CH 334

Final Exam Tuesday, December 5, 2017

Name_____KEY_____

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

1																	18
1 H hydrogen 1.008 [1.0078, 1.0082]	2		Key: atomic number **Symbol** name conventional atomic weight standard atomic weight									13	14	15	16	17	2 He helium 4.0026
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.948
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 [79.901, 79.907]	36 Kr krypton 83.798(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	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 copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

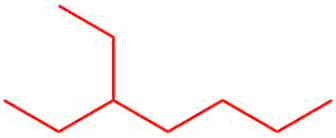
57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 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

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

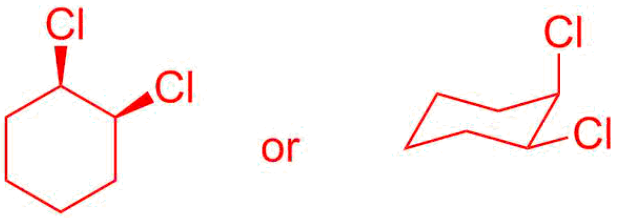
For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.

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

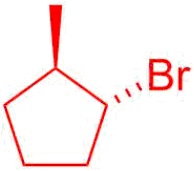
A. 3-ethylheptane



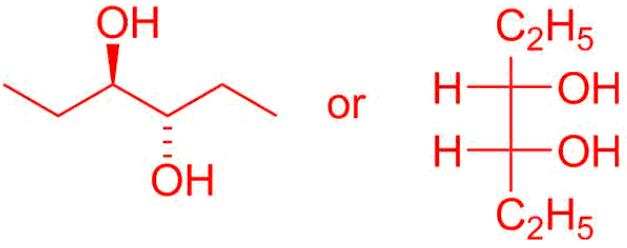
B. *cis*-1,2-dichlorocyclohexane



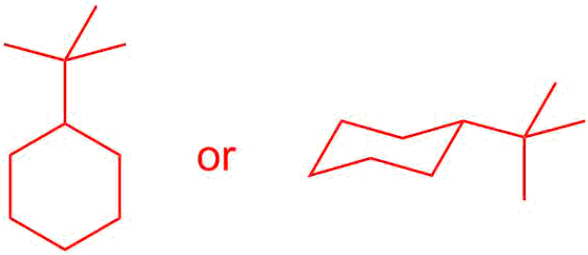
C. R, R-2-bromomethylcyclopentane



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

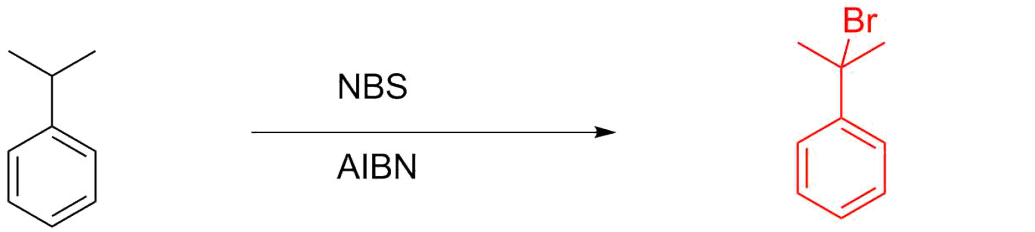


E. *tert*-butylcyclohexane

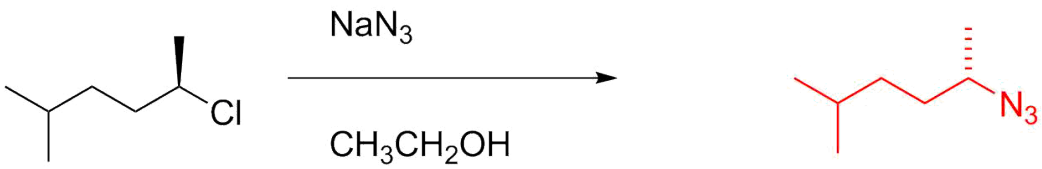


2. (30 points) Draw the structure of the major product for each reaction. Include stereochemistry where appropriate; you may designate a racemic product by designating "+ enantiomer."

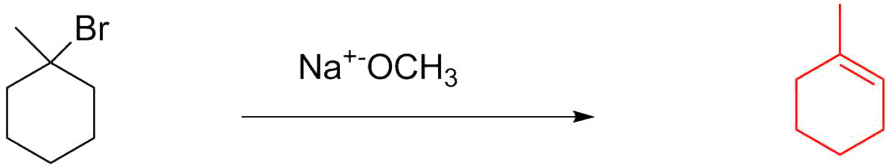
A.



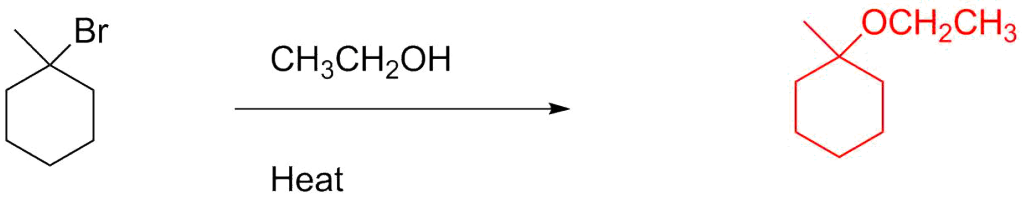
B.



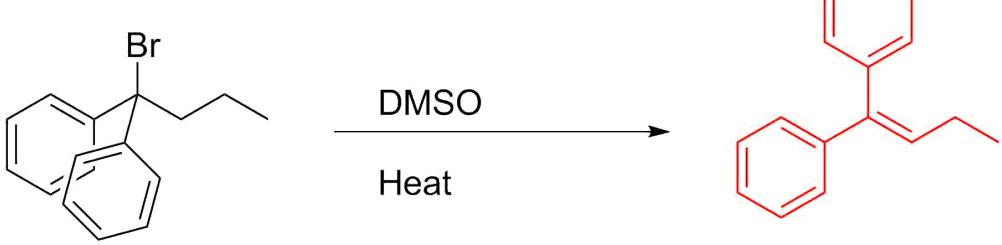
C.



D.

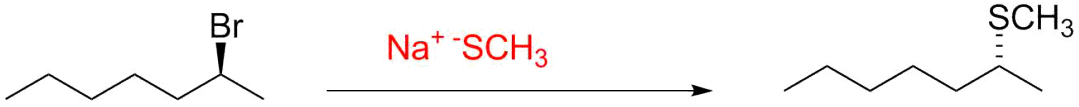


E.

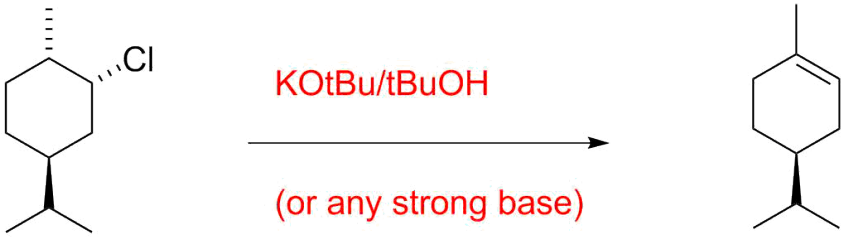


3. (30 points) Write (over the arrow) the reagents and conditions (as appropriate) that will accomplish the following transformations.

A 

B 

(typo in original)

C 

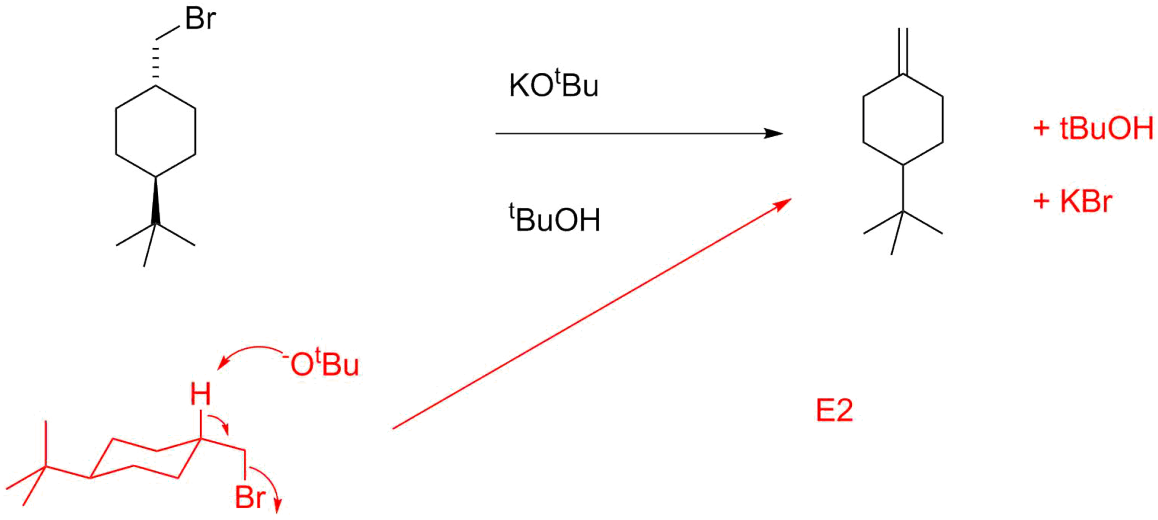
D 

(racemic)

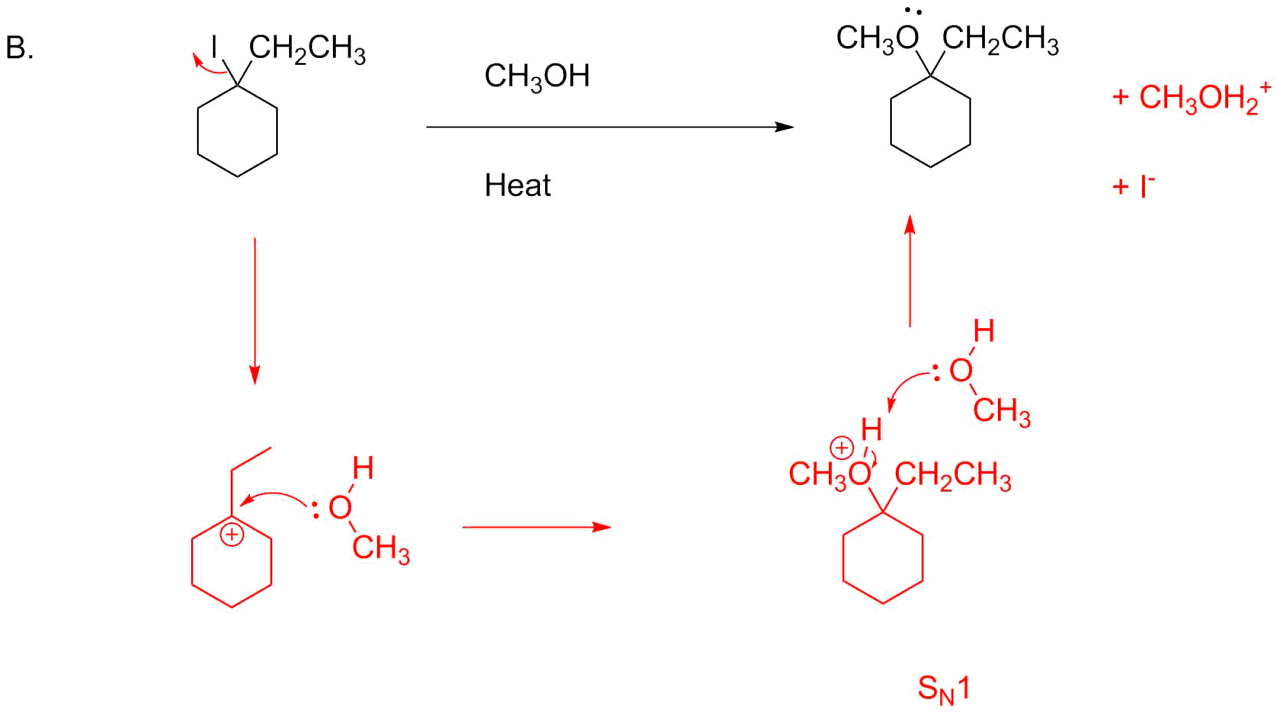
E 

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.

A.

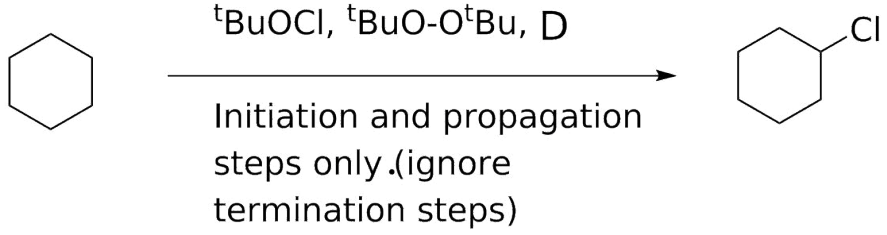


B.



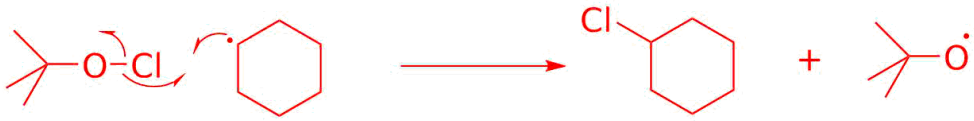
4. (Continued)

C.



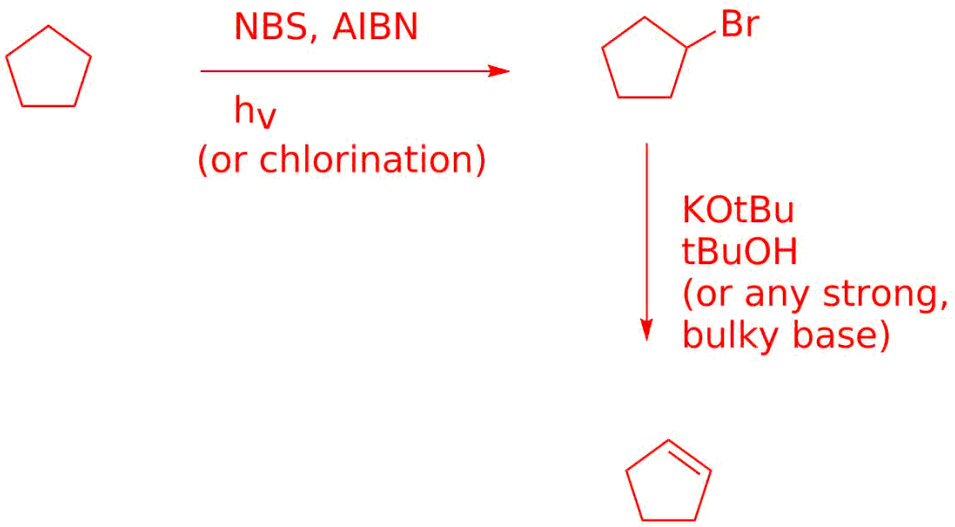
Initiation:

Propagation:

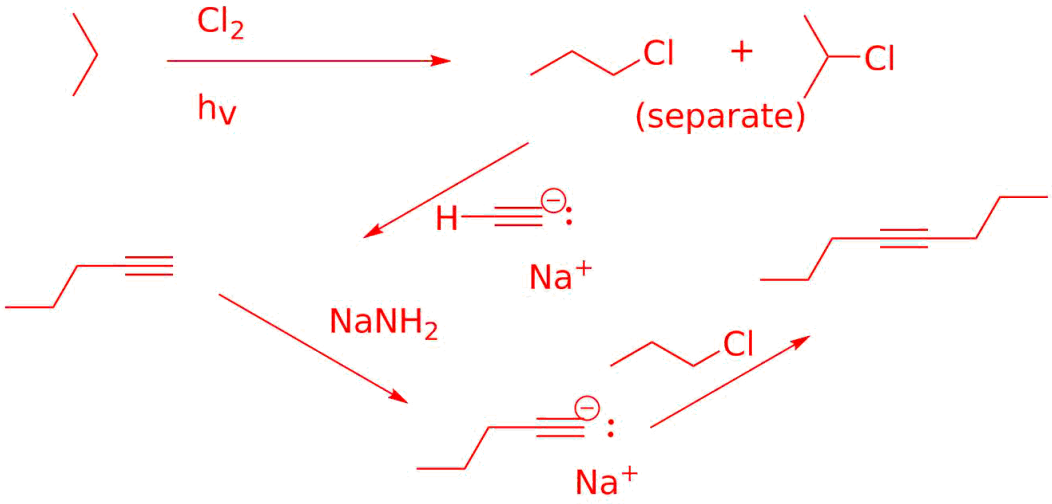


5. (30 points) Each of the following short syntheses can be accomplished with chemistry you know in several steps. Show how to do each, providing reactants and reagents/conditions needed.

A. Cyclopentane to cyclopentene

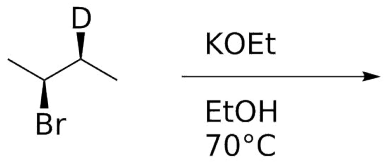


B. Propane to 4-octyne

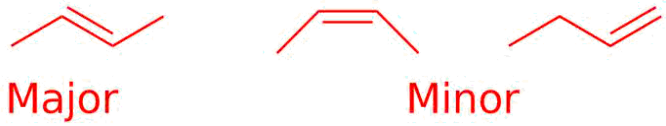


6. (30 points) Deuterium is an isotope of hydrogen that has an extra neutron in its nucleus. Because it is chemically identical to normal hydrogen but can be detected by its heavier mass, it is often used to help determine reaction mechanisms.

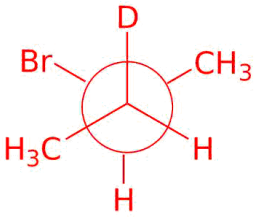
The following deuterated form of 2-bromobutane was reacted under E2 conditions:



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

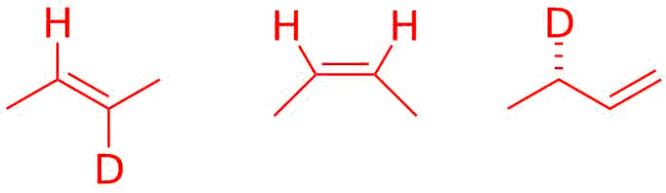


B. For the deuterated form of 2-bromobutane shown, draw the Newman projection for the most stable rotamer looking down the C2-C3 bond.



(Anti-methyls; gauche Br-CH_3 better than gauche CH_3-CH_3

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

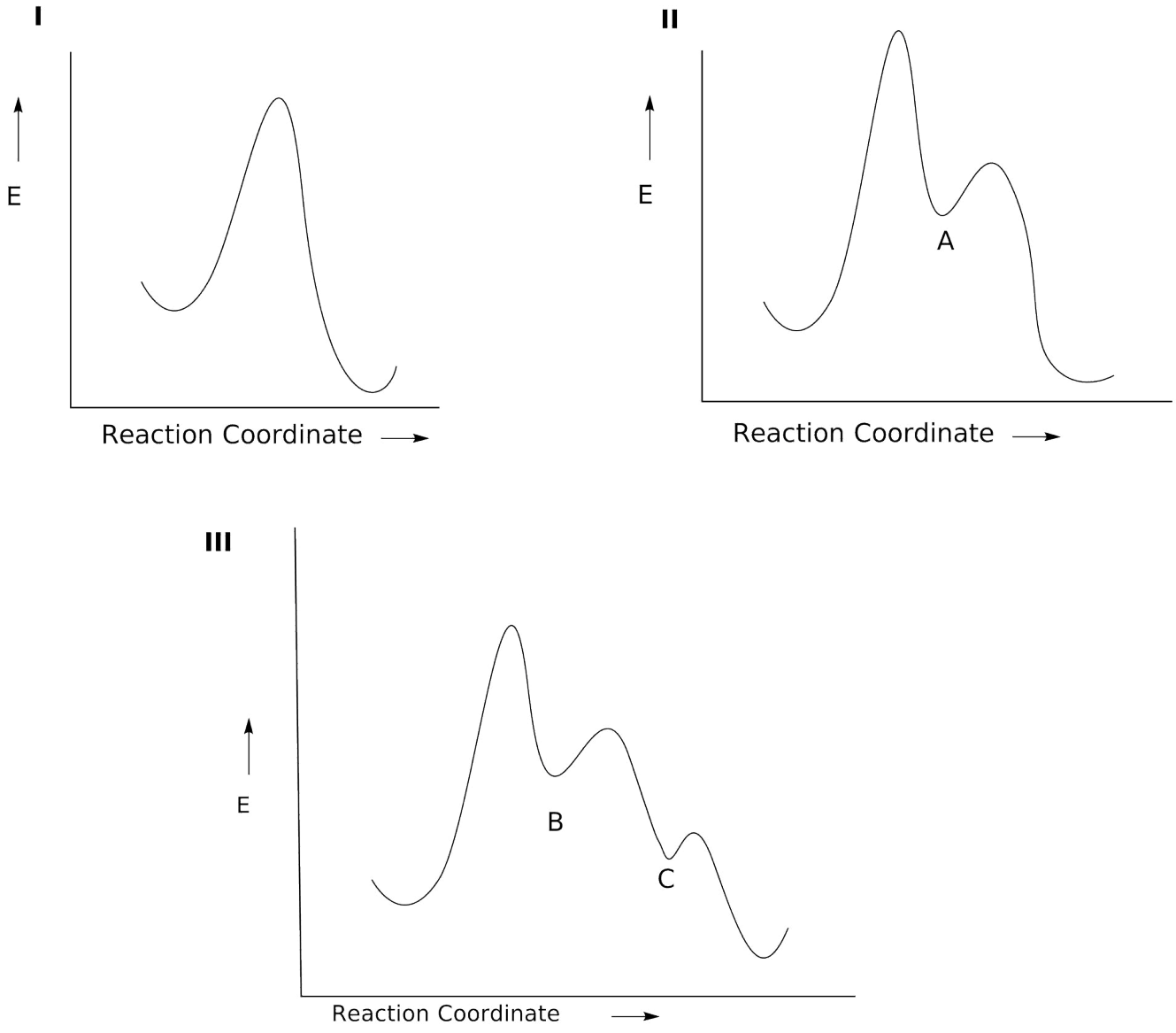


From the Newman projection for (B), we see that H (and not D) will be lost in forming the trans isomer. To get the cis, rotate the bond; this places D anti to Br and so Dbr will be eliminated.

The 1-ene does not involve the deuterated center, so the deuterium will be retained there.

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.



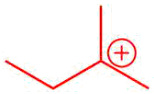
a. $(CH_3)_3CBr + HOCH_2CH_3$ S_N1, with fast loss of proton in the final step: **III**.

b. $CH_3CH_2Br + NaOCH_2CH_2CH_3$ S_N2: **I**.

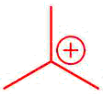
c. $CH_3CH_2C(CH_3)_2Cl + Na^+$ $CH_3CO_2^-$ S_N1: **II**.

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

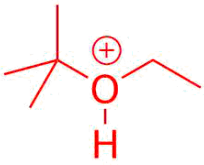
A:



B:



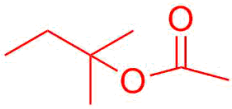
C:



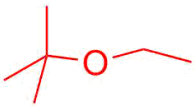
C. Draw the product you expect from each reaction.

I/b.:

II/c:



III/a:



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_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-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
^{i}Pr	2.1
^{t}Bu	>4.5
O-Me	0.75
Cl	0.52
Br	0.55
I	0.46

R = 1.987 cal/(mol-K)
= 8.314 J/(mol-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_{rel} for CH_3Br + Nu: in CH_3OH/25°C)

Et_3P	8.7
HS^-	8.0
I^-	7.4
CN^-	6.7
Et_3N	6.7
CH_3O^-	6.7
HO^-	6.0
Br^-	5.8
N_3^-	5.8
NH_3	5.5
$(CH_3)_2S$	5.3
Cl^-	4.3
$CH_3CO_2^-$	4.3
F^-	2.7
CH_3OH	0
H_2O	0