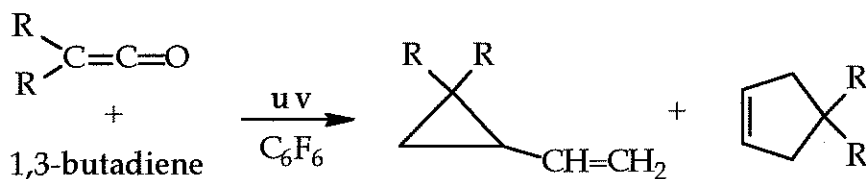
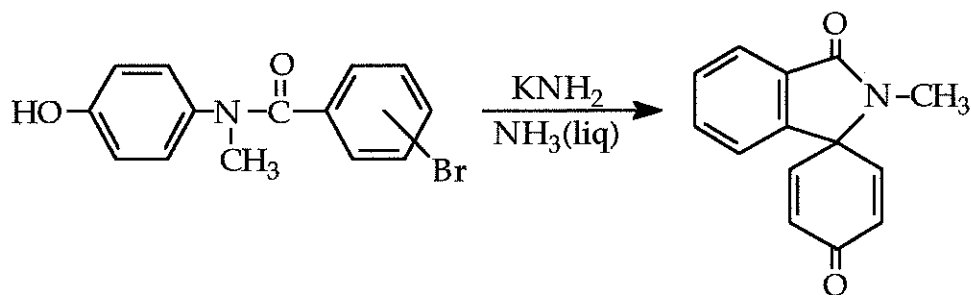


- (5) 1. Consider the following carbene cycloaddition reaction:



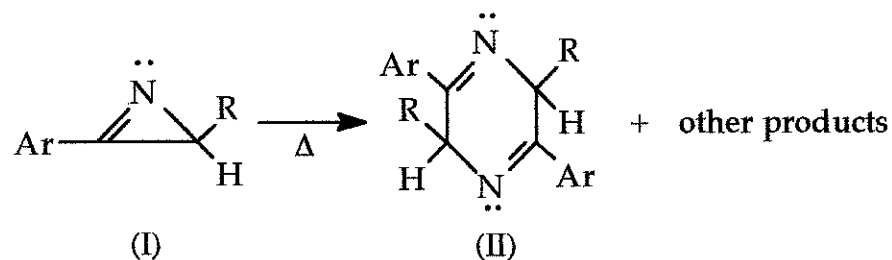
If product formation involves only one type of carbene species (i.e. singlet or triplet), which one is it? Explain and/or illustrate.

- (6) 2. The reaction shown below occurs only when the bromo-substituent is oriented **ortho** or **meta**, but not para, to the amido group.

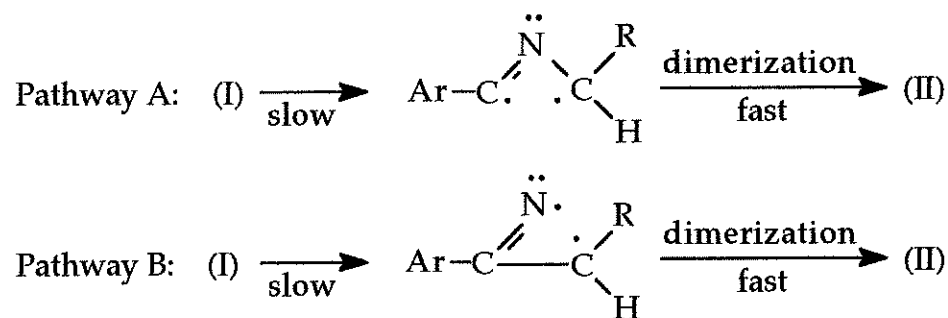


Propose a plausible mechanism to account for the reaction.

- (5) 3. Consider the following thermal rearrangement of the 2H-azirine derivative (I) shown below:



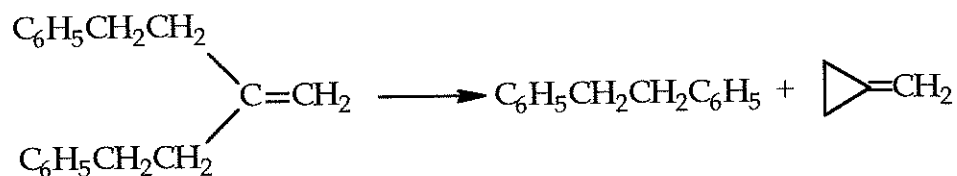
Two conceivable mechanistic pathways are presented below to account for the formation of (II):



Devise an experiment to differentiate between the two pathways shown above.

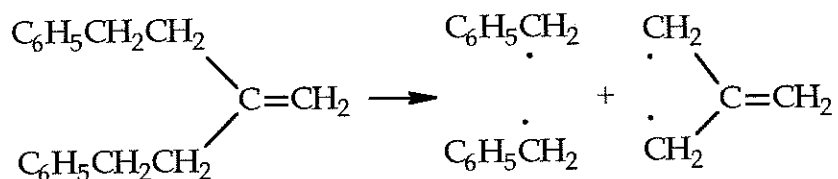
Hint: Consider the bond being broken in the slow step of each pathway.

(5) 4. Consider the following hypothetical reaction:

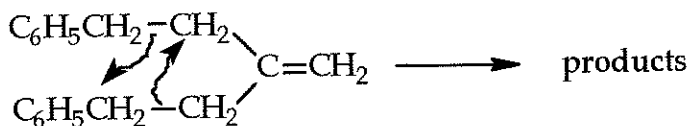


Product formation can be envisioned (by some astute individuals) as arising from either a radical recombination pathway or from a 1,4-concerted shift pathway (see below):

Radical recombination

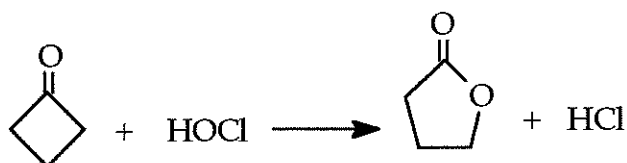


1,4-Concerted shift

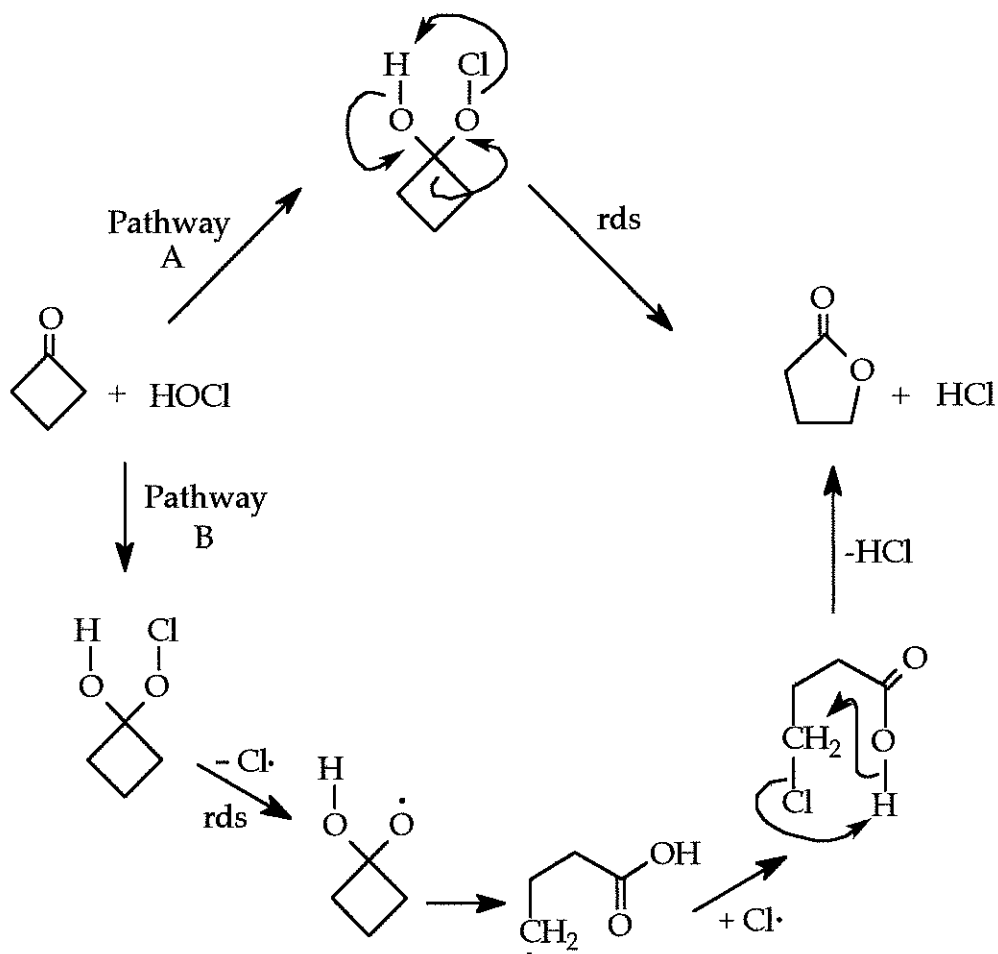


Explain how running the above reaction using $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2)_2\text{C}=\text{CD}_2$ might allow one to determine the actual pathway taken by the reaction.

5. Consider the reaction of cyclobutanone with hypochlorous acid:



Two mechanisms that can account for product formation are shown below:

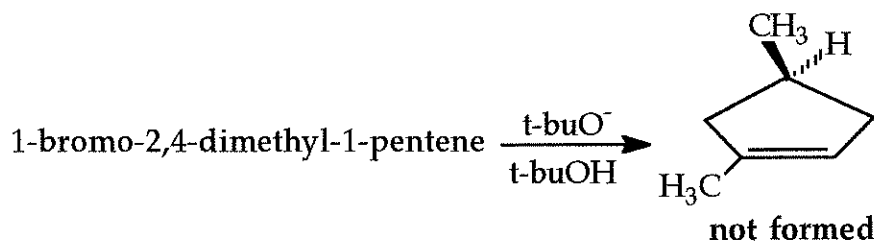
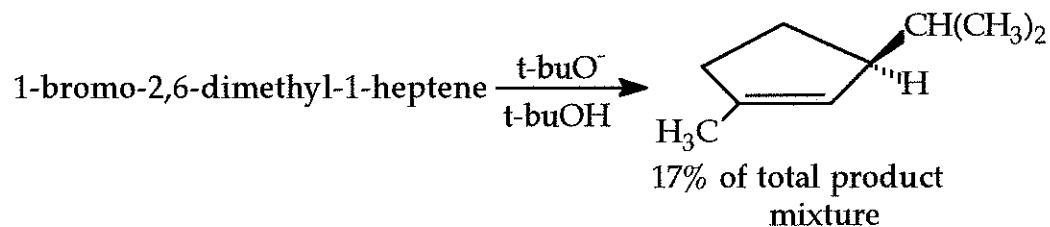
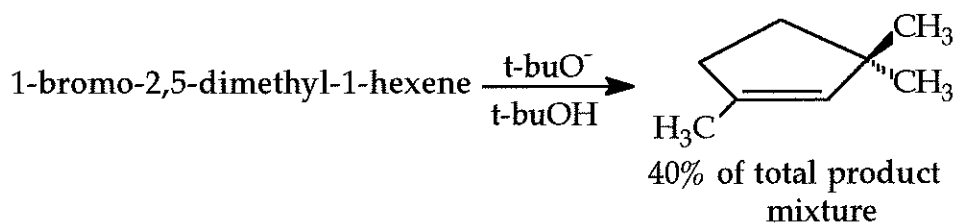


- (5) a) Devise a labeling experiment to differentiate between the pathways presented. Specify what results would be expected in each case.
- (5) b) Devise a crossover experiment to differentiate between the pathways presented. Specify what results would be expected in each case.
- (4) c) Could a 1° kinetic isotope effect study using ^{37}Cl -labeled reactant differentiate between the pathways presented? Explain briefly.

- (8) 6. When triplet methylene, $\cdot\dot{\text{C}}\text{H}_2$, reacts with 1,3-cyclohexadiene, two structurally isomeric products of formula C_7H_{10} are formed. Product (J) is the result of 1,2-addition, whereas product (K) is the result of 1,4-addition. Draw the structures of (J) and (K) in the space provided below:

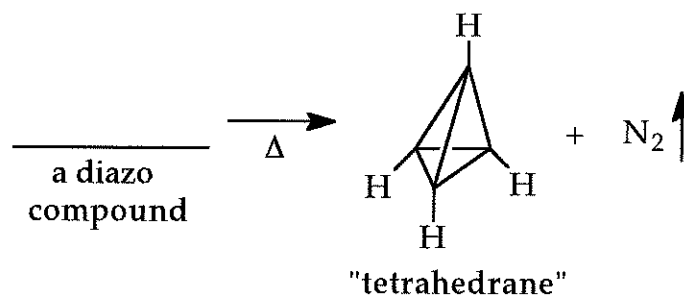
(J) _____ (K) _____

- (5) 7. Consider each of the following reactions in which vinyl carbenes are known intermediates:

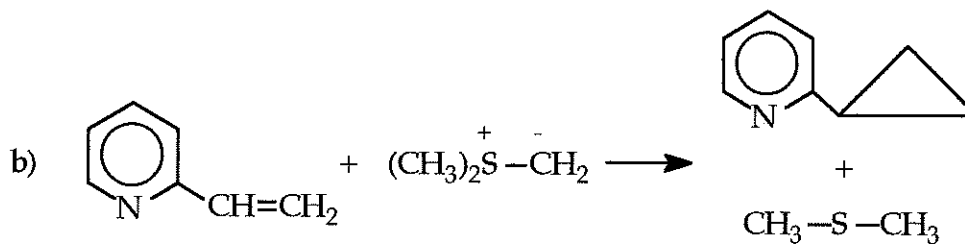
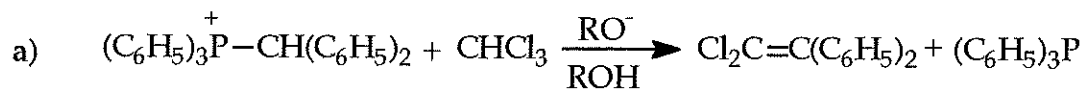


What conclusion can one draw about the nature of vinyl carbene 1,5-insertion reactions from the data presented?

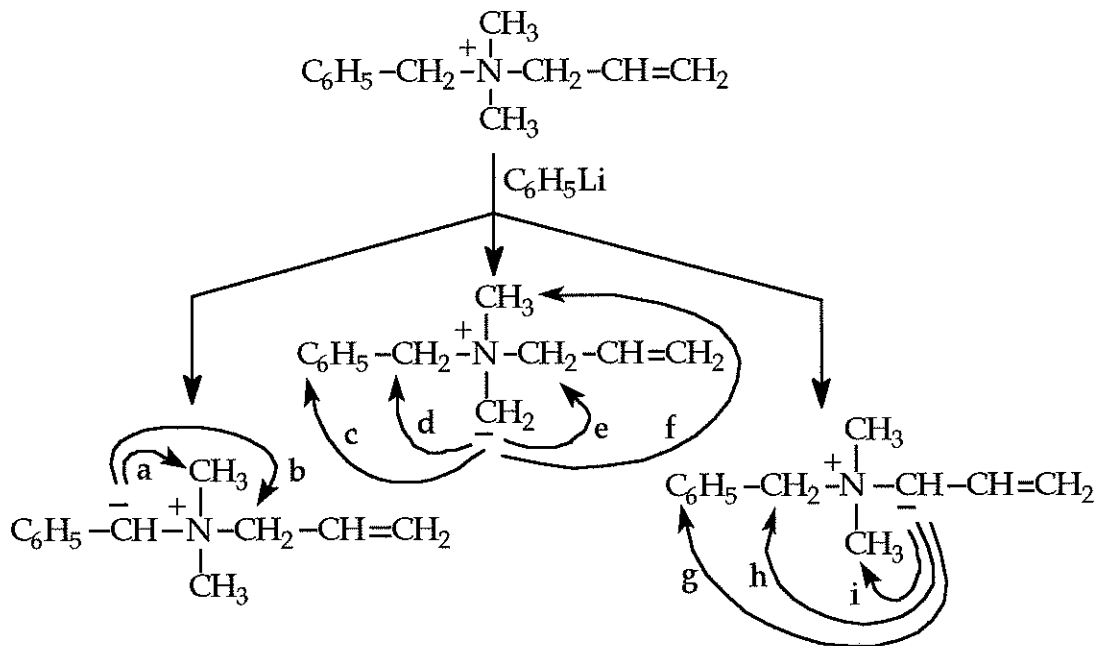
- (5) 8. Complete the following chemical equation by supplying the structure of the missing reactant:



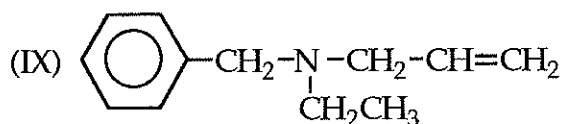
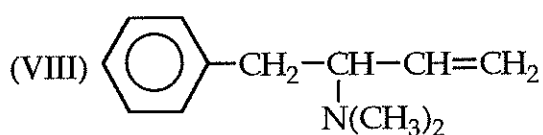
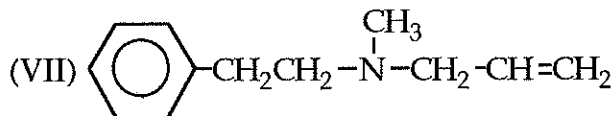
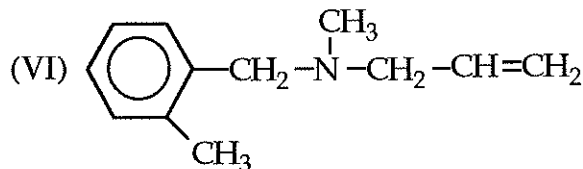
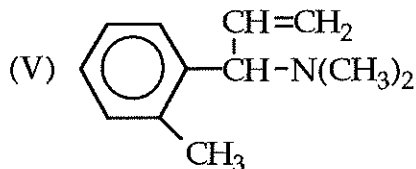
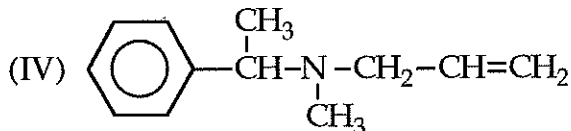
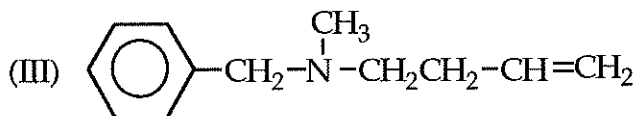
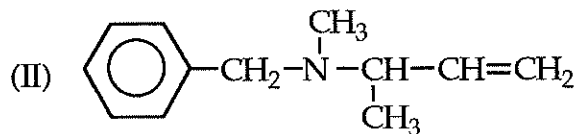
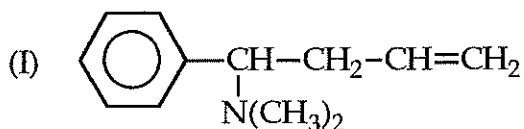
- (12) 9. Provide a plausible mechanism to account for each of the following reactions:



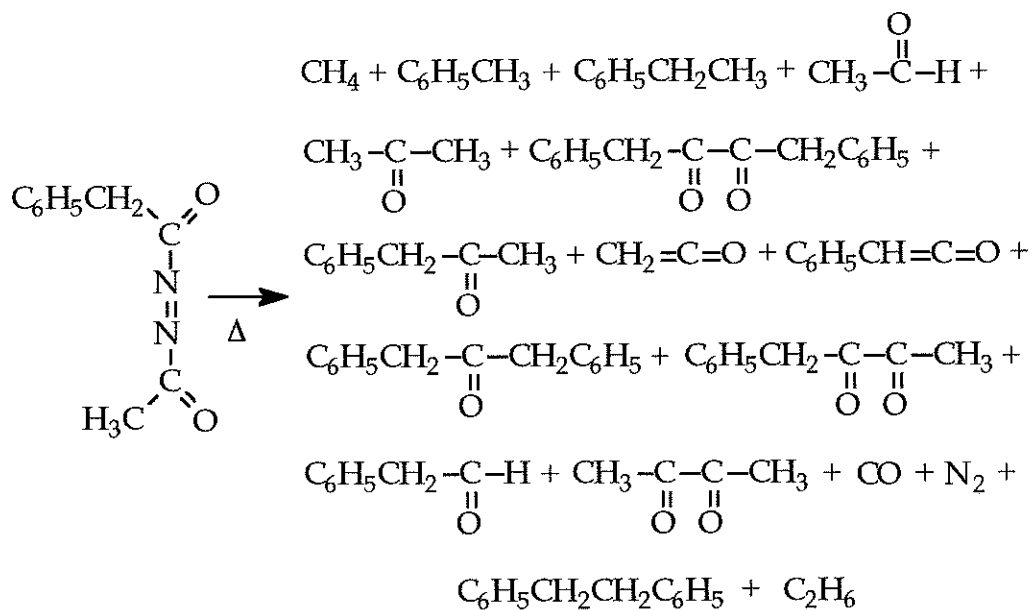
- (18) 10. Reaction of the quarternary ammonium salt shown below with strong base produces the nitrogen ylides indicated from which rearrangement products are ultimately obtained (via pathways a-i).



Match each letter with the corresponding rearrangement product by placing the letter next to the correct Roman numeral.



(17) 11. Consider the thermal decomposition of the following azo compound:



Propose a mechanism to account for all the products obtained.