Chemistry 2542, Fall 2016 Midterm Exam 3

(100 points)

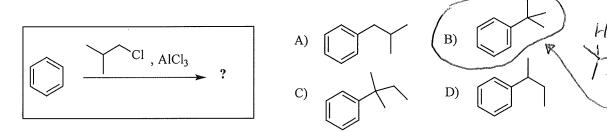


Important notes:

- Please use the provided Scantron form for your answers; you can keep the sheet with the questions and can use it as scratch paper
- Do not forget to write your name on the Scantron form
- You will not receive credit for unmarked answers or for more than one mark on answer line
- Your scores will be posted on eGradebook; graded Scantron forms will not be returned to students.

Questions 1-28: Please mark the appropriate box on the front of the Scantron form (3 pts each).

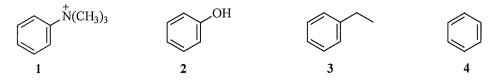
1. Which of the following compounds is a product of rearrangement formed by a 1,2-hydride shift in the reaction shown in the box?



2. Predict which one of the following groups will be **meta-directing** in the **electrophilic** aromatic substitution reaction?

B) $-N(CH_3)_2$ C) -OH (D) -CHOA) –Cl

3. Arrange the following compounds according to their reactivity in electrophilic aromatic substitution reaction.



- A) (most reactive) 1 > 4 > 2 > 3 (least reactive)
- B) (most reactive) 4 > 1 > 2 > 3 (least reactive)
- C) (most reactive) 2 > 3 > 4 > 1 (least reactive) D) (most reactive) 3 > 4 > 2 > 1 (least reactive)

4. For the compound shown in a box, which labeled position is the most reactive in electrophilic aromatic substitution reactions?

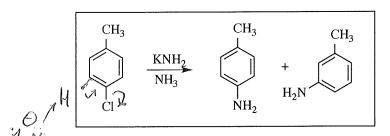
5. Which of the following is a key intermediate for the transformation in the box?

6. Predict which one of the following groups will be **ortho/para-directing** in the electrophilic aromatic substitution reaction?

A)
$$-CF_3$$
 B) $-S - CH_3$ C) $-F - CH_3$ CH₃

7. Which one of the following four schemes (A-D) gives the best representation of the initial step of the **mechanism** of the reaction in the box?

8. What is the structure of the intermediate for the reaction in the box?



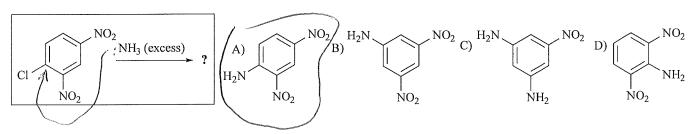
9. What is the structure of the intermediate for the reaction in the box?

10. What is the name of the product formed in the following reaction?

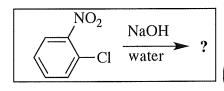
$$O_2N \xrightarrow{\sqrt{\sqrt[4]{2}]{2}}} NH_2 \xrightarrow{Cl_2} ?$$

- A) 3-chloro-4-nitrophenol
- B) 2-chloro-4-nitroaniline
- C) 2-chloro-4-nitrophenol
- D) p-chloroaniline

11. What is a major **product** in the following reaction?

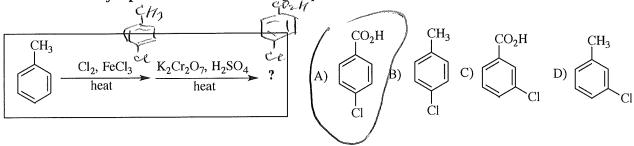


12. What is the name of the **product** formed in the following reaction?



- A) m-nitrophenol B) o-chlorophenol
- C) o-nitrophenol D) m-chlorophenol

13. What is a major product of the following sequence of reactions?

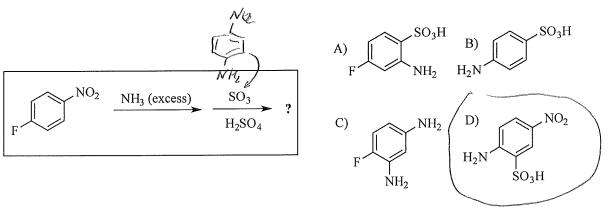


14. Which one of the following compounds is the most reactive towards **nucleophilic** aromatic substitution reaction with NaOH?

A)
$$I$$
 NH_2 NH_2

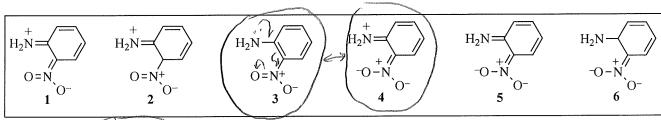
15. What is a major **product** in the following reaction?

16. What is a major product of the following sequence of reactions?



- 17. Which is the correct order of **basicity** of the following compounds:
- (1) ethylamine; (2) NH₃; (3) 2,4-dimethylaniline; (4) 2,4-dinitroaniline; (5) p-nitroaniline
- (A) 1 (strongest) > 2 > 3 > 5 > 4 (weakest) C) 3 (strongest) > 1 > 2 > 5 > 4 (weakest) D) 4 (strongest) > 5 > 3 > 2 > 1 (weakest) D) 4 (strongest) > 5 > 3 > 2 > 1 (weakest)

18. Which of the following structures represent reasonable **resonance contributors** of *o*-nitroaniline?

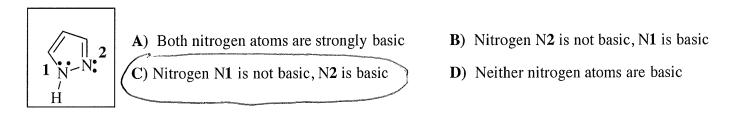


- A) 1 and 2 (B) 3 and 4 (C) 3 and 5 (D) 4 and 6
- 19. Which one of the following amines is the strongest base?
- A) *o*-nitroaniline B) 4-methylaniline C) butanamine D) aniline
- 20. Which is the most acidic hydrogen in the compound shown in a box?

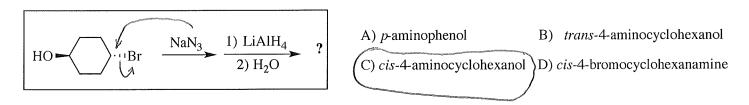
$$(A) \longrightarrow HO \longrightarrow C-CH_2NH_2 \longrightarrow (C) N \longrightarrow D$$

$$CO_2H \longrightarrow CO_2H \longrightarrow$$

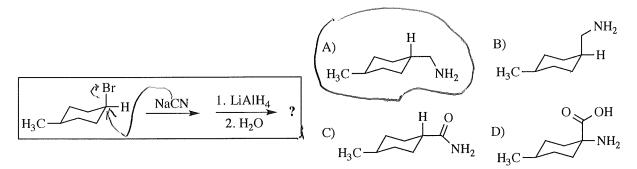
21. Which statement regarding the basicity of the aromatic heterocycle shown in the box is correct?



22. What is the name of the major product of the reaction shown in the box?



23. What is the major **product** of the reaction shown in the box?



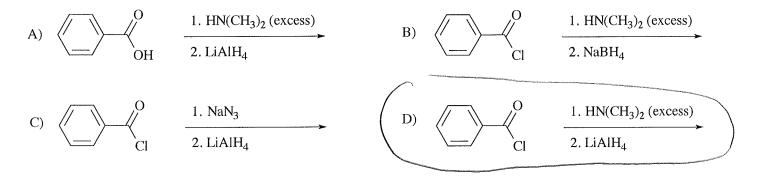
24. What is the name of the major **product** of the reaction shown in the box?

$$H_3C$$
 NO_2 NO_2

25. What is the major product of the reaction shown in the box?

26. What is the major product of the reaction shown in the box?

27. Which reaction sequence will give $PhCH_2N(CH_3)_2$ in high yield?



28. Which reaction sequence will accomplish transformation shown in the box?

Questions 29, 30: Please put your answers into the appropriate space on the back of the Scantron form (16 pts). PLEASE SHOW FORMULAS, DO NOT WRITE NAMES.

29. Provide substituent at the end of the bond in the box (4 pts):

30. Provide the reagents or reactant that give the indicated product in high yield (4 pts each):

$$\begin{array}{c|c}
\hline
 & HNO_3 & Fe(vis_n) \\
\hline
 & line 67 & line 68 \\
\hline
 & HCI & H_2N \longrightarrow OCH_3 \\
\hline
 & CI \longrightarrow NH_2 & NaNO_2, HCI \\
\hline
 & H_2O, 0-5°C & VY & IGO
\end{array}$$