

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.
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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

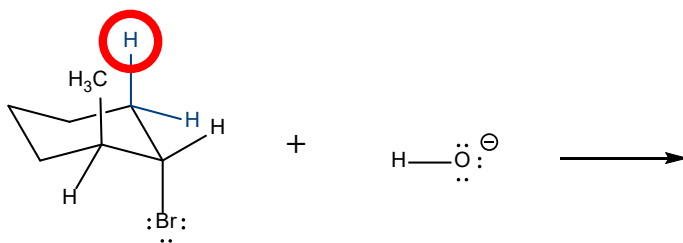
Q1	/ 8
Q2	/ 4
Q3	/ 4
Q4	/ 8
Q5	/ 7
Q6	/ 11
Q7	/ 8

Total	/ 50
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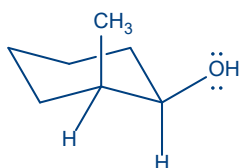
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1. Consider the following reaction mixture:

[8 marks]



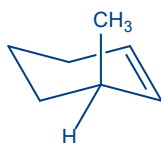
(a) Draw the major organic product obtained if the reaction proceeds according to an S_N2 mechanism. Briefly explain why this isomer is obtained. [4 marks]



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]

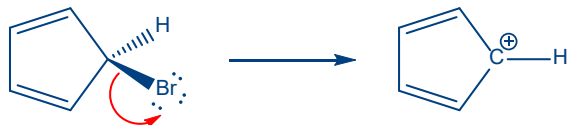


3-methylcyclohexene

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.

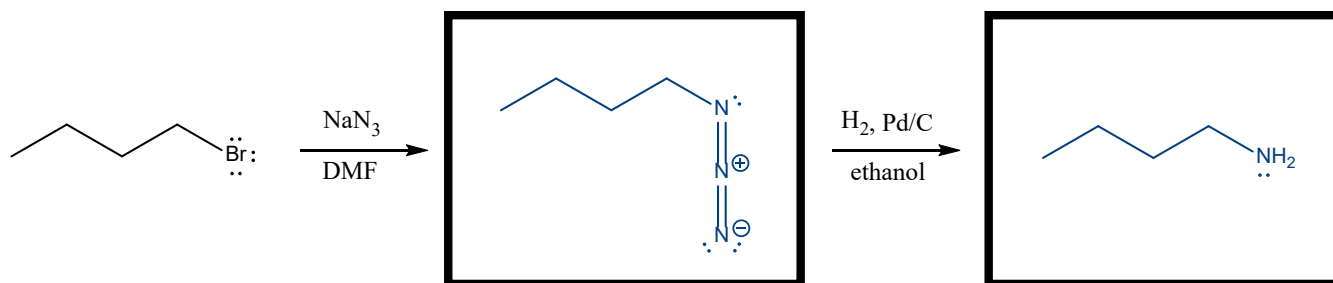


The first step in an S_N1 or $E1$ mechanism is departure of the leaving group, generating a carbocation (shown above for 5-bromo-1,3-cyclopentadiene). If the carbocation is not reasonably stable, this step will not occur and the reaction will therefore not proceed.

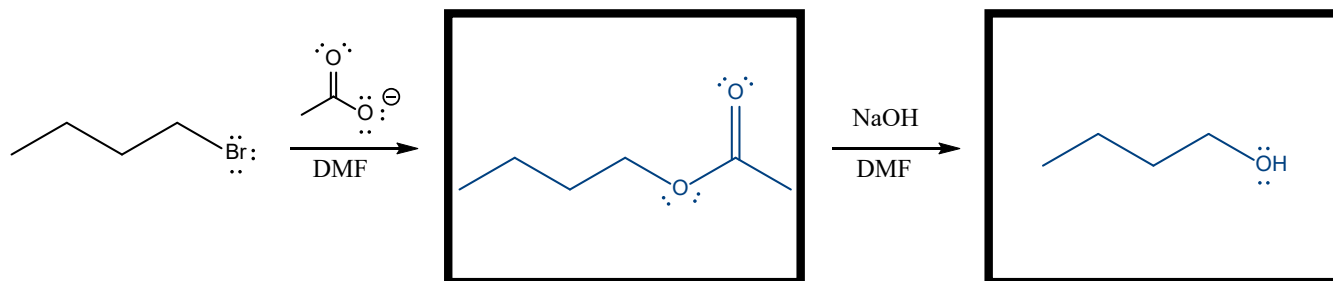
The carbocation shown above is antiaromatic so it is not expected to form.

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

(a)



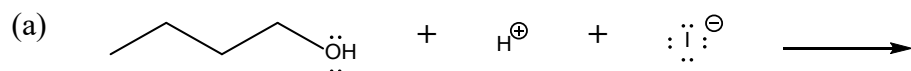
(b)




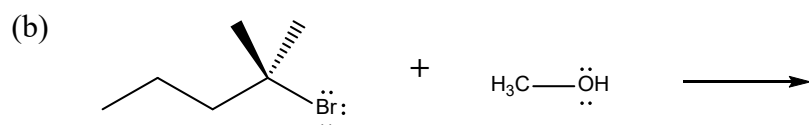
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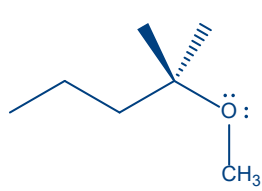
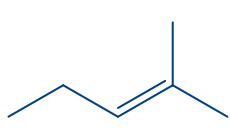
4. Indicate whether or not you would expect to see a significant amount of reaction according to each mechanism type by circling 'yes' or 'no'. In the bottom row of each table, justify your answer by: **[8 marks]**

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



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



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

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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]

$[RCl]$ ($\frac{mol}{L}$)	$[base]$ ($\frac{mol}{L}$)	Rate of reaction ($\frac{mol}{L \cdot s}$)
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

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

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

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

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

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

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

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]

$E2$

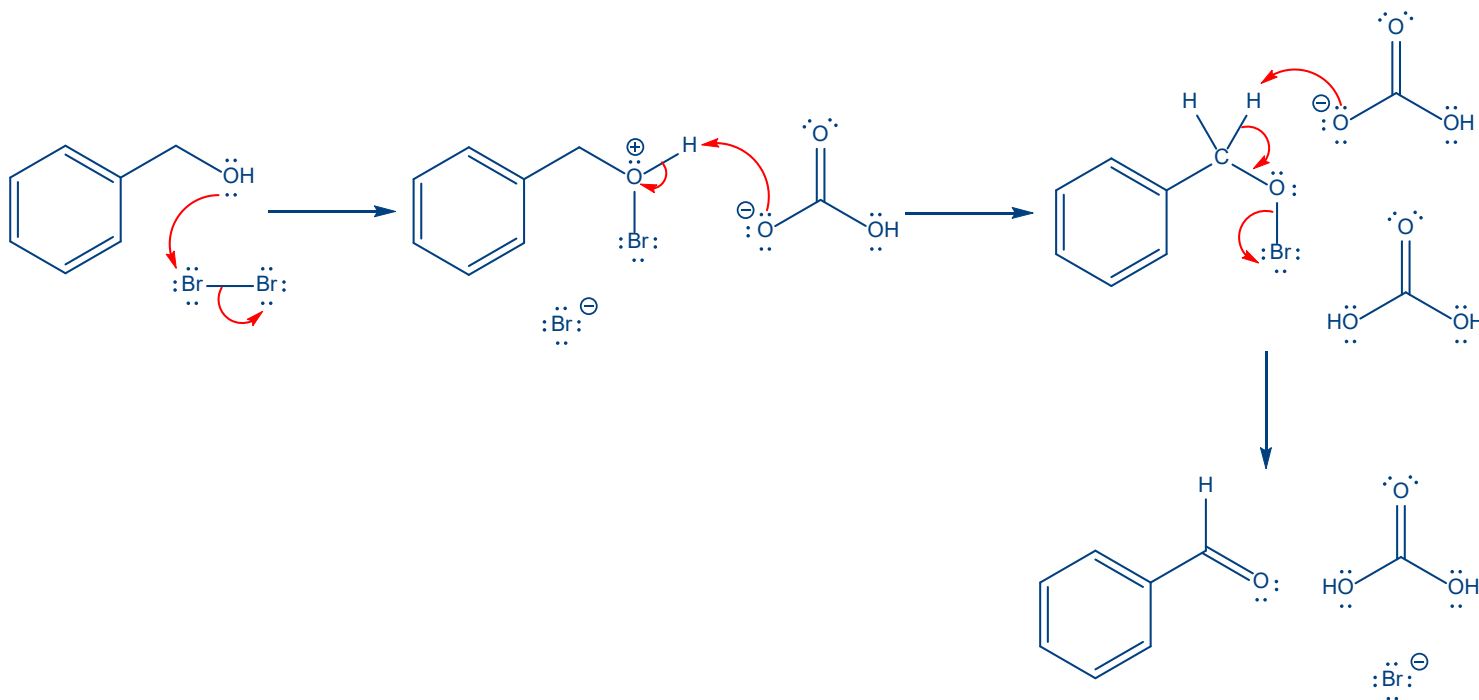
The reaction is second order therefore it cannot be $E1$ or S_N1 (both are first order).

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.
(a) Draw a reasonable mechanism for the following reaction.

[11 marks]
[5 marks]



Notes: Br⁻ is a very very weak base. It cannot deprotonate anything in this mechanism. NaHCO₃ is not a strong enough base to deprotonate an alcohol, but it can deprotonate O⁺. Overall, two Br⁻ and two H₂CO₃ 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. ¹H NMR

- The reactant would give a sharp singlet at ~4.5 ppm (for CH₂O) and a broad singlet (for OH) that exchanges with D₂O. These peaks would disappear as reactant was consumed.
- The product would give a sharp singlet at 9-10 ppm for the aldehyde hydrogen.

ii. ¹³C NMR

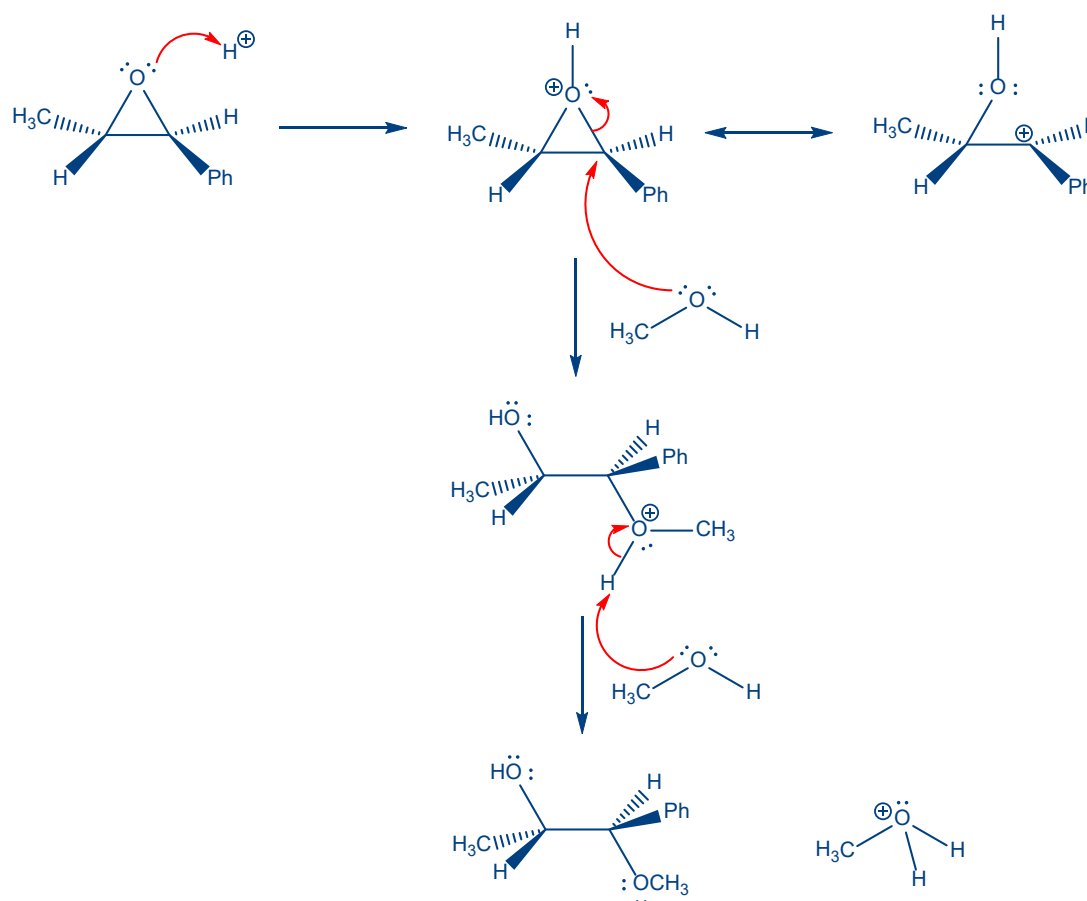
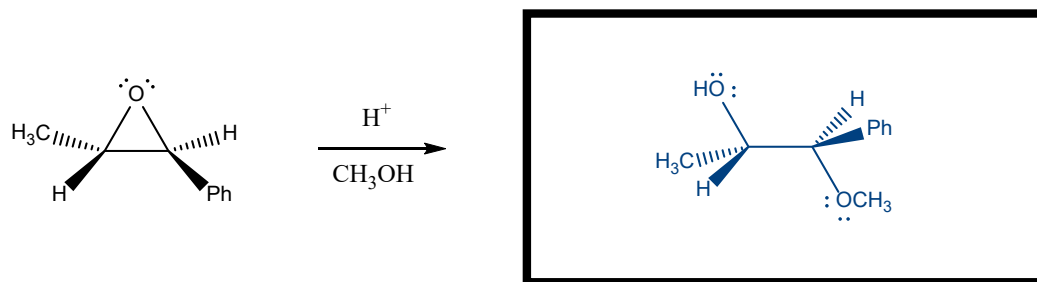
- The reactant would give a peak at ~50-80 ppm (for CH₂O). This peak would disappear as reactant was consumed.
- The product would give a peak at 170-200 ppm for the C=O conjugated to an aromatic ring.

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																	18																														
1.0079 H 1																			4.0026 He 2																												
2												13	14	15	16	17																															
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																														
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>138.906 La 57</td> <td>140.115 Ce 58</td> <td>140.908 Pr 59</td> <td>144.24 Nd 60</td> <td>(145) Pm 61</td> <td>150.36 Sm 62</td> <td>151.965 Eu 63</td> <td>157.25 Gd 64</td> <td>158.925 Tb 65</td> <td>162.50 Dy 66</td> <td>164.930 Ho 67</td> <td>167.26 Er 68</td> <td>168.934 Tm 69</td> <td>173.04 Yb 70</td> <td>174.967 Lu 71</td> </tr> <tr> <td>227.028 Ac 89</td> <td>232.038 Th 90</td> <td>231.036 Pa 91</td> <td>238.029 U 92</td> <td>237.048 Np 93</td> <td>(240) Pu 94</td> <td>(243) Am 95</td> <td>(247) Cm 96</td> <td>(247) Bk 97</td> <td>(251) Cf 98</td> <td>(252) Es 99</td> <td>(257) Fm 100</td> <td>(258) Md 101</td> <td>(259) No 102</td> <td>(262) Lr 103</td> </tr> </table>																		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
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Developed by Prof. R. T. Boéré (updated 2016)