NAME:_____ Section:_____ Student Number:_____

Fall 2019 **Chemistry 2600 Midterm 2** ____/ 50 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 6 pages of questions in addition to this cover page and a periodic table.
2) You have also been given a 6 page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE!** If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) You may use a molecular model kit and ruler. You may not have any papers or other written materials in your model kit.
4) Electronic devices (including calculators) are **not** allowed for this test.
5) If your work is not legible, it will be given a mark of zero.
6) For full credit, explanations must be complete. In many cases, complete explanations include drawing relevant structures. If delocalization of electrons is invoked, the relevant resonance structures must be drawn.
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 2 hours to complete this test.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 5:00pm Mountain Time on Wednesday, November 6th, 2019 (the day after the test). I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/50 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____

Course: CHEM 2600 (Organic Chemistry II)
Semester: Fall 2019
The University of Lethbridge

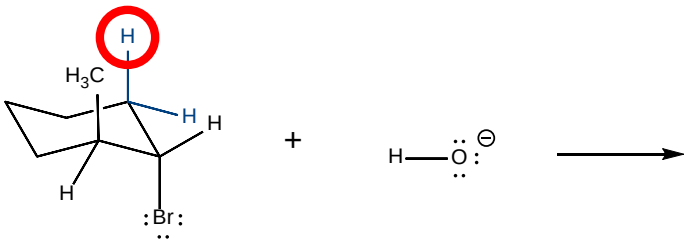
Question Breakdown

Q1	/ 8
Q2	/ 4
Q3	/ 4
Q4	/ 8
Q5	/ 7
Q6	/ 11
Q7	/ 8

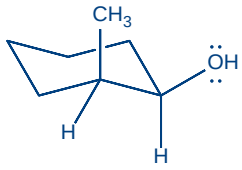
Total	/ 50

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1. Consider the following reaction mixture: **[8 marks]**



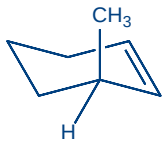
(a) Draw the major organic product obtained if the reaction proceeds according to an S_N2 mechanism. Briefly explain why this isomer is obtained. *[4 marks]*



cis-2-methylcyclohexanol

S_N2 reactions proceed via backside attack, inverting the configuration of the electrophilic site.

(b) Draw the major organic product obtained if the reaction proceeds according to an E2 mechanism at high temperature. Briefly explain why this isomer is obtained. *[4 marks]*



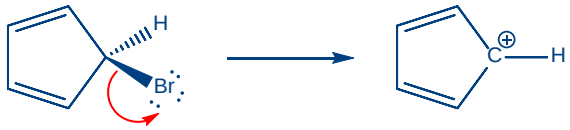
3-methylcyclohexene

In an E2 reaction, the base removes a β-hydrogen that is antiperiplanar to the leaving group. The only such hydrogen atom in the starting material shown has been circled on the diagram at the top of the page.

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2. 5-Bromo-1,3-cyclopentadiene is a bad substrate for S_N1 or E1 reactions. Why? **[4 marks]**

For full credit, your answer must include the structure of 5-bromo-1,3-cyclopentadiene and any other relevant structures. If you need a hint, start drawing the mechanism for an S_N1 or E1 reaction involving 5-bromo-1,3-cyclopentadiene.

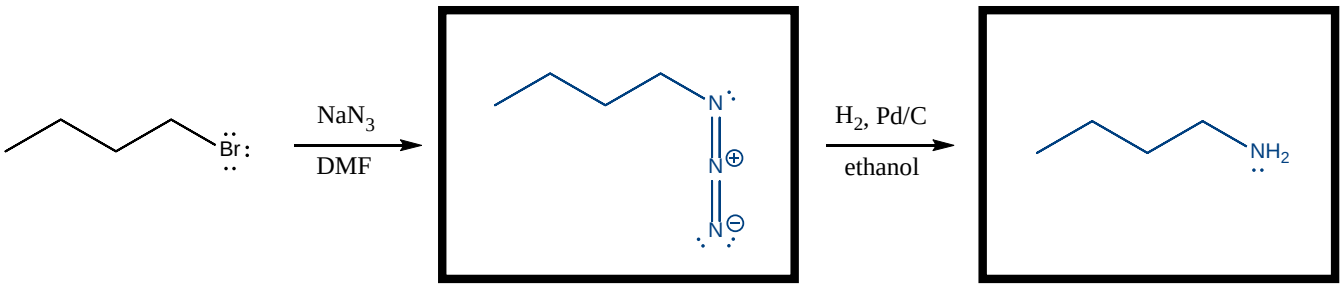


The first step in an S_N1 or E1 mechanism is departure of the leaving group, generating a carbocation (shown above for 5-bromo-1,3-cyclopentadiene). If the carbocation is not reasonably stable, this step will not occur and the reaction will therefore not proceed.

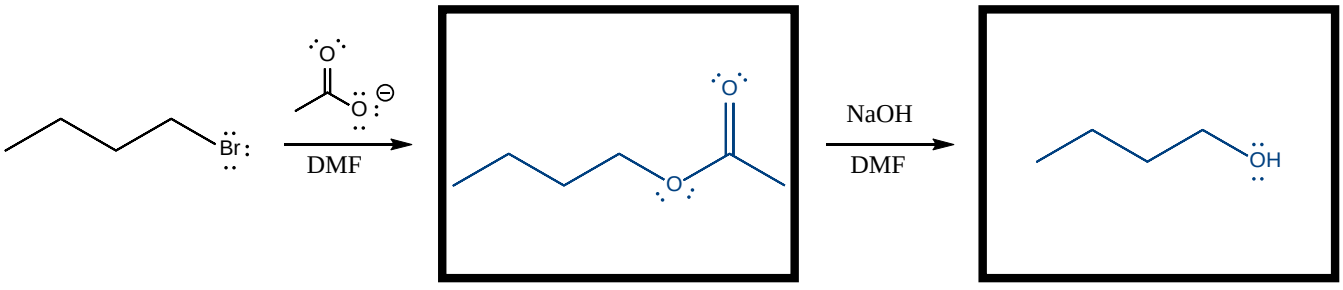
The carbocation shown above is **antiaromatic** so it is not expected to form.

3. For each of the following multi-step processes, draw the major organic product of each step in the appropriate box. **[4 marks]**

(a)



(b)

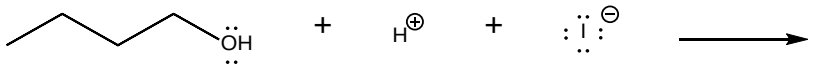


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4. Indicate whether or not you would expect to see a significant amount of reaction according to each mechanism type by circling 'yes' or 'no'. In the bottom row of each table, justify your answer by: **[8 marks]**

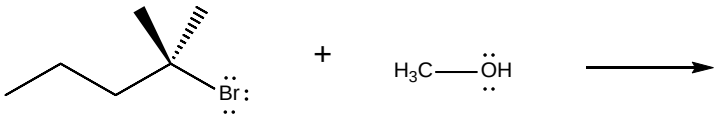
- For each 'yes', drawing the organic product(s) that will be observed.
- For each 'no', briefly explaining why you expect little-to-no reaction.

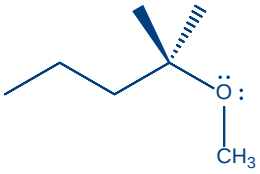
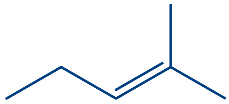
(a)



SN1? yes / no	**SN2?** yes / no	**E1?** yes / no	**E2?** yes / no
The carbocation intermediate formed after the alcohol was protonated and left would be 1° (and therefore unstable).		The carbocation intermediate formed after the alcohol was protonated and left would be 1° (and therefore unstable). Also, there is no base available to remove a β-hydrogen.	E2 reactions require a strong base, and there is no base available in this system.

(b)



SN1? yes / no	**SN2?** yes / no	**E1?** yes / no	**E2?** yes / no
 *Credit was also given for protonated product.*	S_N2 reactions require a strong nucleophile and methanol is a weak nucleophile. Also, the electrophilic site is not accessible (since it is 3°).	 *E1 reactions give the thermodynamic product as the major product.*	E2 reactions require a strong base, and methanol is a weak base.

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5. A kinetic study of the reaction between an alkyl chloride (RCl) and a non-nucleophilic base ($base$) provided the following data: **[7 marks]**

$[RCl]$ $\left(\frac{mol}{L}\right)$	$[base]$ $\left(\frac{mol}{L}\right)$	Rate of reaction $\left(\frac{mol}{L \cdot s}\right)$
1	1	10
1	2	20
2	4	80
4	4	160

(a) Write the rate law for this reaction. Include a numerical value and units for k. *[4 marks]*
Clearly identify the order of each reactant.

Step 1: Write generic rate law

$rate = k[RCl]^m[base]^n$

Step 2: Solve for n by comparing rows 1 and 2

$\frac{20\frac{mol}{L\cdot s}}{10\frac{mol}{L\cdot s}} = \frac{k\left(1\frac{mol}{L}\right)^m\left(2\frac{mol}{L}\right)^n}{k\left(1\frac{mol}{L}\right)^m\left(1\frac{mol}{L}\right)^n}$ therefore $2 = \frac{\left(2\frac{mol}{L}\right)^n}{\left(1\frac{mol}{L}\right)^n}$ therefore $2 = 2^n$ therefore $n = 1$

Step 3: Solve for m by comparing rows 3 and 4 (or any other pair that isn't rows 1 and 2)

$\frac{160\frac{mol}{L\cdot s}}{80\frac{mol}{L\cdot s}} = \frac{k\left(4\frac{mol}{L}\right)^m\left(4\frac{mol}{L}\right)^0}{k\left(2\frac{mol}{L}\right)^m\left(4\frac{mol}{L}\right)^0}$ therefore $2 = \frac{\left(4\frac{mol}{L}\right)^m}{\left(2\frac{mol}{L}\right)^m}$ therefore $2 = 2^m$ therefore $m = 1$

Step 4: Solve for rate constant (k) using any row

$10\ \frac{mol}{L\cdot s} = k\left(1\ \frac{mol}{L}\right)^1\left(1\ \frac{mol}{L}\right)^1$ therefore $10\ \frac{mol}{L\cdot s} = k\left(1\ \frac{mol}{L}\right)\left(1\ \frac{mol}{L}\right)$

therefore $k = \frac{6\frac{mol}{L\cdot s}}{\left(1\frac{mol}{L}\right)\left(1\frac{mol}{L}\right)}$ therefore $k = 10\frac{L}{mol\cdot s}$

Step 5: Answer question (i.e. write rate law)

$rate = 10\frac{L}{mol\cdot s}[RCl][base]$

(b) Did this reaction proceed via an S_N1, S_N2, E1 or E2 mechanism? Explain your choice. It must be clear why all three alternative options were rejected. *[3 marks]*

E2

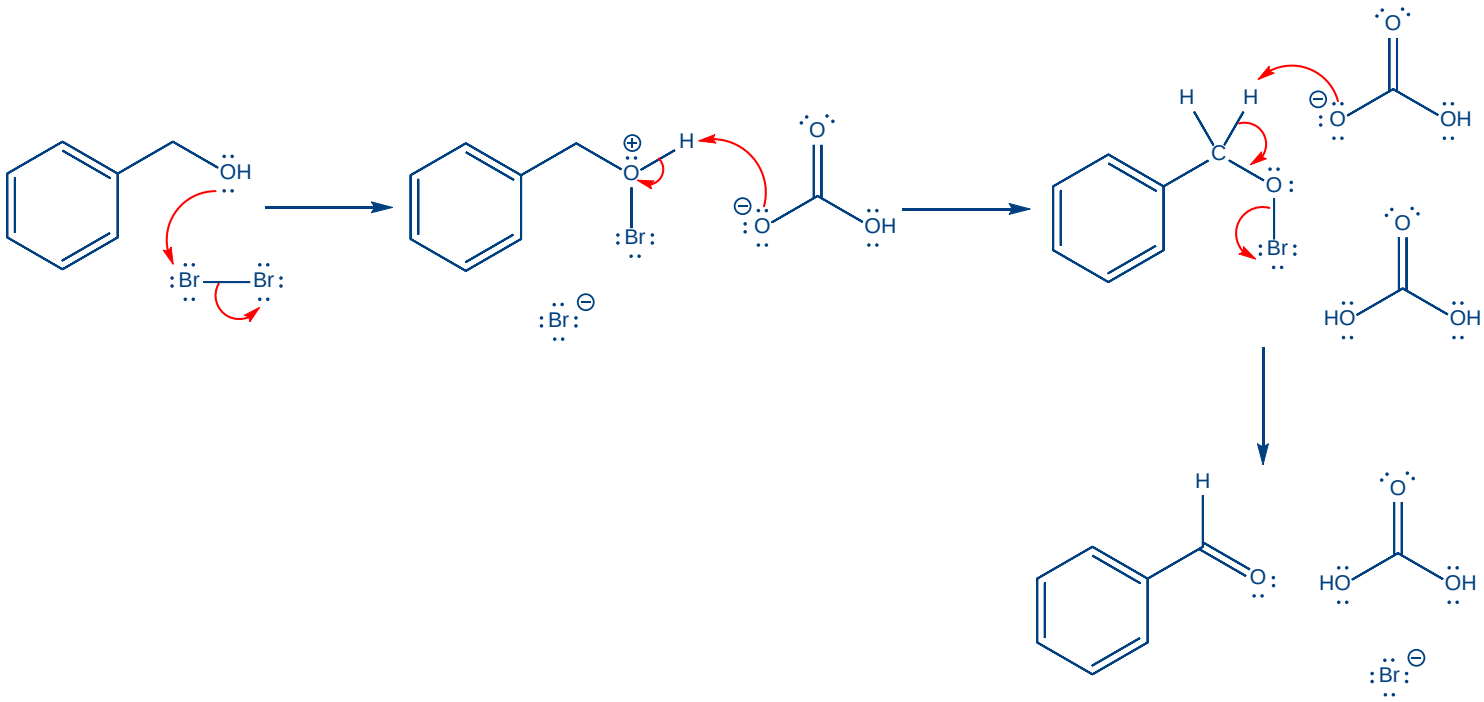
The reaction is second order therefore it cannot be E1 or S_N1 (both are first order).

There is no nucleophile ("non-nucleophilic base") therefore it cannot be a substitution reaction (cannot be S_N1 or S_N2).

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6. **[11 marks]**

(a) Draw a reasonable mechanism for the following reaction. *[5 marks]*



Notes: Br^- is a very very weak base. It cannot deprotonate anything in this mechanism. $NaHCO_3$ is not a strong enough base to deprotonate an alcohol, but it can deprotonate O^+. Overall, two Br^- and two H_2CO_3 were produced in addition to the aldehyde. I showed each as a product in the step in which it was generated.

(b) Briefly explain how you would use each of the following spectroscopic methods to determine whether or not this reaction had gone to completion. *[6 marks]*
Your answers should address how you would monitor for both reactant and product.

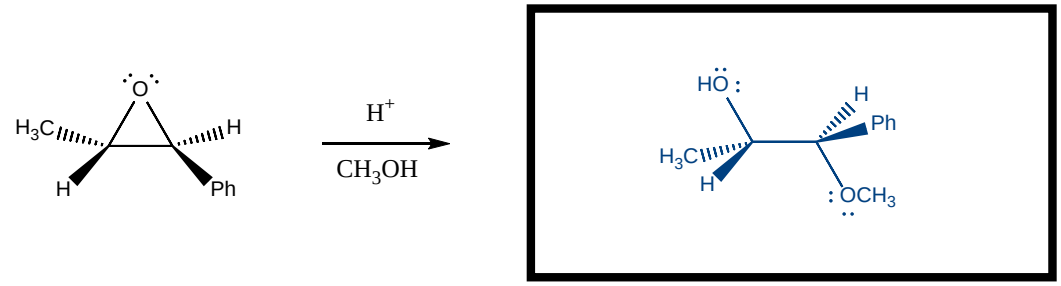
i. ^{1}H NMR
- The reactant would give a sharp singlet at ~4.5 ppm (for CH_2O) and a broad singlet (for OH) that exchanges with D_2O. These peaks would disappear as reactant was consumed.
- The product would give a sharp singlet at 9-10 ppm for the aldehyde hydrogen.

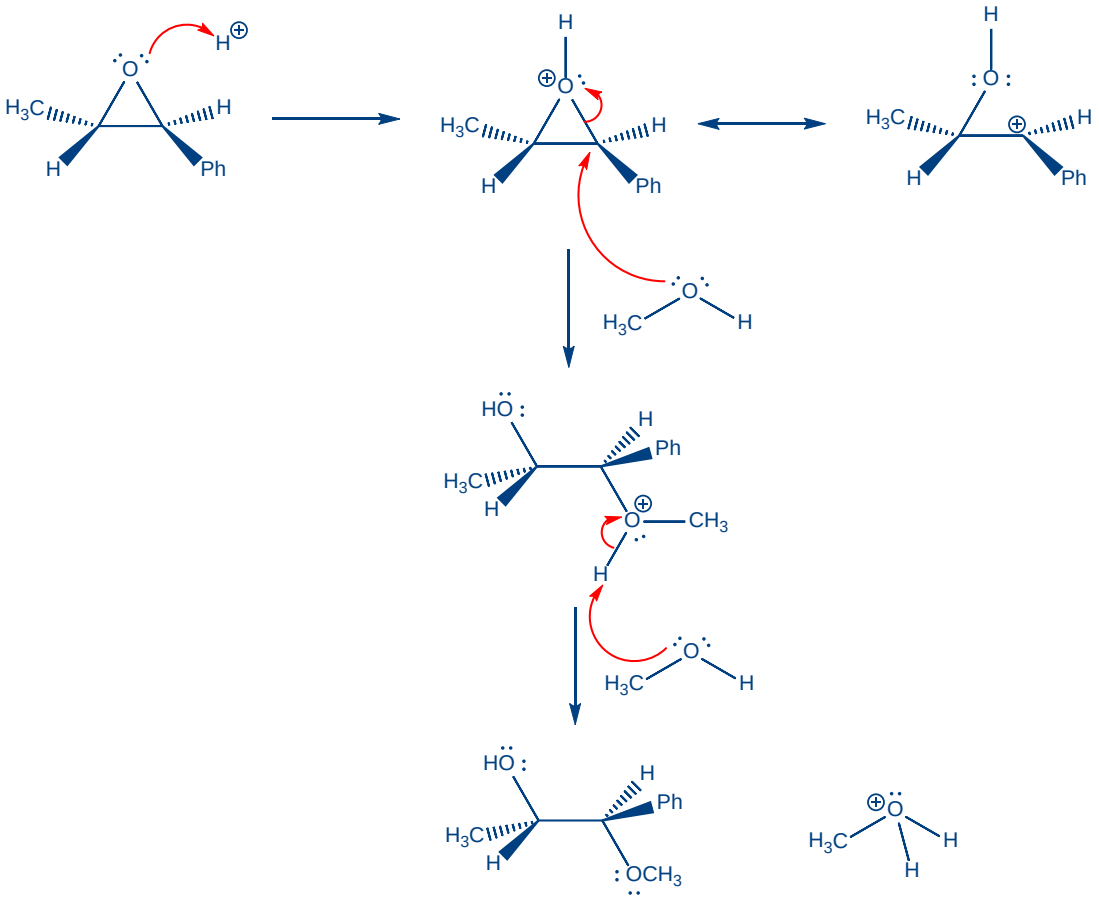
ii. ^{13}C NMR
- The reactant would give a peak at ~50-80 ppm (for CH_2O). This peak would disappear as reactant was consumed.
- The product would give a peak at 170-200 ppm for the C=O conjugated to an aromatic ring.

iii. IR
- The reactant would give a broad peak at ~3300 cm^{-1} for the O-H bond. This peak would disappear as reactant was consumed.
- The product would give a strong peak at 1680-1715 cm^{-1} for the aldehyde C=O conjugated to an aromatic ring.

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7. Draw a reasonable mechanism for the following reaction and draw the final product in the box provided. *Clearly show any relevant stereochemistry of the final product.* **[8 marks]**





Notes: In an acid-catalyzed reaction of a nucleophile with an epoxide, the nucleophile will attack at the carbon which would give the more stable carbocation (the benzylic carbon, in this case) because that carbon has the greater partial positive charge so it is the more electrophilic of the two carbons in the protonated epoxide..
Because the carbocation is only one resonance structure contributing to the average (along with the resonance structure that looks like a protonated epoxide), there is not free rotation so the configuration at the electrophilic carbon is inverted (as it would be in an S_N2 reaction).

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CHEM 1000 Standard Periodic Table

1												13	14	15	16	17	18
1.0079 **H** 1	**2**																4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)