

LAB REPORT: REACTIONS OF ALKYL HALIDES: RADICAL SUBSTITUTION

NAME: _____

PARTNER'S NAME: _____

LAB SECTION: _____

DATE: _____

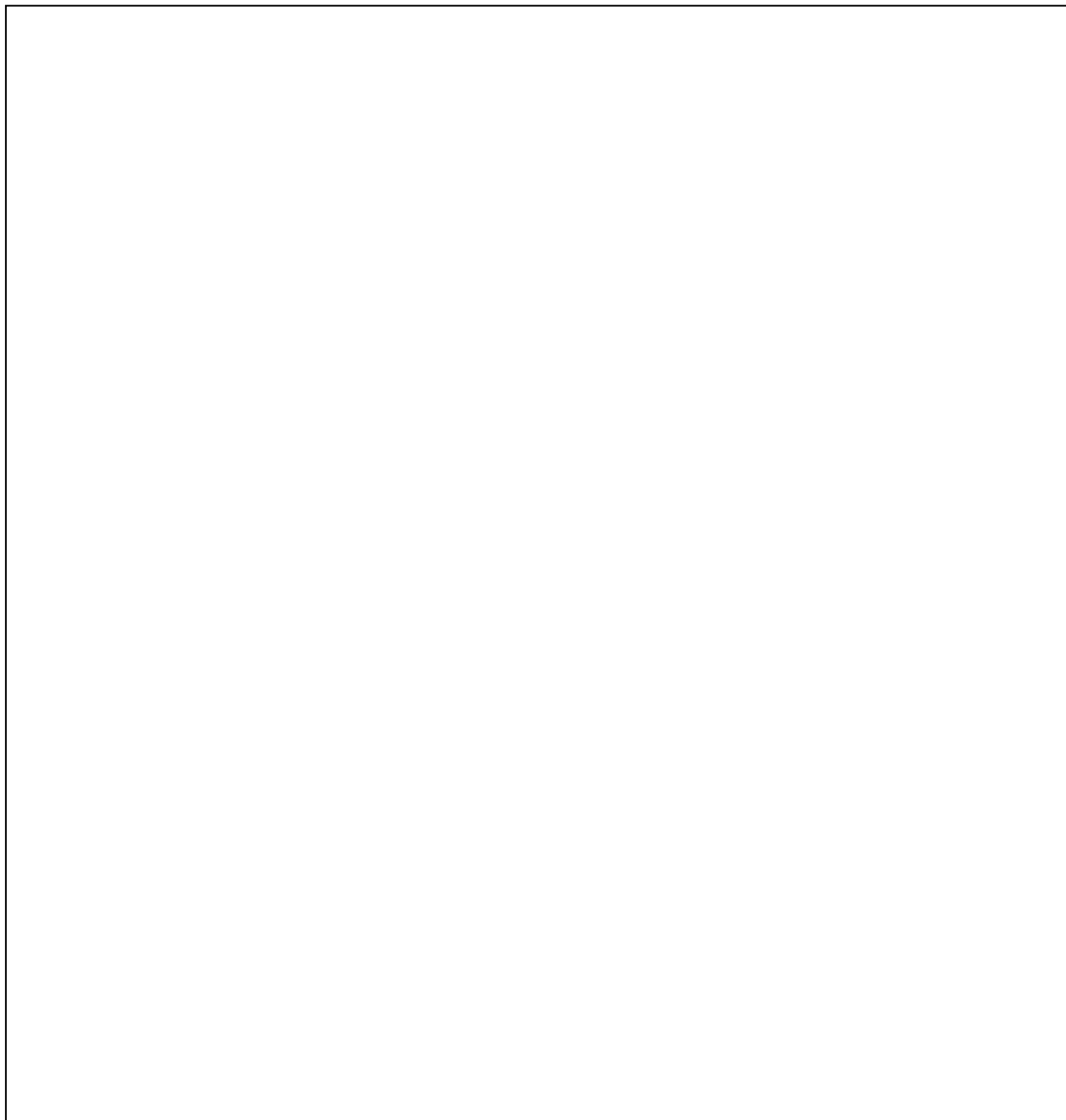
% SCORE:

Lab Notebook	
Abstract	
Mechanism of radical substitution	
Radical Chlorination Statistical Prediction, reactivity	
HNMR 1-Chlorobutane	
Questions	
Essay: Discuss & Interpret your results	
Total	

A. ABSTRACT: CHLORINATION OF 1-CHLOROBUTANE

B: CHLORINATION OF 1-CHLOROBUTANE

Show the Reaction mechanism- include initiation, propagation and 1 termination step. Use structures and arrows. Include the initiator, AIBN, in your mechanism. You only need to show formation of one possible product.



C. DATA ANALYSIS

Table 1. GC Results

Compare the **statistical prediction** of product distribution with the **actual ratio obtained** in the experiment, determined from the GC analysis. Attach (staple) the chromatogram to your report.

Compound	B.P. (°C)	RT (min)	Statistical ratio	Statistical %	GC area	Calculated % Area
1, 1-dichlorobutane	114					
1, 2-dichlorobutane	124					
1,3-dichlorobutane	134					
1,4-dichlorobutane	162					
						Total product area =100%

- The statistical ratio is the ratio of the number of equivalent hydrogen atoms at the position that has been substituted to the total number of hydrogen atoms in chlorobutane.
- GC area should be obtained from your chromatogram
- To obtain Calculated % Area for each compound, divide the GC area of the compound by the sum of the GC area for all disubstituted products.

Table 2. Reactivity Analysis

Calculate relative reactivity of each position in 1-Chlorobutane per hydrogen.

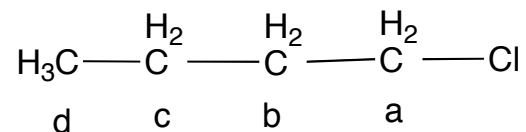
Express the reactivity of C1, C2, and C3 per Hydrogen atom in comparison with the reactivity at C4, the farthest from chlorine and the least influenced by its electronegativity.

Carbon T #	Hydrogen position on 1-chlorobutane	Area % per H atom	Relative reactivity (vs. reactivity at C4)
o 1	Cl-CH ₂ -CH ₂ -CH ₂ -CH ₃		
a 2	Cl-CH ₂ -CH ₂ -CH ₂ -CH ₃		
b 3	Cl-CH ₂ -CH ₂ -CH ₂ -CH ₃		
t 4	Cl-CH ₂ -CH ₂ -CH ₂ -CH ₃		
i			

- To obtain the Area % per H atom: First, divide the Calculated % Area (last column in 1 above) of the dichlorinated structure by the number of hydrogens that can be substituted at that particular position.
- To calculate the relative reactivity for C1, C2, and C3, divide the **Area % are per H** by the **Area % per H value for C4**. C4 has 3 hydrogen attached, is primary and the same base used for references in specifying the relative reactivity of alkanes, the group used as reference. Since we are dividing by C4 the relative reactivity of this position is 1.

3. NMR data analysis: 1-Chlorobutane

Label the provided HNMR of 1-chlorobutane with the each proton signal as shown in the structure below.



Briefly discuss how you assigned each signal based upon proximity to the chlorine and splitting into multiplets.

Ha

Hb

Hc

Hd

Show a calculation of the coupling constants between Ha and Hb, (J_{ab}) and Hc and Hd (J_{cd}). Do you expect these coupling constants to be identical? Explain.

D. QUESTIONS:

1. Draw a Lewis Dot structure of the reaction byproduct, sulfur dioxide.
2. According to your overall reaction what is the mole ratio of sulfuryl chloride to 1-chlorobutane? Did you use a stoichiometric amount of sulfuryl chloride in the reaction? Offer an explanation for your experimental ratio of these reactants.

3. The initiation of the reaction uses AIBN which decomposes to N_2 and a “relatively stable radical”. Draw the structure of the radical formed and explain how the structure of the radical influences its stability.
4. The reaction is worked up by washing with sodium bicarbonate. Why is this solution used instead of sodium chloride or water?
5. One of the four products you obtained via chlorination from 1-chlorobutane, would show a different number of ^{13}C NMR peaks than the other three. Give the **name, the structure of this product, and a brief explanation of why it would have a different CNMR spectrum.**
6. What products would you expect from the chlorination of 2-methylpropane? In what statistical ratio? Draw each product structure and state % expected. Remember that the average reactivity per hydrogen in free radical chlorination of unsubstituted alkanes is $3^\circ > 2^\circ > 1^\circ$ in a ratio of 5.0: 3.8 : 1.

E. DISCUSSION:

Based on your experience with this lab and the amount of information you collected and analyzed write A short essay regarding:

Radical substitution and relative reactivity.

First, compare the percent of each product from **Table 1. GC Results** to the statistical percent predicted. Does your Calculated % Area follow the statistical % predicted? Offer an explanation for any observed differences.

Second using your results from **Table 2. Relative Reactivity**, discuss how chlorine at the C1 affects the reactivity toward reactivity to chlorination of each of the four positions. Recall that average reactivity of the hydrogens in unsubstituted butane is $2^\circ > 1^\circ$ in a ratio of 3.8 : 1.

Finally, offer an explanation for why the addition of a chlorine atom to butane affects the radical reaction.