Columbia University C99ORG13.DOC S3443D Summer 99
Professor Grace B. Borowitz **Exam No. 3** **June 22, 1999**

Name: **Ann Sursheet and Al Kene** ***Grade:***

Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses **( ).** ***Good Luck!***

Question	Points	Max. Points	Points Earned
1.	**4 + 3 + 3 + 4 + 3**	**= 17**	
2.	**4 + 4 + 5 + 5**	**= 18**	
3.	**(4 + 4 + 4) + (4 + 4)**	**= 20**	
4.	**(4 + 6 + 4) +6**	**= 20**	
5.	**4 + 3**	**= 7**	
6.	**3 + 3 + 6 + 3 + 3**	**= 18**	
Total		**= 100**	

1. **(17)** a. Which of the following reagents will react with an alkene in an anti addition? Check all that apply.

(1) BH_3/Et_2O * (2) Br_2/H_2O (3) $KMnO_4$, , HO^-

(4) H_2/Pt * (5) Br_2/CH_2Cl_2

4

b. Define **regioselective** reaction.

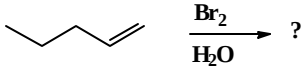
3 **A <u>regioselective</u> reaction is a reaction that yields only 1 or predominantly 1 constitutional isomer when 2 or more constitutional isomers are possible products.**

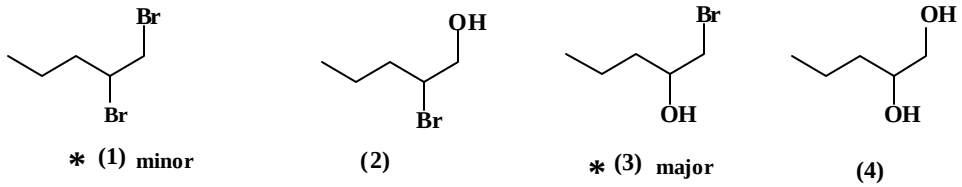
c. Which of the following reagents will add to an alkene to result in a Markovnikov orientation? Check all that apply.

* (1) $Hg(OAc)_2$ / H_2O * (2) HI/ROOR * (3) HI

3 (4) H_2/Pt * (5) 1. BH_3/Et_2O, then 2. HOOH, HO^- (Markovnikov Addn followed; anti-Mark type resultant orientation; both answers accepted).

d. According to the mechanism proposed for electrophilic addition of bromine to alkenes, which products do you predict will be formed from the bromination of 1-pentene in water. Check all that apply.





* (1) minor (2) * (3) major (4)

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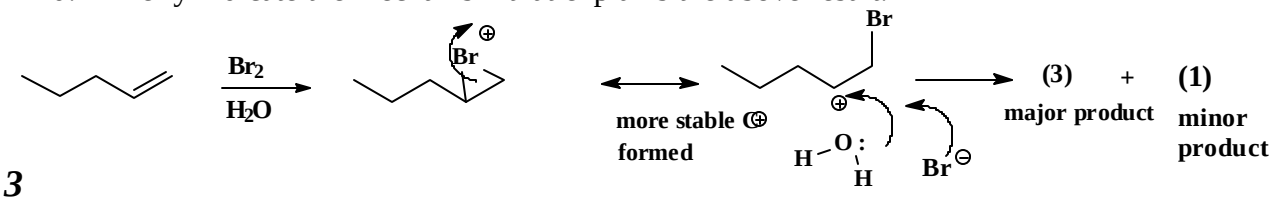
d. Briefly indicate the mechanism that explains the above result.



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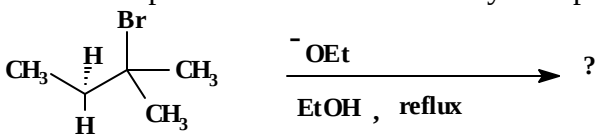
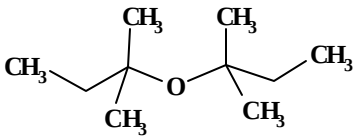
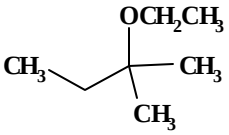
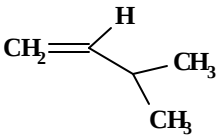
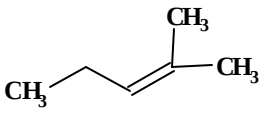
2. **(18)** Which compound listed below would you expect to be the major product of this reaction?

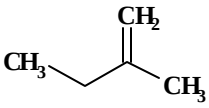


(1) 

(2) 

(3) 

* (4) 

(5) 

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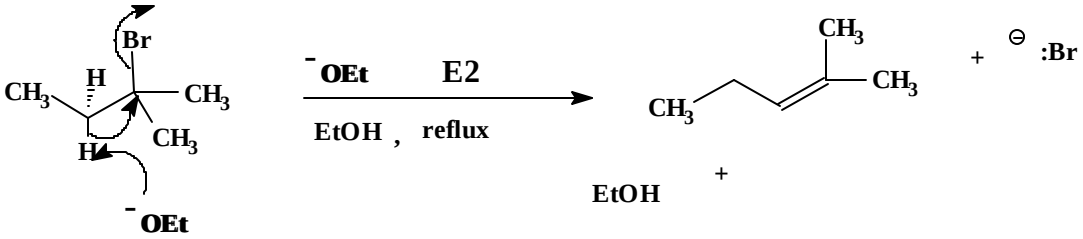
b. Using arrows to show the direction of electron flow, show and name the mechanism.



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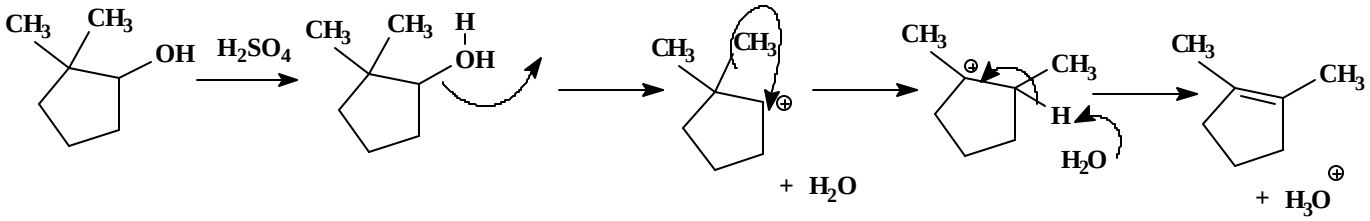
e. Predict the major product resulting from the direct dehydration of 2,2-dimethyl-1-cyclopentanol with H_2SO_4. Show the mechanism of the reaction leading to that major product.



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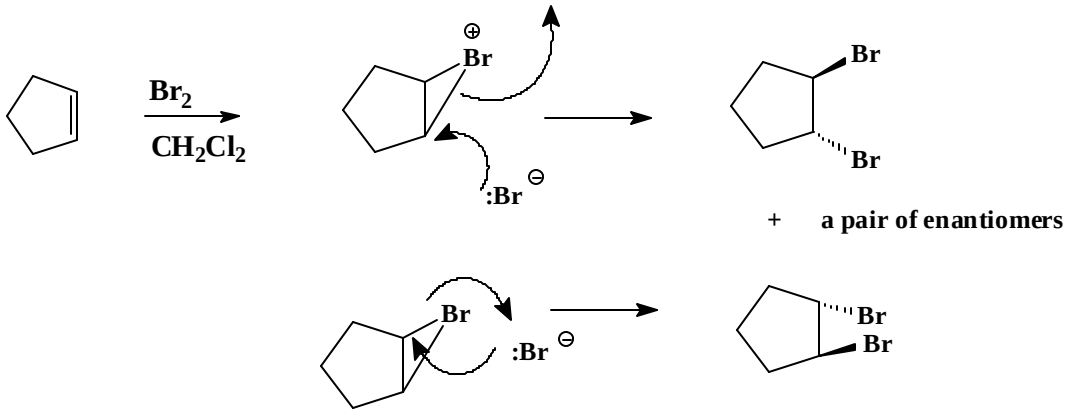
d. Using arrows to show the direction of electron flow, show the mechanism for the bromination of cyclopentene in methylene chloride solution. Make sure to show any important intermediates and give the structure of the product(s) including the stereochemistry. Name the type(s) of stereoisomers formed.



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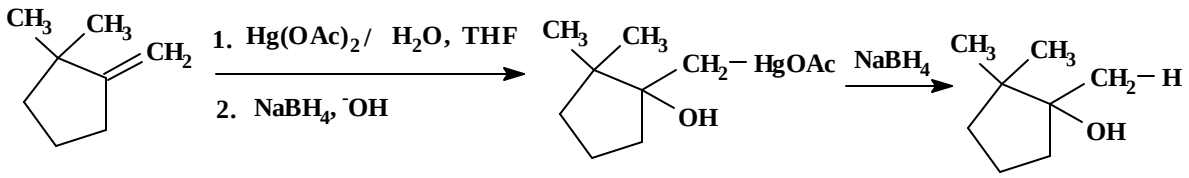
3. **(20)** a. Fill in the missing products in the following reaction sequences. Note any special stereospecificity or regiospecificity.

(1) 

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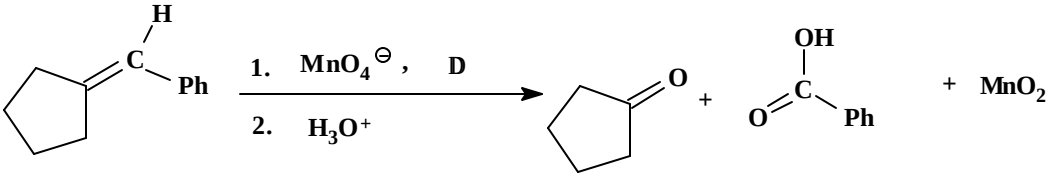
(2) 

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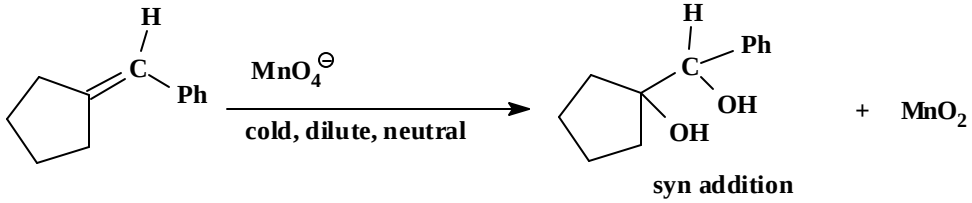
(3) 

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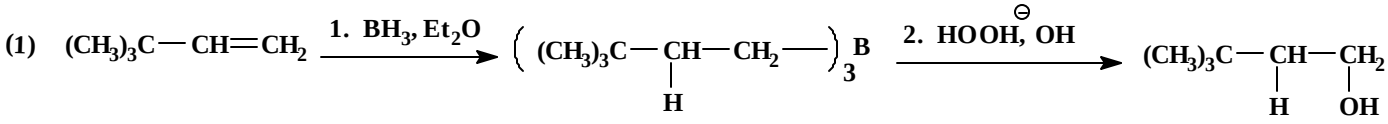
b. Fill in the missing reagents, intermediates, or organic products, including stereochemistry when appropriate, for the following reaction sequences.

(1) 

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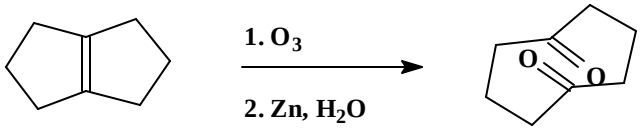
(2) 

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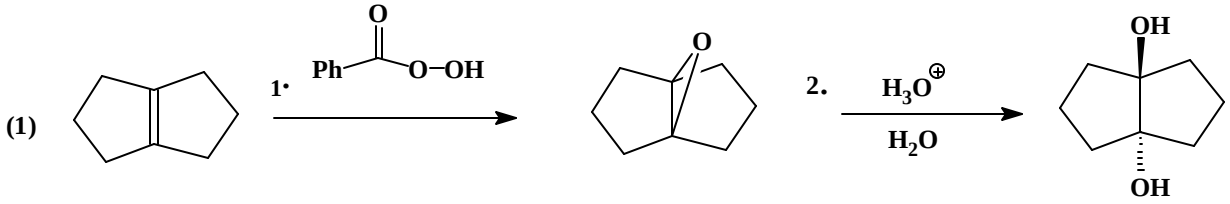
4. **(20)** a. Fill in the missing reagents, intermediates, or organic products, including stereochemistry when appropriate, for the following reaction sequences.



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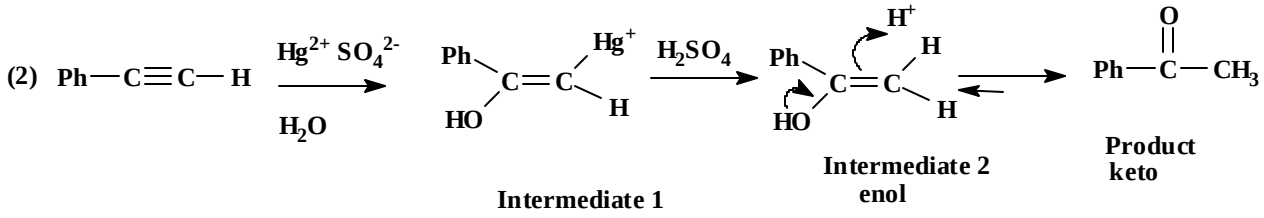

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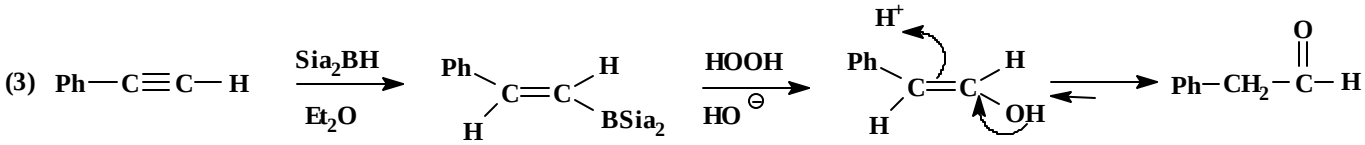

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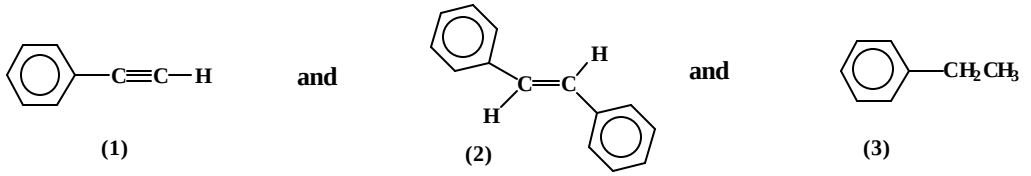
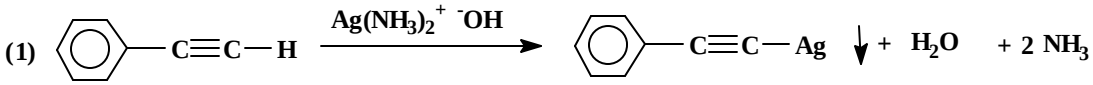
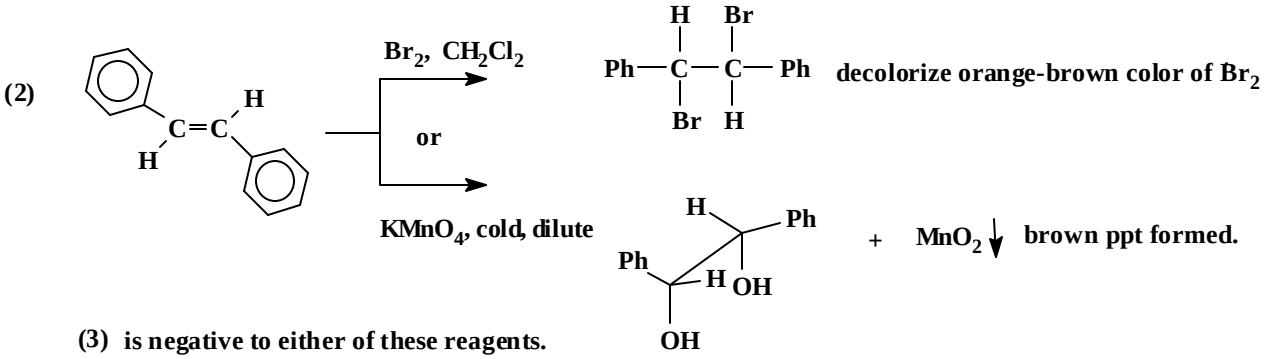
b. Devise a scheme that will distinguish among the following compounds. Cite all visible results and write the equations for the positive reactions.





(2) and (3) are negative with $Ag(NH_3)_2^+$ ^-OH.



(3) is negative to either of these reagents.

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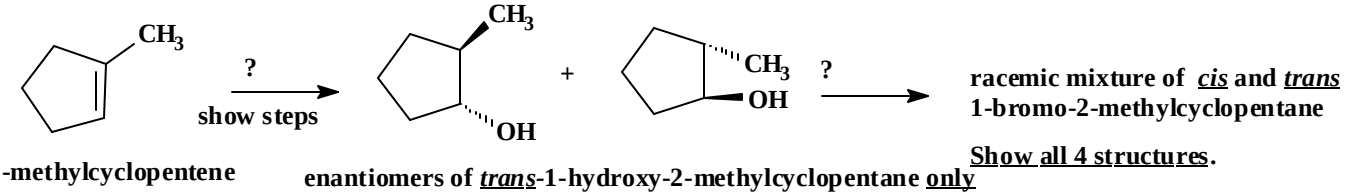
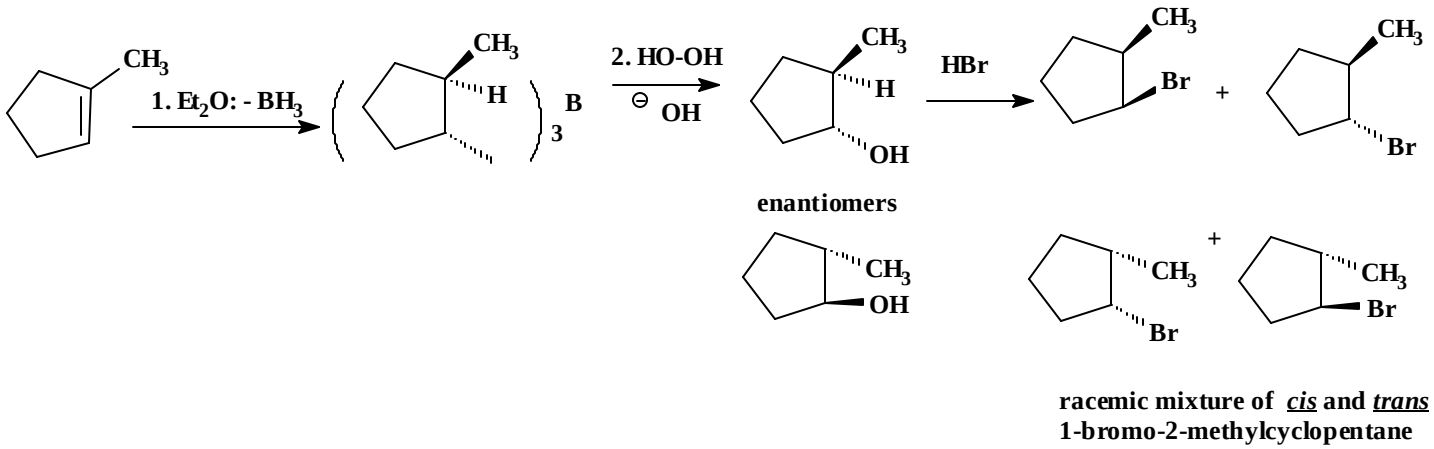
5. **(7)** a. Carry out the following conversion using organic and inorganic reagents as needed. Clearly indicate the reaction steps, showing the intermediates formed.





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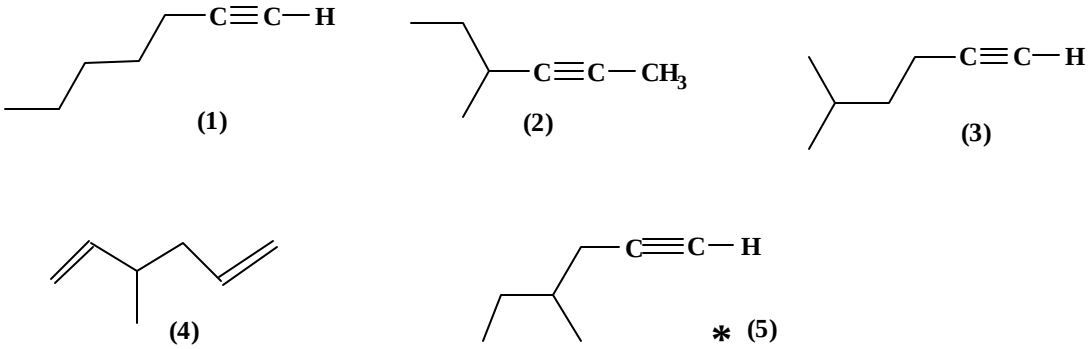
b. An optically active compound, **A**, with the molecular formula C_7H_{12} reacts with **cold dilute $KMnO_4$** (**MnO_2** precipitates**).** It also gives a precipitate when treated with **$Ag(NH_3)_2OH$.** On catalytic hydrogenation, **A** is converted to **B (C_7H_{16})** and **B** is also optically active. Which is a possible structure for **A**.



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6. **(18)** 1. a. A chain reaction is one that:

(1) is one that can be initiated by light.

(2) involves free radicals that have an unusual stability and thereby cause a large quantum yield.

* (3) involves a series of steps, each of which generates a reactive intermediate that brings about the next step.

(4) involves a series of steps.

(5) involves two steps of equal activation energy.

3

b. Which of the following statements is true when used to compare the reaction of chlorine and of bromine with isobutane (2-methylpropane)?

(1) Chlorine is the less reactive and the more selective.

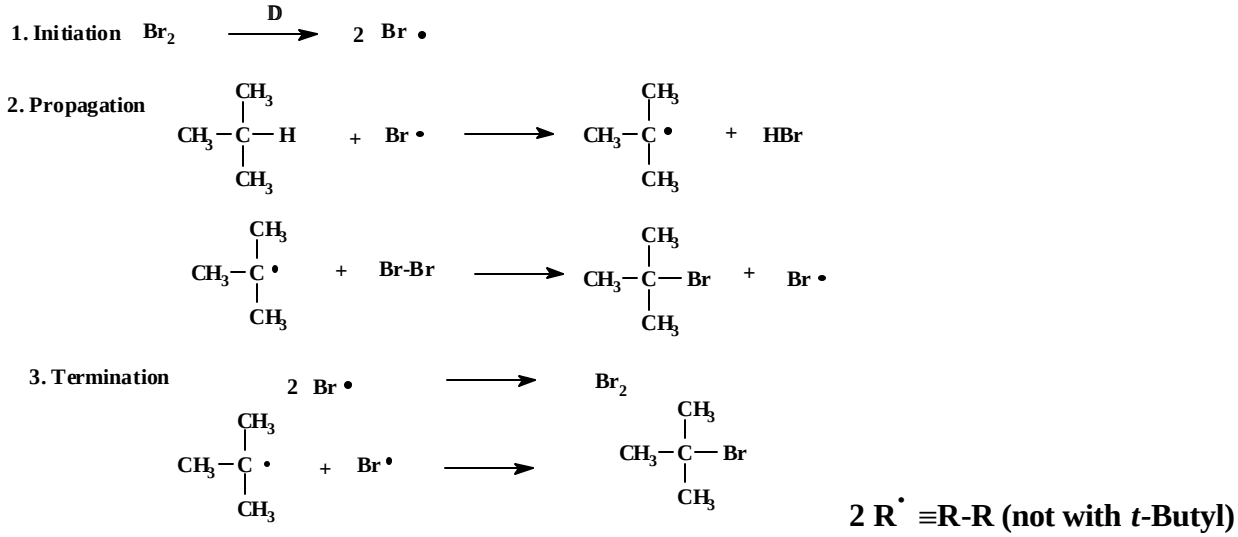
* (2) Bromine is the less reactive and the more selective.

(3) Chlorine is the more reactive and the more selective.

(4) Bromine is the more reactive and the more selective.

3

c. Show the mechanism, including the steps involved in initiation, propagation, and termination, for the free radical bromination of isobutane, **$(CH_3)_3CH$**, to give the predominant product. Calculate the % predominant product if the reactivity ratio for removal of primary to tertiary hydrogen by Br· is **1:1600**.



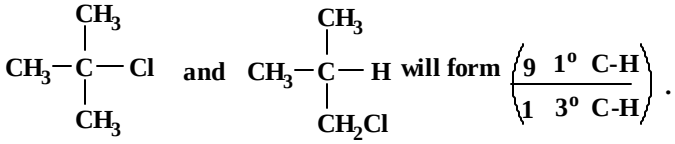
2 R· ≡R-R (not with *t*-Butyl)

6

d. Qualitatively describe the results, in terms of nature and structure of the product(s), of the free radical chlorination of isobutane, **$(CH_3)_3CH$.**

X	1° C-H	2° C-H	
Cl	1.0	3.8	5.0
Br	1.0	79	1600

Since Cl• is more reactive and less selective both products,



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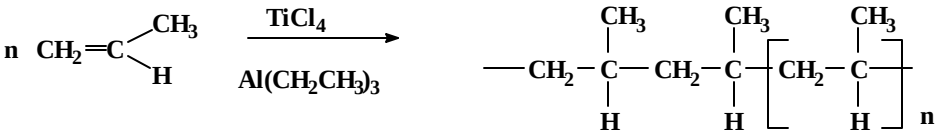
e. Complete the following reaction. Name it and tell what is significant about it.

Reacton Name: Ziegler-Natta Polymerization

Reaction Significance: Stereoregular Polymerization (more crystalline)

Nalgene polymer (isotactic)

Show a representative section including stereochemistry.



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