Chemistry 3A –
Midter

CHEMISTRY 3A – MIDTERM 1 – SPRING 2001 – FRECHET

Professor Jean Fréchet

February 28, 2002

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Please check the section number and name of yo

_____ 161 Margot Paulick
_____ 171 Danielle Dube
_____ 181 Matt Pratt
_____ 191 Laurie Schenkel
_____ 111 Cathleen Yung
_____ 121 Priya Sonik
_____ 131 Paul Furuta
_____ 141 Zach Fresco
_____ 261 Aaron Stutz
_____ 271 Vanessa Sun
_____ 211 Jamey Kain
_____ 221 Laura Anderson
_____ 361 Reema Thalji
_____ 371 Warren Wood

_____ 471 Alex Kollias
_____ 411 Andrew Chi
_____ 421 Shahed Ghoghawala
_____ 431 Mike Slater
_____ 561 Jean Han
__X__ 571 Ognjen Miljanic
_____ 511 Joe Kwon
_____ 521 Catherine Chan
_____ 531 Olga Fedin
_____ 541 Jason Serin

If you are making up an I-grade, indicate the semester you took 3A
_____ and the Professor _____

Do not write in this box.

This exam has **10** pages; **make sure that you have them all.**

Please be sure to use the very useful data given on page 10.

We will only grade answers that are in the designated spaces. Pl
do your scratch work on the backs of the exam pages. Write only
answer to each problem; multiple answers will receive **no** credit,
one of them is correct.

Note: This examination runs for a total of 90 minutes. No questic
be answered by proctors after the exam begins. Please write leg
ambiguous or messy answers will receive **no credit**.

1. (15 points) (a) The elemental analysis of an unknown alcohol reveals that it contains 50% oxygen, 37.5% carbon, and 12.5% hydrogen. What is its empirical formula (show your calculation). Use the following atomic weight values: C = 12, H =1, O = 16.

Answer:

(b) Write Kekule structures for **three** resonance forms of $[CH_2NCH_2]^+$ Show the location of the charge, circle the resonance form that contributes most and explain your choice.

(c) Draw the Lewis-dot structure of the methylene dianion CH_2^{2-} as well as a 3-D structure showing all the orbitals and state the hybridization of the C atom in this dianion.

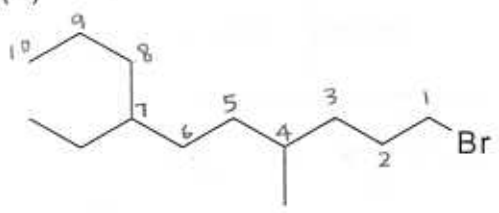
Answer. Hybridization of C is:

Lewis-dot

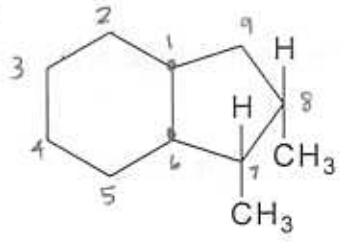
3-D with orbitals

2. (10 points) Name (IUPAC) or draw, as appropriate, the following molecules.

(a)



(b)



(c)

cis-1-chloro-2-ethylcyclohexane

(Most stable chair conformation)

(d)

1,7,7-trimethylbicyclo[2.2.1]heptane

(e)

2,2-dibromo-3-cyclopropylnonane

3. (14 points) (a) What is the SHAPE of the methyl cation CH_3^+, explain using VSEPR (1 sentence!)

Shape:

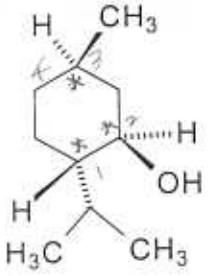
Explanation:

(b) what is the approximate H-C-H bond angle in the methyl anion CH_3^-

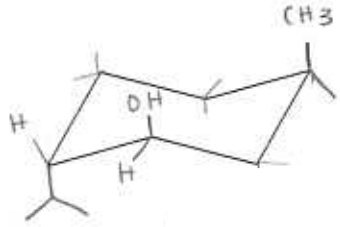
Bond angle:

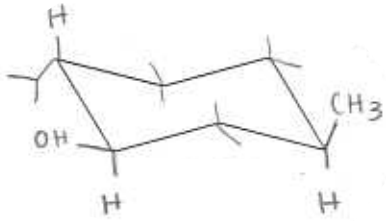
(c) How many stereoisomers are possible for menthol? Answer:
(see structure below)

(d) Draw the two chair conformations of menthol (peppermint oil) and circle the most stable.
*Note: show **all** axial and equatorial bonds corresponding to those on the structure below.*



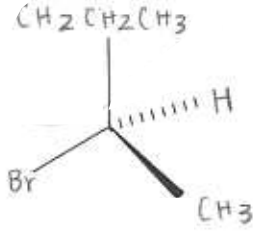
Menthol





(e) How many optically active stereoisomers are obtained by monobromination of pentane C_5H_{12}?
Draw a clear stereochemical representation of each stereoisomer using the template below as a model
Do not write the same structure twice!

Answer:



4. (12 points) (a) Removal of two protons from propyne $HC\equiv C-CH_3$ leads to the propyne dianion $[\ CCCH_2\ ]^{2-}$. Write Lewis-dot structures for two resonance forms of the propyne dianion ***in which all three carbon atoms have an octet***. Do not forget to show the location of any charges! Circle the most important resonance form and explain why it is the most important.

(b) Calculate the change in free energy (expressed in Kcal $mole^{-1}$) needed to change the equilibrium constant of a reaction that takes place at 27°C from 1 to 100? Show the equation(s) you use and the detail of your work.

Answer:

5. (13 points). (a) Name the scientist who discovered that the plane of polarization of plane polarized light is rotated when the light is passed through a solution of camphor

Answer :

(b) Name the scientist who discovered and quantified the dependence of reaction rates on temperature.

Answer :

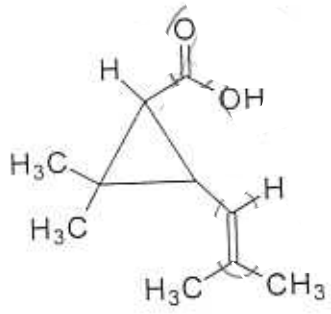
(c) Write the Lewis-dot structure for the sulfate anion SO_4^{2-} in which each oxygen is bound to sulfur in an equivalent manner and indicate the formal charge (if any) assigned to each atom.

(d) Consider the equilibrium: $HA + H_2O \rightleftharpoons A^- + H_3^+O$

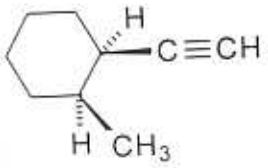
Determine the concentration of $[H_3^+O]$, $[A^-]$, and undissociated acid [HA] for a 1M solution of acid having $pK_a = -2$. Show the details of your work.

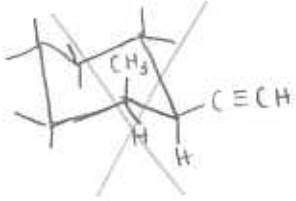
Answers; $[H_3^+O]$ = $[A^-]$ = [HA] =

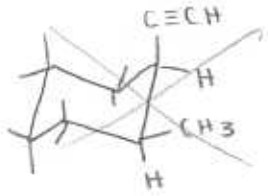
6. (13 points) (a) circle the functional groups in the molecule below and name them



(b) Draw the more stable chair conformation of cis-1-ethynyl-2-metnylcyclohexane (show all bonded atoms on C1 and C2) and explain why this chair is more stable than the other chair conformation.



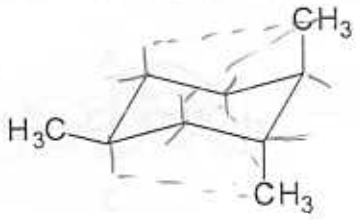




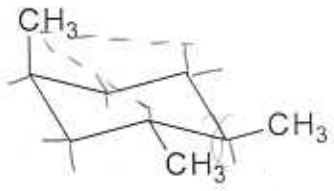
(c) A sample containing both enantiomers of lactic acid has a specific rotation $[\alpha]_D = +0.95°$ Given that the specific rotation of PURE (-)-lactic acid is $[\alpha]_D = -3.8°$, what is the percentage of (-)-lactic acid contained in this sample? Explain and show your detailed work.

Answer: ____ %

7. (13 Points) (a) Consider the two chair conformations of the 1,2,4-trimethylcyclohexane shown below. Name and tally the strains present in each conformation, calculate the total amount of strain in each, and circle the most stable chair.

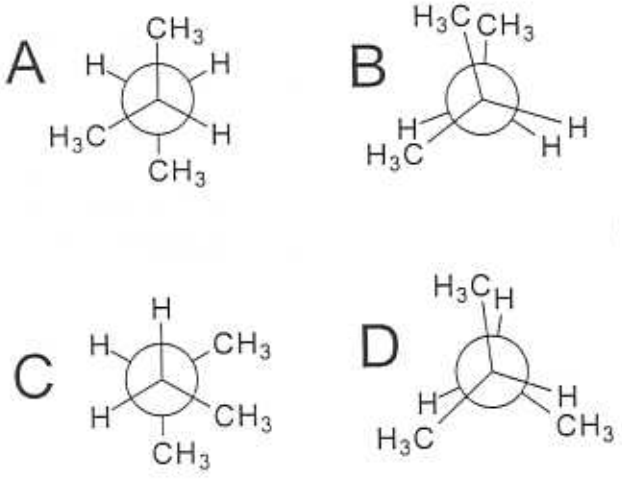


Answer:
Total strain =



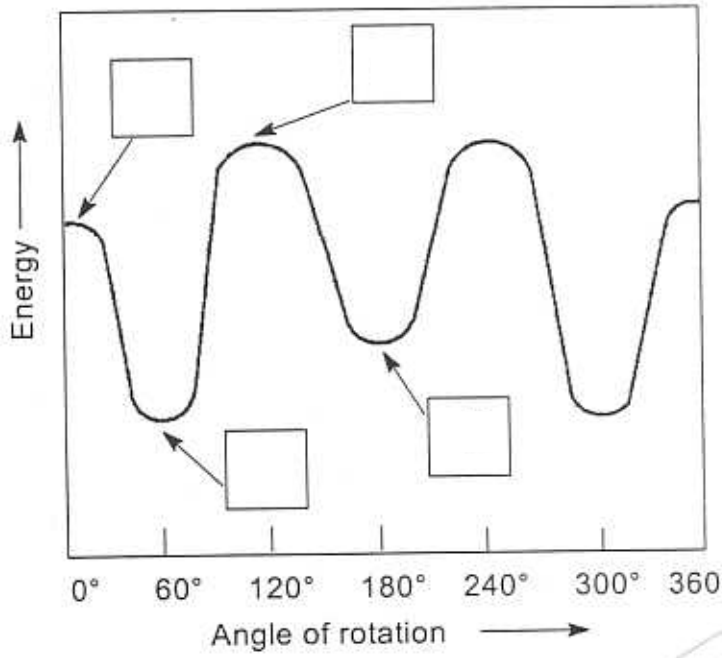
Answer:
Total strain =

(b) Match the letters of the staggered and eclipsed Newman projections below to the indicated positions on the diagram describing the relative energies of different conformations of 2-methylbutane.

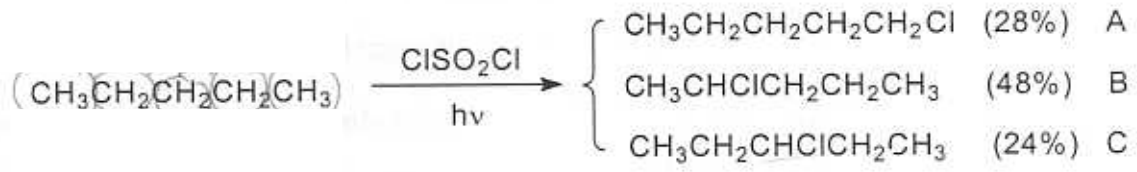


Staggered conformations

Eclipsed conformations



8. **(10 points)** (a) The free radical chlorination of alkanes with sulfuryl chloride $ClSO_2Cl$ does not produce the same mixture of monochlorinated products as would be obtained using Cl_2 and light. Using the product compositions below, calculate the selectivity of the $^{\cdot}SO_2Cl$ radical for primary, and secondary hydrogens. Show the details of your work.



Answer. Relative reactivity **secondary/primary =**

(b) Consider the chlorination of alkanes with chlorine in the presence of light.

(i) Alkane A (C_5H_{12}) reacts to produce only one monochlorinated product. Write the **IUPAC name** of the monochlorinated product.

Answer:

(ii). Alkane B (C_7H_{16}) reacts to produce seven monochlorinated products (ignore stereoisomers). Write the **structure** of alkane B.

Answer:

/5

Note: **There are no questions to be answered on this page**, it only contains data that may be of use in solving the questions contained in this exam. Not all of the data given is needed.

Value of gas constant: R = 2.0 cal deg^{-1} mol^{-1} Value of absolute zero (kelvin) = -273°C

Value of e (base for natural logarithms) e = 2.718

Bond dissociation energies (in kcal $mole^{-1}$): RCH_2—H 98; R_2CH—H 95; R_3C—H 91; Cl—Cl 58; Br—Br 46; I—I 36; H—Cl 103; H—Br 88; H—I 71; RCH_2—Cl 81; RCH_2—Br 68; RCH_2—I 53; R_2CH—Cl 80; R_2CH—Br 68; R_3C—Cl 79; R_3C—Br 65;

Values of strain energies:

Each CH_3 - H eclipsing interaction: 1.5 kcal mol^{-1}

Each H - H eclipsing interaction: 1.0 kcal mol^{-1}

Each CH_3 - CH_3 eclipsing interaction: 2.5 kcal mol^{-1}

Each CH_3 - CH_3 gauche interaction: 0.9 kcal mol^{-1}

Each t-Butyl - CH_3 gauche interaction: 2.0 kcal mol^{-1}

Each CH_3 - H 1,3-diaxial interaction: 0.8 kcal mol^{-1}

Each Cl - H 1,3-diaxial interaction: 0.25 kcal mol^{-1}

Each CH_3 - CH_3 1,3-diaxial interaction: 1.6 kcal mol^{-1}

Each H - CN 1,3-diaxial interaction : 0.1 kcal mol^{-1}

Each H - $C(CH_3)_3$ 1,3-diaxial interaction: 2.5 kcal mol^{-1}

Formulae used in solving quadratic equations:

$ax^2 + bx + c = 0$ $x = [-b \pm (\textit{square root of } (b^2 - 4ac)] / 2a$

Partial periodic table of the elements.

IA	IIA	IIIA	IVA	VA	VIA	VIIA	O
1 H 1.00794							2 He 4.00260
3 Li 6.941	4 Be 9.01218	5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80