Chem 41c Final Exam

Stoltz, Spring 2006, June 5, 2006

The exam begins when you turn to page 2. You have 4 hours to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table on the last page of this packet. You may not use any other materials. The exam has a total of 180 points and counts for 40% of your course grade. Good luck.

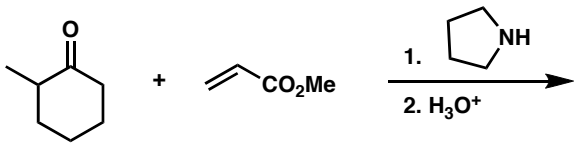
There are 17 pages in this exam packet.

The Exam is due by Friday June 9, 2006 by 5 PM.

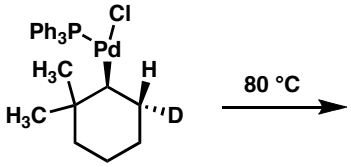
*Name:*_____

1. Predict the major non-volatile products (if any) of the following reactions or sequences. Clearly mark your answers by placing a **box** around the compound that you believe to be the major product. (5 points each).

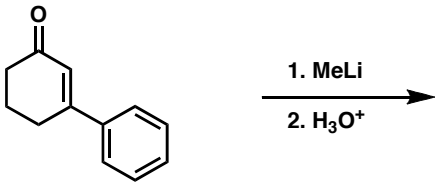
a.



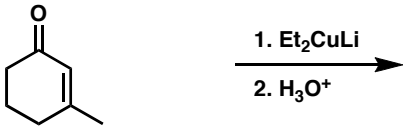
b.



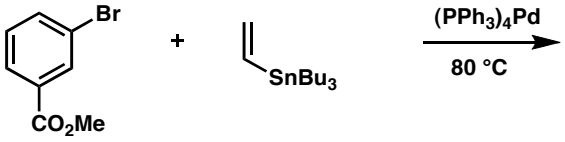
c.



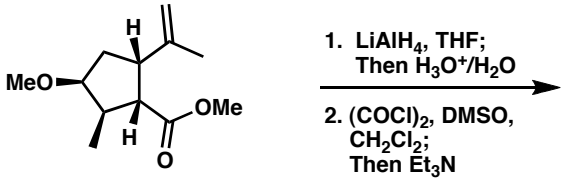
d.


O
1. Et_2CuLi
2. H_3O^+

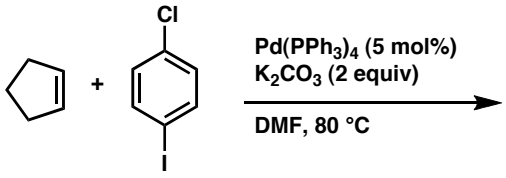
e.


Br
CO_2Me
+
$SnBu_3$
$(PPh_3)_4Pd$
80 °C

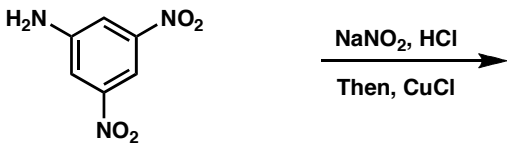
f.


H
MeO
OMe
H
O
1. $LiAlH_4$, THF;
Then H_3O^+/H_2O
2. $(COCl)_2$, DMSO,
CH_2Cl_2;
Then Et_3N

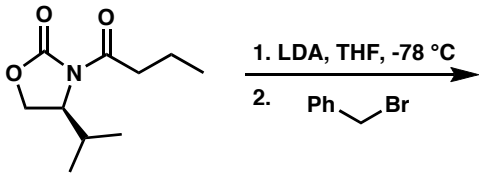
g.



h.

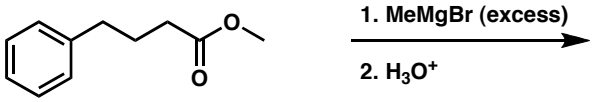


i.



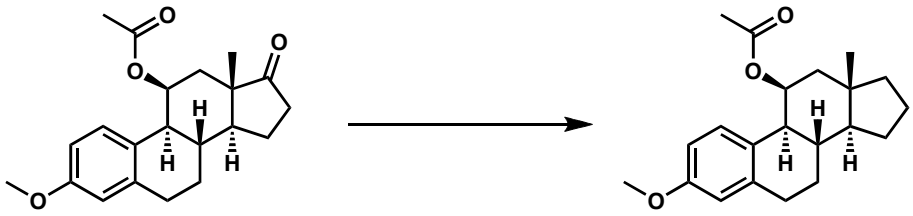
5 point bonus: what is the structure of LDA?

j.

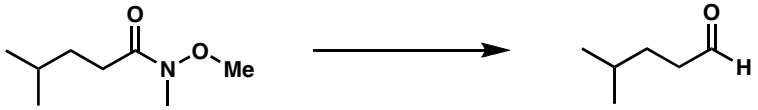


2. Provide reagents for the following transformations. They may be multistep processes, but should not be longer than 5 steps. (5 points each)

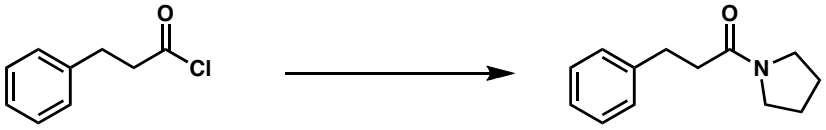
a.



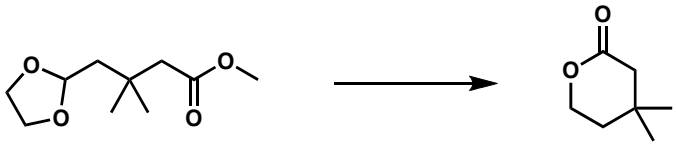
b.



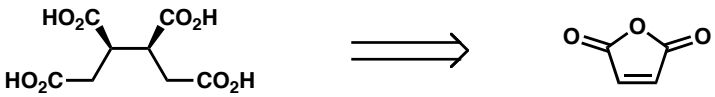
c.



d.

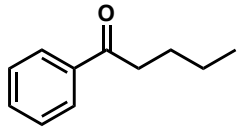


3. Design a synthesis of tetracarboxylic acid **1** starting from maleic anhydride (**2**) and any other materials containing 4 carbons or less. (15 points)

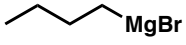


1 ***2***

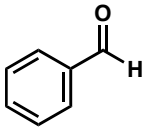
4. a) In the lab on an unusually hot and humid Sunday afternoon, you set out to prepare ketone **1**. The door to the stockroom is unfortunately locked, and you have left your keys at your friends home in Newport Beach. Due to a big game between the Los Angeles Angels of Anaheim and the Boston Red Sox, the freeways are too clogged to drive and pick them up in time to complete the synthesis of **1**. Your boss is counting on the your preparation of **1** for a big project grant that is due on the following day. Luckily, you happen to find some butyl magnesium bromide (**2**), benzaldehyde (**3**), benzene (**4**), and you have access to the inorganic stockroom full of common reagents and plenty of dry-ice (solid CO_2), solvents, and N_2 gas. Design a synthesis of **1** from any of these simple staring materials. (15 points total)



1



2



3

4

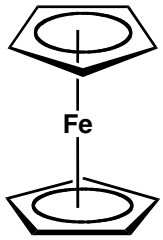
b) Unfortunately, the keys to the NMR lab were on the same key ring and are lost at the beach as well. Provide two analytical tools that you can use other than NMR that will allow you to elucidate the structure of your synthetic **1**. Explain your answer and specifically how you will know that your synthesis was a success.

c) Because you are so industrious, you realize that from the given resources, a second independent route is possible to generate **1**. If successful, this independent route will provide you with additional evidence that you have successfully prepared the key molecule **1**. Provide this synthesis for final confirmation of your ketone **1**.

d) All the while as you sweat through the day you wish you had some pentanoic acid. Why? Which reagent would you want to avoid on a very humid day **2**, **3**, or **4** and why?

5. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (5 points each-no partial credit)

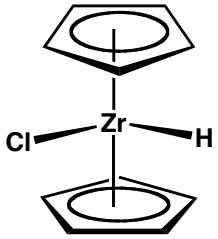
a.



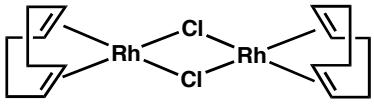
b.

$(PPh_3)_3RhCl$

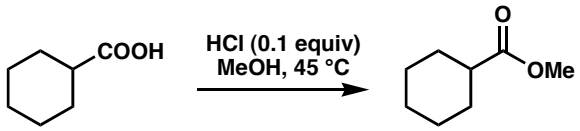
c.



d.

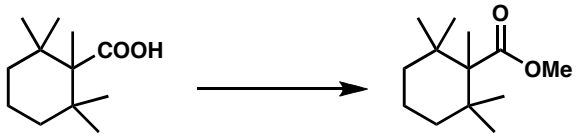


6. a) Provide a detailed curved arrow mechanism for the following reaction. What drives the equilibrium to the product side? (10 points)



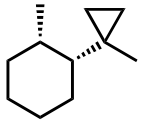
1 *2*

b) In contrast to part a of this problem, under the same conditions the following reaction (**3**→**4**) is extremely slow. Why do you think this is the case? Provide an alternative method for preparing the methyl ester **4** from carboxylic acid **3** that you believe would be fast and high yielding. Provide a detailed curved arrow mechanism for your new synthesis of **4** from **3** and explain why the new method should be better. (10 points)

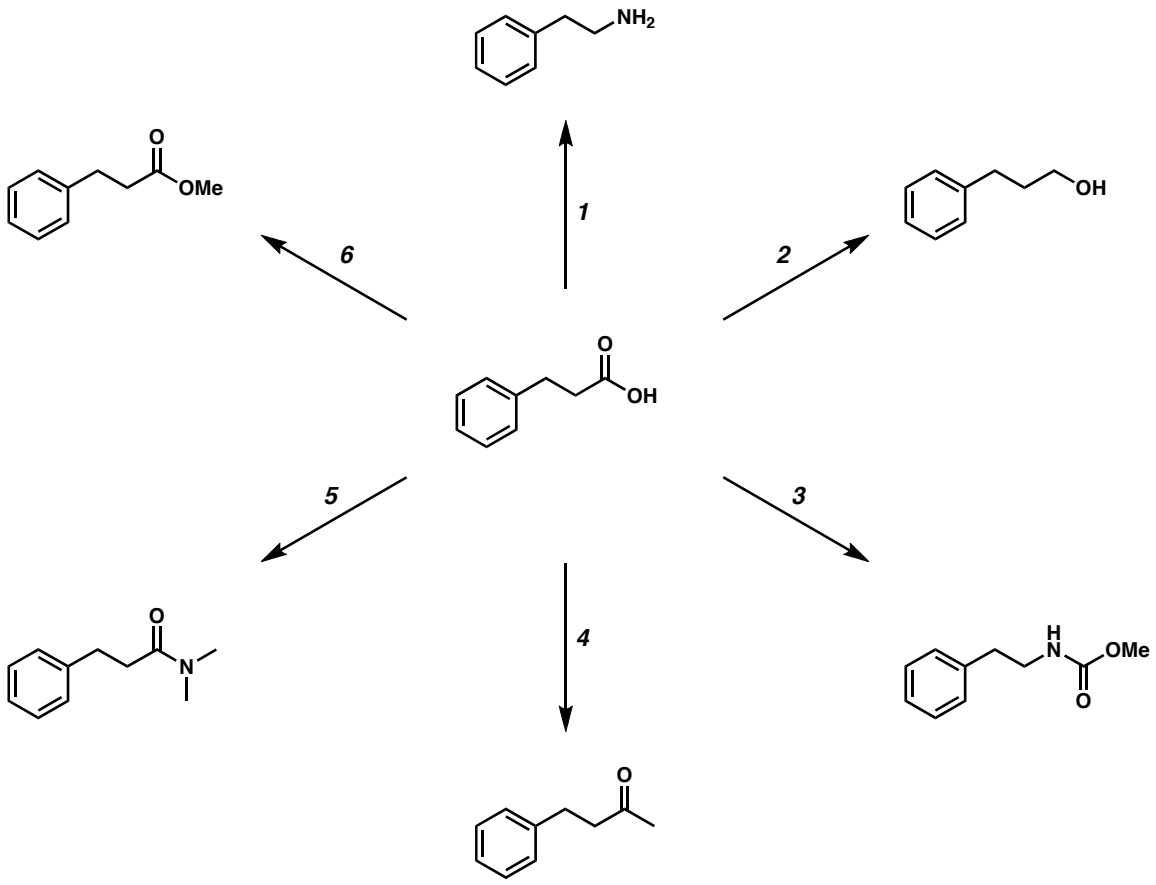


3 *4*

7. Design a retrosynthesis and a complete forward process for the synthesis of the following compound as a single diastereomer (in racemic form) starting from fragments of less than 6 carbons (or benzene). (20 points) (hint: disconnect the cyclopropane first!)



8. As you can see, carboxylic acids are valuable synthons in organic chemistry. Provide reagents for each of the following six transformations in the spaces below the figure. Keep in mind that some transformations may require more than one step. (15 points)



1. _____

_____

_____

2. _____

_____

_____

3. _____

_____

_____

4. _____

_____

_____

5. _____

_____

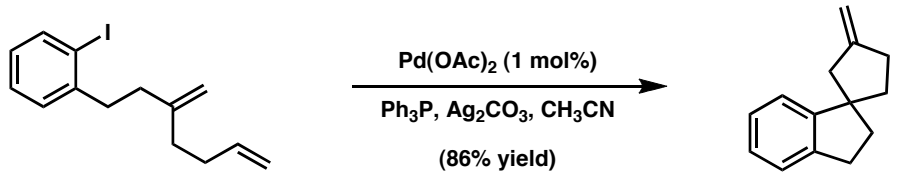
_____

6. _____

_____

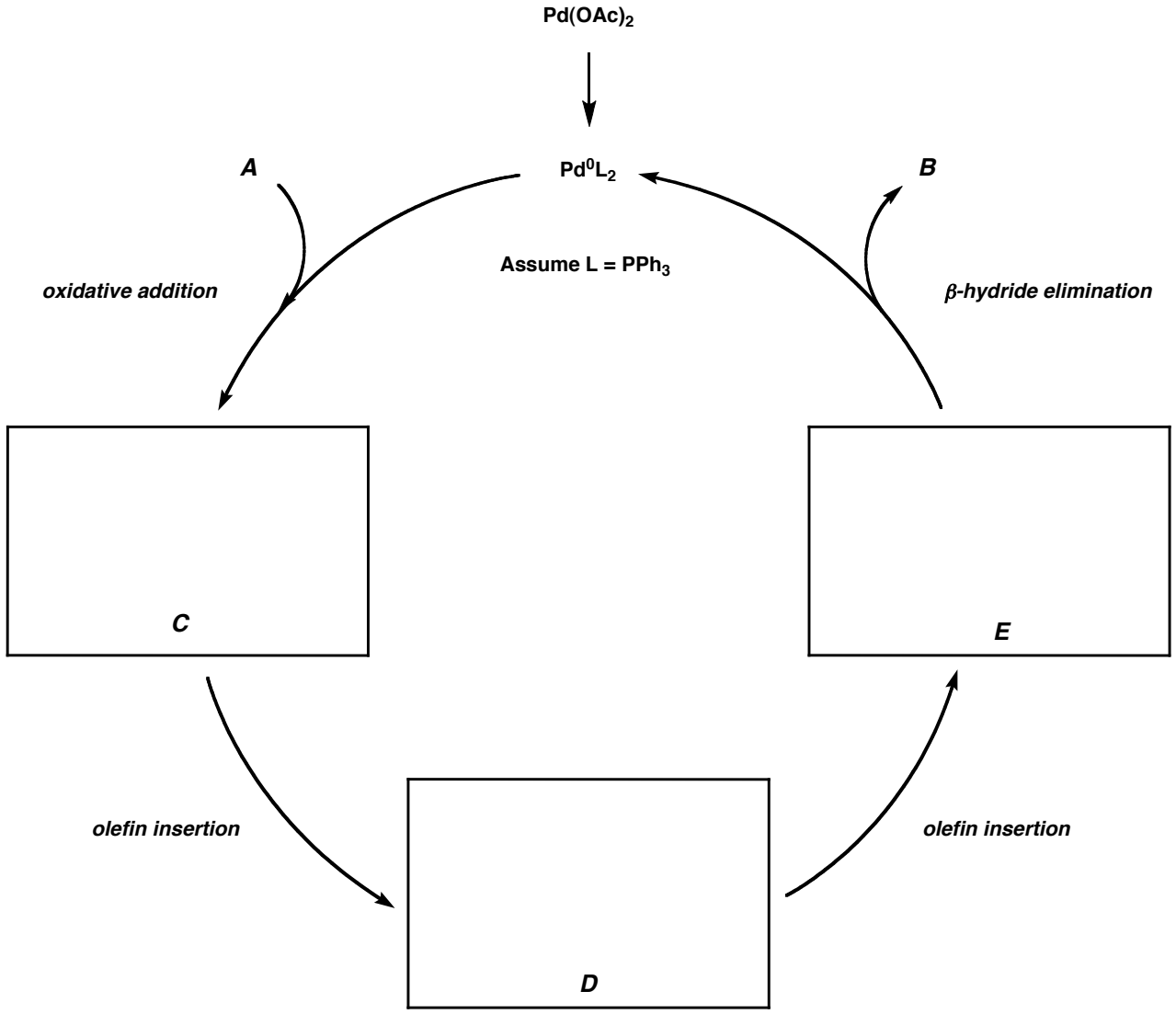
_____

9. In 1988, Larry Overman at the University of California, Irvine, showed that polyenes such as compound **A** could be cyclized to form spiro arenes (e.g., **B**) using palladium-catalyzed "zipper" reaction sequences.



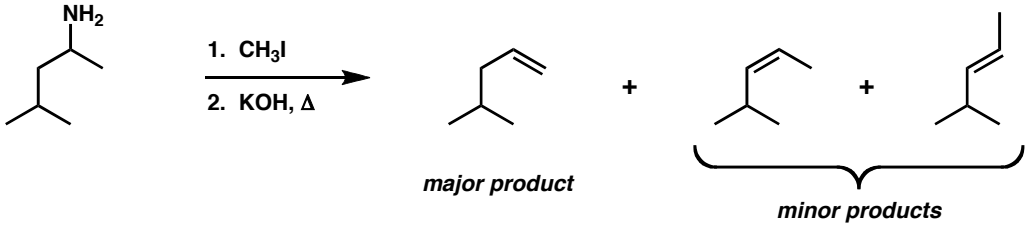
A ***B***

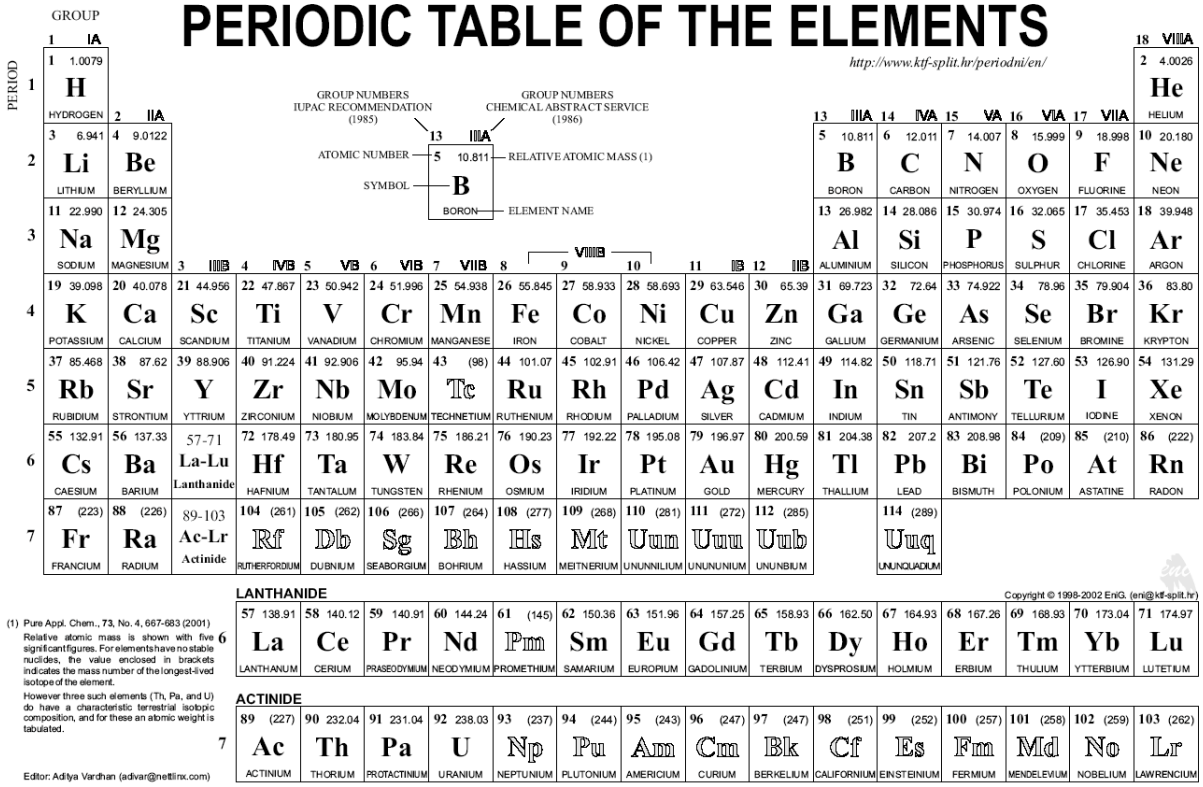
A catalytic cycle for this reaction is shown below. Each of the key steps is labeled next to the arrows. Using these clues, fill in each of the boxes with the structure of intermediates **C**, **D**, and **E**. (15 points) (5 point Bonus: What is the name of this reaction?)



Reaction Name: _____

10. The following reaction, known as the Hofmann elimination, generates the product bearing the terminal olefin in much greater yield than the combined internal olefins products. Using arrow pushing conventions, provide a detailed mechanistic explanation of how the product is formed, and *why* the terminal olefin is produced preferentially. (10 points)




PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
ATOMIC NUMBER
SYMBOL
RELATIVE ATOMIC MASS (1)
ELEMENT NAME
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9
10
VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.922 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have 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)

The End