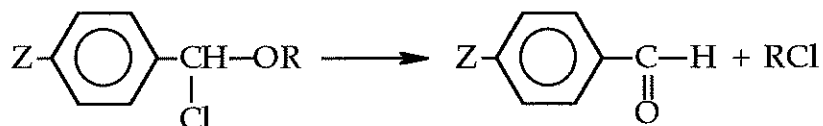
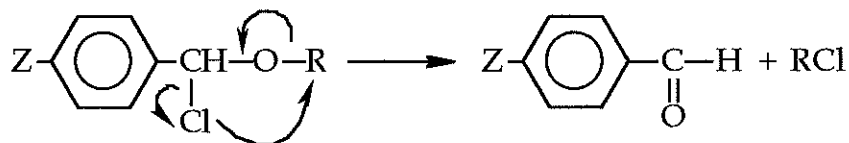


- (30) 1. Consider the thermolysis of para-substituted α -chlorobenzylalkyl ethers to give para-substituted benzaldehydes and alkyl chlorides:

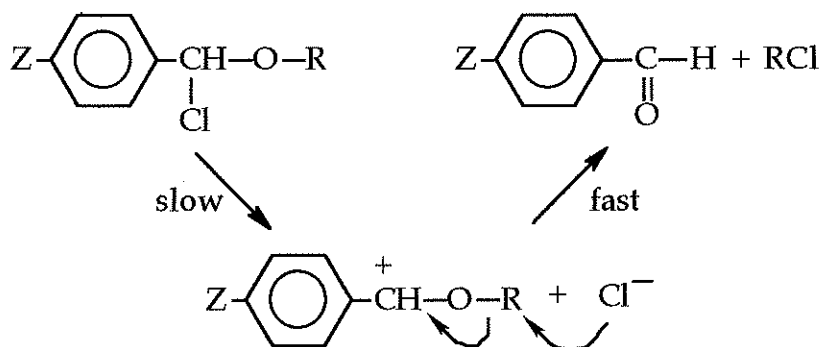


Two possible pathways leading to product formation are shown below:

Pathway (I) - One step concerted reaction:



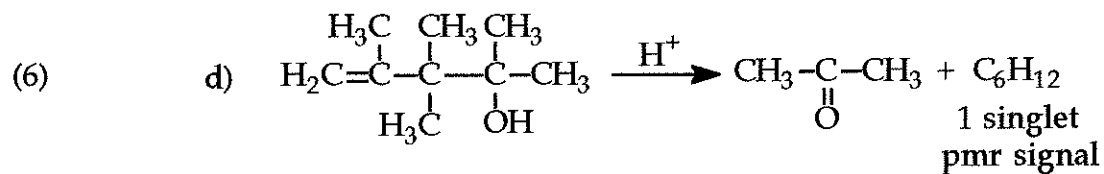
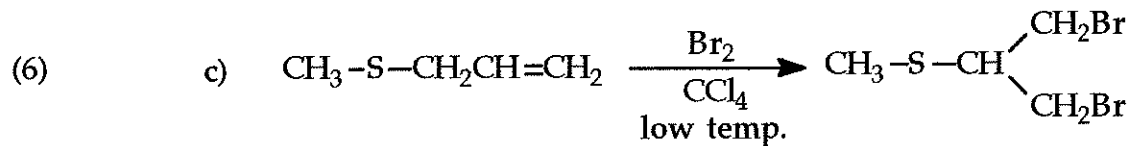
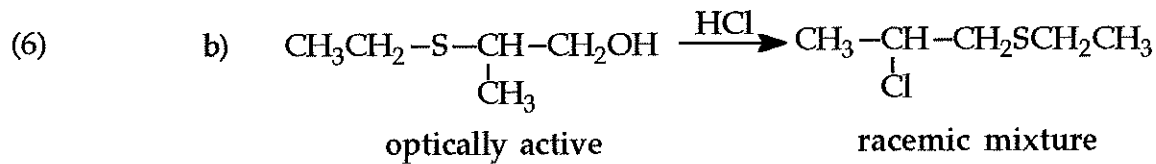
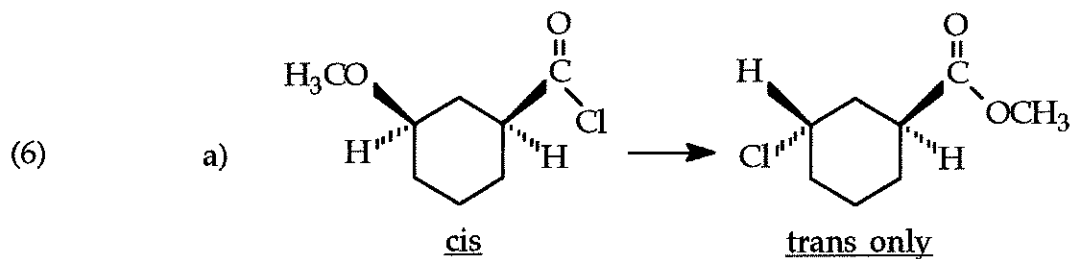
Pathway (II) - Carbocation intermediate:



Explain in detail whether or not each of the following considerations would permit one to differentiate between the two proposed pathways:

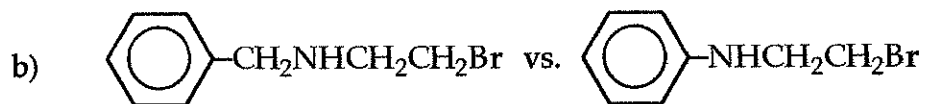
- A kinetic study to determine the order of the reaction
- A study of reaction rates as a function of the size of the R-group
- A $^{35}\text{Cl}/^{37}\text{Cl}$ kinetic isotope study
- A study to determine whether or not reaction rates can be correlated best with "normal" or "modified" Hammett substituent constants
- A study of reaction rates as a function of solvent polarity

2. Provide a plausible mechanism for each of the following transformations:



(16) 3. For which member of each of the following pairs of compounds would Neighboring Group Participation be **more likely** during hydrolysis? Briefly explain and/or illustrate your response.

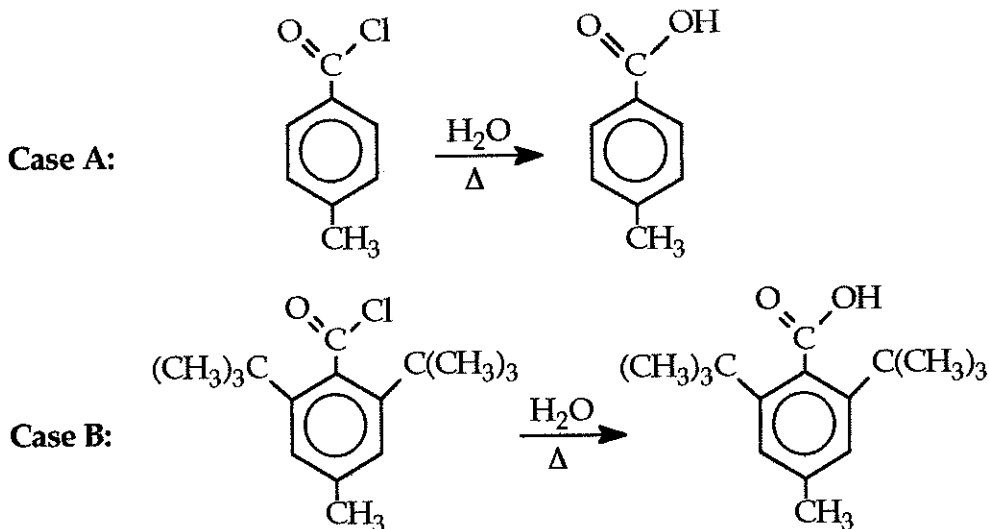
a) $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Br}$ vs. $\text{CH}_3\text{SeCH}_2\text{CH}_2\text{Br}$



c) $\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$ vs. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cl}$

d) Threo vs. Erythro $\text{CH}_3\text{CH}_2\text{SCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{Br}$

- (8) 4. Compare the hydrolyses of the following substituted benzoyl chlorides:

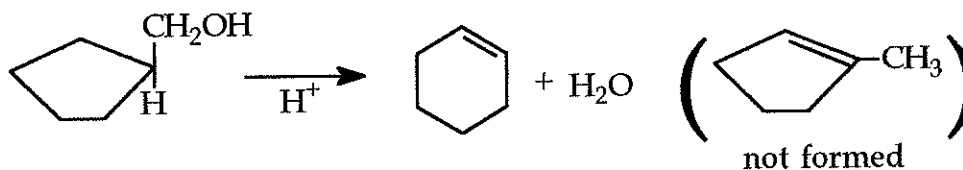


Under comparable conditions, ρ for the hydrolysis in Case A is a positive value, whereas ρ for hydrolysis in Case B is a large negative value.

When para-methyl is replaced by para-methoxy, the rate of hydrolysis decreases in Case A but increases in Case B. Furthermore, the rate of hydrolysis in Case B is best correlated using $\sigma_{p\text{-OMe}^+}$ rather than $\sigma_{p\text{-OMe}}$.

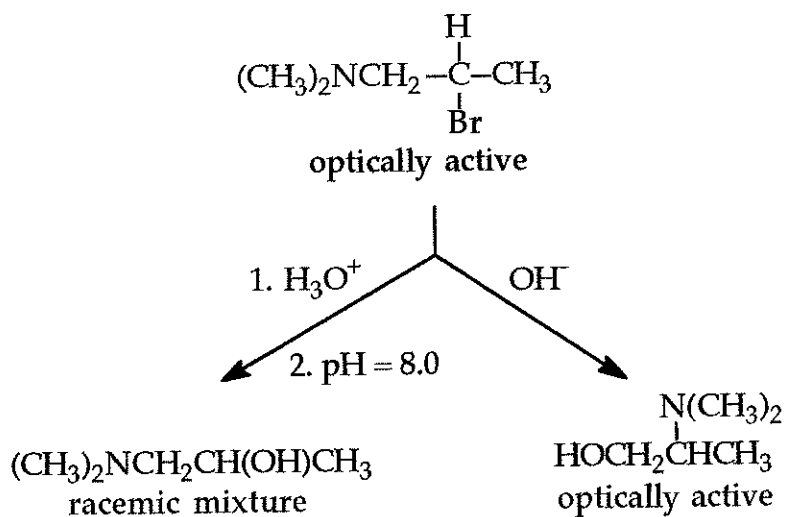
Provide a plausible explanation for all of the above data. In your explanation, be sure to address the difference in the nature of the intermediate in Case A versus that involved in Case B and how this difference accounts for the contrasting ρ values.

(6) 5. Consider the following reaction:



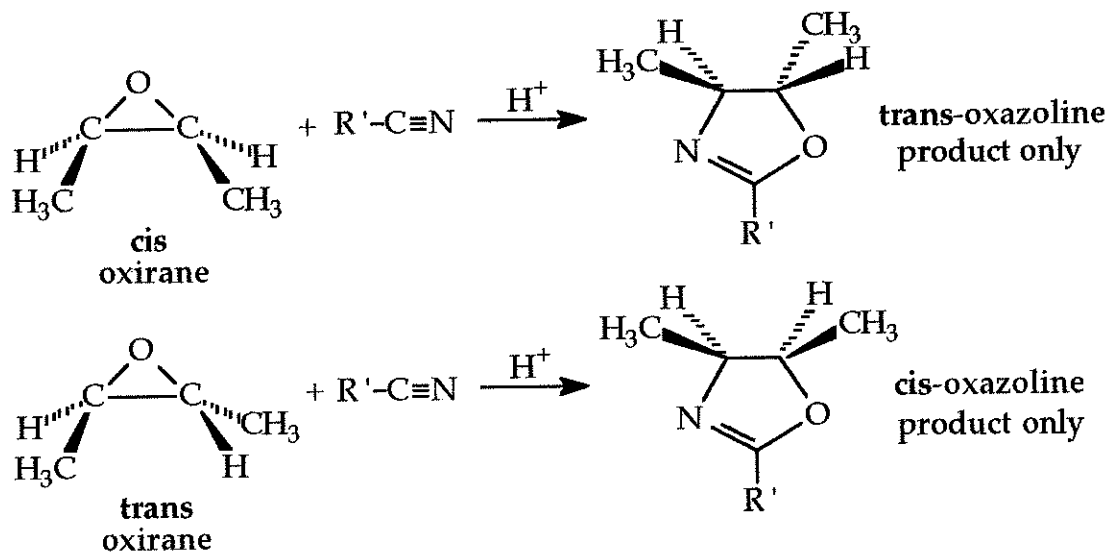
Provide a plausible mechanism to explain the above results.

(8) 6. Consider the following data:



Show how the above chiral reactant leads to racemic product under acidic conditions, whereas, under basic conditions, an optically active product is obtained.

- (8) 7. The data shown below allow one to differentiate between nitrile attack on an open carbocationic intermediate versus nitrile attack on/ring opening of a protonated oxirane (epoxide):



Which possible pathway do the data support? Justify your decision by providing a plausible mechanism leading to the results shown.