

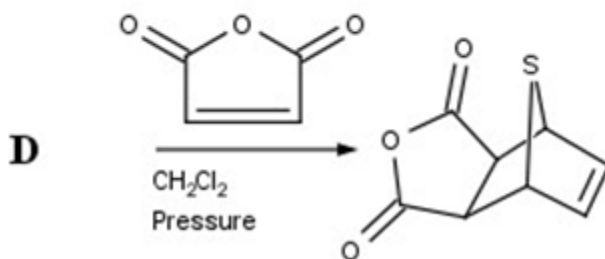
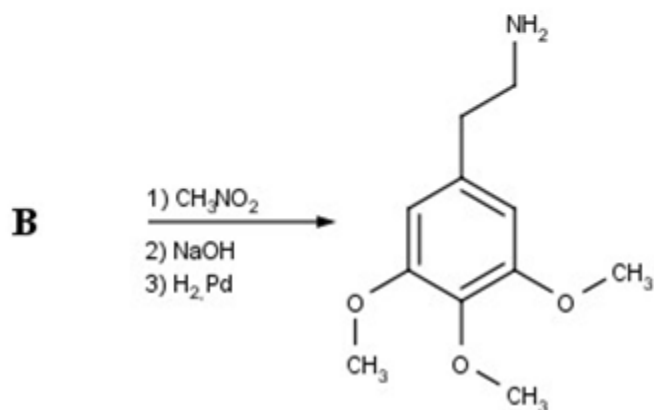
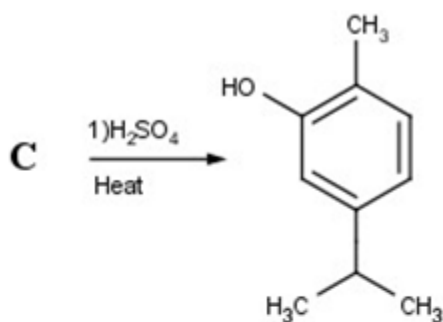
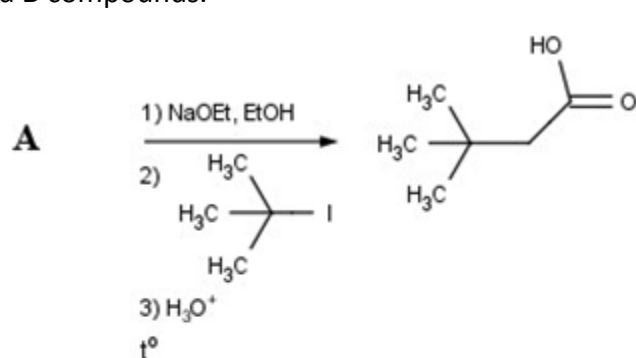


PART II.d – Organic chemistry

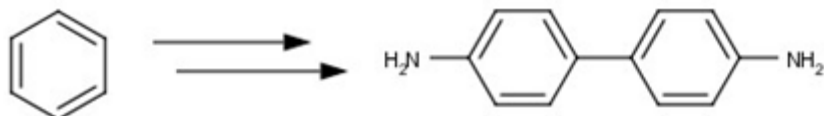
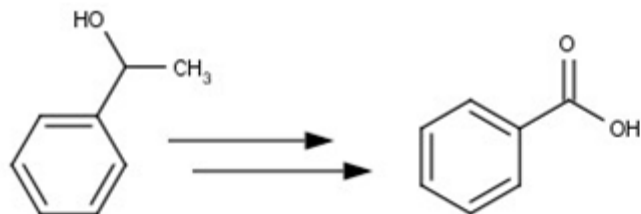
Problem 1

A little bit of organic chemistry

1. Determine and write the structure of **A**, **B**, **C**, **D** starting compounds. Write reaction mechanisms with **A** and **B** compounds.

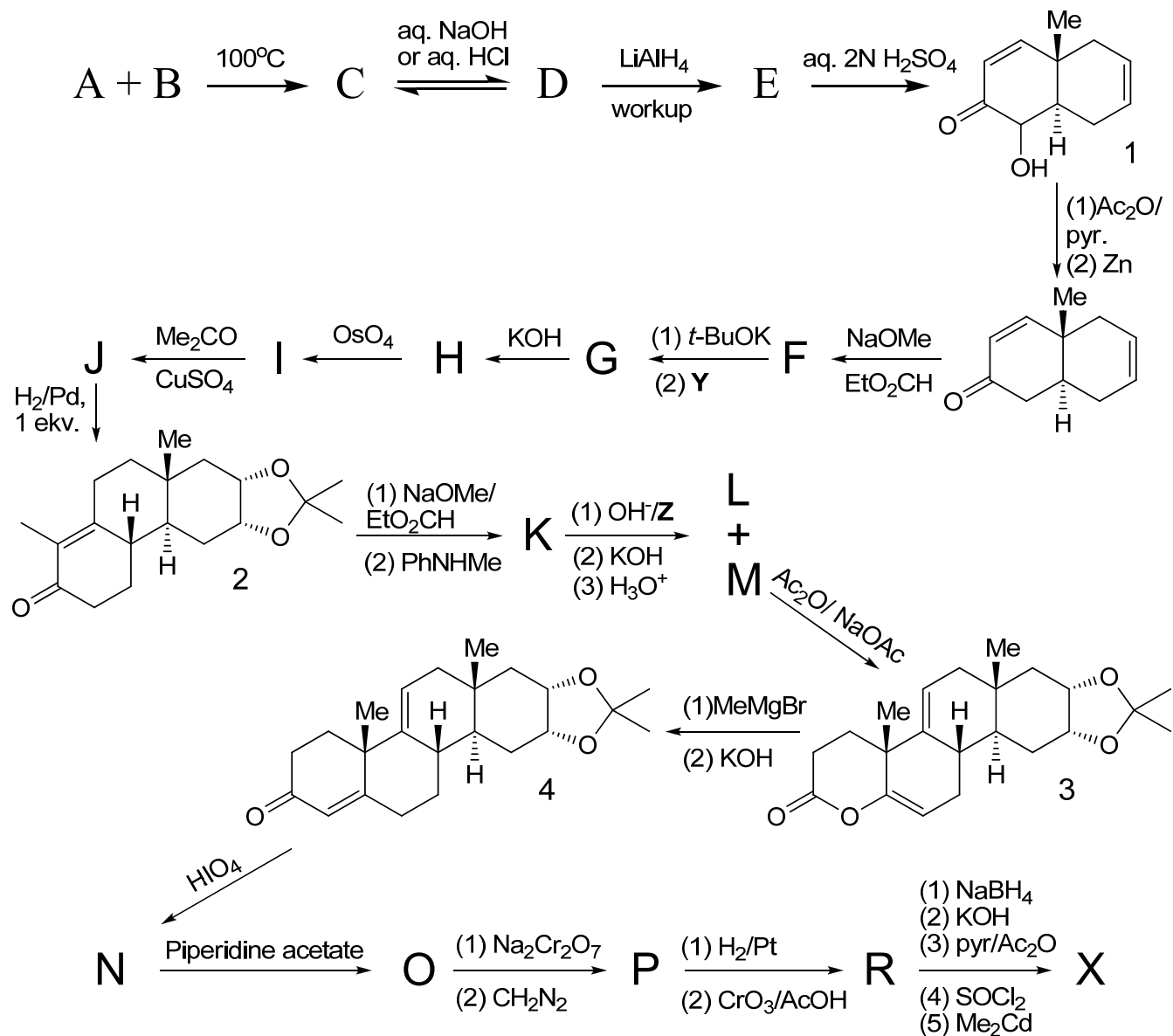


2. Provide plausible synthesis plans with reagents and intermediate compounds.



Problem 2

Lord of the rings



A: $\text{C}_8\text{H}_8\text{O}_3$

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 2.26 (d, $J=0.8$ Hz, 3H), 3.7 (s, 3H), 5.98 (s, 1H), 6.84 (d, $J=0.8$ Hz, 1H)

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 14.3, 57.1, 106.7, 132.6, 143.7, 159.9, 182.0, 185.8

B: C_4H_6

^1H NMR (600 MHz, CDCl_3) δ 5.06 (dd, $J=9.2$ Hz, 2.3 Hz, 2H), 5.16 (dd, $J=14.8$ Hz, 2.3 Hz, 2H), 6.25 (dd, $J=14.8$ Hz, 9.2 Hz, 2H)

^{13}C NMR (150 MHz, CDCl_3) δ 115.2, 135.4

Y: $\text{C}_5\text{H}_8\text{O}$

^1H NMR (600 MHz, CDCl_3) δ 1.21 (t, $J = 6.7$ Hz, 3H), 3.04 (q, $J = 6.7$ Hz, 2H), 6.23 (dd, $J = 16.8, 9.3$ Hz, 1H), 6.10 (dd, $J = 9.3, 2.8$ Hz, 1H), 6.28 (dd, $J = 16.8, 2.8$ Hz, 2H)

^{13}C NMR (150 MHz, CDCl_3) δ 8.4, 34.3, 124.9, 133.2, 200

Z: $\text{C}_3\text{H}_3\text{N}$

^1H NMR (600 MHz, CDCl_3) δ 5.52 (dd, $J = 15.3$ Hz, 10.0 Hz, 1H), 5.88 (dd, $J = 10.0, 2.1$ Hz, 1H), 6.01 (dd, $J = 15.3, 2.1$ Hz, 1H)

Notes:

1. L and M compounds have identical molecular formulas, weigh and produce very similar HRMS spectra.
2. Me_2Cd converts acid chloranhydrides into corresponding methyl ketones.
3. Some of the reactions are stereospecific or highly stereoselective, don't forget that. You are required to provide formulae with correct absolute configuration.

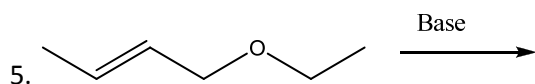
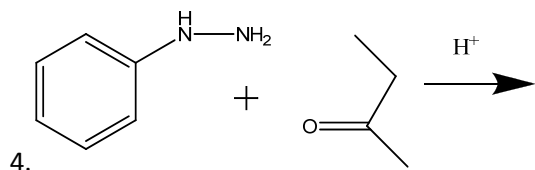
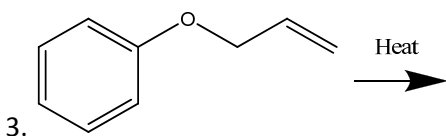
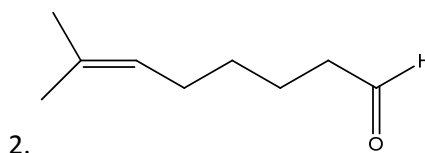
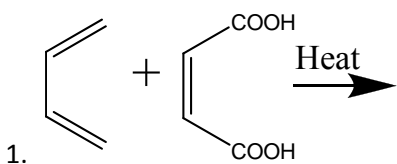
Tasks:

1. Determine the structures of compounds A – R and X.
2. Provide reasonable mechanisms for the given conversions: $\text{E} \rightarrow 1$, $\text{G} \rightarrow \text{H}$, $2 \rightarrow \text{K}$, $3 \rightarrow 4$
3. Determine the number of stereogenic centers in compound 4, assign absolute configurations to each of them.
4. Assign chemical shifts and coupling constants to each hydrogen of the compounds A and Y. Which signals do you expect to disappear after exposure to excess of $\text{D}_2\text{O}/\text{NaOD}$ solution?
5. How are the compounds L and M called in relation to each other?
6. Many biologically active compounds share the ring system of compound X. Name the group of those compounds.

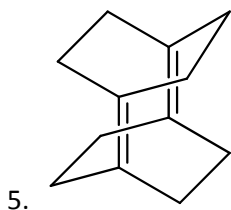
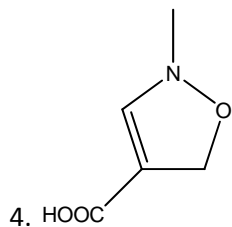
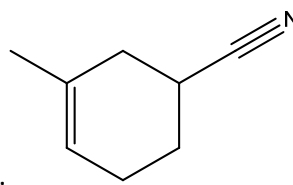
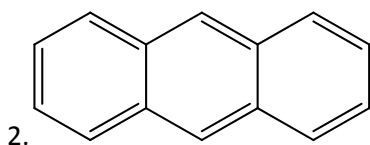
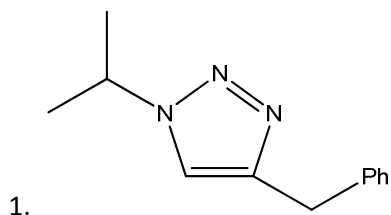
Problem 3

Pericyclic reactions

1. What's the main difference between pericyclic reactions and substitution/elimination reactions?
2. Name three main types of pericyclic reactions?
3. Here you have 5 examples of named pericyclic reactions. Write the products and give names to these reactions.



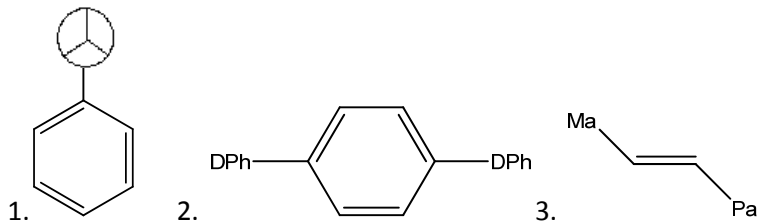
4. 5 different compounds are given, recognize which of them was made using pericyclic reactions. Give names of those reactions.



5. Butadiene reacts with itself when heated to yield compound A. Under presence of catalyst the reaction gives product B. Draw structures of A and B and explain why A is formed instead of B when butadiene is heated.

6. Compound A gives this HNMR spectra: 2.90(2H, t), 6.40(2H, m), 6.50(2H, m). Salt of compound A(BF_4^-) is reduced to compound B. B also could be made from A using NaH in THF and I_2 with CuBr and Me_2S . B reacts with dimethyl but-2-ynedioate to yield products C and D. Then an intramolecular reaction occurs in both C and D to give E and F respectively. Finally E and F reacts with NaOH in water to give final products G and H. Draw the structural formulae for compounds A-H. Write mechanisms for reactions B \rightarrow C, C \rightarrow E.

7. And now the fun part :D. Just give the „systematic“ names to these compounds.



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