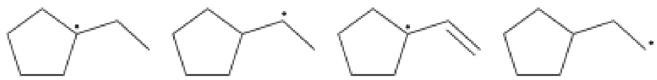
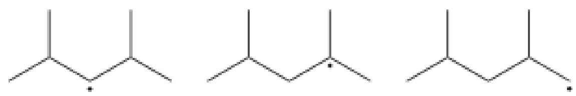
1. Explain why alkanes are generally considered unreactive compounds.

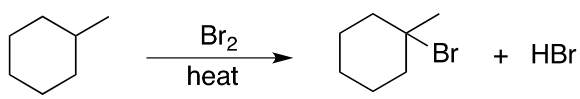
2. Rank each group of radicals in order of increasing stability:

   a) 

   b) 

   c) Abstraction of a hydrogen atom from 3-ethylpentane can yield three different radicals, depending on which hydrogen atom is abstracted. Draw all three radicals and rank them in order of increasing stability.

3. Provide the full mechanism (initiation, propagation and termination) to account for the following reaction:



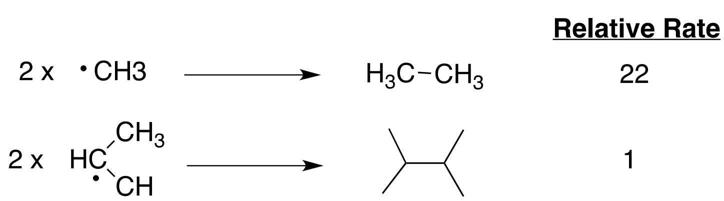
4. How many products are formed from the monochlorination of ethylcyclohexane? Draw the structures of all products and identify the major product. If bromine, more selective reagent, is used to react instead, how many products are expected?

5. Draw four dibromo products that could be obtained by radical bromination of propane. Show the reaction pathway or mechanism for the compound that you think would be the major product. Also, which of the four dibromo products are chiral?

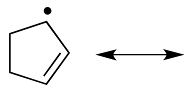
6. Provide the full mechanism for the radical chlorination of 2,2-dichloropropane to produce 1,2,2-trichloropropane.

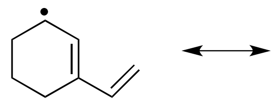
7. In practice, the chlorination of methane often produces many by-products. For example, ethyl chloride (CH_3CH_2Cl) is obtained in small quantities. Can you suggest a mechanism for the formation of ethyl chloride?

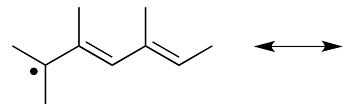
8. The relative rates of termination of methyl and isopropyl radicals are quite different. Give two possible reasons for this difference.

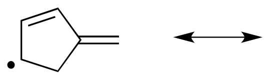


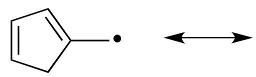
9. For each radical, draw all resonance structures using curved-arrow. For resonance structures involving radicals, single barbed arrows are used.

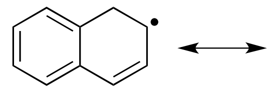
a) 

b) 

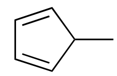
c) 

d) 

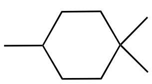
e) 

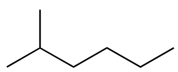
f) 

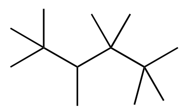
10. 5-methylcyclopentadiene, shown to the right, undergoes homolytic bond cleavage of a C-H bond to form a radical that exhibits five resonance structures. Determine which hydrogen is abstracted and draw all five resonance structures of the resulting radical.



11. Draw the structure of the major product upon radical <u>mono</u>bromination of each of the following compounds:

a) 

b) 

c) 

12. Compound A has molecular formula C_5H_{12} and undergoes monochlorination to produce four different constitutional isomers.

(a) Draw the structure of compound A
(b) Draw all four monochlorinated products
(c) If compound A undergoes monobromination (instead of monochlorinaion), one product predominates. Draw that product.

13. Using the steps provided below, calculate the theoretical percent yields of the four monochlorinated products that result when 2- methylbutane is subjected to free radical chlorination. Assume that the relative ease of hydrogen abstraction in the chlorination process is 5 for 3°; 3.8 for 2°; and 1 for 1°hydrogens.

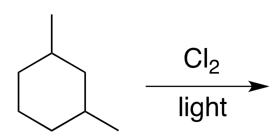
Step 1 - Draw out the structures and label (ex. A, B and so on) all monochlorinated products, and identify them as primary (1°), secondary (2°) and tertiary (3°) alkyl halides.

Step 2 - **Determine the total number of hydrogen atoms <u>from the starting alkane</u>** that are potentially subject to the radical substitution to yield a monochlorinated product you labeled in step 1. Then, identify the hydrogens as primary (1°), secondary (2°) and tertiary (3°). Repeat this process for all other monochlorinated products.

Step 3 - For each monochlorinated product, **multiply** the number of the hydrogens you determined from step 2 by their corresponding rate of abstraction. (*i.e.* if the hydrogens identified in step 2 are primary, multiply the number of hydrogens by rate 1).

Step 4 Sum up all results from the multiplication involving all monochlorinated products. Then divide each multiplication result for each monochlorinated product by the sum, followed by x 100. There, it gives the theoretical percent yield for each product.

14. For the free radical reaction below, answer the following questions for the monochlorination of 1,3-dimethylcyclohexane:



a) Draw the structures of the five monochlorinated constitutional isomers. (ignore stereoisomers)
b) For chlorination, the relative reactivities of the hydrogens in this reaction are 1 : 3.9 : 5.2 for 1º (Primary) : 2º (Secondary) : 3º (Tertiary), respectively. Calculate the percentage yield for the five products drawn in question (a) above. (i.e. please refer to the guideline in Q13 for calculation)

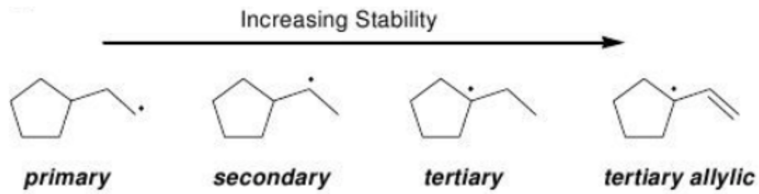
Solutions

1. Explain why alkanes are generally considered unreactive compounds.

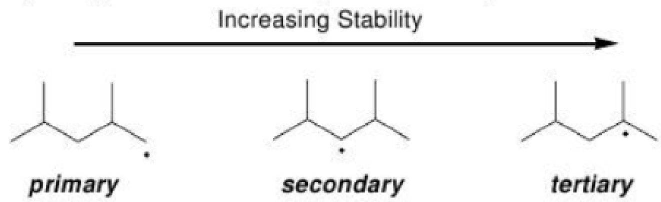
Alkanes are unreactive because they only have very strong, non-polar C-H and C-C σ (sigma) bonds. These bonds are extremely difficult to break unless a large amount of heat or light is provided.

2. Rank each group of radicals in order of increasing stability:

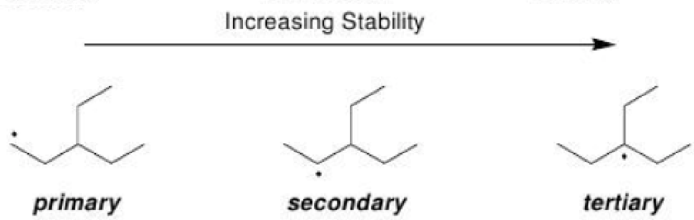
a)



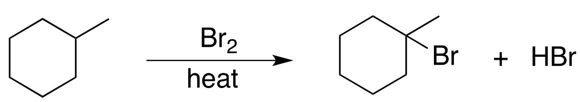
b)



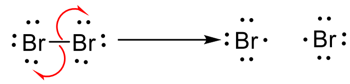
c)



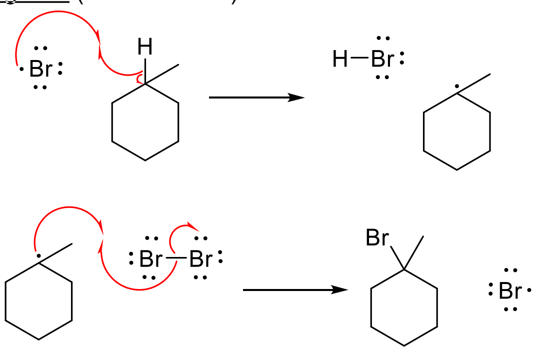
3. Provide the full mechanism (initiation, propagation and termination) to account for the following reaction:



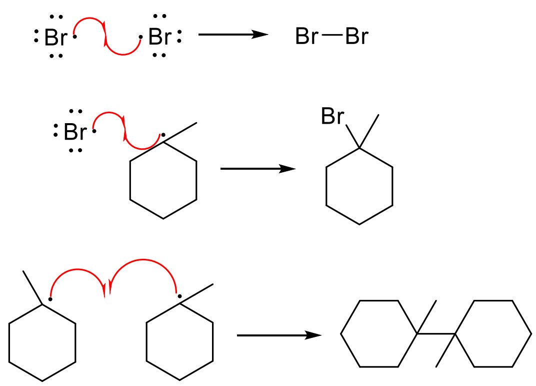
Initiation (birth of radicals)



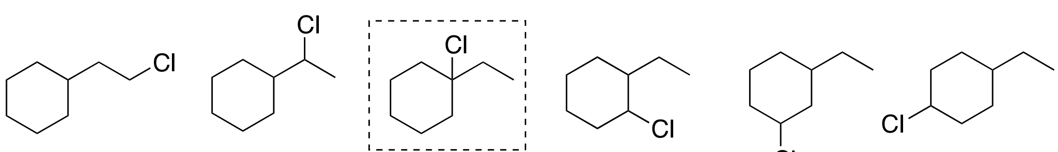
Propagation (life of radicals)



Termination (death of radicals)



4. How many products are formed from the monochlorination of ethylcyclohexane? Draw the structures of all products and identify the major product. If bromine, more selective reagent, is used to react instead, how many products are expected?

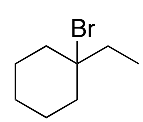


Major Product

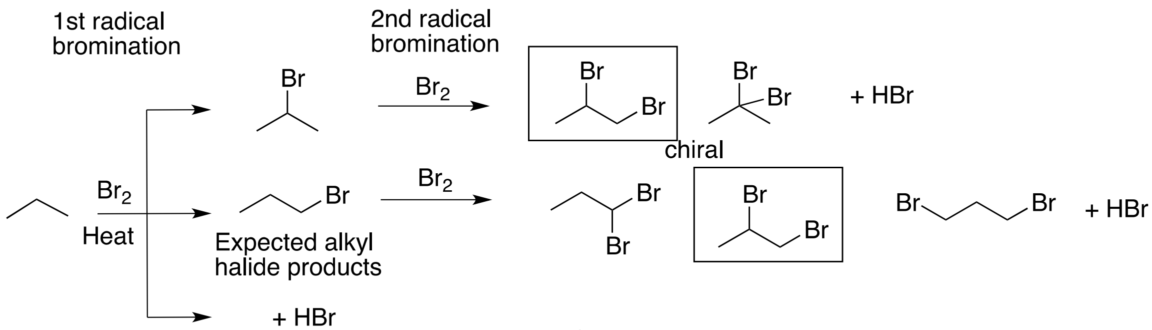
(involves a more stable 3º carbon radical in RDS; hence, the fastest to form)

With Bromine, more selective towards the stability of carbon radicals, as reagents,

only



5. Draw four dibromo products that could be obtained by radical bromination of propane. Show the reaction pathway or mechanism for the compound that you think would be the major product. Also, which of the four dibromo products are chiral?



Mechanism of Initiation, propagation and termination not drawn. You should however practice to see how you can arrive at each product

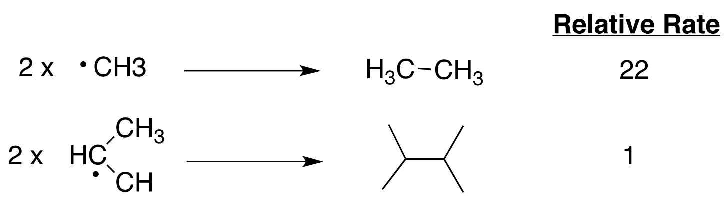
6. Provide the full mechanism for the radical chlorination of 2,2-dichloropropane to produce 1,2,2-trichloropropane.

See answer for question 3 for mechanism pattern

7. In practice, the chlorination of methane often produces many by-products. For example, ethyl chloride (CH_3CH_2Cl) is obtained in small quantities. Can you suggest a mechanism for the formation of ethyl chloride?

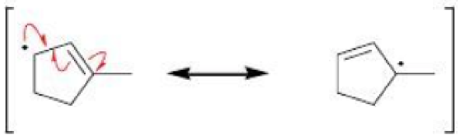
In the termination step of the chlorination of methane, ethane is produced as a by-product, which can undergo a propagation step with chlorine radical to generate ethyl chloride

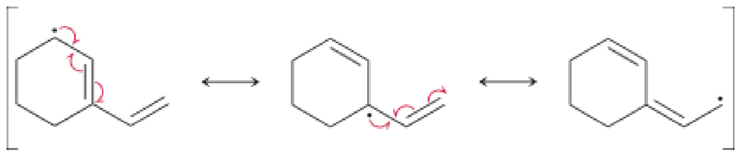
8. The relative rates of termination of methyl and isopropyl radicals are quite different. Give two possible reasons for this difference.

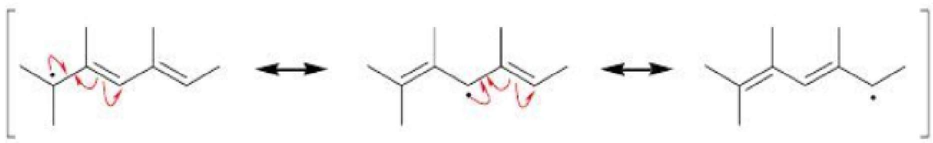


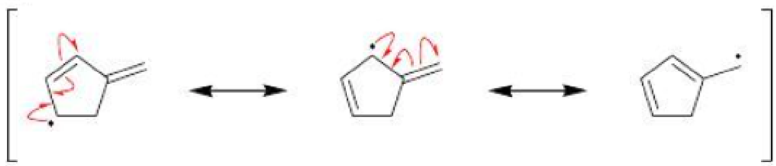
1) The less stable methyl radical recombines <u>faster</u> than the more substituted, more stable, and thus longer lived isopropyl radical (i.e. hyperconjugation). 2) The <u>bulkier</u> (meaning more branching; hence, more electron repulsion due to steric strain) isopropyl radical has more difficulty in recombining than does the smaller methyl radical.

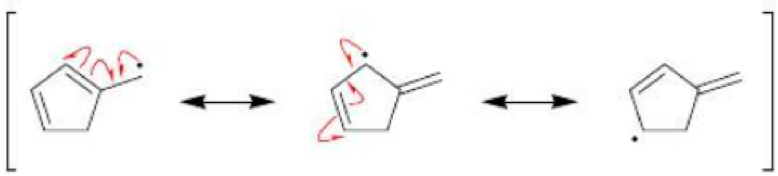
9. For each radical, draw all resonance structures using curved-arrow. For resonance structures involving radicals, single barbed arrows are used.

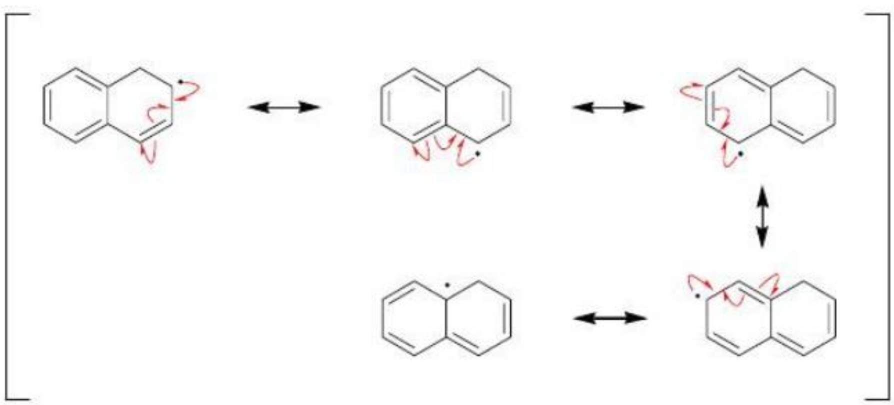
a)


b)


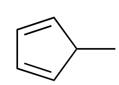
c)


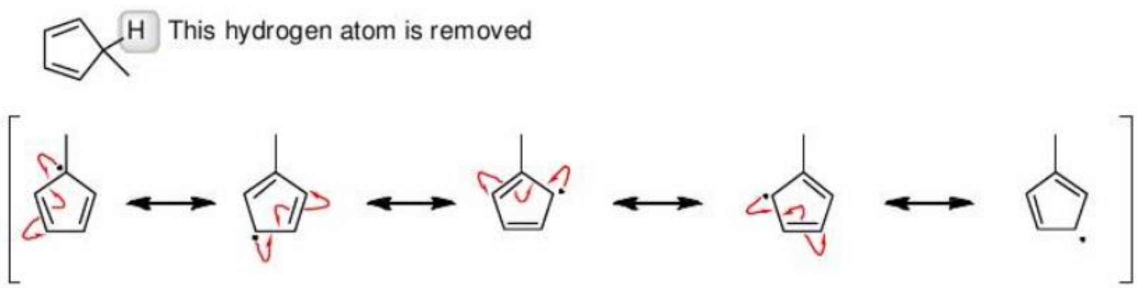
d)


e)


f)


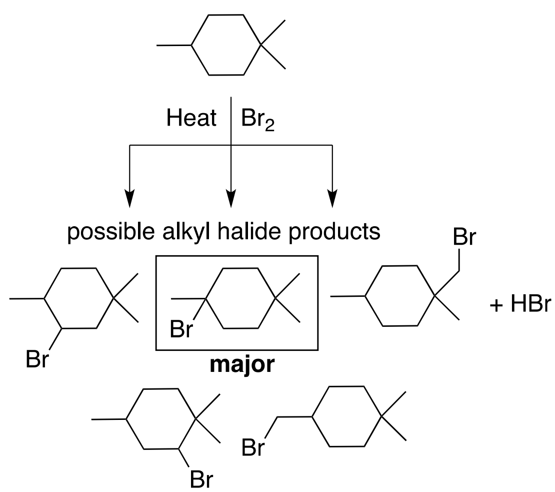
10. 5-methylcyclopentadiene, shown to the right, undergoes hemolytic bond cleavage of a C-H bond to form a radical that exhibits five resonance structures. Determine which hydrogen is abstracted and draw all five resonance structures of the resulting radical.



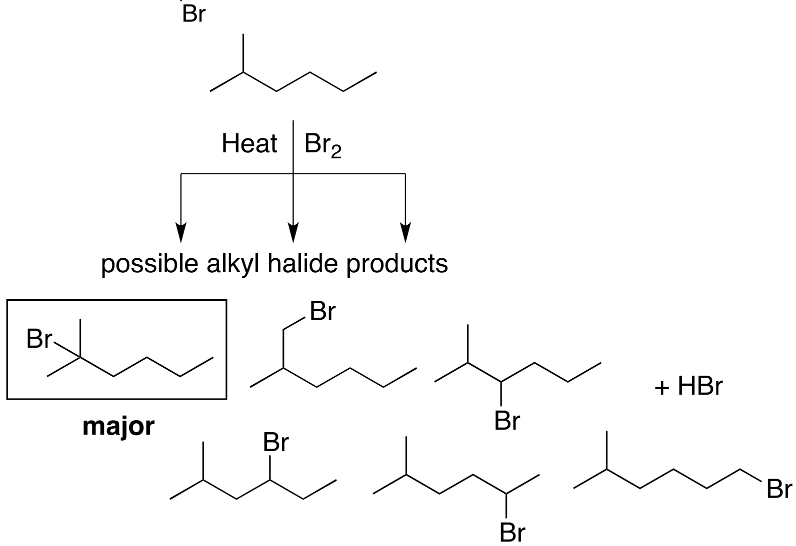


11. Draw the structure of the major product upon radical monobromination of each of the following compounds:

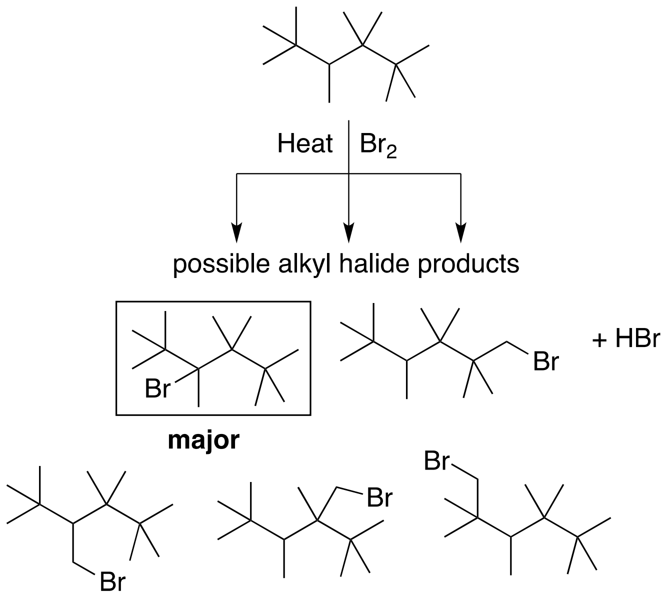
a)



b)

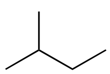


c)



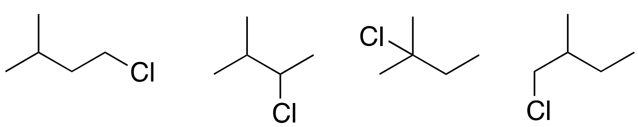
12. Compound A has molecular formula C_5H_{12} and undergoes monochlorination to produce four different constitutional isomers.

(a) Draw the structure of compound A.

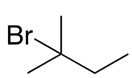


A

(b) Draw all four monochlorinated products

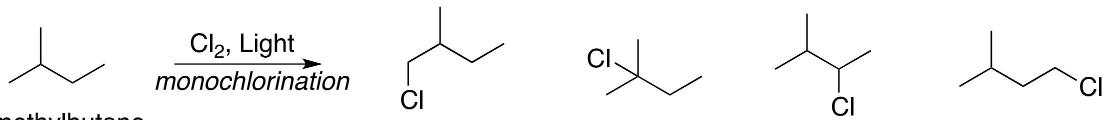


(c) If compound A undergoes monobromination (instead of monochlorinaion), one product predominates. Draw that product.



13. Using the steps provided below, calculate the theoretical percent yields of the four monochlorinated products that result when 2- methylbutane is subjected to free radical chlorination. Assume that the relative ease of hydrogen abstraction in the chlorination process is 5 for 3°; 3.8 for 2°; and 1 for 1°hydrogens.

<u>Step1 and 2</u>



2-methylbutane

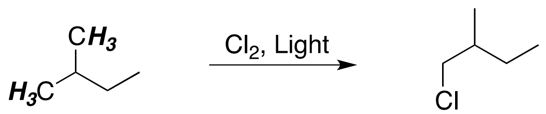
1-chloro-2-methylbutane **A**

2-chloro-2-methylbutane **B**

2-chloro-3-methylbutane **C**

1-chloro-3-methylbutane **D**

For **A**,

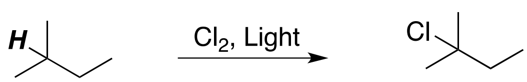


1-chloro-2-methylbutane

A

There are total **6 primary hydrogens** that are potentially subject to H abstraction to yield A

For **B**,

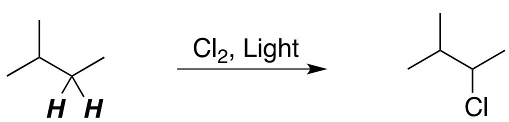


2-chloro-2-methylbutane

B

There is only **1 tertiary hydrogen** that is subject to H abstraction to yield B

For **C**,

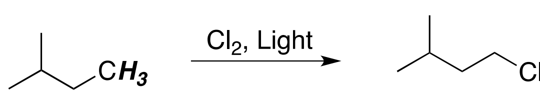


2-chloro-3-methylbutane

C

There are total **2 secondary hydrogens** that are potentially subject to H abstraction to yield A

For **D**,



1-chloro-3-methylbutane

D

There are total **3 primary hydrogens** that are potentially subject to H abstraction to yield A

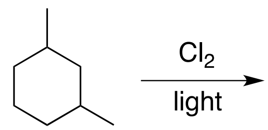
<u>Step 3 and 4</u>

The rate of hydrogen abstraction

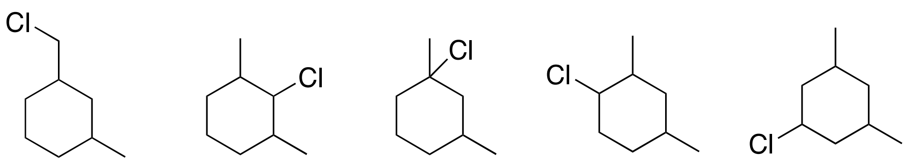
Class of hydrogen	Relative Rate of Abstraction
1°	**1**
2°	**3.8**
3°	**5**

	Product of # of Hydrogens x Relative Rate	Theoretical Yield for each product
A	6 x 1 = **6**	(6 / 21.6)*100 = **27.8%**
B	1 x 5 = **5**	(5 / 21.6)*100 = **23.1%**
C	2 x 3.8 = **7.6**	(7.6 / 21.6)*100 = **35.2%**
D	3 x 1 = **3**	(3 / 21.6)*100 = **13.9 %**
	Sum = 21.6	

14. For the free radical reaction below, answer the following questions for the monochlorination of 1,3-dimethylcyclohexane:



a) Draw the structures of the five monochlorinated constitutional isomers. (ignore stereoisomers)



A B C D E

b) For chlorination, the relative reactivities of the hydrogens in this reaction are 1 : 3.9 : 5.2 for 1º (Primary) : 2º (Secondary) : 3º (Tertiary), respectively. Calculate the percentage yield for the five products drawn in question (a) above. (i.e. please refer to the guideline in Q13 for calculation)

	Product of # of Hydrogens x Relative Rate	Theoretical Yield for each product
A	6 x 1 = **6**	(6 / 47.6)*100 = **12.6%**
B	2 x 3.9 = **7.8**	(7.8 / 47.6)*100 = **16.4%**
C	2 x 5.2 = **10.4**	(10.4 / 47.6)*100 = **21.8%**
D	4 x 3.9 = **15.6**	(15.6 / 47.6)*100 = **32.8 %**

E	2 x 3.9 = **7.8**	(7.8 / 47.6)*100 = **16.4 %**
	Sum = 47.6	