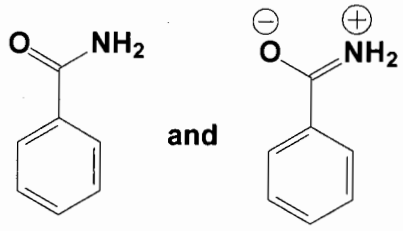
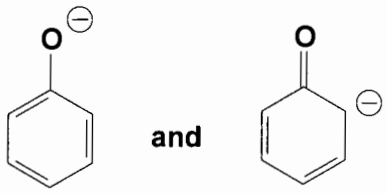
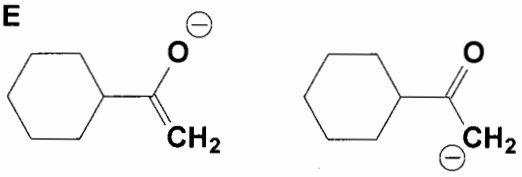
1. (11 Points)

(a) Choose one answer to the question: which of the following pairs are not resonance structures of each other? Circle the letter corresponding to your answer in the appropriate box.

A  and

D  and

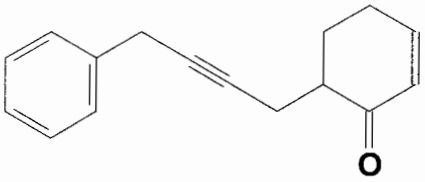
(B) All are pairs of resonance structures

E 

C $H_2C-C\equiv C-H$ and $H_2C=C=C-H$

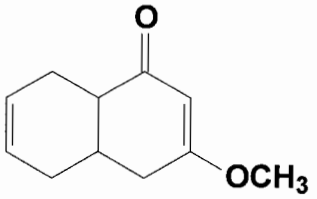
(b) Consider the following molecules (for each, write your answer in the box provided).

How many carbons are in the sp^2 hybridization state?



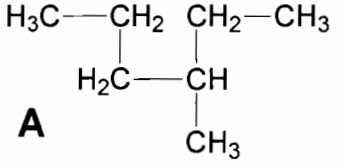
Answer: 9

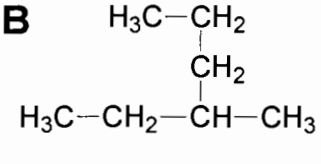
How many carbons are in the sp^3 hybridization state?

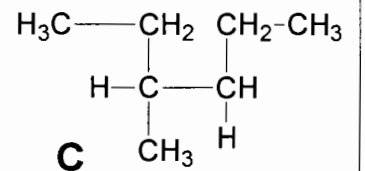


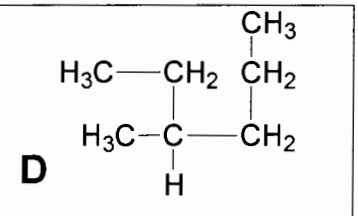
Answer: 6

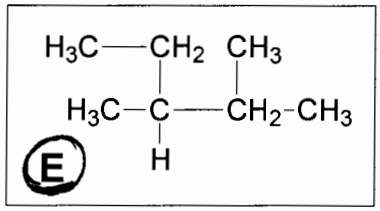
(c) Which of the following molecule is not chemically identical to the others. Circle the letter corresponding to your answer in the appropriate box.

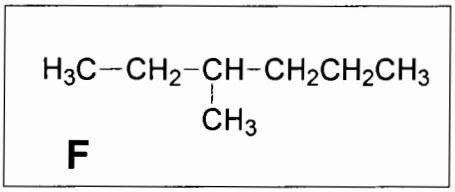
A 

B 

C 

D 

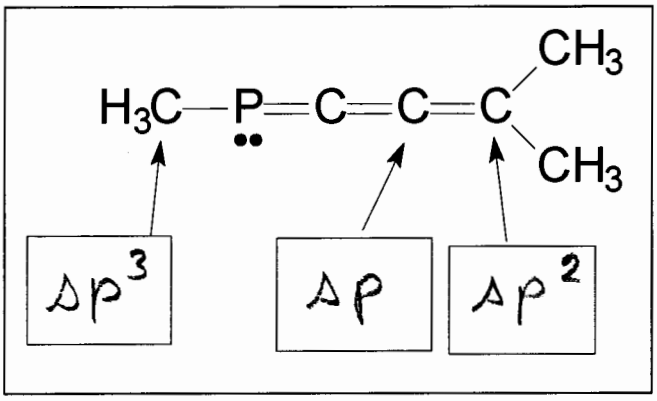
(E) 

F 

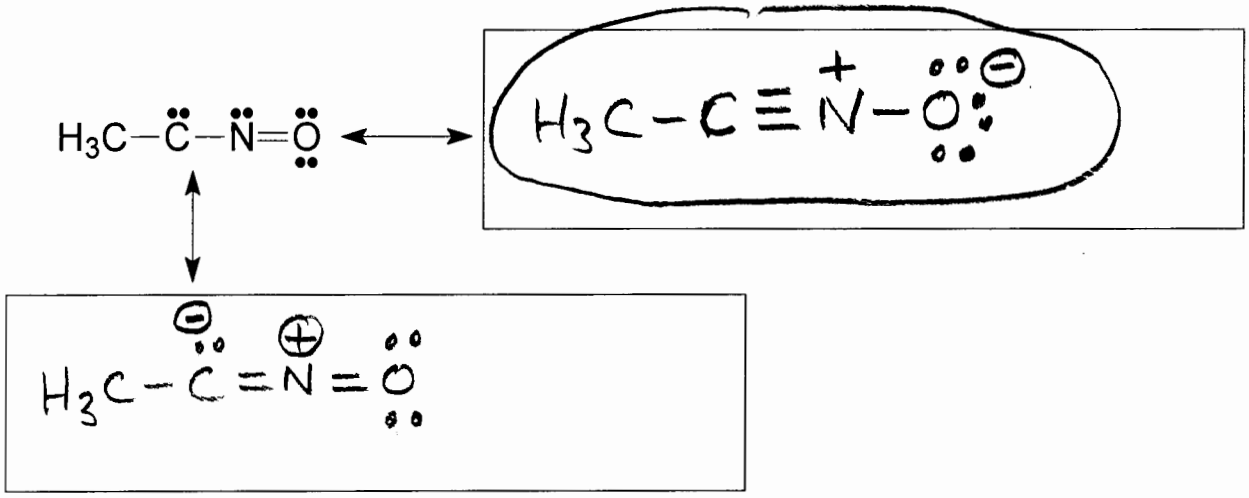
(d) What is the value of the H-O-H bond angle in water? Answer: 104.5° (± 1.5° ok)

(e) Using VSEPR deduce the shape of the molecule of BeH_2? Answer: linear

2. (13 Points) (a) What is the hybridization state of each atom highlighted with an arrow pointing to it. Place each individual answer in the box provided at the end of each arrow.



2. (b) An unimportant resonance form of acetonitrile oxide is shown below. Write two additional resonance forms that are more important as all C, N, and O atoms have an octet and some have +1 and -1 formal charges. Which is the most important resonance form? Circle it and explain.



Explanation: The circled structure is the most important resonance form because

Negative charge is on oxygen (more electronegative)

2. (c) How many σ (sigma) and how many π (pi) bonds are present in each of the molecules below. Write your answers in the appropriate boxes.

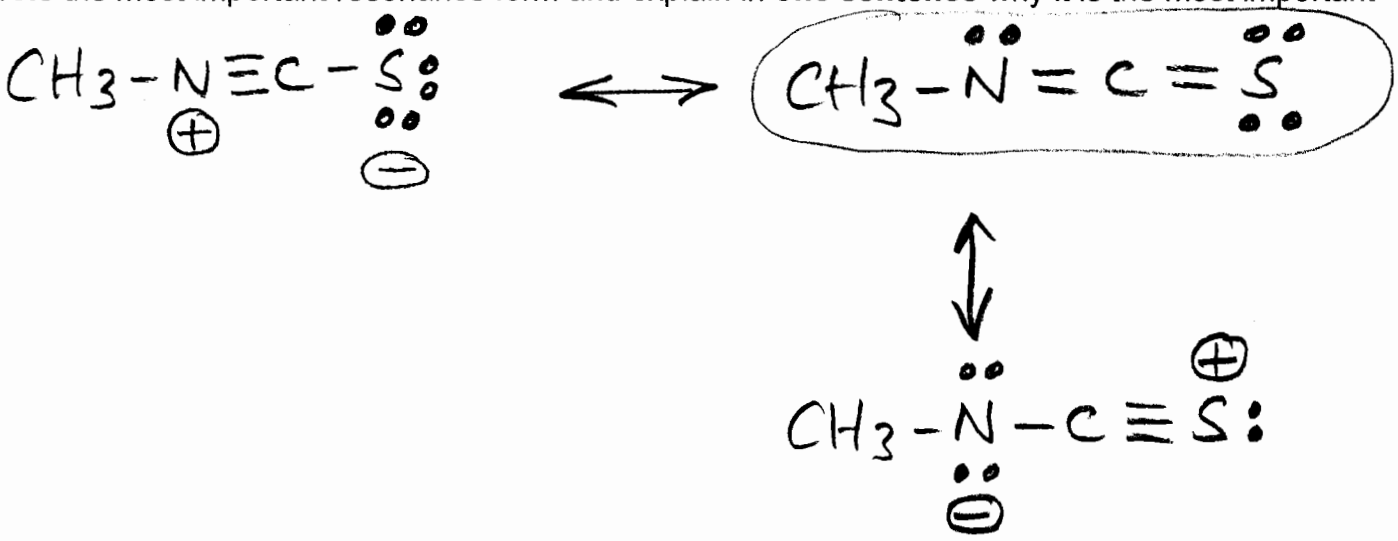
$H-C\equiv C-C\equiv C-H$

σ bonds:	5
π bonds:	4

$H_2C=CH-C\equiv N$

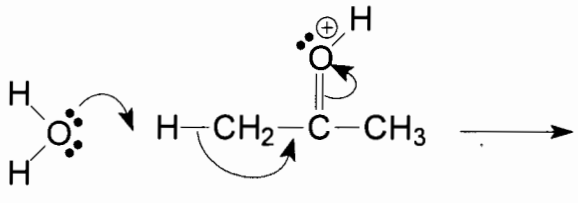
σ bonds:	6
π bonds:	3

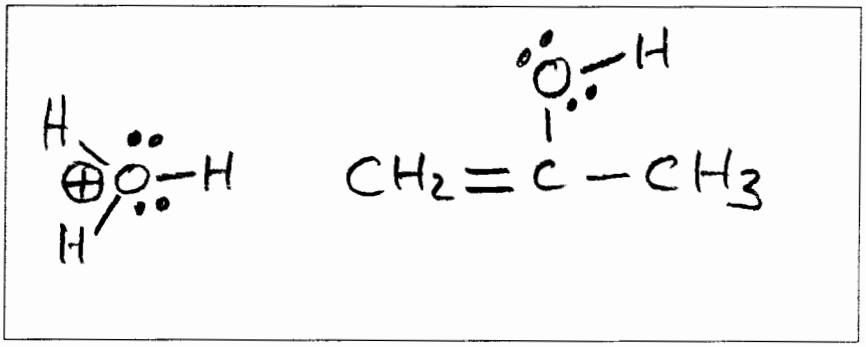
3. (12 Points). (a) Draw **three** resonance forms (showing all unshared doublets and charges) for methyl isothiocyanate H_3C-NCS (in which the atoms are linked in this order). All C, N, S atoms must have an octet and some may have formal charges of 0, +1, or -1. *(Do not show more than three!).* **Circle** the most important resonance form and explain in **one sentence** why it is the most important

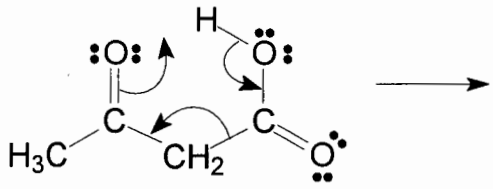


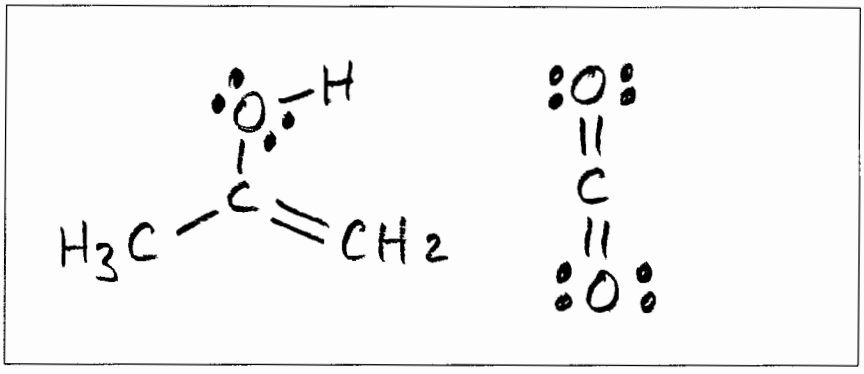
Explanation: There are no charges on any atom

(b) Using the curved arrows suggesting the mechanism of the reactions, **show the product(s)** obtained in each of the reactions below (show all unshared doublets and all charges if any)



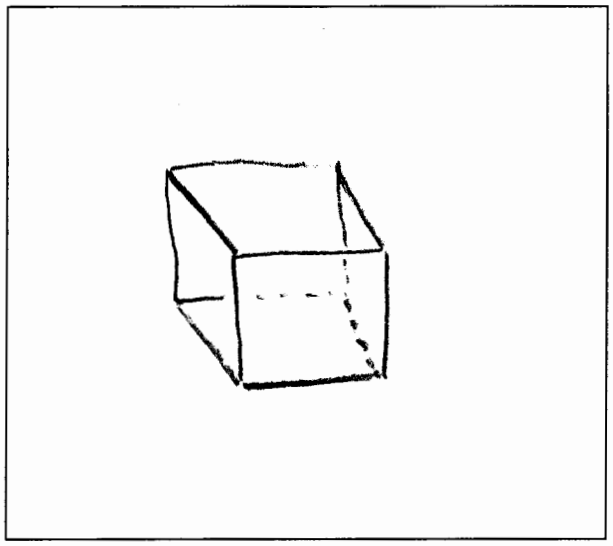




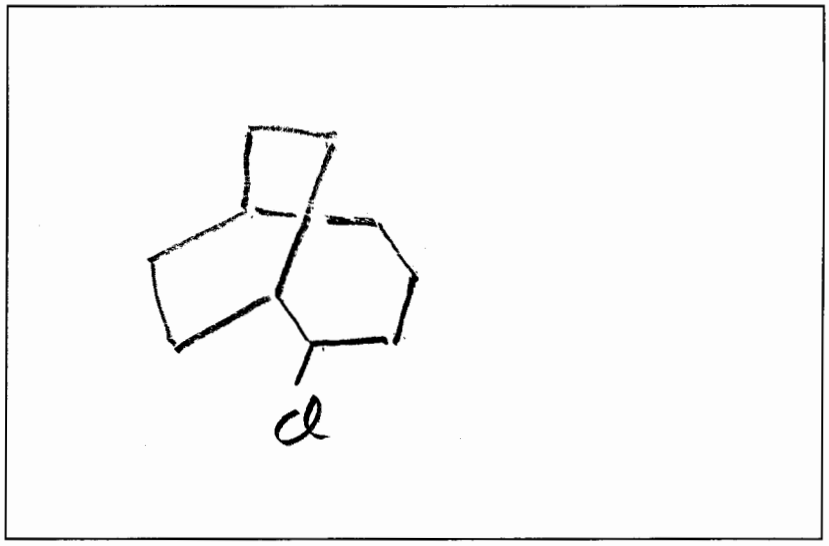


4. (12 Points). (a) DRAW a clear structure for each of the following molecules

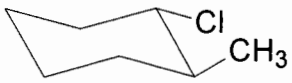
(i) Cubane



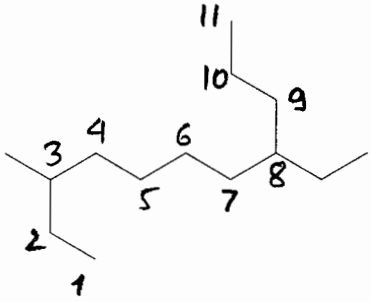
(ii) 2-chlorobicyclo[4.2.2]decane



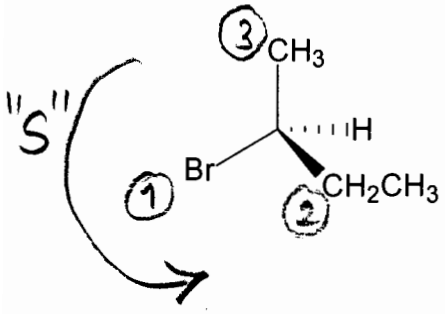
(b) Name the following compounds (IUPAC nomenclature)



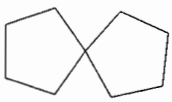
Trans-1-chloro-2-methyl cyclohexane



8-ethyl-3-methyl undecane

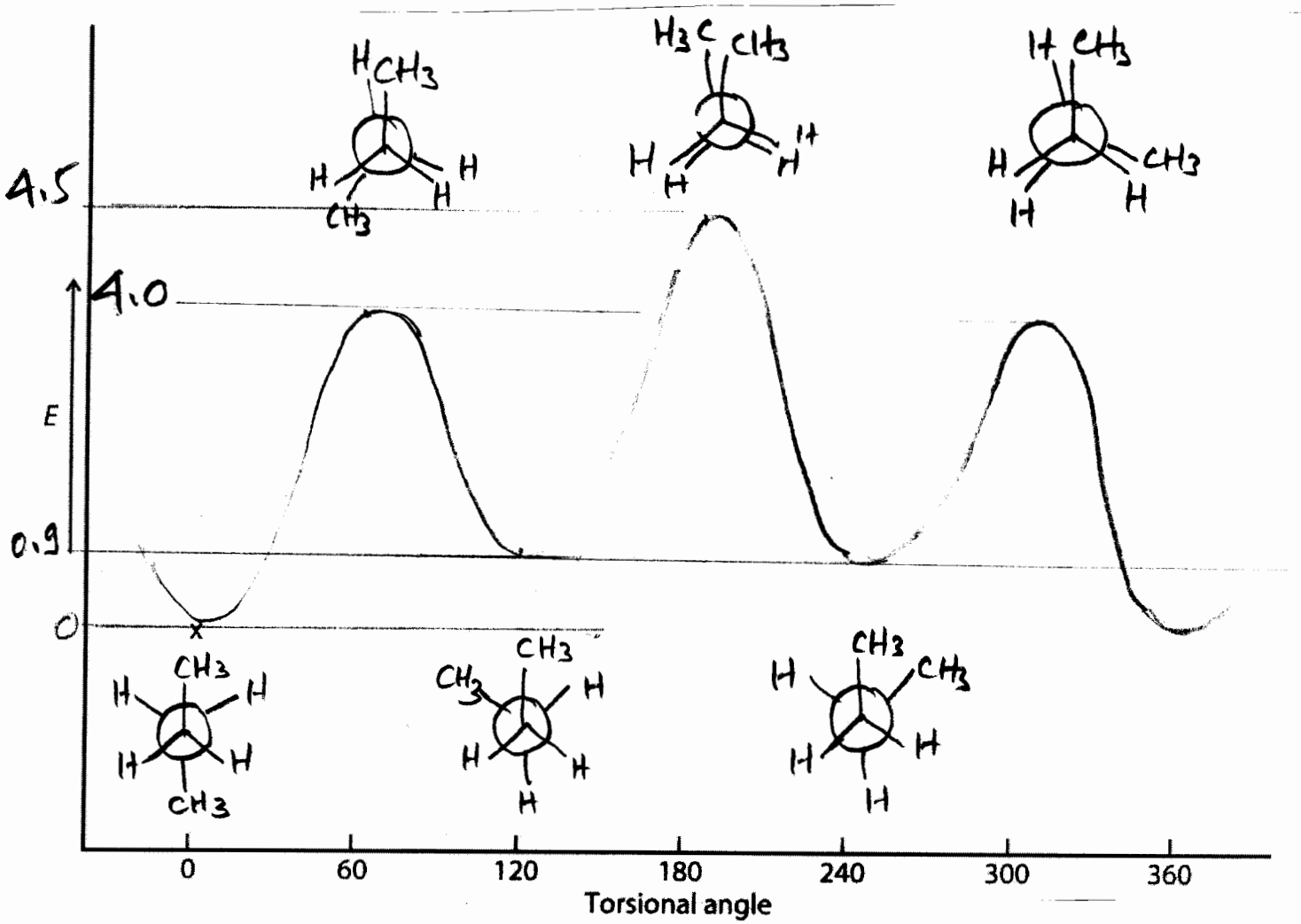


(S)-2-Bromobutane



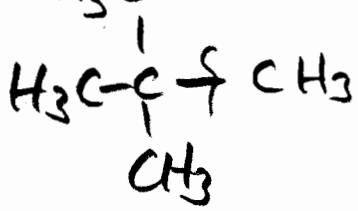
spiro [4.4] nonane

5. (13 Points). (a) Draw a potential energy diagram for the rotation about the C2-C3 bond of butane. Show Newman projections for all conformations located at the maximum and minimum points on your graph. Start the potential energy curve with the lowest energy conformation at the location marked with an x on the graph below and assign relative energy values to all the conformations at energy maxima and minima on your diagram.



(b) Which C-C bond would break first in a pyrolysis reaction: a C-C bond of ethane or a C-C bond of 2,2-dimethyl propane? Provide a quantitative explanation using the data on page 10.

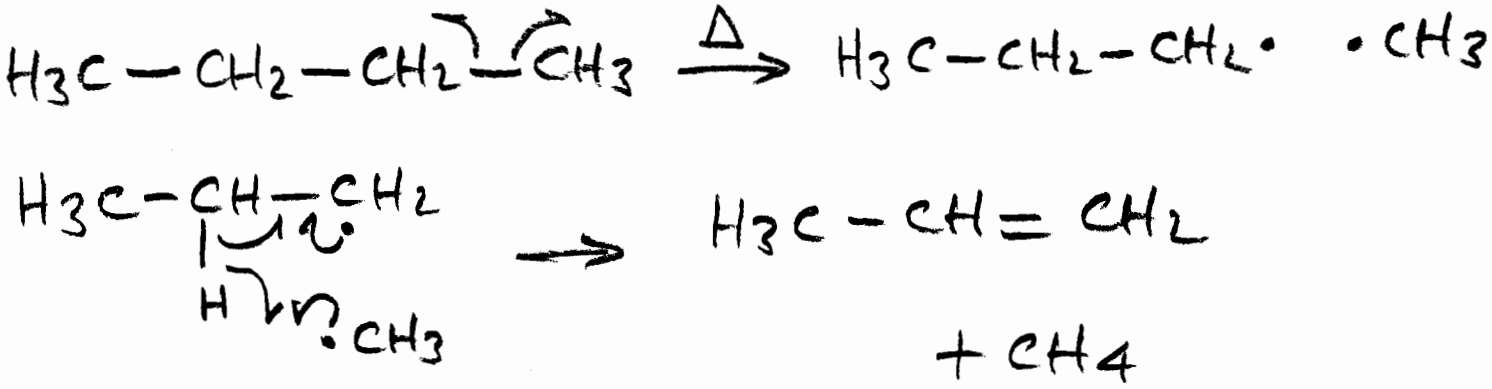
H_3C–CH_3 Bond dissociation E = 90 Kcal mole^{-1}



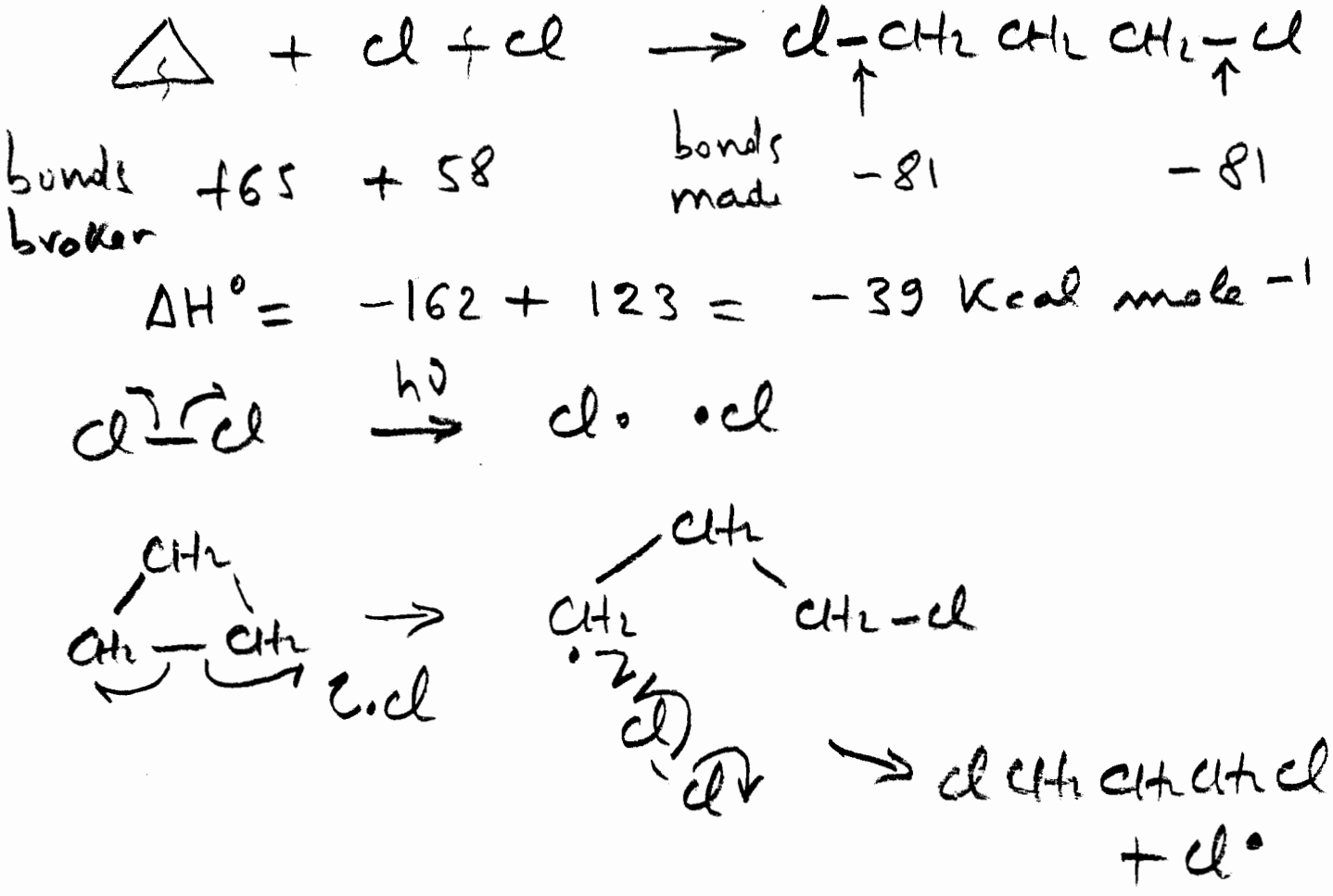
BDE = 87 Kcal mole^{-1}

The bond of 2,2-dimethylpropane would break first due to lower value of BDE

6. (12 Points). (a) Show a mechanism (equations with the appropriate curved or "fishhook" arrows) for the formation of $H_2C{=}CH{-}CH_3$ during the thermal cracking (pyrolysis) of butane $H_3C{-}CH_2{-}CH_2{-}CH_3$



(b) The reaction of **cyclo**propane with chlorine (Cl_2) in the presence of light is known to produce 1,3-dichloropropane. Write an overall equation for this process and show a step by step mechanism for the formation of this unexpected product. Calculate the change in enthalpy for this reaction



Answer: Change in Enthalpy = −39 Kcal mole^{-1}

7. (12 Points) (a) Calculate the optical purity (% ee) and the percentage of each enantiomer in a mixture of (+) and (-) isomers of alanine with an optical rotation of -1.70° given that pure (+) alanine has a specific rotation of +8.5°. Show the detail of your calculation

Optical purity = $\frac{-1.70}{-8.5} \times 100 = 20\%$

20% (+) + 80% racemic 50% Racemic = { 40% (+) / 40% (-)

Optical purity = 20 % % of (+) isomer = 40 % of (-) isomer = 60

(b) A solution containing 0.7g per 10 mL of coniine is placed in a 5cm long polarimeter cell exhibits a clockwise optical rotation of 0.6°. Calculate its specific rotation [α].

$[\alpha] = \frac{\alpha}{l \times c} = \frac{0.6}{0.5 \times 0.07} = 17^\circ$

Answer: [α] = 17°

(c) Calculate ΔG° for the dissociation of fluoroacetic acid at 25°C (pK_a = 2.66). Show the details of your calculation.

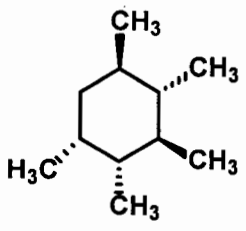
$\Delta G^\circ = -RT \ln K_a = -2.3\, RT \log K_a$

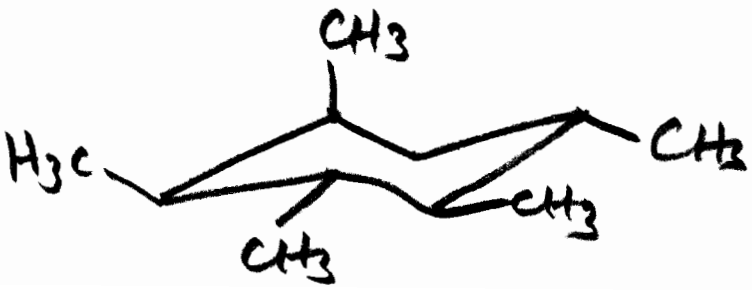
$= 2.3\, RT\, pK_a$

$= 2.3 \times 2 \times 298 \times 2.66 = 3646$ cal/mole

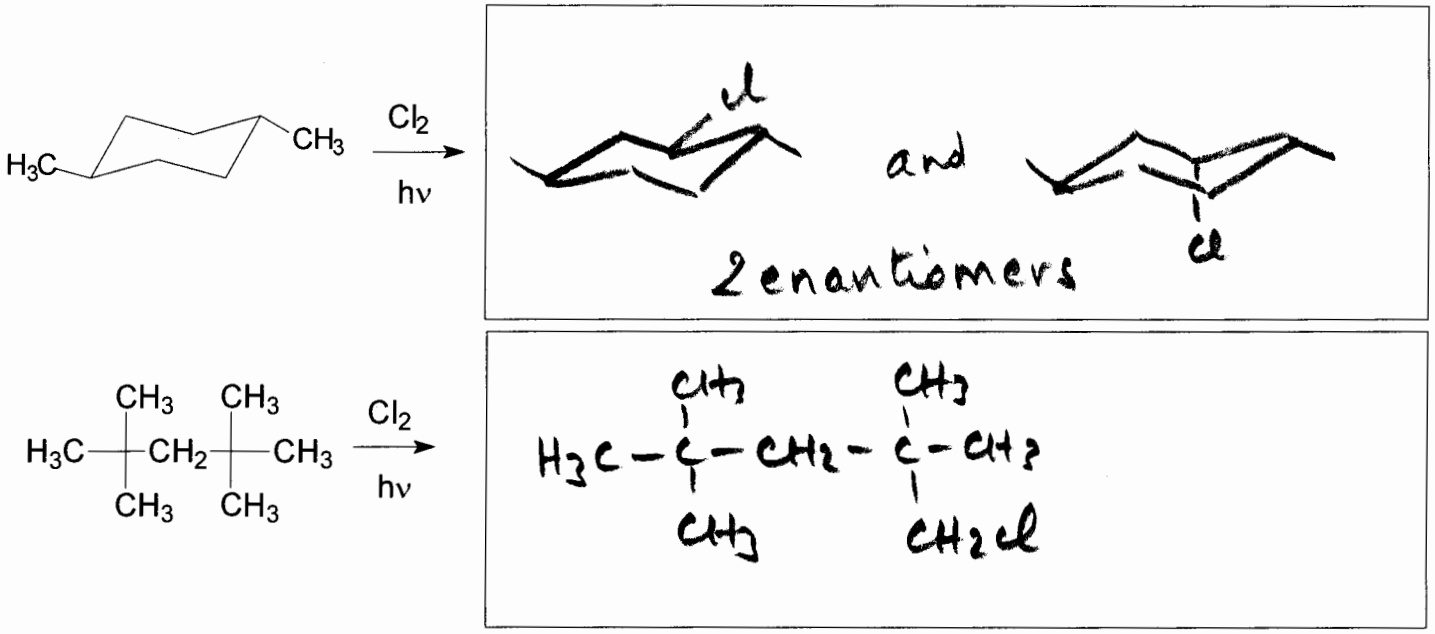
Answer: 3.64 Kcal mole^{-1}

(c) Draw a structure of the compound below in its more stable chair conformation





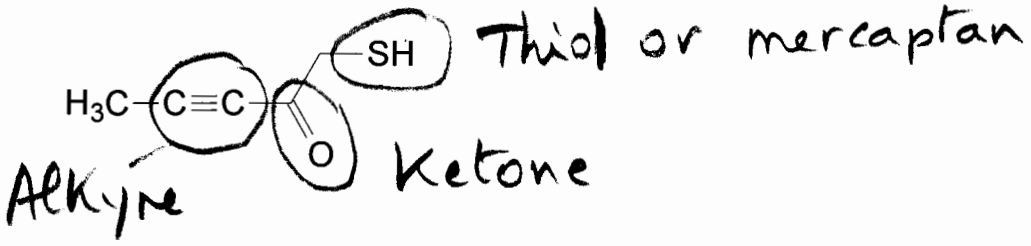
8. (15 Points) (a) Show a clear structure for the major product(s) obtained in each of the following monochlorination reactions initiated with light at room temperature.



(b) Name the scientist who established the scale of electronegativity of elements

Answer: PAULING

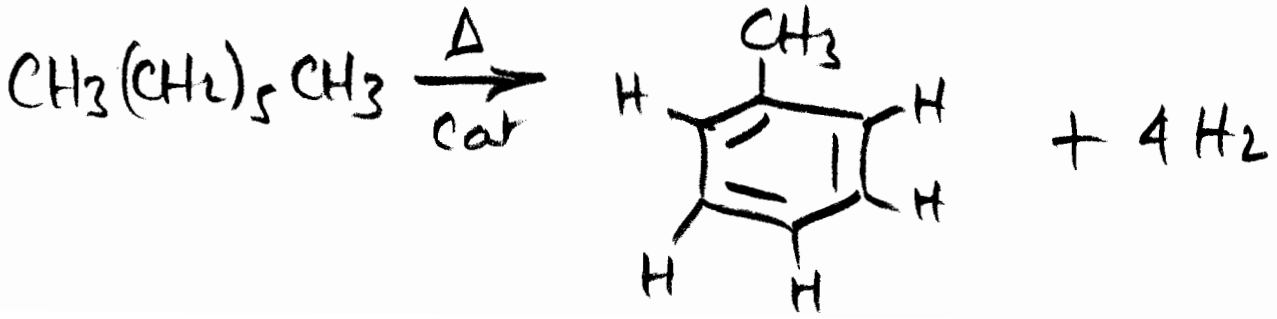
(c) Circle the functional groups in the molecule below and name them.



(d) Name the scientist who proposed that bonds are made by the in-phase overlap of atomic orbitals.

Answer: PAULING

(e) Write a balanced equation showing the catalytic **reforming** of heptane $CH_3(CH_2)_5CH_3$ into a C7 aromatic hydrocarbon and a gaseous by-product.



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 for Alkanes

Compound	$DH°$ [kcal mol^{-1} (kJ mol^{-1})]	Compound	$DH°$ [kcal mol^{-1} (kJ mol^{-1})]
CH_3–H	105 (439)	CH_3–CH_3	90 (377)
C_2H_5–H	101 (423)	C_2H_5–CH_3	89 (372)
C_3H_7–H	101 (423)	C_2H_5–C_2H_5	88 (368)
$(CH_3)_2CHCH_2$–H	101 (423)	$(CH_3)_2CH$–CH_3	88 (368)
$(CH_3)_2CH$–H	98.5 (412)	$(CH_3)_3C$–CH_3	87 (364)
$(CH_3)_3C$–H	96.5 (404)	$(CH_3)_2CH$–$CH(CH_3)_2$	85.5 (358)
		$(CH_3)_3C$–$C(CH_3)_3$	78.5 (328)

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}

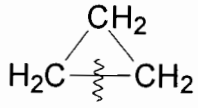
Each CH_3 - CH_3 1,3-diaxial interaction: 1.6 kcal mol^{-1}

Each H - CN 1.3-diaxial interaction : 0.1 kcal mol^{-1}

Bond dissociation Energies

Cl–Cl 58 Kcal $mole^{-1}$

RCH_2–Cl 81 Kcal $mole^{-1}$



65 Kcal $mole^{-1}$