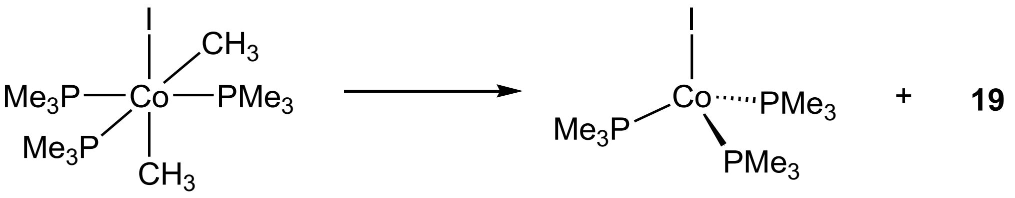
e) To what class of phosphorus compound does $P(OR)_3$ belong? [1 mark]

f) Describe, with suitable orbital diagrams, the bonding of carbon monoxide to metals such as those in **16**–**18**. [6 marks]

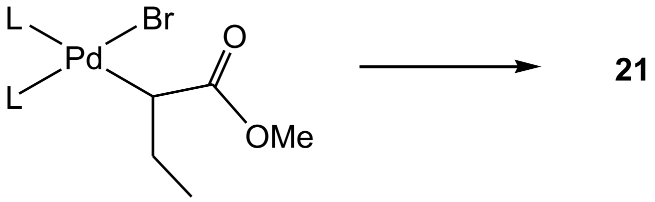
g) Discuss a spectroscopic technique that can be used to distinguish the different bonding modes of CO in **16**–**18**. [3 marks]

h) For the following equation, identify the class of reaction (including the structure of **19**) and explain your reasoning.

[4 marks]



i) The palladium(II) compound **20** eliminates an alkene, **21**. Draw only the structure of **21** and name this class of reaction. Ignore any contribution from the ligands (L/Br).
[2 marks]



**20**

**S.D.R. Christie, M.B. Smith, G.W. Weaver**