

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353

Version

1

WEDNESDAY MARCH 12th, 2025

Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

ENTER YOUR NAME, STUDENT I.D. NUMBER AND VERSION NUMBER 1 ON **BOTH**
YOUR MULTIPLE CHOICE ANSWER SHEET AND WRITTEN ANSWER SHEET.

The exam consists of **Parts 1 - 7**, each of which should be attempted. Some Parts provide you with a choice of questions, e.g. answer any 5 out of 6. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. **Parts 1 - 4** are to be answered on the multiple choice answer sheet, and **Parts 5 - 7** are to be answered **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1 - 4 consist of a series of multiple choice questions numbered **1 - 34** which are to be answered by completely blackening out the appropriate space, A, B, C, D or E on the answer sheet for that specific question. Use a soft pencil only, **not ink**. In some cases it is required that you indicate **multiple** items for a complete and/or correct answer by blackening out **more than one space**. In some other cases, more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out **both** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be **erased cleanly**.

A periodic table with atomic numbers and atomic weights and spectroscopic data tables and 2 pages of scrap paper for rough work are included with this examination paper.

Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**. Absolutely no other electronic devices are allowed.

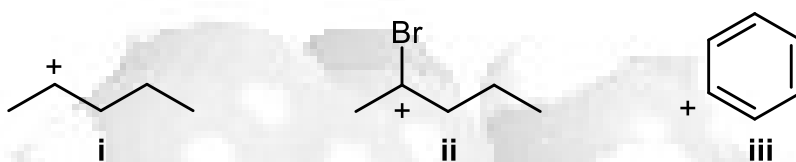
16% PART 1: RELATIVE PROPERTIES**ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

Arrange the items in each of the questions in this section in **DECREASING ORDER** (*i.e.* greatest first) with respect to the indicated property.

Use the following code to indicate your answers.

- | | | | |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

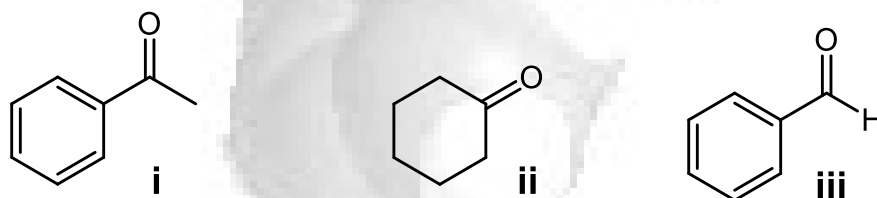
1. The relative stability of each of the following:



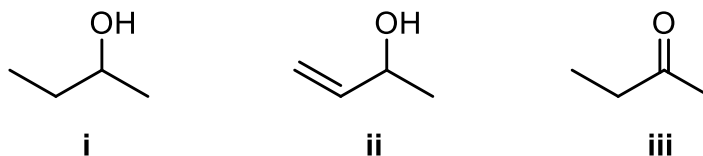
2. The relative reactivity of each of the following towards 1-hexene:



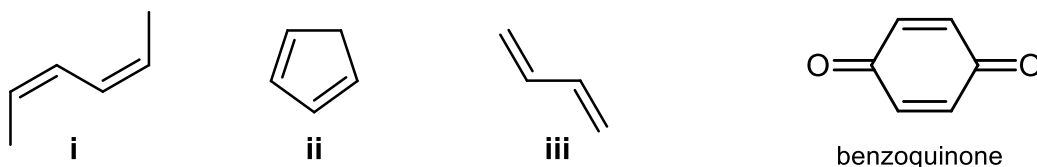
3. The number of alpha-H in each of the following:



4. The relative yields of each of the following products from the reaction of but-3-en-2-one with H₂ / Pd:



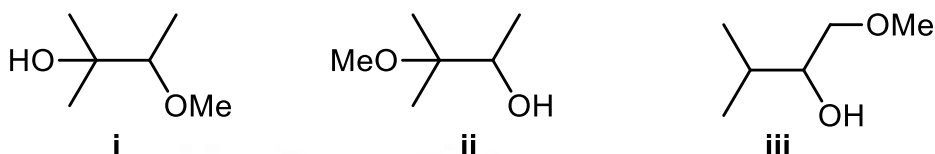
5. The relative reactivity towards benzoquinone (shown below) of each of the following:



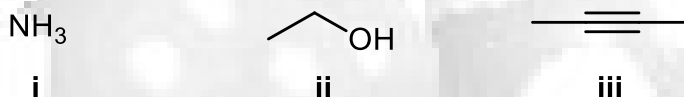
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

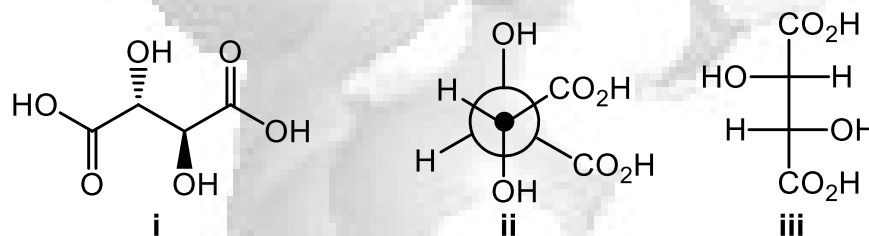
6. The relative yields of each of the following products from the reaction of 2-methyl-2-butene with MCPBA followed by sodium methoxide in methanol:



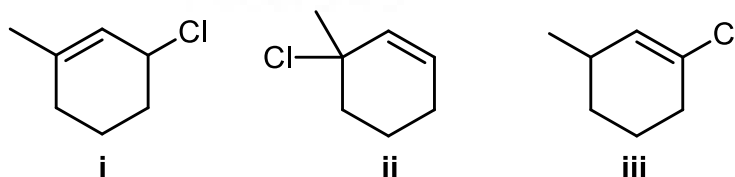
7. The relative pK_a of the most acidic proton in each of the following:



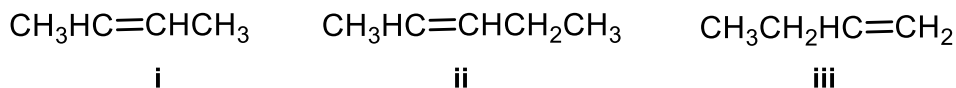
8. The specific rotations of each of the following molecules given that (R,R)-2,3-dihydroxybutanedioic acid $[\alpha]_D = +12.7$:



9. The relative yields of each of the following from the reaction of 2-methylcyclohexa-1,3-diene with HCl at 0 °C:

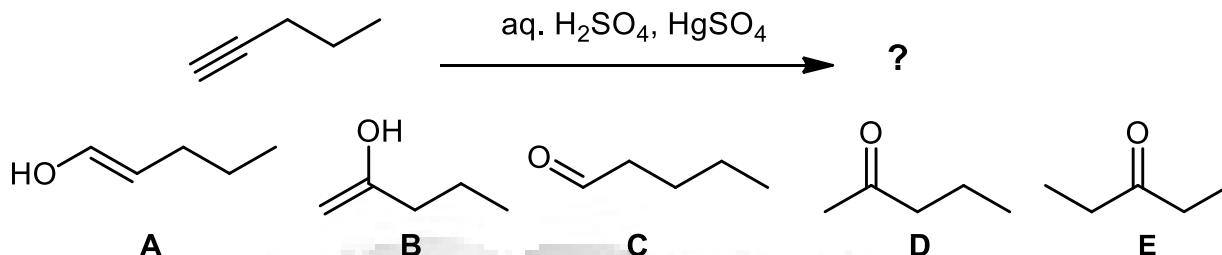


10. The relative yields of an alkan-2-ol from the reactions of each of the following with (1) BH_3/THF then (2) aq. $H_2O_2/NaOH$:

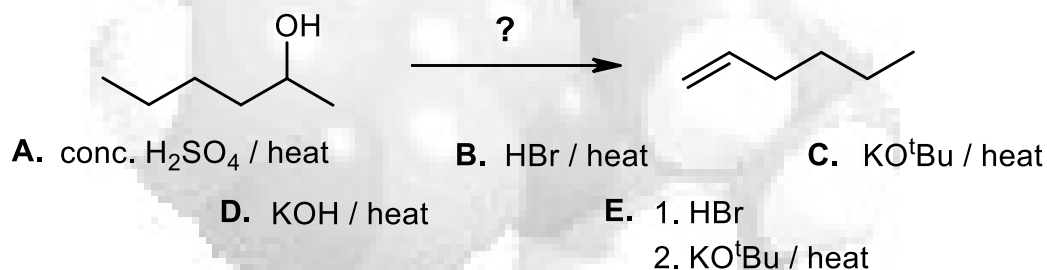


14% PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS**ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**For each of questions 11-18 select the **MISSING** component (starting material, product or reagents) required in order to **BEST** complete each reaction scheme.

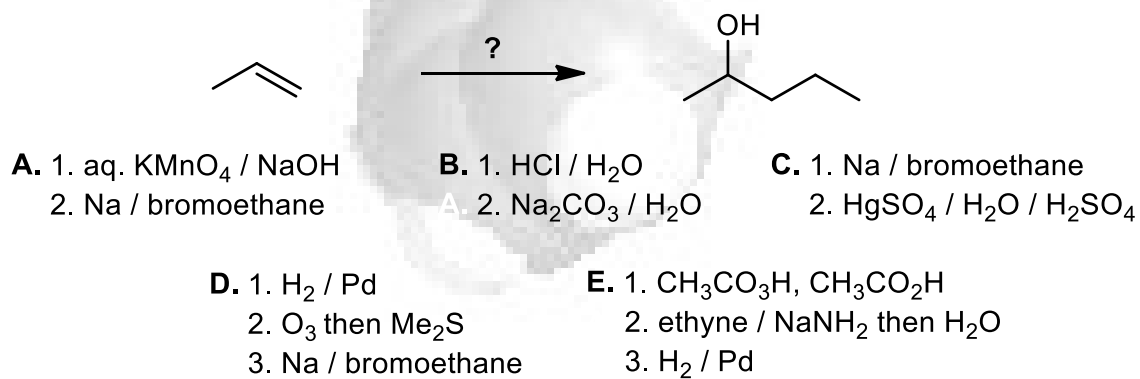
11.



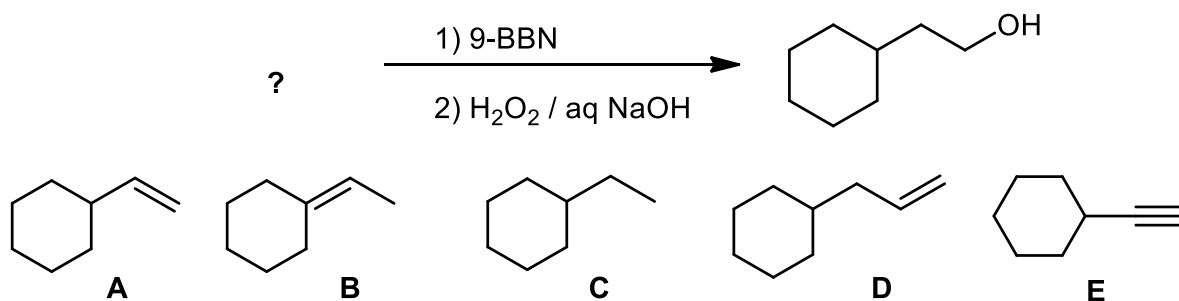
12.



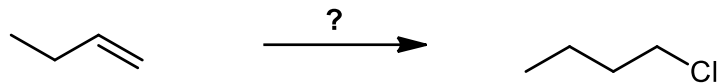
13.



14.



15.



A. 1. HBr / uv
2. Cl₂

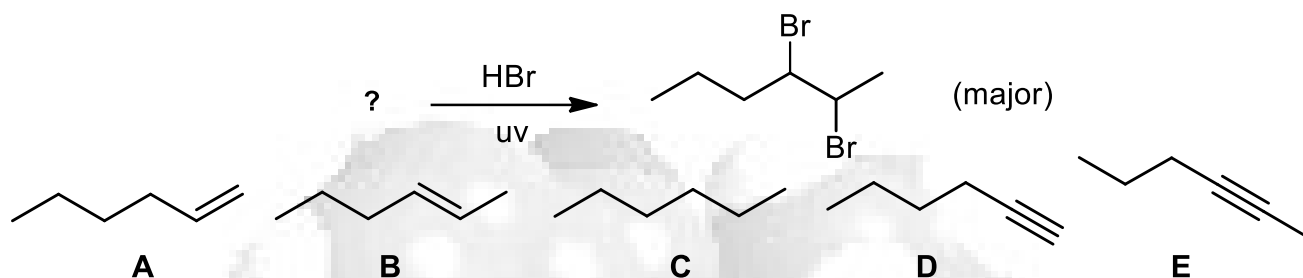
B. HCl / uv

C. 1. BH₃-THF
2. aq NaOH / H₂O₂
3. SOCl₂ / Et₃N

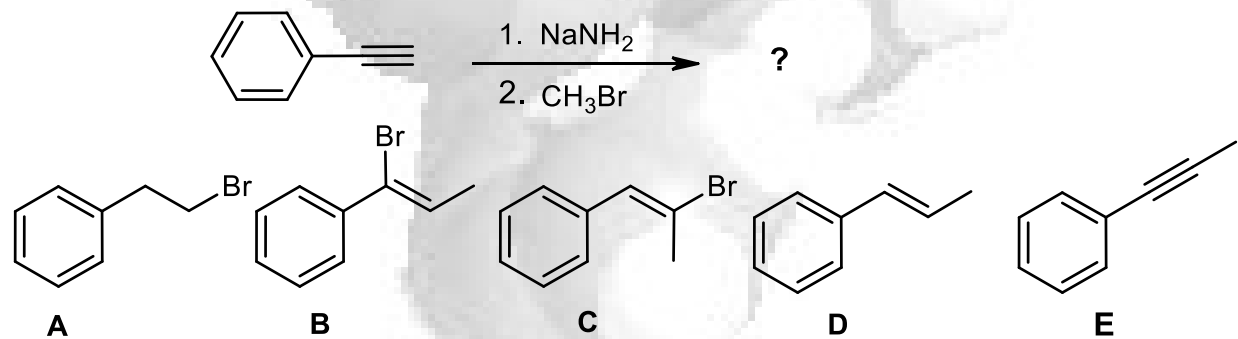
D. 1. H₂ / Pd
2. Cl₂ / uv

E. 1. Cl₂ / uv
2. H₂ / Pd

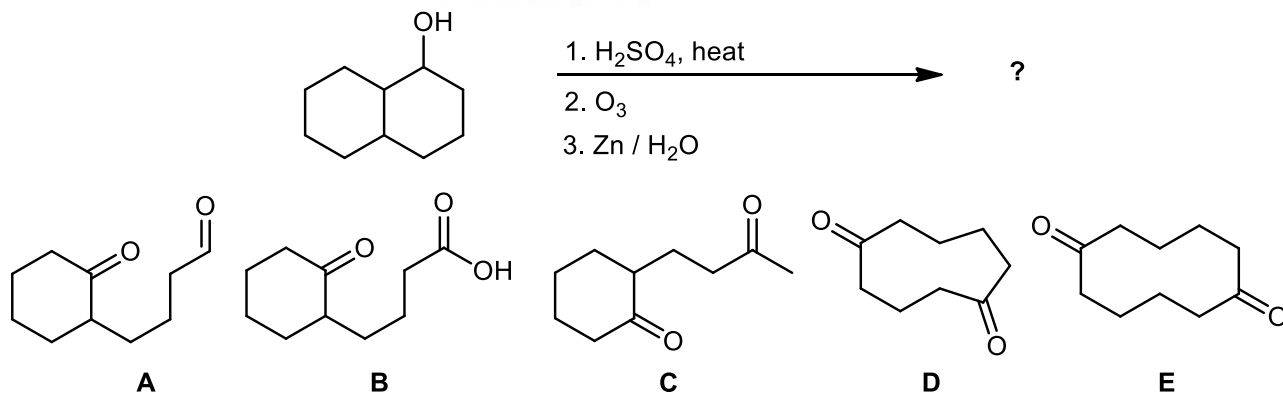
16.



17.

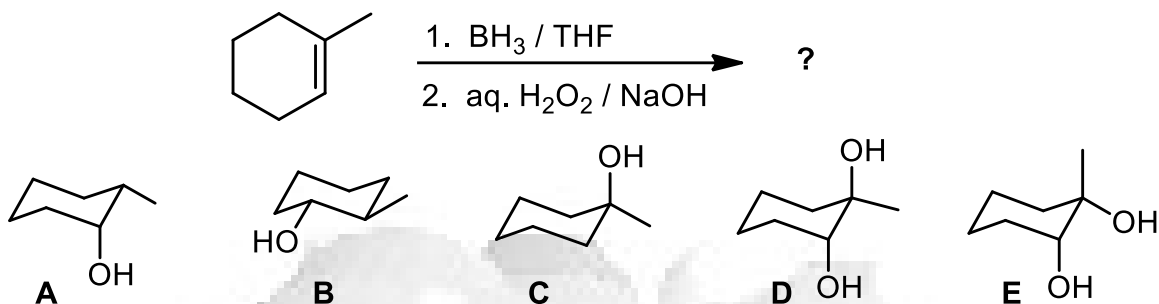


18.

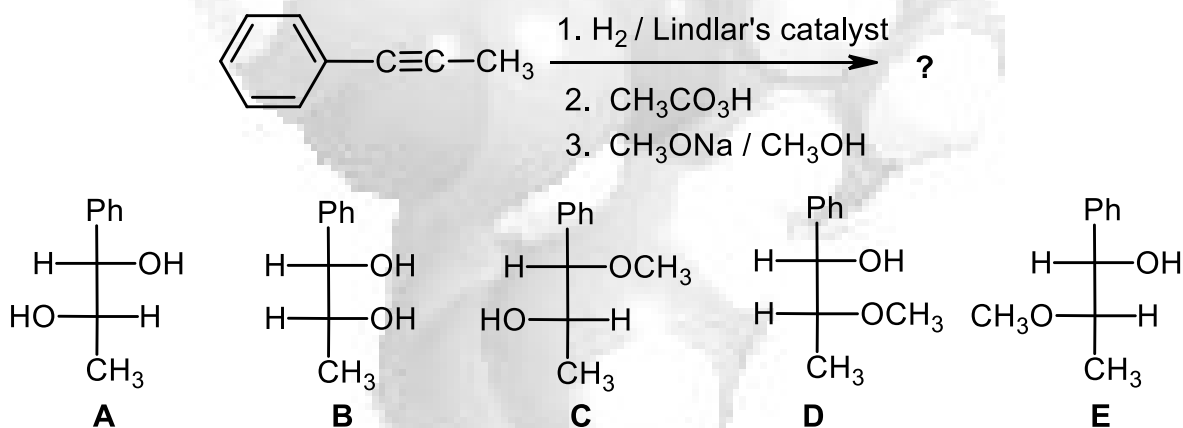


18% **PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS****ANSWER ANY SIX (6) OF QUESTIONS 19-25.**For each of the questions 19-25, select the structure required to **BEST** complete the reaction shown.

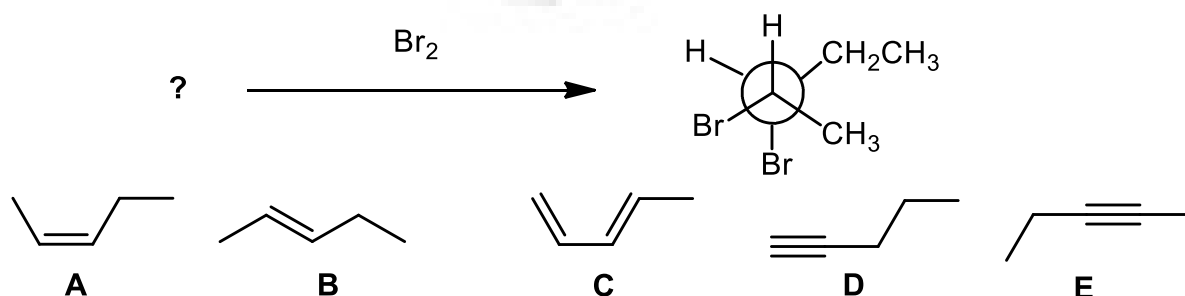
19.



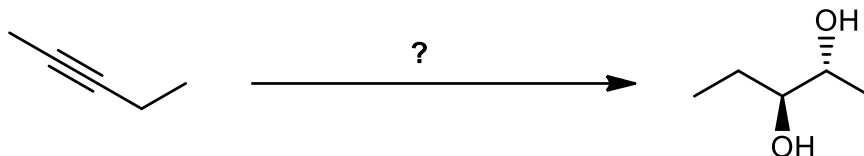
20.



21.

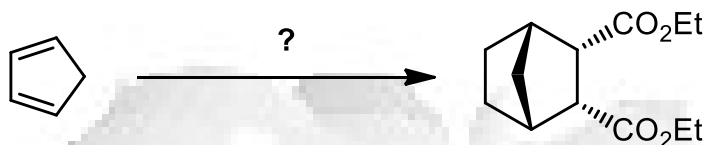


22.



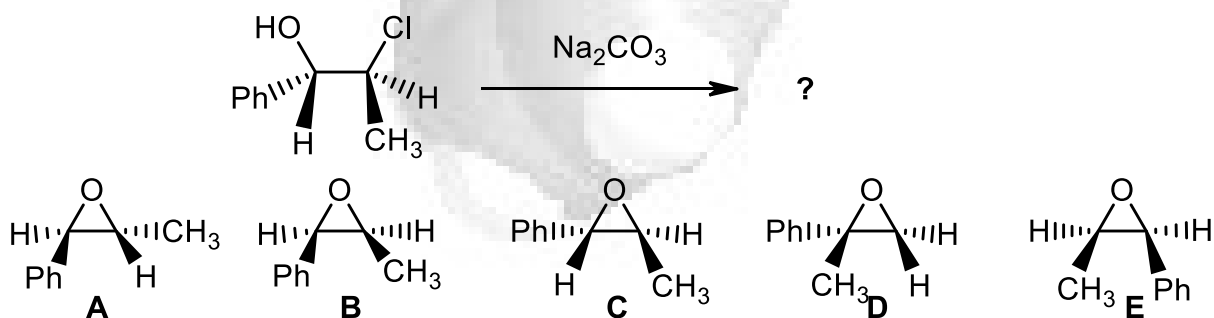
- A. 1) H_2 , Lindlar's cat. 2) KMnO_4 , aq KOH , 0°C
 B. 1) H_2 , Lindlar's cat. 2) MCPBA 3) aq H_2SO_4
 C. 1) Na / NH_3 2) KMnO_4 , aq KOH , 0°C
 D. 1) Na / NH_3 2) $\text{Br}_2 / \text{H}_2\text{O}$ 3) Na_2CO_3 , heat
 E. 1) NaNH_2 2) aq. H_2SO_4 , HgSO_4

23.

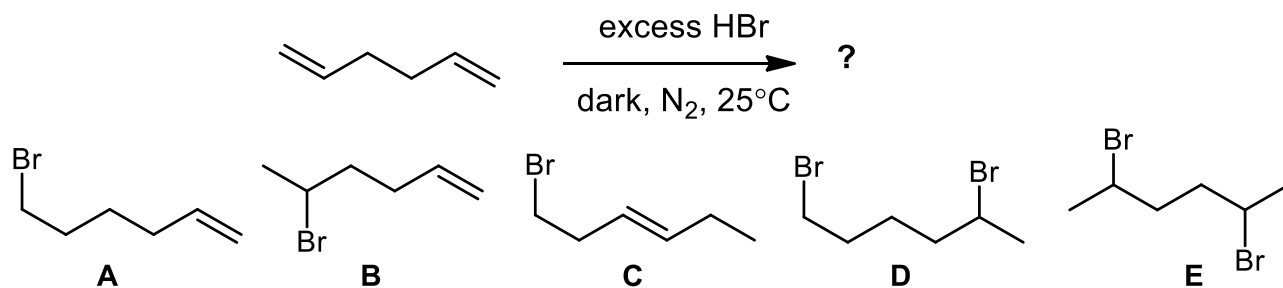


- A. 1. $\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$ / heat 2. Na / NH_3
 B. 1. $\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$ / heat 2. H_2 / Pd
 C. 1. $\text{EtO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{Et}$ / heat 2. $\text{H}_2 / \text{Lindlar's cat.}$
 D. 1. $\text{EtO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{Et}$ / heat 2. H_2 / Pd
 E. $\text{EtO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{Et}$ / heat

24.



25.

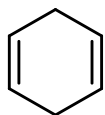


16% **PART 4: PI SYSTEMS**

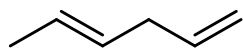
ANSWER ANY EIGHT (8) of the questions 26 - 34.

For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

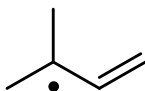
26. Which of the following contain conjugated systems? (select all that apply)



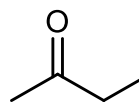
A



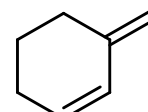
B



C

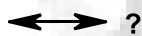
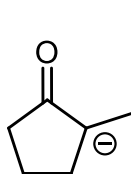


D

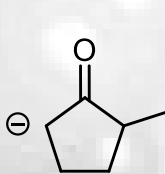


E

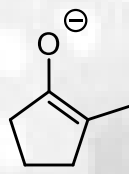
27. Which of the following systems are resonance contributors of the anion shown below? (select all that apply)



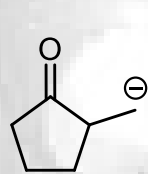
?



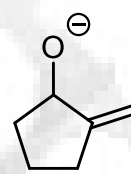
A



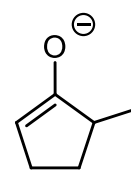
B



C



D

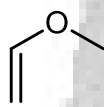


E

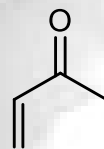
28. Which of the following is the **most** reactive towards 1,3-butadiene:



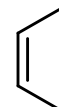
A



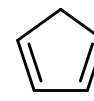
B



C

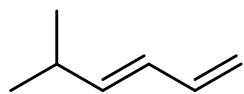


D

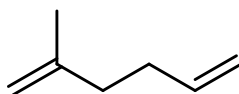


E

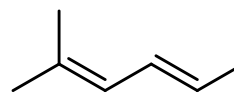
29. Which of the following isomers has the **least exothermic** heat of hydrogenation?



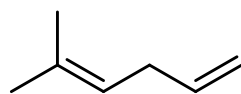
A



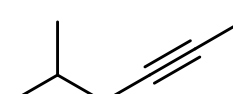
B



C

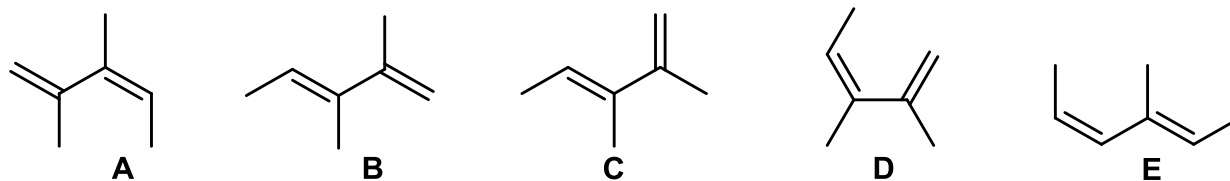


D

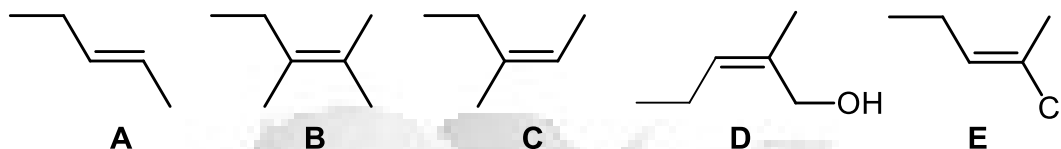


E

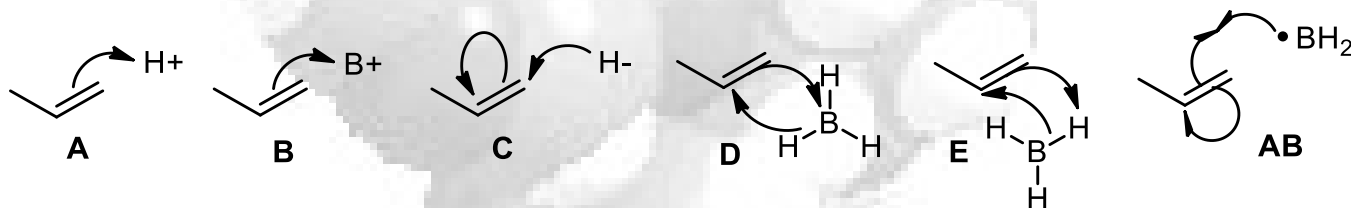
30. Which of the following molecules is the *s-trans* form of (3E)-2,3-dimethylpenta-1,3-diene?



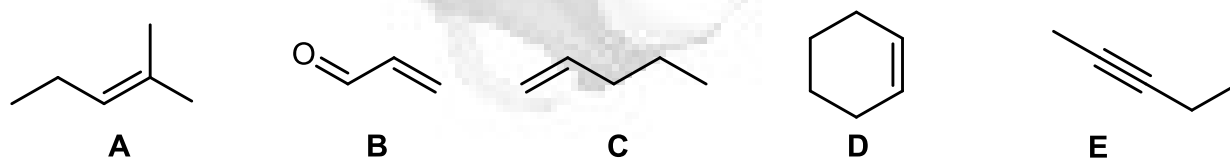
31. Which of the following molecules would be named as *Z*? (select all that apply)



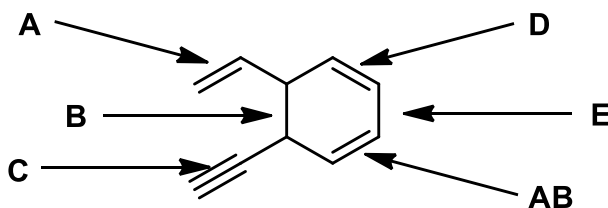
32. Which of the following **best** represents a step in the mechanism of the reaction of propene with BH_3 ?



33. Which of the following systems react with H_2 / Lindlar's catalyst (select all that apply)?



34. Which of the **CC** bonds indicated below is the **shortest**?



15% PART 5: SYNTHESIS

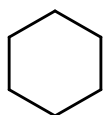
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

ANSWER THREE (3) QUESTIONS, ONE FROM EACH OF 5.1, 5.2 AND 5.3

**Design an efficient synthesis of THREE (3) of the following target molecules
SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE
REAGENT REQUIRED AND PRODUCT OF EACH STEP**

DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

Allowed starting materials and reagents:



and / or

Any hydrocarbons with 3 or less C atoms

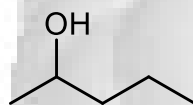
Any solvents or reagents that do not contribute carbon atoms to the final structure.

A

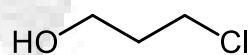
or

B

5.1

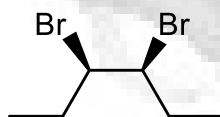


or

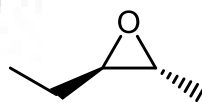


AND

5.2

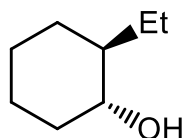


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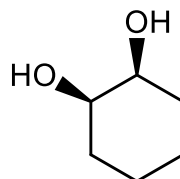


AND

5.3



or



10% PART 6: MECHANISMS

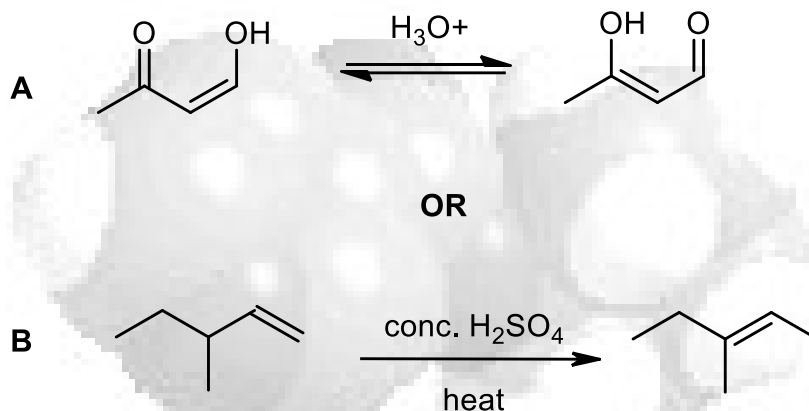
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE FROM PART 6.1 AND ONE FROM PART 6.2

Draw curly arrow mechanisms to explain the following reactions / observations.

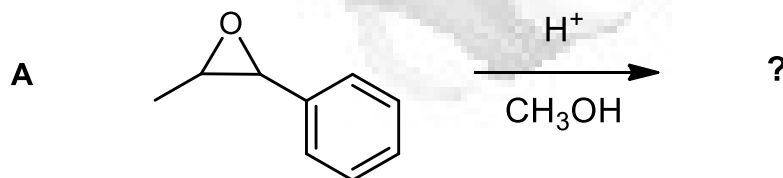
No other reagents are required.

6.1. Show the mechanism for **one** of the following reactions:

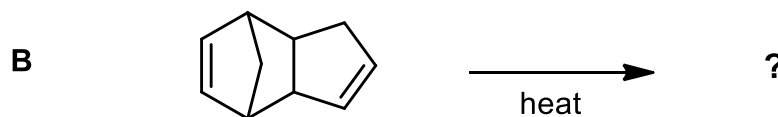


AND

6.2. Show the mechanism for **one** of the following reactions to predict the major product :



OR



11% PART 7: STRUCTURE DETERMINATION

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

Use the information in the following paragraph to answer the questions below.

None of the materials **A - F** are chiral.

A, $C_6H_{14}O$, IR = 3500 cm^{-1} . When **A** was reacted with hot conc. H_2SO_4 , **B**, C_6H_{12} was the major product. **B** was found to give a colourless solution when reacted with Br_2 in chloroform from which compound **C**, $C_6H_{12}Br_2$ was isolated as the major product. When **C** was then reacted with excess hot KOH / EtOH, **D** was obtained as the major product.

D spectral data : H-NMR / ppm: 5.00 (m, 2H) and 1.92 (s, 3H); ^{13}C -NMR / ppm 143, 113, and 21; IR : 1601 cm^{-1} MS : $M^+ = 82$.

When **D** was heated in a sealed tube with ethene, it gave **E** as the major product. **E** also gave a colourless solution with Br_2 in chloroform and 4 peaks in the ^{13}C -NMR. Subsequent reaction of **E** with ozone followed by zinc in aqueous acid work up gave octan-2,7-dione.

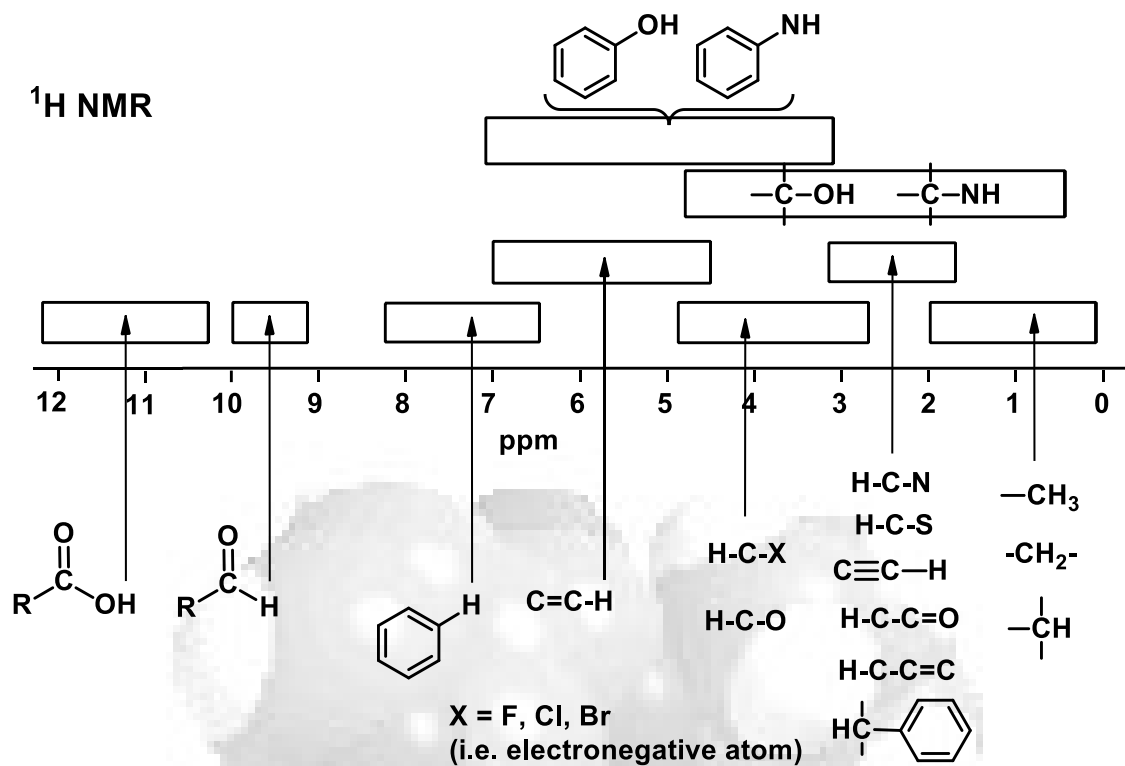
The reaction of **E** with H_2 / Pd gave **F**, C_8H_{16} .

- Identify the compounds **A - F** (structures are sufficient)

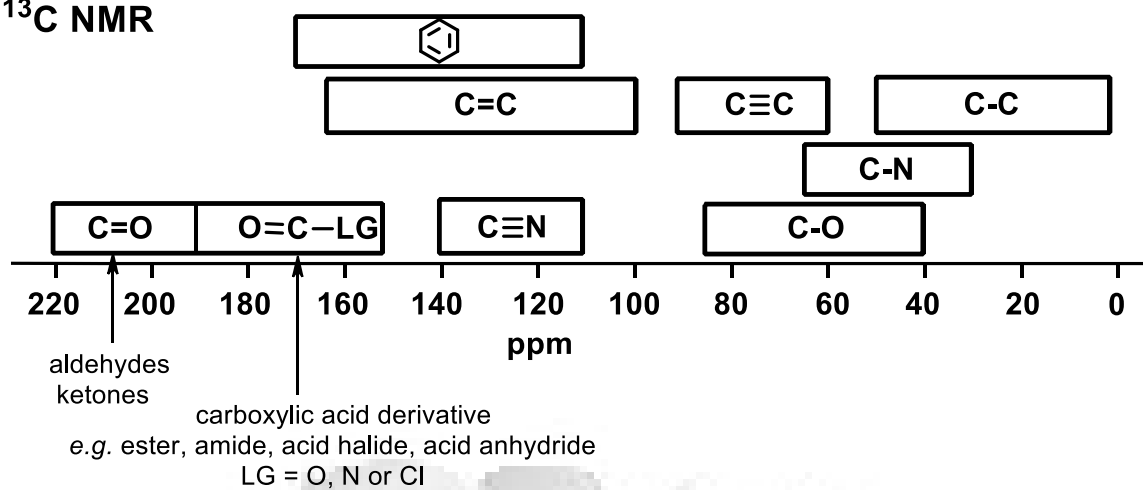
Draw the structures of A to F. Include 3D stereochemistry where appropriate.

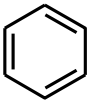
What is the IUPAC name for D ?

***** THE END *****

SPECTROSCOPIC TABLES **^1H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
$-\text{CH}_3$				
$\text{R}-\text{C}-$	0.9	1.4	1.5	$\text{sp}^3\text{C}-\text{OH}$ 1-5
$\text{R}-\text{C}=\text{C}$	1.6	2.3	2.6	$\text{sp}^3\text{C}-\text{NH}$ 1-3
$\text{R}-\text{C}(=\text{O})-$	2.1	2.4	2.5	$\text{C}\equiv\text{CH}$ 2.5
$\text{R}-\text{N}$	2.2	2.5	2.9	$\text{C}=\text{C}-\text{H}$ 4.5-6.5
$\text{R}-\text{C}_6\text{H}_5$	2.3	2.7	3.0	$\text{H}-\text{C}_6\text{H}_5$ 6.5-8
$\text{R}-\text{Br}$	2.7	3.3	4.1	$\text{R}-\text{C}(=\text{O})\text{H}$ 9-10
$\text{R}-\text{Cl}$	3.1	3.4	4.1	$\text{R}-\text{C}(=\text{O})\text{OH}$ 9-12
$\text{R}-\text{O}-$	3.3	3.4	3.7	

¹³C NMR**¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C(=O)—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-25	—C(=O)OH 160-185
 110-170		—C—Cl 15-30	—C=O—H 190-210
		—C—OH 45-75	>C=O 190-220
		—C—N 30-65	$\text{—C}\equiv\text{N}$ 110-140

INFRA-RED GROUP ABSORPTION FREQUENCIES

	<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
C-H	Alkanes (stretch)	3000-2850	3.33-3.51	s	
	-CH ₃ (bend)	1450 and 1375	6.90 and 7.27	m	
	-CH ₂ - (bend)	1465	6.83	m	
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne (stretch)	ca. 3300	ca.3.03	s	
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C-C	Alkane	not usually useful			
C=C	Alkene	1680-1600	5.95-6.25	m-w	
	Aromatic	1600-1400	6.25-7.14	m-w	
C≡C	Alkyne	2250-2100	4.44-4.76	m-w	
C=O	Aldehyde	1740-1720	5.75-5.81	s	
	Ketone	1725-1705	5.80-5.87	s	
	Carboxylic acid	1725-1700	5.80-5.88	s	
	Ester	1750-1730	5.71-5.78	s	
	Amide	1700-1640	5.88-6.10	s	
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride	1800	5.55	s	
C-O	Alcohols, Ethers, Esters,				
	Carboxylic acids	1300-1000	7.69-10.0	s	
O-H	Alcohols, Phenols				
	Free	3650-3600	2.74-2.78	m	
	H-Bonded	3400-3200	2.94-3.12	m	
	Carboxylic acids (2)	3300-2500	3.03-4.00	m	
N-H	Primary and secondary amines	ca. 3500	ca. 2.86	m	
C≡N	Nitriles	2260-2240	4.42-4.46	m	
N=O	Nitro (R-NO ₂)	1600-1500	6.25-6.67	s	
		1400-1300	7.14-7.69	s	
C-X	Fluoride	1400-1000	7.14-10.0	s	
	Chloride	800-600	12.5-16.7	s	
	Bromide, Iodide	<600	>16.7	s	

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.

PERIODIC TABLE

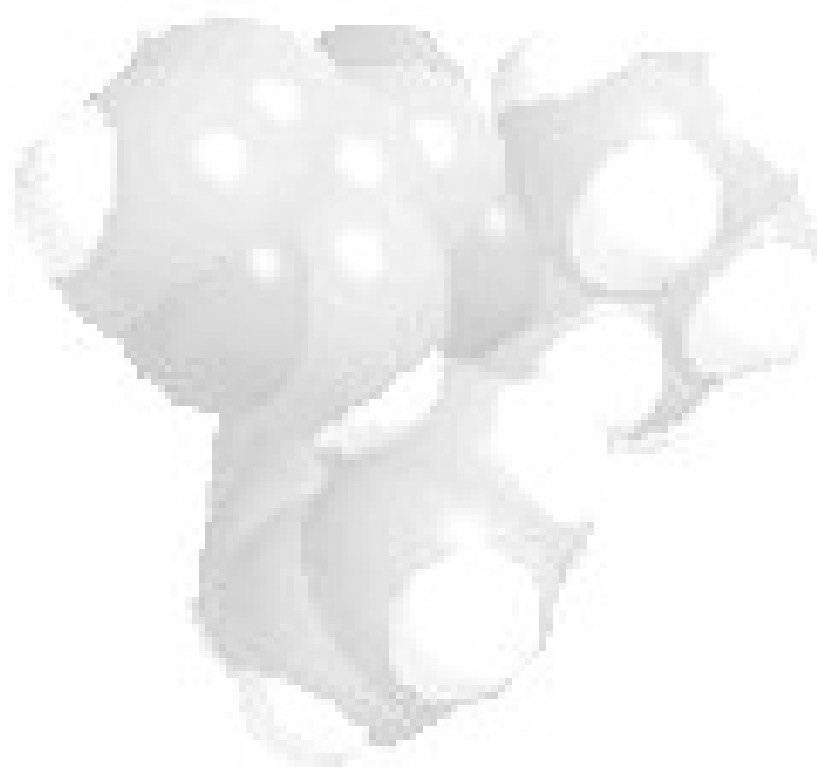
																18	
1											13	14	15	16	17	2	
1A											3A	4A	5A	6A	7A	8A	
1 H 1.008											B 10.81	C 12.01	N 14.01	O 16.00	F 19.00	He 4.003	
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89** Ac (227)	104 Rf (261)	105 Ha (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)							

Lanthanides *

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Actinides **

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