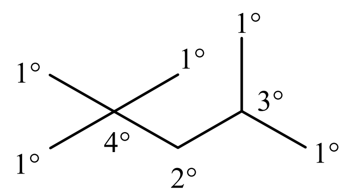
Chem 2P20 Assignment 2 Name: ___________________
Due Monday Oct. 21, 5 pm ID Number: ___________________

1.
"Gasoline" is a mixture of C_5-C_{11} alkanes refined from crude mixtures of hydrocarbons found in deposits all over the surface of the Earth. Branched alkanes burn better than unbranched ones in a car (less engine "ping"), and a desirable alkane for fuel is 2,2,4-trimethylpentane (common name "isooctane"). The quality of the automobile fuel is rated by the Octane Number in the petroleum industry. Isooctane has been given the highest possible Octane Number of 100, while heptane is assigned an Octane Number of 0. The higher the Octane number in a gasoline mixture, the better the combustion in a car. Note at the pumps how cheaper fuels have a lower number ... they contain less branched hydrocarbons!

a) Neatly draw 2,2,4-trimethylpentane in the space provided below: (2 marks)



In your drawing, carefully label each carbon in isooctane as either primary, secondary, tertiary, or quaternary. (4 marks)

b) The heat of combustion of isooctane is -5461 kJ/mol at 25°C. Draw the products of the following reaction: (1 mark)

isooctane + excess O_2 —spark→ $8CO_2 + 9H_2O$

Some economy cars have gas tanks with 40 liter capacities. How much energy is released when such a full gas tank of isooctane is burned? Answer: 1.32×10^6 kJ
Octane has a density of 0.692 g/mL. (1 mark)

For how many days could a 60 Watt light bulb burn with this much energy? 255 days
A Watt is a unit of power; 1 Watt = 1 Joule/second. (2 marks)

Feel free to use this space for your calculations in Question 1:

40 L = 40,000 mL
0.692 g/mL x 40,000 mL = 27,680 g
m.w. of C_8H_{18} = 114 g/mol

27,680 g / 114 g/mol = 242 mols

242 mols x 5416 kJ/mol = 1.32×10^6 kJ
1 day = 24x60x60 = 86,400 seconds
60 W bulb burning for a day consumes 86,400 s x 60 Js^{-1} = 5184 kJ
Bulb burns for 1.32×10^6 / 5184 = 255 days

2. Saturated hydrocarbons have a generic formula C_nH_{2n+2}, e.g., hexane is C_6H_{14}.

Each double bond or ring in a molecule reduces the number of H atoms by 2, e.g., cyclohexane is C_6H_{12} and 1-hexene is also C_6H_{12}. Both cyclohexane and 1-hexene are said to have an *Index of Hydrogen Deficiency* of 1.

For halogen-containing molecules, the halogen atoms are counted as H atoms.
For oxygenated molecules, the oxygen atoms may be ignored for the purposes of computing the Index of Hydrogen Deficiency.
Nitrogen-containing compounds increase the total number of hydrogen atoms expected by one per N atom. For example, methylamine is CH_5N.

Using the rules above, calculate the Index of Hydrogen Deficiency in the following molecules and write the answer on the line provided.

a) (5 marks)

i) Vitamin D3, formula: $C_{27}H_{44}O$ ______6______

ii) Aspartame, formula: $C_{14}H_{18}O_5N_2$ ______7______

iii) Kumepaloxane, formula: $C_{11}H_{17}OBrCl$ ______2______
(an interesting compound found in an marine organism that is used in defense against predators)

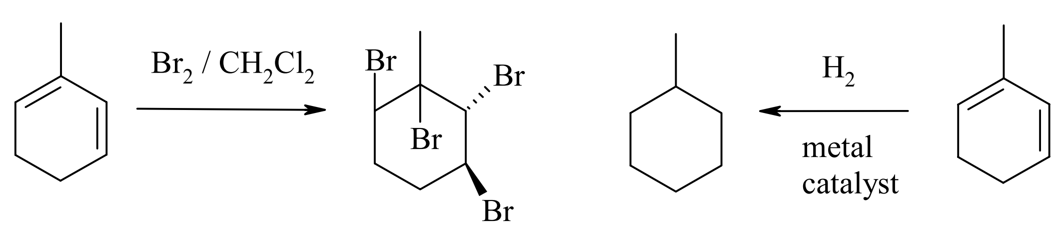
iv) *cis*-Jasmone, formula: $C_{11}H_{16}O$ ______4______
(compound responsible for the smell of Jasmine flowers)

v) Vitamin E, formula: $C_{29}H_{50}O_2$ ______5______

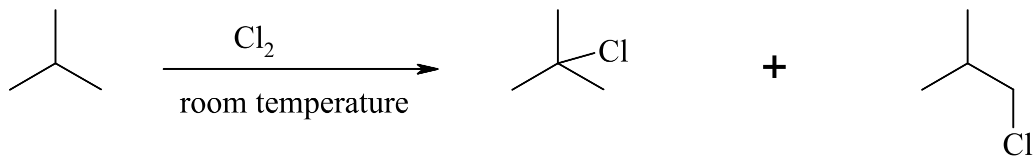
b) Describe a potential method that a chemist could use to determine the actual number of double bonds versus rings in a molecule. (3 marks)

The *Index of Hydrogen Deficiency* only gives the SUM of double bonds and rings in a molecule.

One way to determine the actual number of double bonds is *via* chemical reaction. For example, electrophilic addition with excess bromine or catalytic hydrogenation will both fully saturate a molecule. Then the remaining contribution to the index must come from the number of rings.



3. Chlorination of 2-methylpropane at room temperature yields *tert*-butyl chloride and 1-chloro-2-methyl-propane in about a 1:2 ratio.



36%   64%

a) What is the expected statistical ratio of the two products?

Numerical Answer: 1 to 9 (2 marks)

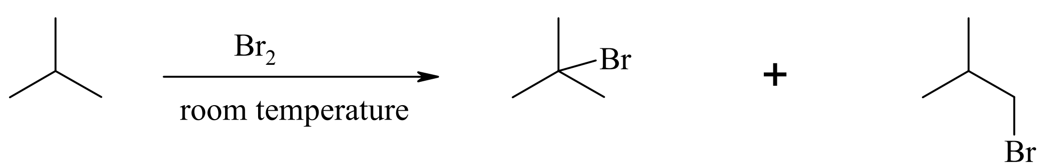
b) Given that the observed ratio differs from the statistical one, calculate the relative reactivity of the tertiary hydrogen compared to the primary one. Please show your work.

The tertiary site yields 36% of the reaction product *but is 9 fold less numerous*.

Therefore the reactivity ratio is 36*9 : 64. Dividing the ratio by 64 yields 5.06:1

Numerical Answer: 5.06 to 1 (3 marks)

Now consider the bromination of the identical hydrocarbon to yield similar brominated products:



99%   1%

d) What is the relative reactivity of the tertiary hydrogen compared to the primary hydrogen in this reaction?

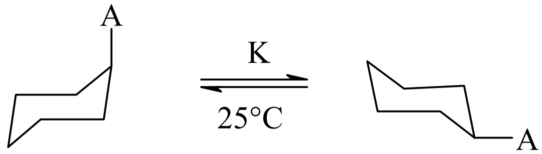
The tertiary site yields 99% of the reaction product *but is 9 fold less numerous*.

Therefore the reactivity ratio is 99*9 : 1, or 891:1

Numerical Answer: 891 to 1 (3 marks)

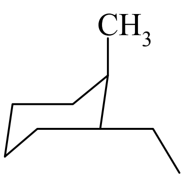
4.

Consider the following data for the equilibrium where A is a substituent group.



A	ΔG°	A	ΔG°
CH_3	-7.1 kJ/mol	F	-1.05 kJ/mol
CH_2CH_3	-7.3 kJ/mol	Br	-2.3 kJ/mol
C(Me)$_3$	-21 kJ/mol	OH	-3.9 kJ/mol

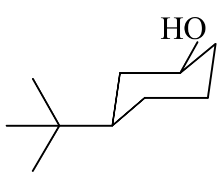
For each equilibrium below, i) provide the IUPAC name of the molecule, ii) Circle YES or NO to indicate if the most stable chair conformation has been drawn, and iii) calculate the % of the most stable chair conformation at equilbrium. Note that substituent effects are *additive*. (9 marks)



a) i) *cis*-1-ethyl-2-methylcyclohexane

ii) YES or NO

iii) ΔG° = (+7.1 - 7.3) kJ/mol = -0.2 kJ/mol; K = exp(-ΔG°/RT)
R = 8.314 $Jmol^{-1}Kelvin^{-1}$ and T = 298 Kelvin
K = 1.084; % = K/(K+1)x100% = 52%

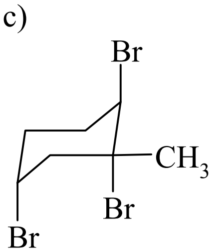


b) i) *cis*-3-tert-butylcyclohexanol or *cis*-3-(dimethylpropyl)cyclohexanol

ii) YES or NO

iii) ΔG° = (-21 - 3.9) kJ/mol = -24.9 kJ/mol
K = 2.32 x10^4; % = K/(K+1)x100% = 99.996% or 100%

c)



i) 1(*R*), 2(*R*), 4(*R*)-tribromo-2-methylcyclohexane or
1(*R*), 2(*R*), 5(*R*)-tribromo-1-methylcyclohexane

ii) YES or NO

iii) ΔG° = (2.3+2.3+2.3 - 7.1) kJ/mol = -0.2 kJ/mol
K = 1.084; % = K/(K+1)x100% = 52%