

Name \_\_\_\_\_

You may use model kits but no other material with chemical information without instructor approval. Tables of possibly useful data are included on the last page.

Please do not use any electronic gadgets (calculators, music players, phones, etc.).

**IUPAC Periodic Table of the Elements**

Key:																																																																										
atomic number		Symbol		name		conventional atomic weight		standard atomic weight																																																																		
1	H	hydrogen	1.008	[1.0078, 1.0082]	2	He	helium	4.0026	13	B	boron	10.81	[10.806, 10.821]	14	C	carbon	12.011	[12.009, 12.012]	15	N	nitrogen	14.007	[14.006, 14.008]	16	O	oxygen	15.999	[15.998, 16.000]	17	F	fluorine	18.998	18	Ne	neon	20.180																																						
3	Li	lithium	6.94	[6.938, 6.997]	4	Be	beryllium	9.0122	11	Na	sodium	22.990	[22.989, 22.991]	12	Mg	magnesium	24.304	[24.304, 24.307]	13	Al	aluminum	26.982	[26.981, 26.983]	14	Si	silicon	28.086	[28.085, 28.087]	15	P	phosphorus	30.974	[30.972, 30.976]	16	S	sulfur	32.06	[32.059, 32.076]	17	Cl	chlorine	35.45	[35.446, 35.457]	18	Ar	argon	39.948	[39.942, 39.949]																										
19	K	potassium	39.098	20	Ca	calcium	40.078(4)	21	Sc	scandium	44.956	22	Ti	titanium	47.867	23	V	vanadium	50.942	24	Cr	chromium	51.996	25	Mn	manganese	54.938	26	Fe	iron	55.845(2)	27	Co	cobalt	58.933	28	Ni	nickel	58.693	29	Cu	copper	63.546(3)	30	Zn	zinc	65.38(2)	31	Ga	gallium	69.723	32	Ge	germanium	72.630(8)	33	As	arsenic	74.922	34	Se	selenium	78.971(8)	35	Br	bromine	79.904	36	Kr	krypton	83.796(2)			
37	Rb	rubidium	85.468	38	Sr	strontium	87.62	39	Y	yttrium	88.906	40	Zr	zirconium	91.224(2)	41	Nb	niobium	92.906	42	Mo	molybdenum	95.95	43	Tc	technetium	101.07(2)	44	Ru	ruthenium	101.07(2)	45	Rh	rhodium	102.91	46	Pd	palladium	106.42	47	Ag	silver	107.87	48	Cd	cadmium	112.41	49	In	indium	114.82	50	Sn	tin	118.71	51	Sb	antimony	121.76	52	Te	tellurium	127.60(3)	53	I	iodine	126.90	54	Xe	xenon	131.29			
55	Cs	caesium	132.91	56	Ba	barium	137.33	57-71	lanthanoids					72	Hf	hafnium	178.49(2)	73	Ta	tantalum	180.95	74	W	tungsten	183.84	75	Re	rhenium	186.21	76	Os	osmium	190.23(3)	77	Ir	iridium	192.22	78	Pt	platinum	195.08	79	Au	gold	196.97	80	Hg	mercury	200.59	81	Tl	thallium	204.38	[204.38, 204.39]	82	Pb	lead	207.2	83	Bi	bismuth	208.98	84	Po	polonium		85	At	astatine		86	Rn	radon	
87	Fr	francium		88	Ra	radium		89-103	actinoids					104	Rf	rutherfordium		105	Db	dubnium		106	Sg	seaborgium		107	Bh	bohrium		108	Hs	hassium		109	Mt	meitnerium		110	Ds	darmstadtium		111	Rg	roentgenium		112	Cn	coppernium		113	Nh	nihonium		114	Fl	flerovium		115	Mc	moscovium		116	Lv	livermorium		117	Ts	tennessine		118	Og	oganesson		
57	La	lanthanum	138.91	58	Ce	cerium	140.12	59	Pr	praseodymium	140.91	60	Nd	neodymium	144.24	61	Pm	promethium		62	Sm	samarium	150.36(2)	63	Eu	europium	151.96	64	Gd	gadolinium	157.25(3)	65	Tb	terbium	158.93	66	Dy	dysprosium	162.50	67	Ho	holmium	164.93	68	Er	erbium	167.26	69	Tm	thulium	168.93	70	Yb	ytterbium	173.05	71	Lu	lutetium	174.97															
89	Ac	actinium		90	Th	thorium	232.04	91	Pa	protactinium	231.04	92	U	uranium	238.03	93	Np	neptunium		94	Pu	plutonium		95	Am	americium		96	Cm	curium		97	Bk	berkelium		98	Cf	californium		99	Es	einsteinium		100	Fm	fermium		101	Md	mendelevium		102	No	nobelium		103	Lr	lawrencium																



1. (15 points) Draw structures, including stereochemistry where appropriate, for each of the following.

A. 3-ethylheptane

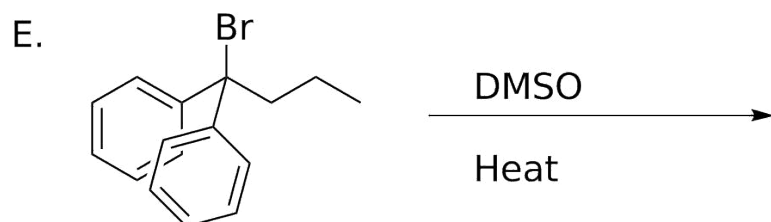
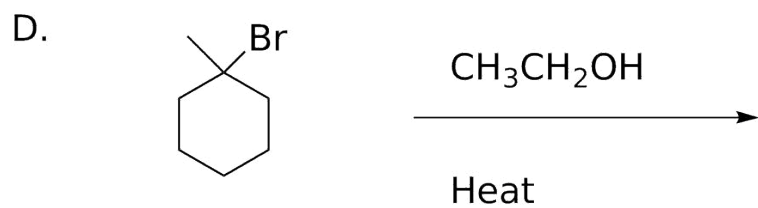
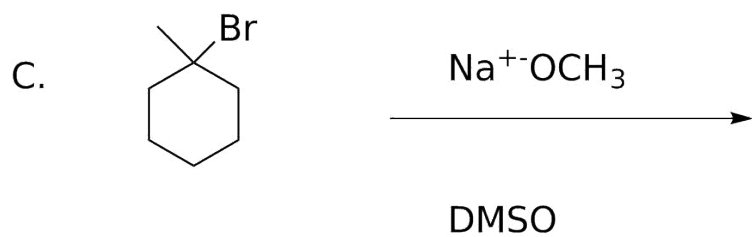
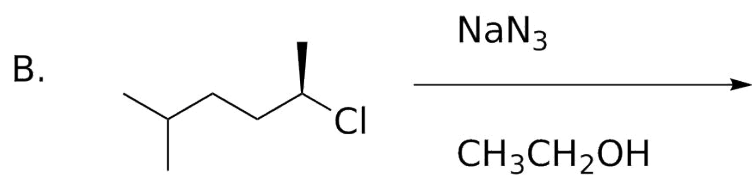
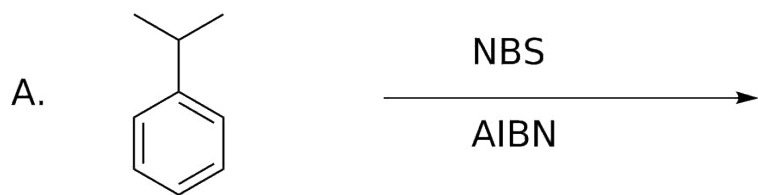
B. *cis*-1,2-dichlorocyclohexane

C. *R, R*-2-bromomethylcyclopentane

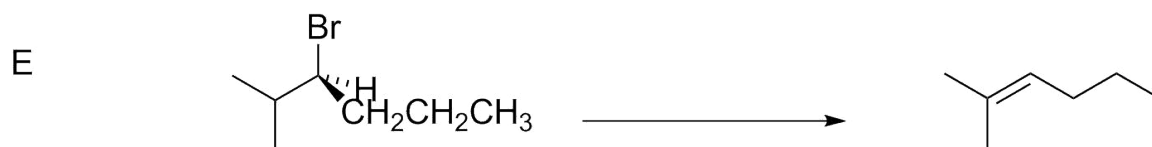
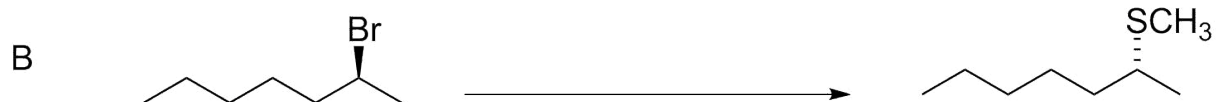
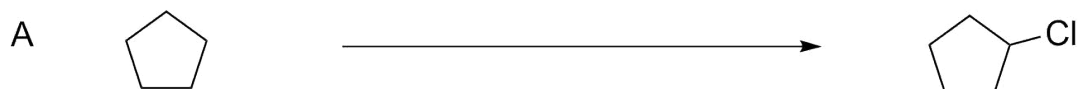
D. *R, S*-3,4-dihydroxyhexane

E. *tert*-butylcyclohexane

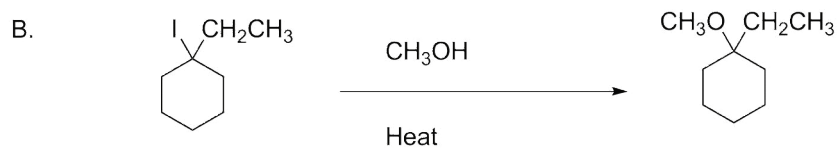
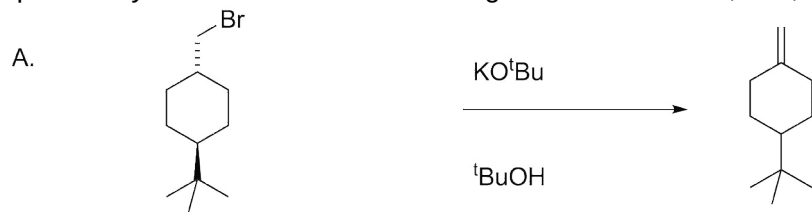
2. (30 points) Draw the structure of the major product for each reaction. Include stereochemistry where appropriate; you may designate a racemic product by designating "+ enantiomer."



3. (30 points) Write (over the arrow) the reagents and conditions (as appropriate) that will accomplish the following transformations.

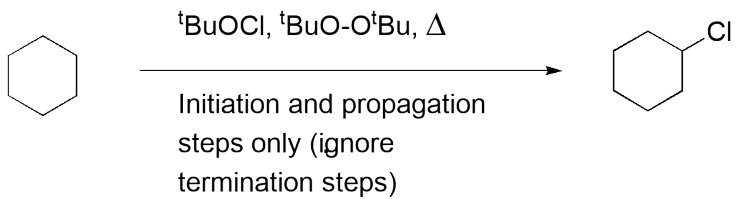


4. (40 points) For each reaction below, write a mechanism using the electron-pushing formalism for each step. Classify each as one of the following: free radical chain,  $S_N1$ ,  $S_N2$ , E1 or E2.



4. (Continued)

C.



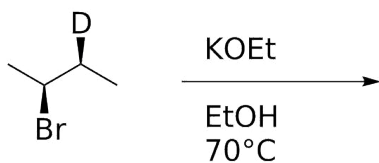
5. (30 points) Each of the following short syntheses can be accomplished with chemistry you know in several steps. Show how to do each, providing reactants and reagents/conditions needed.

A. Cyclopentane to cyclopentene

B. Propane to 4-octyne

6. (30 points) Deuterium is an isotope of hydrogen that has an extra neutron in its nucleus. Because it is chemically identical to normal hydrogen but can be detected by its heavier mass, it is often used to help determine reaction mechanisms.

The following deuterated form of 2-bromobutane was reacted under E2 conditions:



A. When (undeuterated) 2-bromobutane reacts under these conditions, one major and two minor products are observed. Draw them.

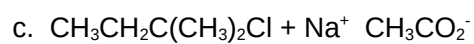
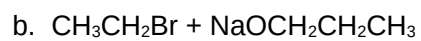
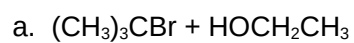
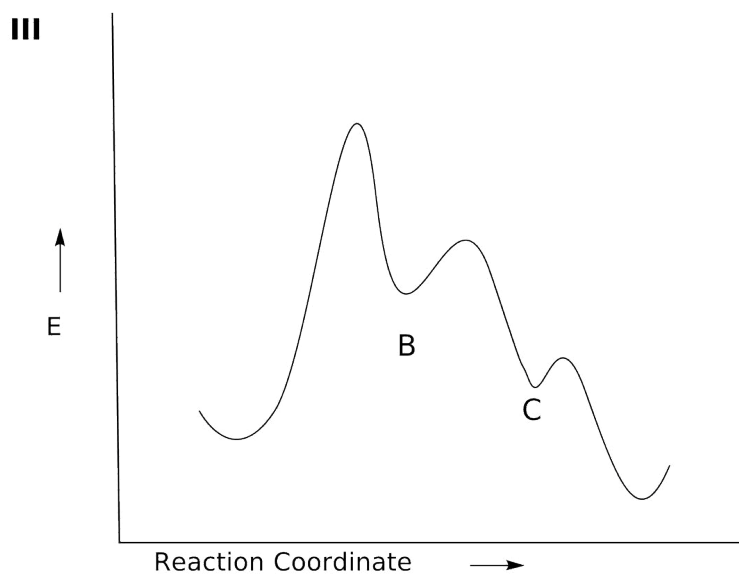
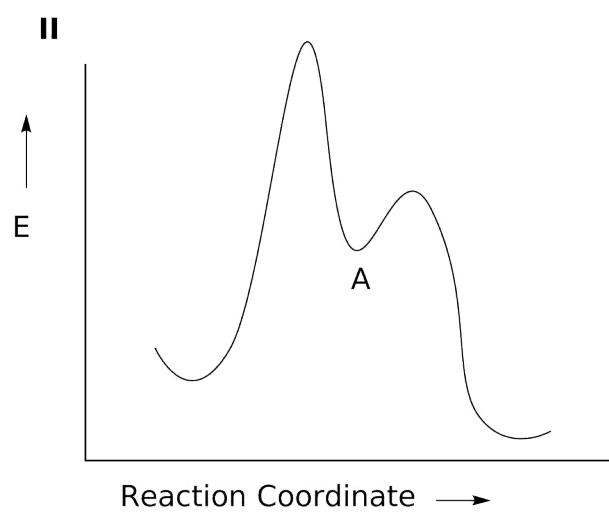
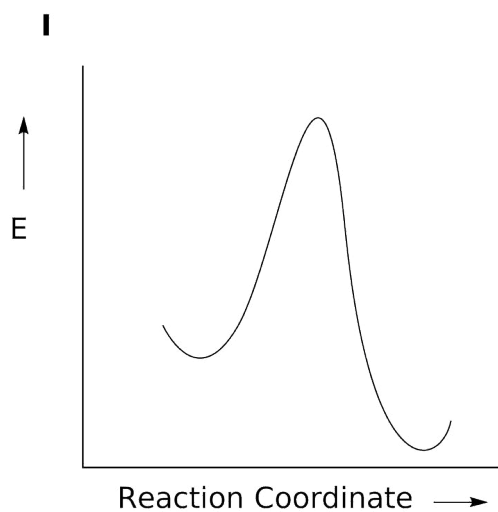
B. For the deuterated form of 2-bromobutane shown, draw the Newman projection for the most stable rotamer looking down the C2-C3 bond.

C. For the three products you drew in part A, predict whether each will have deuterium or not. Explain the basis of your prediction.



7. (25 points)

A. Match each of the following reaction energy diagrams with one of the reactions shown below. Each reaction is in DMSO solvent.



B. For each of the reactive intermediates indicated in the reaction energy diagrams (labeled A, B, C), draw its likely structure.

C. Draw the product you expect from each reaction.

## Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH <sub>3</sub> -H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH <sub>3</sub> -F	110
CH <sub>3</sub> -Cl	85
CH <sub>3</sub> -Br	70
CH <sub>3</sub> -I	57
CH <sub>3</sub> CH <sub>2</sub> -F	111
CH <sub>3</sub> CH <sub>2</sub> -Cl	84
CH <sub>3</sub> CH <sub>2</sub> -Br	70
CH <sub>3</sub> CH <sub>2</sub> -I	56
(CH <sub>3</sub> ) <sub>2</sub> CH-F	111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	84
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	71
(CH <sub>3</sub> ) <sub>2</sub> CH-I	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	85
(CH <sub>3</sub> ) <sub>3</sub> C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-I	55

## Solvent Polarities

Solvent	Dielectric Const.
Hexane	1.9
Diethyl Ether	4.3
Acetic Acid	6.1
THF	7.6
t-Butyl Alcohol	12.5
Acetone	21
Ethanol	24.5
Nitromethane	36
DMSO	47
Water	78

## A values for monosubstituted cyclohexanes (kcal/mol)

Substituent	A
Me	1.8
Et	1.8
<sup>i</sup> Pr	2.1
<sup>t</sup> Bu	>4.5
O-Me	0.75
Cl	0.52
Br	0.55
I	0.46

$$R = 1.987 \text{ cal}/(\text{mol}\cdot\text{K})$$

$$= 8.314 \text{ J}/(\text{mol}\cdot\text{K})$$

*cis*-1,3-diaxial interaction energies

Me-Me	1.5 kcal/mol
Me-Br	1.0 kcal/mol

(relative to R-H diaxial interactions)

Nucleophilicities

(= log  $k_{\text{rel}}$  for CH<sub>3</sub>Br + Nu: in CH<sub>3</sub>OH/25°C)

Et <sub>3</sub> P	8.7
HS <sup>-</sup>	8.0
I <sup>-</sup>	7.4
CN <sup>-</sup>	6.7
Et <sub>3</sub> N	6.7
CH <sub>3</sub> O <sup>-</sup>	6.7
HO <sup>-</sup>	6.0
Br <sup>-</sup>	5.8
N <sub>3</sub> <sup>-</sup>	5.8
NH <sub>3</sub>	5.5
(CH <sub>3</sub> ) <sub>2</sub> S	5.3
Cl <sup>-</sup>	4.3
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.3
F <sup>-</sup>	2.7
CH <sub>3</sub> OH	0
H <sub>2</sub> O	0