

Chem 41c Midterm Exam

Stoltz, Spring 2007, April 27, 2007

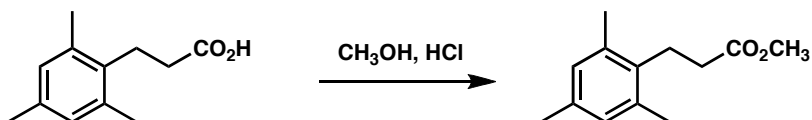
The exam begins when you turn to page 2. You have 55 minutes to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table at the front of the room or the one on the last page of this packet. You may not use any other materials. The exam has a total of 135 points. Your grade will be calculated based on 120 points (i.e., you have 15 bonus points built-in). (Also, remember that your midterm counts 60 points toward your final grade, e.g., 5 quiz points = 10 points here). Good luck.

There are 11 pages in this exam packet.

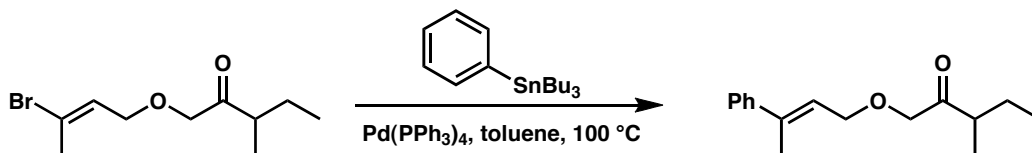
Name: _____

1. Predict the major non-volatile products (if any) of the following reactions or sequences. (5 points each)

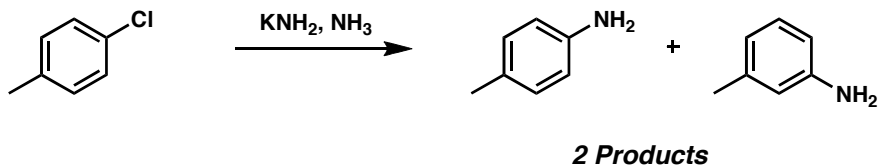
a.



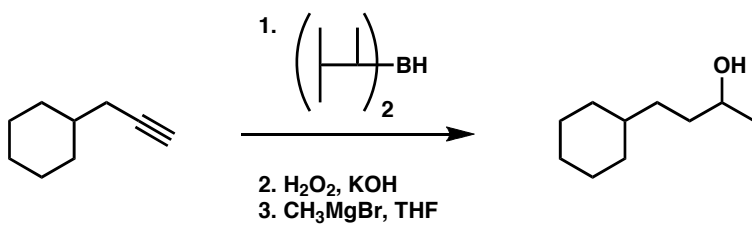
b.



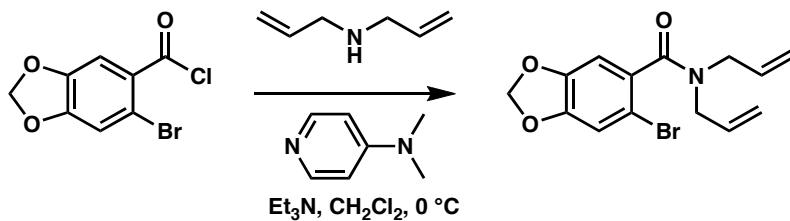
c.



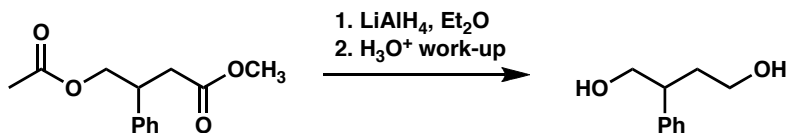
d.



e.

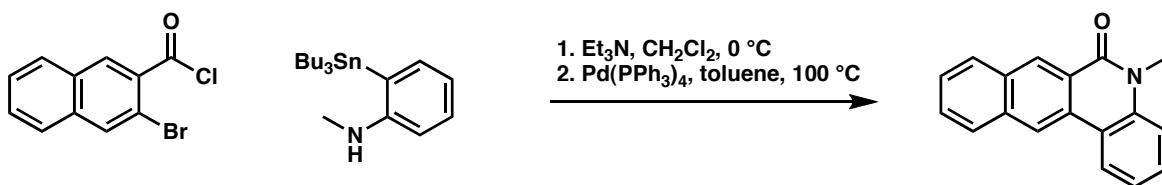


f.

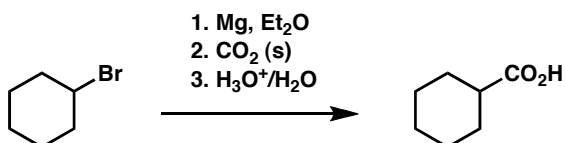


2. Provide reagents for the following transformations. They may be multistep processes (none are longer than 3 steps). (5 points each)

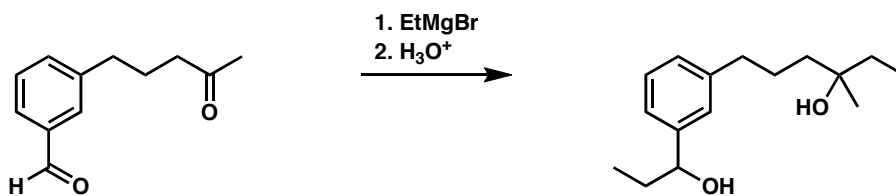
a.



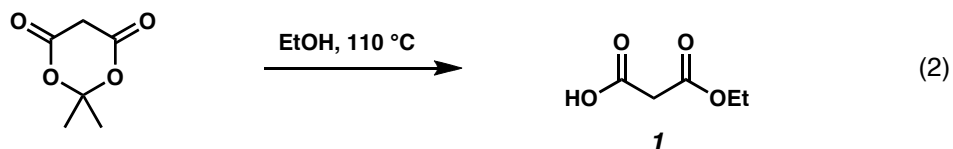
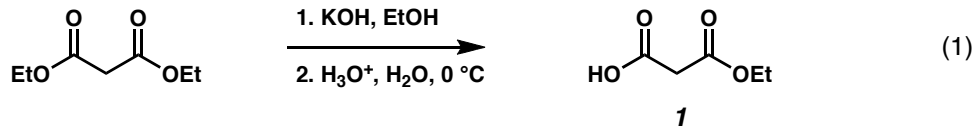
b.



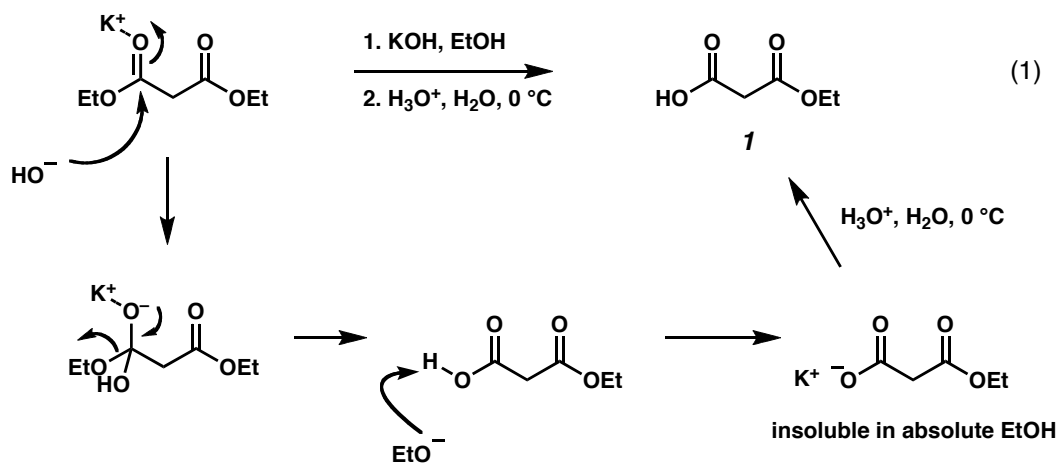
c.

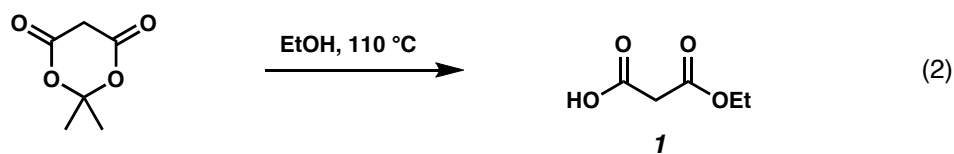


3. Malonic acid monoethyl ester (**1**) is an important building block for synthetic chemists. It can be prepared in high yield by a number of methods. Two methods are shown below in equations 1 and 2.

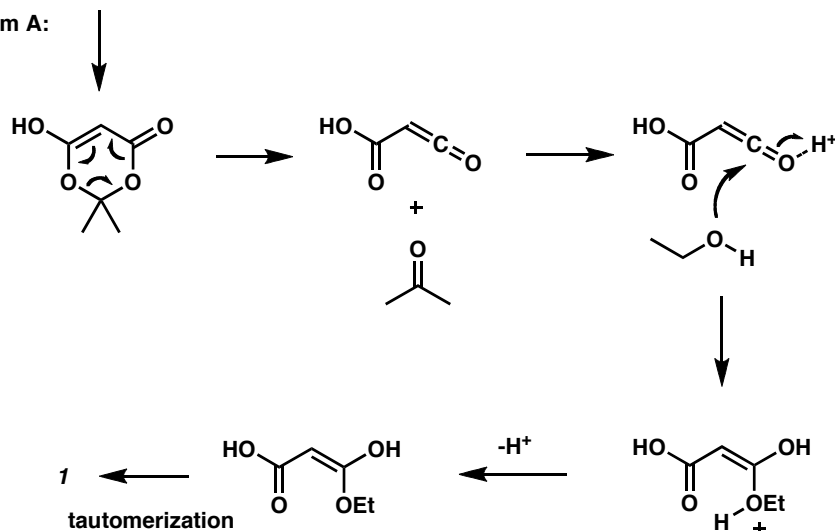


For each reaction, draw a mechanism that describes the formation of **1** (10 points each).

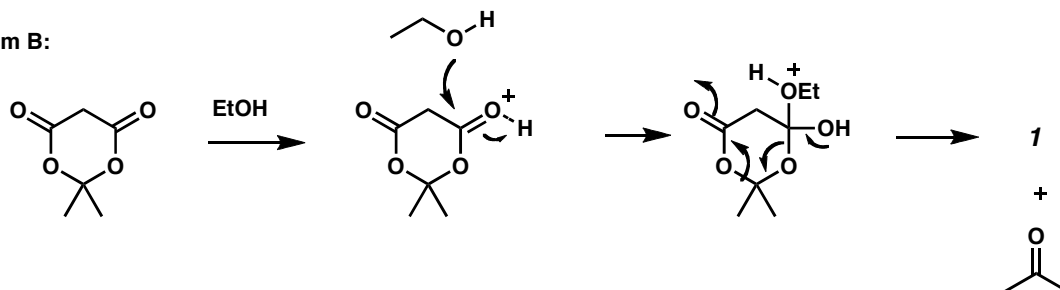




Mechanism A:



Mechanism B:



Either A or B is correct although A is currently the accepted mechanism for this reaction.

Based on your knowledge of esters and acids from this term, you should have some concerns about the success of the reactions in equations 1 and 2. You might even be surprised that the yields in each case are >90%. Describe your concerns and, if you can, how you think they were overcome in these reactions (5 points).

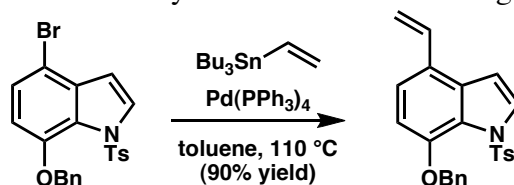
Equation 1 possible concerns:

- over saponification to malonic acid. This is overcome by the insolubility of the intermediate potassium salt in absolute ethanol.
- Possible decarboxylation upon protonation in step 2. Overcome with the low temp.

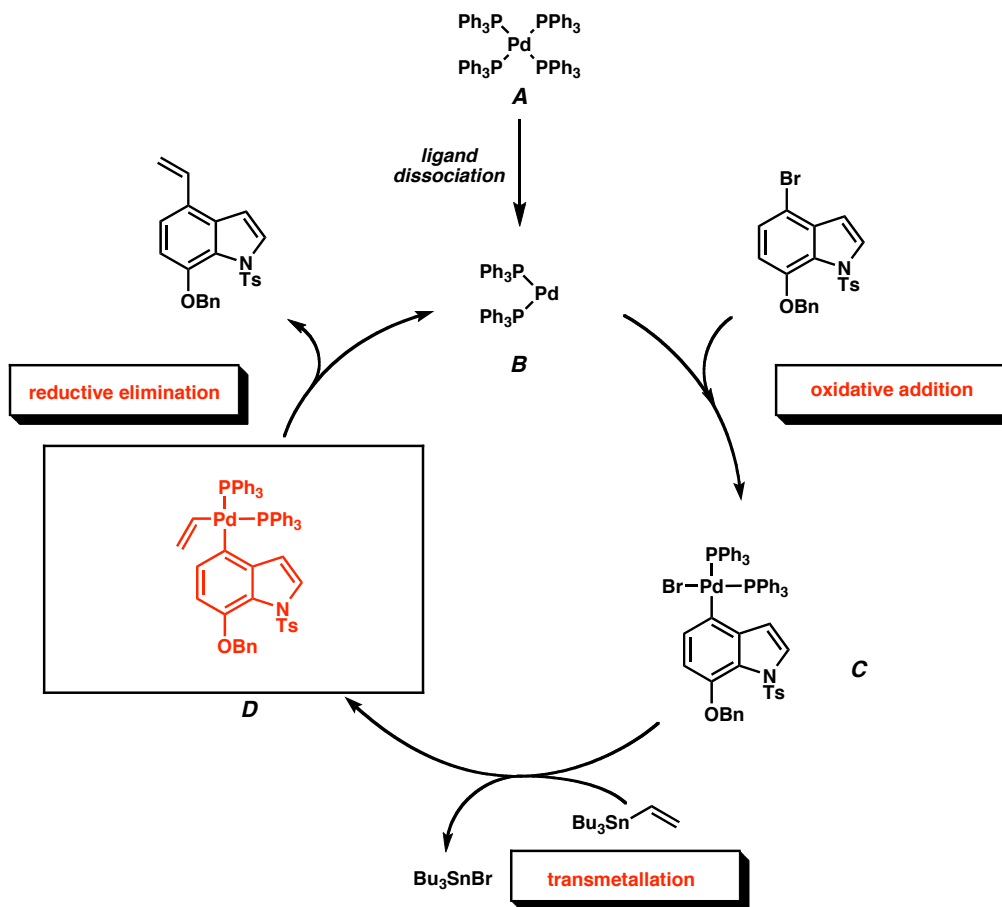
Equation 2 possible concerns:

- Possible double esterification. Overcome by the formation of acetone as a stable leaving group. Also, there is no strong acid in solution to catalyze a Fischer esterification.
- Possible decarboxylation by heating. Overcome with the slightly lower temp than needed for decarboxylation (135 °C given in class for these kinds of compounds).

4. The following reaction produces a valuable synthetic intermediate in high yield.



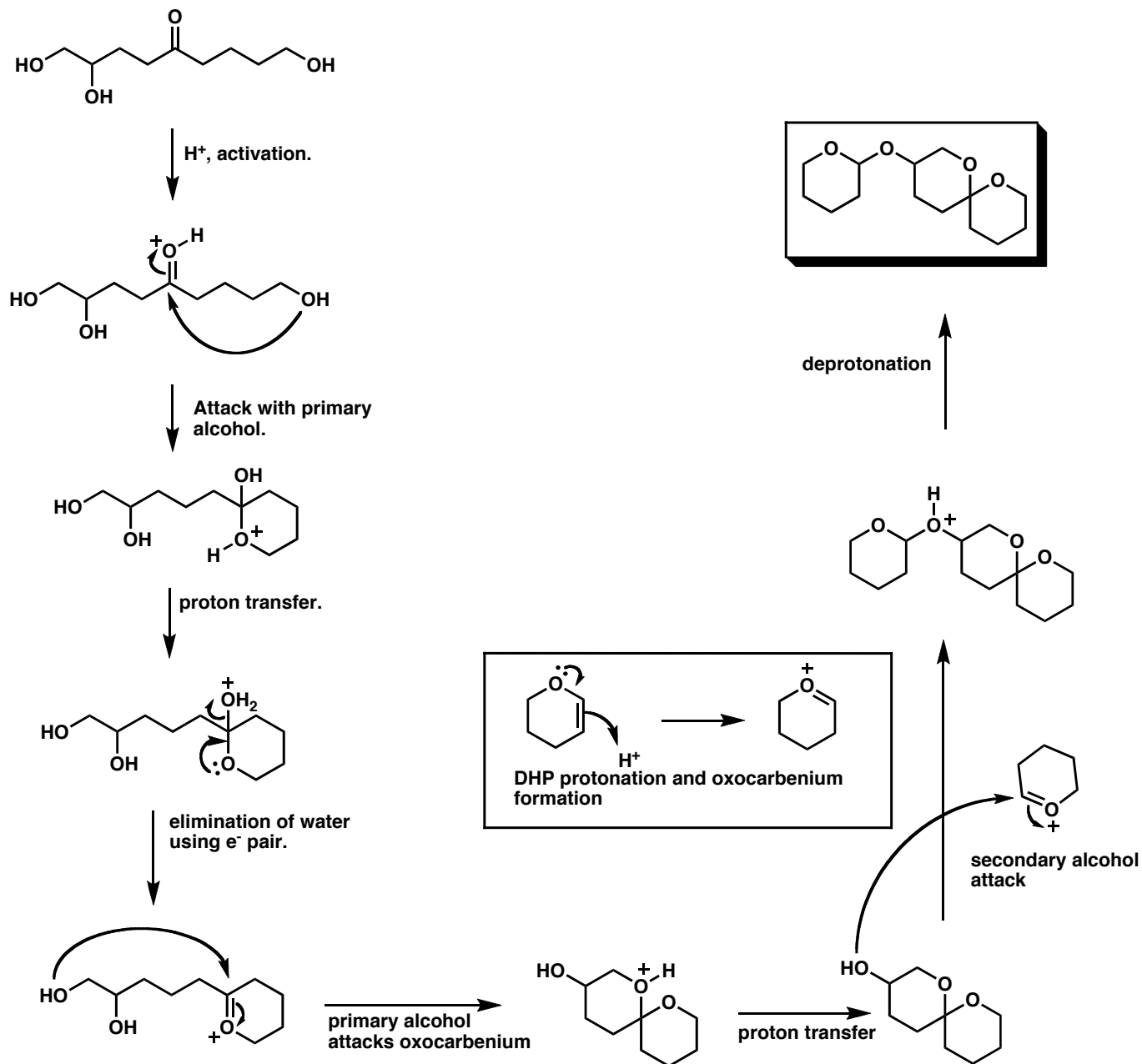
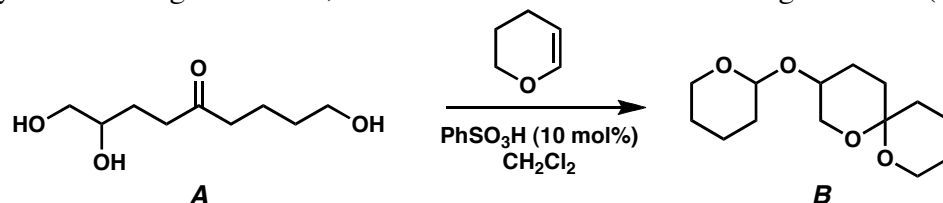
5) A catalytic cycle for this reaction is shown below. Fill in the boxes with names (e.g., associative ligand substitution) describing each of the key steps and provide the structure of intermediate **D**. Next, fill in the blanks indicating the oxidation state, *d* electron count and the total electron count of the metal species involved. Last, what is the name of this reaction? (25 points-5 points bonus)



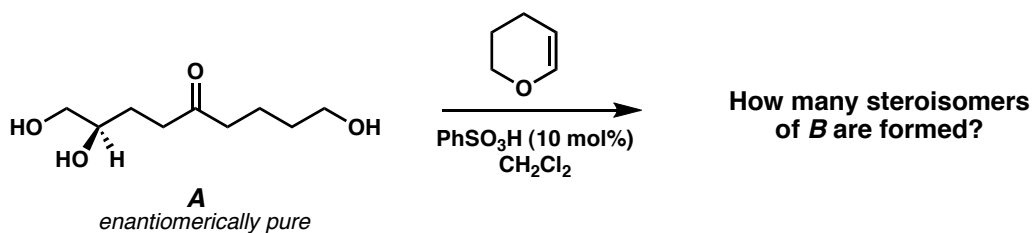
	Compound A	Compound B	Compound C
Metal oxidation state:	0	0	+2
Metal <i>d</i> count:	d^{10}	d^{10}	d^8
Total electron count:	18	14	16

(bonus-5 points) Name of reaction: Stille Coupling

5. (a) Based on your knowledge of acetals, draw a mechanism for the following reaction. (20 points)

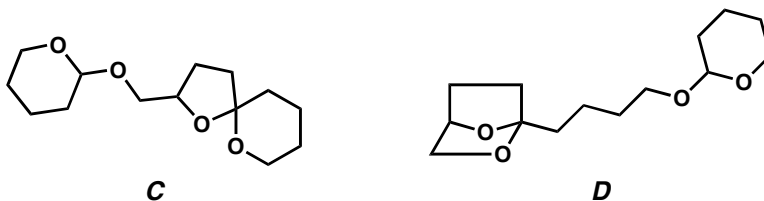


(b) Assuming that **A** is a single enantiomer (as below), how many stereoisomers (i.e., diastereomers) of **B** are possible (5 points).



4 Diastereomers

(c) For the reaction shown above (i.e., **A** + dihydropyran in the presence of acid), there are at least two alternative products possible (i.e., **C** and **D**) that are constitutional (structural) isomers of **B**. In other words they have different connectivity to **B**, but have the same molecular formula (C₁₄H₂₄O₄). Can you predict the structures of **C** and **D**? Hint: Neither **C** nor **D** has an IR resonance at 1710 cm⁻¹. (5 points each)



PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

[illegible]

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

LANTHANIDE														Copyright © 1998-2002 ENG. jeni@k8-split.hr															
57	138.91	58	140.12	59	140.91	60	144.24	61	(145)	62	150.38	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
LANTHANUM		CERIUM		PRASEODYMIUM		NEODYMIUM		PROMETHIUM		SAMARIUM		EUROPIUM		GADOLINIUM		TERBIUM		DYSPROSIUM		HOLMIUM		ERBIUM		THULIUM		YTTERBIUM		LUTETIUM	

ACTINIDE																													
89	(227)	90	232.04	91	231.04	92	238.03	93	(237)	94	(244)	95	(243)	96	(247)	97	(247)	98	(251)	99	(252)	100	(257)	101	(258)	102	(259)	103	(262)
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
ACTINIUM		THORIUM		PROTACTINIUM		URANIUM		NEPTUNIUM		PLUTONIUM		AMERICIUM		CURIUM		BERKELIUM		CALIFORNIUM		ENSTENIUM		FERMIUM		MENDELIUM		NOBELIUM		LAWRENCIUM	

The End