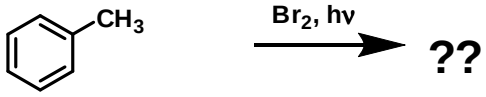
UNIVERSITY OF WINDSOR
Chemistry and Biochemistry

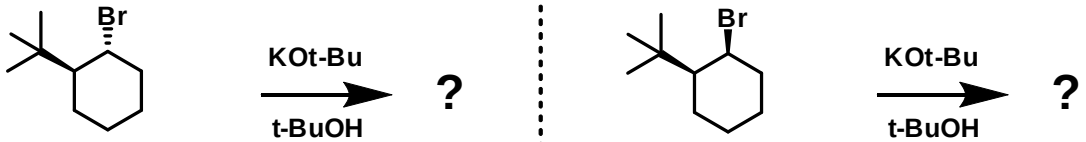
Chemistry 59-235 **Apr. 18, 2013**
Final Exam **Time: 3 hours**

Answer all questions in the exam booklet(s). ***Note: there is an option in question 4***. Once again, if 'complex' functional groups such as nitro, sulfonic acid, diazonium ions, or azides, a proper valence structure once (anywhere) is required for full marks. Use the following values for molecular weights: C, 12.011; H, 1.008; Br, 79.904; Cl, 35.453; O, 15.999; N, 14.007

1. Give a complete mechanism for the following halogenation reaction. Your answer should include an initiation step, the propagation steps, and any one plausible termination step. Show the product, and all small molecules given off. (**10 marks**)

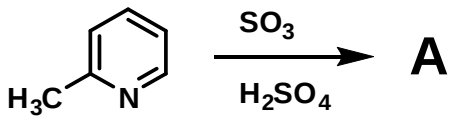


2. The following two reactions may or *may not* give different products, and one of them proceeds more slowly than the other. Indicate which product(s) are obtained, which reaction is faster (or slower), and for both clearly explain the reasons why with any convincing set of 3-dimensional structures. Note: In terms of size, *tert*-butyl >> bromide > H. (**10 marks**).



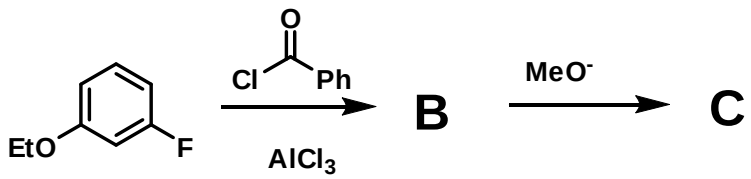
3. Predict the major products of the following transformations. Mechanisms are not necessary, but showing your work may be useful. In any *ortho/para* forming reaction, show both and take the major on to any next step. (**5 marks each, 50 total**).

a)

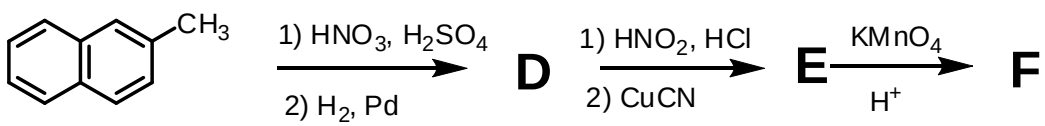


Note: a reaction *does* go

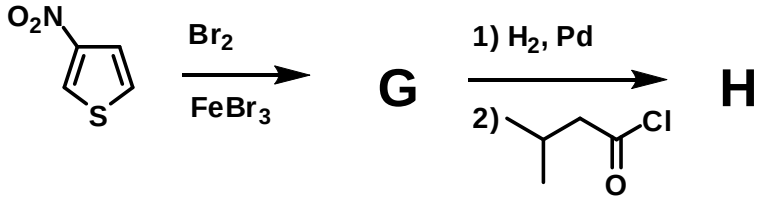
b)



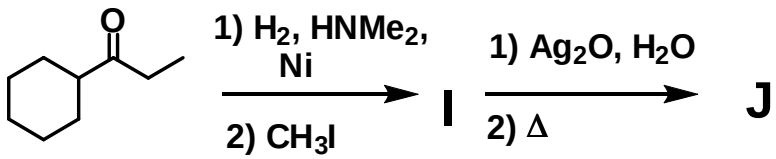
c)



d)

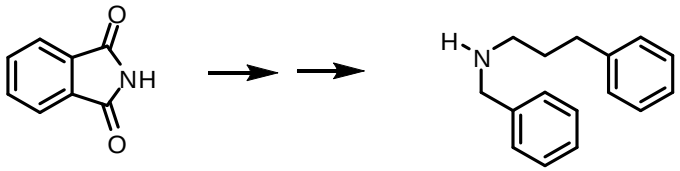


e)

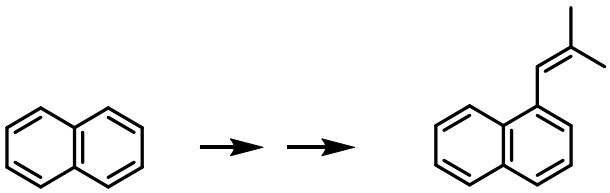


4. Show by equation (normally several steps) how you could prepare the products illustrated below from the given starting materials. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but showing your work may be a help. **Do any four (40 marks).**

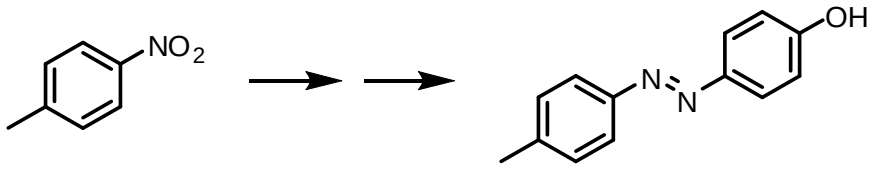
a)



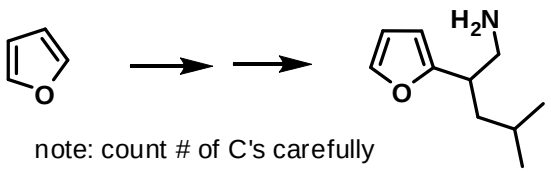
b)



c)

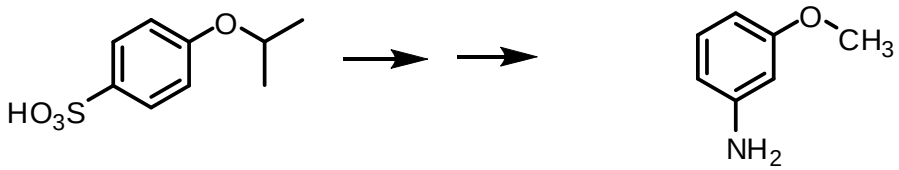


d)



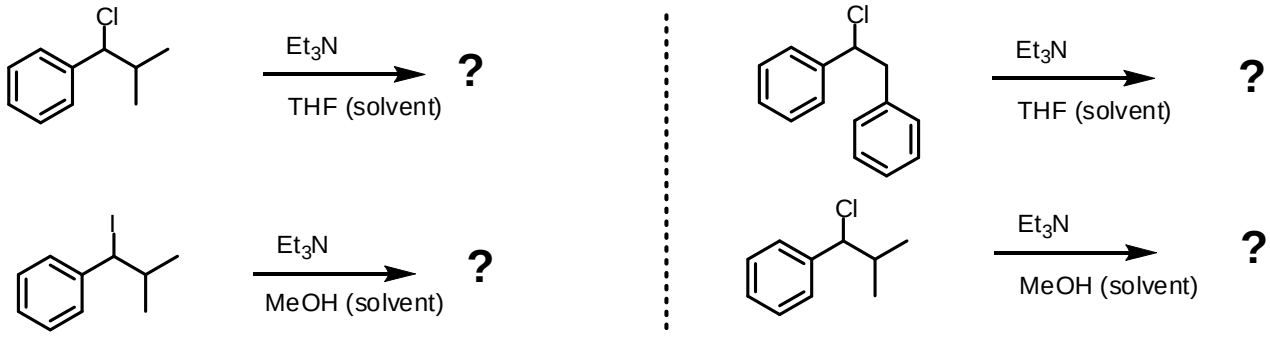
note: count # of C's carefully

e)

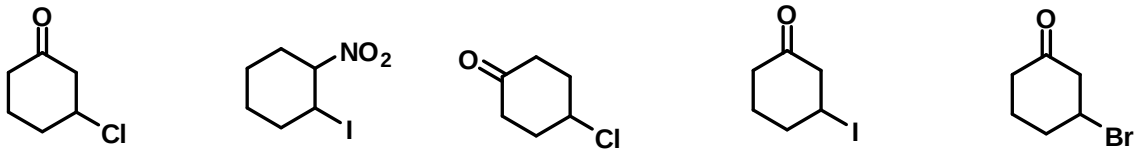


5. Rank *all four* of the following reactions in their *relative* ability to undergo E2 elimination as opposed to an E1. Include the reasons for your ordering and the product structures. It

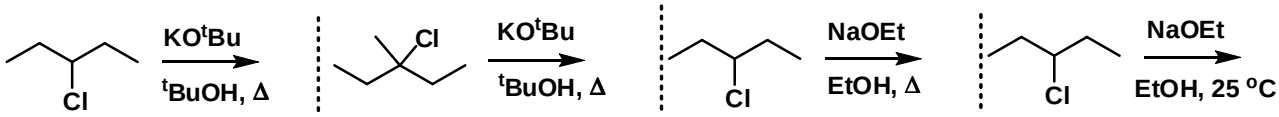
is possible that there might be small amounts of substitution products in some cases; *you may ignore the substitution products*. Dielectric constants, THF = 7.6, , MeOH = 33.1, H_2O = 78.3 (**15 marks**).



6a. Rank the following in terms of their *relative* rate in an $E1_{cb}$ elimination . I am ***not*** asking for products or rationale. Consider the conditions for each to be $KO^tBu/^tBuOH$. For reference, some pK_a's….. O_2N-C<u>H</u>$_3$, 10; R-C(=O)-C<u>H</u>$_3$, 20; R-CH_2-C<u>H</u>$_3$, 50. (**5 marks**)

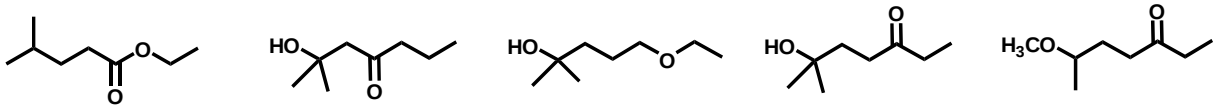


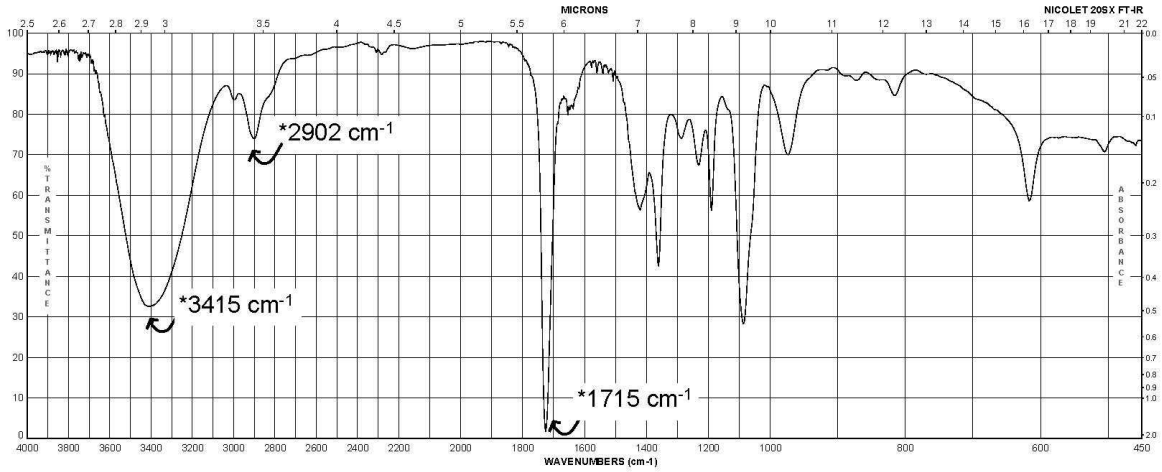
b. Rank the following in terms of their tendency to undergo elimination relative to substitution. Again, I am ***not*** asking for rationale or products (**4 marks**).

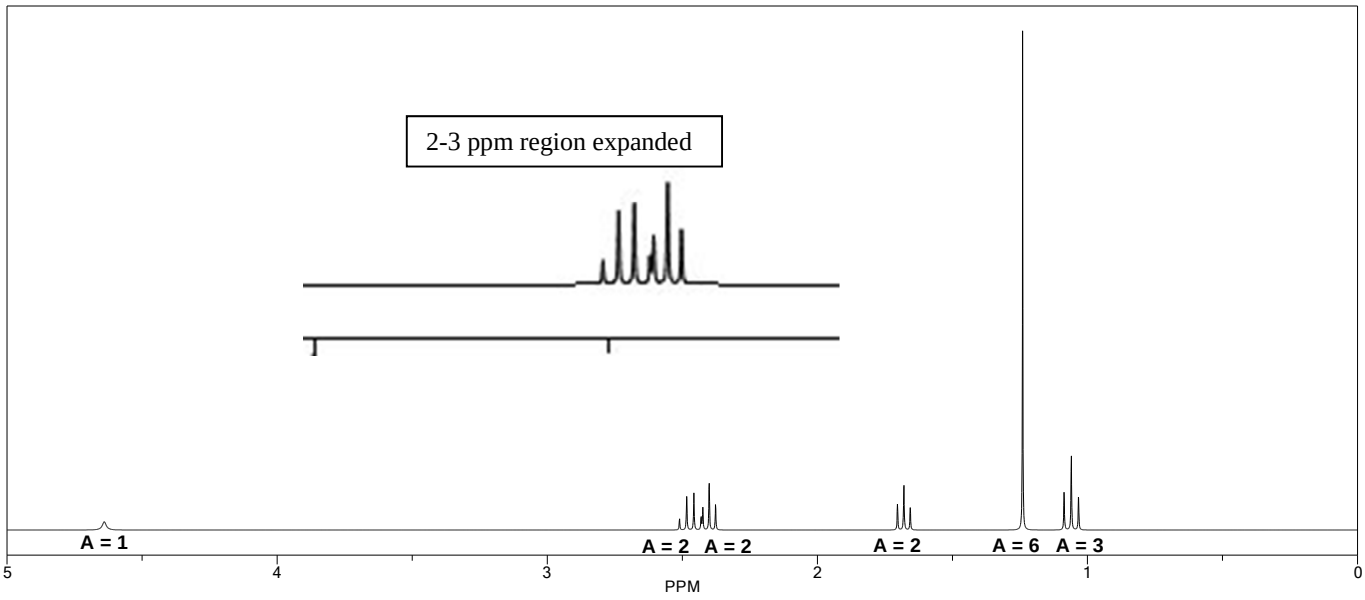


c. This refers to question **7**, but will added to the marks for **6**. For your assigned compound in **7**, what is its index of hydrogen deficiency (IHD)? (**1 mark**)

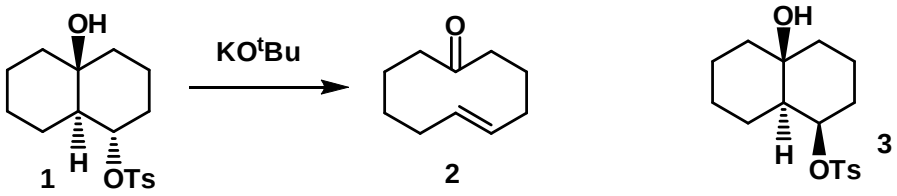
7. The following compound has been analyzed, revealing a composition C, 66.63%; H, 11.18%; O, 22.19%. The mass spectrum gives a highest m/e of 144. The IR (infrared) and ^1H NMR spectra are also included below. Which of the following structures is the most reasonable candidate for the compound in question, and why? <u>Assign the NMR spectrum</u>, showing the comparison of your calculated chemical shifts with the observed ones. Your answer should include the assignment of the most important features (i.e., <u>the starred ones</u>) of the IR spectrum. (**15 marks**)







Bonus: The following ring expansion (**1** → **2**) is one of a class of reactions called Grob fragmentations, which gives a cyclodecenone as product. Curiously, the other diastereomer **3**, really doesn't do anything very well. Can you propose a mechanism….and if possible indicate why **1** reacts but **3** doesn't?



^{1}H Nuclear Magnetic Resonance Chemical Shifts

Chemical Shifts in ppm downfield from tetramethylsilane (defined as $\delta = 0.000$ ppm). Values are approx. ± 0.2 ppm).

Protons on a Carbon Adjacent to a Functional Group

Functional Group	CH_3		CH_2		CH	
	δ	(Δδ)	δ	(Δδ)	δ	(Δδ)
saturated system	0.8		1.2		1.6	
M-C=C	1.6	(0.8)	2.0	(0.8)	2.4	(0.8)
M-C≡C	1.7	(0.9)	2.2	(1.0)	2.8	(1.2)
M-Phenyl	2.2	(1.4)	2.6	(1.4)	2.8	(1.2)
M-Cl	3.0	(2.2)	3.4	(2.2)	4.0	(2.4)
M-Br	2.7	(1.9)	3.4	(2.2)	4.1	(2.5)
M-I	2.2	(1.4)	3.1	(1.9)	4.2	(2.6)
M-OH	3.2	(2.4)	3.4	(2.2)	3.8	(2.2)
M-OR	3.2	(2.4)	3.4	(2.2)	3.6	(2.0)
M-O-Phenyl	3.9	(3.1)	4.1	(2.9)	4.5	(2.9)
M-OC(=O)R	3.6	(2.8)	4.1	(2.9)	4.5	(2.9)
M-OC(=O)Ph	3.8	(3.0)	4.2	(3.0)	5.0	(3.4)
M-CH=O (aldehyde)	2.2	(1.4)	2.4	(1.2)	2.5	(0.9)
M-C(R)=O (ketone)	2.1	(1.3)	2.3	(1.1)	2.6	(1.0)
M-COOH (acid)	2.1	(1.3)	2.3	(1.1)	2.5	(0.9)
M-COOR (ester)	2.0	(1.2)	2.2	(1.0)	2.5	(0.9)
M-NR_2	2.4	(1.6)	2.6	(1.4)	2.9	(1.3)
M-NHC(=O)R	2.9	(2.1)	3.3	(2.1)	3.9	(2.3)

Protons on a Carbon Once Removed from a Functional Group

Functional Group	CH_3		CH_2		CH	
	δ	(Δδ)	δ	(Δδ)	δ	(Δδ)
M-C-CH_2	0.8		1.2		1.6	
M-C-C=C	1.0	(0.2)	1.55	(0.35)	1.8	(0.2)
M-C-C≡C	1.2	(0.4)	1.5	(0.3)	1.8	(0.2)
M-C-Ph	1.2	(0.4)	1.6	(0.4)	1.8	(0.2)
M-C-Cl	1.5	(0.7)	1.8	(0.6)	2.0	(0.4)
M-C-Br	1.8	(1.0)	1.9	(0.7)	1.9	(0.3)
M-C-I	1.8	(1.0)	1.8	(0.6)	2.1	(0.5)
M-C-OH (or OR)	1.2	(0.4)	1.5	(0.3)	1.8	(0.2)
M-C-OPh	1.3	(0.5)	1.6	(0.4)	2.0	(0.4)
M-C-OC(=O)R	1.3	(0.5)	1.6	(0.4)	1.8	(0.2)
M-C-CH=O	1.1	(0.3)	1.6	(0.4)	2.0	(0.4)
M-C-C(R)=O	1.1	(0.3)	1.6	(0.4)	2.0	(0.4)

M-C-CO_2R	1.1	(0.3)	1.7	(0.5)	1.9	(0.3)
M-C-NR_2	1.0	(0.2)	1.5	(0.3)	1.7	(0.1)
M-C-NH-C(=O)R	1.1	(0.3)	1.5	(0.3)	1.9	(0.3)

Protons on sp^2 and sp Hybridized Carbons

$R_2C=C\underline{H}_2$	4.7-5.3	C=C<u>H</u>-C=O	6.0
$R_2C=C\underline{H}R$	5.1	C=C<u>H</u>-Cl	6.5
RCH=C<u>H</u>R	5.3	C=C<u>H</u>Br	6.5
cyclohexene	5.6	C<u>H</u>=CH-C=O	6.9
ArC<u>H</u>=C-C=O	7.7	RC<u>H</u>=O	9.1
R-C≡C-<u>H</u>	2.3-3.3	R-O<u>H</u> (alcohol)	0.5-5.5
Aromatic hydrogens	6.0-9.0 (mostly 6.7-8.2)	R-N<u>H</u>R (amine)	0.5-5.0
R-C(=O)O<u>H</u>	12-14	R-N<u>H</u>-C(=O)R (amide)	5-8

Nuclear Magnetic Resonance Chemical Shifts

Chemical Shifts in ppm downfield from tetramethylsilane (TMS) (defined as δ = 0.000 ppm).

General Regions:

0 - 1 δ cylopropyl hydrogen s and methyl groups not shifted by electronegative atoms

1 - 2 δ methyl groups β- to O or N atoms, attached to C=C or attached to aromatic rings; methylene groups

2 - 3 δ methyl and methylene groups next to carbonyls or attached directly to nitrogen of amines

3 - 4 δ methyl and methylene groups attached to oxygen or halogens (Br, Cl). $C=CH_2$ groups

4.5 - 6.5 δ hydrogens on sp^2 hybridized carbons of alkenes (not aromatics)

6.8 - 8.5 δ aromatic protons

9 - 10 δ **aldehyde protons**

IMPORTANT AND DIAGNOSTIC INFRARED BANDS
(a very condensed table)

ν (cm^{-1})			**Comments**
3000-3400	O-H stretching		alcohols- unassociated OH's - 2 bands around 3600 (sharp) H-bonded - broad absoprtion at 3400 acids- very broad, centred at ca. 3000
3400-3200	N-H stretching		amines- unassociated NH's - 2 bands around 3400 (sharp) H-bonded - broad absorption at 3200, weaker than OH
3300	C-H stretching of an acetylene		
3100-2850	C-H stretching		sp^2 - hybridized > 3000; sp^3 - hybridized < 3000
2900-2700	C-H stretching of ALDEHYDE		
2250-2100	C≡C stretching of ALKYNE		usually weak (weaker than C≡N), unless conjugated to C=O
2250-2225	C≡N stretching of NITRILE		2250 if not conjugated, 2225 conjugated Band may be weak
1800	C=O stretching of ACID CHLORIDE	>>>>	**Conjugation LOWERS these bands by 30 cm^{-1}**
1735-1740	C=O stretching of ESTER	>>>>	**Being in a 5-membered ring raises these bands by 35 cm^{-1}**
1710	C=O stretching of ALDEHYDE or KETONE	>>>>	
1700	C=O stretching of ACID	>>>>	
1660	C=O stretching of AMIDE	>>>>	
1650-1600	C=C stretch		may be weak. Intensity increases with conjugation, especially to C=O

WebElements: the periodic table on the world-wide web

http://www.webelements.com/

Key: element name / **atomic number** / **symbol** / 2001 atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.00794(7)																		helium 2 **He** 4.002602(2)
lithium 3 **Li** 6.941(2)	beryllium 4 **Be** 9.012182(3)												boron 5 **B** 10.811(7)	carbon 6 **C** 12.0107(8)	nitrogen 7 **N** 14.00674(7)	oxygen 8 **O** 15.9994(3)	fluorine 9 **F** 18.9984032(5)	neon 10 **Ne** 20.1797(6)
sodium 11 **Na** 22.989770(2)	magnesium 12 **Mg** 24.3050(6)												aluminium 13 **Al** 26.981538(2)	silicon 14 **Si** 28.0855(3)	phosphorus 15 **P** 30.973761(2)	sulfur 16 **S** 32.065(5)	chlorine 17 **Cl** 35.453(2)	argon 18 **Ar** 39.948(1)
potassium 19 **K** 39.0983(1)	calcium 20 **Ca** 40.078(4)		scandium 21 **Sc** 44.955910(8)	titanium 22 **Ti** 47.867(1)	vanadium 23 **V** 50.9415(1)	chromium 24 **Cr** 51.9961(6)	manganese 25 **Mn** 54.938049(9)	iron 26 **Fe** 55.845(2)	cobalt 27 **Co** 58.933200(9)	nickel 28 **Ni** 58.6934(2)	copper 29 **Cu** 63.546(3)	zinc 30 **Zn** 65.409(4)	gallium 31 **Ga** 69.723(1)	germanium 32 **Ge** 72.64(1)	arsenic 33 **As** 74.92160(2)	selenium 34 **Se** 78.96(3)	bromine 35 **Br** 79.904(1)	krypton 36 **Kr** 83.798(2)
rubidium 37 **Rb** 85.4678(3)	strontium 38 **Sr** 87.62(1)		yttrium 39 **Y** 88.90585(2)	zirconium 40 **Zr** 91.224(2)	niobium 41 **Nb** 92.90638(2)	molybdenum 42 **Mo** 95.94(1)	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07(2)	rhodium 45 **Rh** 102.90550(2)	palladium 46 **Pd** 106.42(1)	silver 47 **Ag** 107.8682(2)	cadmium 48 **Cd** 112.411(8)	indium 49 **In** 114.818(3)	tin 50 **Sn** 118.710(7)	antimony 51 **Sb** 121.760(1)	tellurium 52 **Te** 127.60(3)	iodine 53 **I** 126.90447(3)	xenon 54 **Xe** 131.293(6)
caesium 55 **Cs** 132.90545(2)	barium 56 **Ba** 137.327(7)	57-70 *	lutetium 71 **Lu** 174.967(1)	hafnium 72 **Hf** 178.49(2)	tantalum 73 **Ta** 180.9479(1)	tungsten 74 **W** 183.84(1)	rhenium 75 **Re** 186.207(1)	osmium 76 **Os** 190.23(3)	iridium 77 **Ir** 192.217(3)	platinum 78 **Pt** 195.078(2)	gold 79 **Au** 196.96655(2)	mercury 80 **Hg** 200.59(2)	thallium 81 **Tl** 204.3833(2)	lead 82 **Pb** 207.2(1)	bismuth 83 **Bi** 208.98038(2)	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [285]		ununquadium 114 **Uuq** [289]				

*lanthanoids	lanthanum 57 **La** 138.9055(2)	cerium 58 **Ce** 140.116(1)	praseodymium 59 **Pr** 140.90765(2)	neodymium 60 **Nd** 144.24(3)	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36(3)	europium 63 **Eu** 151.964(1)	gadolinium 64 **Gd** 157.25(3)	terbium 65 **Tb** 158.92534(2)	dysprosium 66 **Dy** 162.500(1)	holmium 67 **Ho** 164.93032(2)	erbium 68 **Er** 167.259(3)	thulium 69 **Tm** 168.93421(2)	ytterbium 70 **Yb** 173.04(3)
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.0381(1)	protactinium 91 **Pa** 231.03588(2)	uranium 92 **U** 238.02891(3)	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Element symbols and names: symbols, names, and spellings are those recommended by IUPAC (http://www.iupac.org/). After controversy, the names of elements 101-109 are now confirmed (Pure & Appl. Chem., 1997, **69**, 2471–2473). Names have yet to be proposed for the elements 110–112, and 114 - those used here are IUPAC's temporary systematic names (Pure & Appl. Chem., 1979, **51**, 381–384). In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the usual spelling is **sulphur**.

Atomic weights (mean relative masses): Apart from the heaviest elements, these are IUPAC 2001 values (Pure & Appl. Chem., 2001, **73**, 667–683). Elements with values given in brackets have no stable nuclides and are represented by 5-figure values for the longest-lived isotope. The elements thorium, protactinium, and uranium have characteristic terrestrial abundances and these are the values quoted. The last significant figure of each value is considered reliable to ±1 except where a larger uncertainty is given in parentheses.

Periodic table organisation: for a justification of the positions of the elements La, Ac, Lu, and Lr in the WebElements periodic table see W.B. Jensen, "The positions of lanthanum (actinium) and lutetium (lawrencium) in the periodic table", J. Chem. Ed., 1982, **59**, 634–636.

Group labels: the numeric system (1–18) used here is the current IUPAC convention. For a discussion of this and other common systems see: W.C. Fernelius and W.H. Powell, "Confusion in the periodic table of the elements", J. Chem. Ed., 1982, **59**, 504–508.