1. Which one of the following heterocycles does NOT show aromatic stabilization in the ionization state indicated?

A

В

C

D

2. What is the approximate energy of the aromatic stabilization of benzene? IDENTIFY THE VALUE AND THE CORRECT UNITS

10 cal/mol

35 kcal/mol

35 cal/mol

10 kcal/mol

Α

В

C

D

3. Which of the following compounds is MOST likely to lose H2O upon treatment with H_2SO_4 (a source of H^+)?

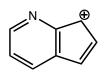


4. Which ONE of the following is NOT a 10-electron AROMATIC system?

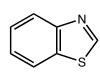


$$\mathbb{Z}_{\mathbb{S}}^{\mathbb{N}}$$

В



C



D

5. Identify the MAJOR product of the reaction shown?

6. What is the FINAL product of the reaction sequence shown below?

ÓН

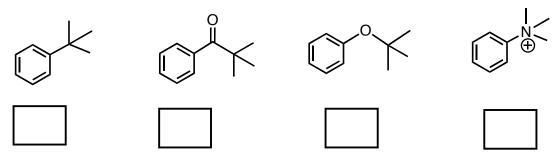
C

D

7. What is the FINAL product of the reaction sequence shown?

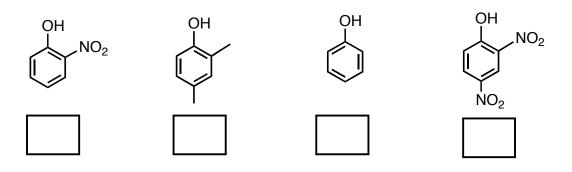
8. Which of the following reaction sequences does NOT give acetophenone as the MAJOR product?

9. Rank the following compounds in order of reactivity in $\underline{\text{ELECTROPHILIC}}$ aromatic substitution.

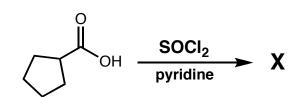


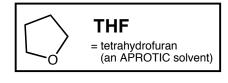
Rank the MOST REACTIVE as 1 and the LEAST REACTIVE as 4

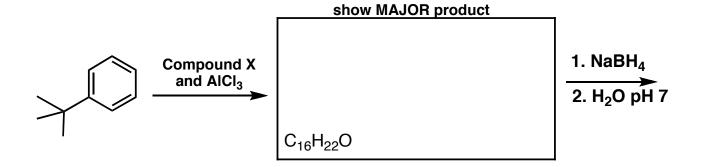
10. Rank the following in terms of acidity. Show the MOST ACIDIC as 1 and the LEAST ACIDIC as 4.



11. (12 points) Give the structures of the compounds in the boxes.







⊕ ⊖ Na NH ₂ in THF	

1. 0	
2. H ₂ O pH 7	
	C ₂₀ H ₃₂ O ₂

Make sure that the molecular formulas match your answer wherever they are provided!

score

12. (18 points) Design a synthesis of compound Z.

The ONLY carbon-containing starting materials that you can use are shown in the square brackets next to the target. You may use any other common reagents (e.g. oxidants, reductants, Lewis acids, metals, and thionyl chloride) and solvents. NO need to show mechanisms!

Note: A retrosynthetic analysis will be useful for figuring this problem out.

Name

- 13. (18 points) Nitrosobenzene undergoes electrophilic aromatic substitution (EAS) when treated with nitric acid and sulfuric acid. (This question continues on p.9 and 10.)
- a) (12 points) DEDUCE whether the nitroso group is "ortho/para" OR "meta" directing by comparing the mechanisms for para and meta substitution.

For full credit you must show the detailed stepwise mechanism, including all arrows, the structure of the electrophile and all of the resonance structures for the key intermediates. Be sure to show all three steps in the EAS reaction.

Mechanism for para substitution:

13 a) (contd.)

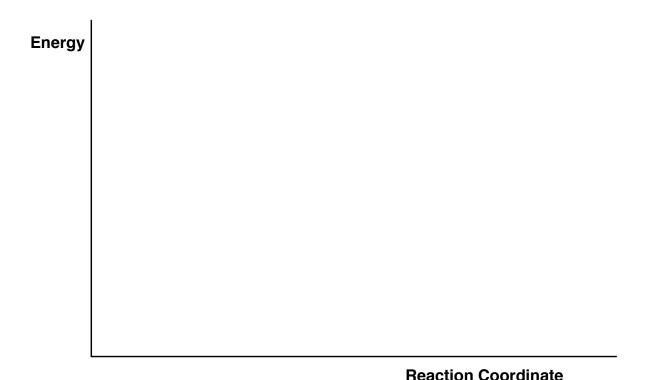
Mechanism for meta substitution

Name		
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13. (contd. 6 points) b) Assuming that the OVERALL reaction is slightly EXOTHERMIC – construct an energy diagram for the EAS reaction of nitrosobenzene leading to the para– and meta-substituted products.

The diagram MUST show:

- The relative energies of the starting material, the σ -complexes and the products.
- The energies of activation for the rate determining steps of the para- and metadirecting EAS processes.



Note: No need to draw out structures – just labels such as SM, PROD, $\sigma\text{-COMPLEX}.$ are fine.

score

15. (16 points) Provide the detailed stepwise mechanisms for the following transformations.

a.

b.

excess H₂SO₄ as a source of H⁺



15. Contd. (16 points) Provide the detailed stepwise mechanisms for the following transformations.

Hint: Write out the Lewis structure for the compound above the arrow.

Name

The following represents part of a synthetic route to Naproxen® (sold under the tradename Aleve), which is an important anti-inflammatory agent.

Provide the best reagents for each transformation (more than one step may be required). No need to show mechanisms!



score

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	it.hr/period		8 K	7 14.007	Z	NITROGEN	5 30.974	Ь	HOSPHORUS	3 74.922	As	_	51 121.76	Sb	ANTIMONY TELLURIUM	33 208.98	Bi	BISMUTH			
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			2 	6.941 4 9.0122	Be	BERYLLIUM	12 24.305	Mg	SODIUM MAGNESIUM 3 IIIB 4 INB 5	19 39.098 20 40.078 21 44.866 22 47.867 23 50.842 24 51.896 25 54.838 26 55.845 27 58.883 28 58.683 29 63.546 30 65.39 31 69.723 32 72.64 33 74.822 34 78.86 35 79.804 36 83.80	Ca		37 85.468 38 87.62 39 88.906 40 91.224 41 92.906 42 95.94	Sr	RUBIDIUM STRONTIUM YTTRIUM	55 13291 56 137.33	Ba	BARIUM	(226)	Ra	RADIUM
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- 1	D	EKIO			2			С			4			ĸ			9			7	_

However three auch elements (Th, Ps, do have a characteristic terrestrial composition, and for these an aboritot tabulated.

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THANUM	CERIUM	PRASEODYMU	W NEODYMIUM	PROMETH	HUM	MANARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULUM	YTTERBIUM	LUTETIUM
TINIDE															
(227)	90 232.04	91 231.04	92 238.03	93 (2	37) 9.	4 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (259)	103 (262)
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Important Electronegativity Values

Н						
2.2						
Li	Be	В	O	N	0	F
1.0	1.6	1.8	2.5	3.0	3.4	4.0
Na	Mg	Al	Si	Р	S	CI
0.9	1.3	1.6	1.9	2.2	2.6	3.2
K						Br
8.0						3.0
	-					1
						2.7

BLANK FOR ROUGH WORK