

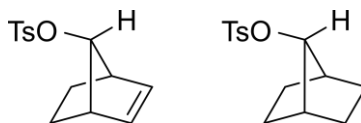
### ❖ Neighbouring Group Participation by $\pi$ and $\sigma$ Bonds

Besides oxygen, nitrogen, sulfur, and halogen;  $\pi$ - and  $\sigma$ -bonds can also act as a nucleophile in ‘neighboring group mechanism’ causing the retention of the original configuration. In this section, we will study the neighboring group participation by  $\pi$  and  $\sigma$  bonds with illustrative examples.

#### ➤ $\pi$ Bond as Neighbouring Group

This type of neighboring group participation can primarily be classified into two categories as discussed below.

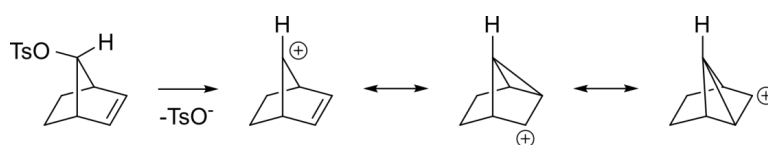
**1. Neighbouring group participation by an alkene:** The  $\pi$  orbitals of an alkene can stabilize a transition state by helping to delocalize the positive charge of the carbocation. For instance, the saturated tosylate will react very slowly ( $10^{11}$  times slower in solvolysis) with a nucleophile than the unsaturated tosylate.



The positively charged intermediate will be stabilized by the phenomenon of resonance where the positive charge is spread over many atoms as shown below.

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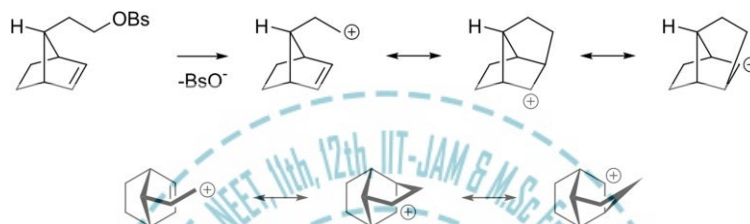
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A different view of the same intermediate is also given below.



Even if the alkene is more distant from the reacting center, it can still act in this way. For instance, in the following alkyl benzenesulfonate, the alkene can delocalize the carbocation's positive charge.

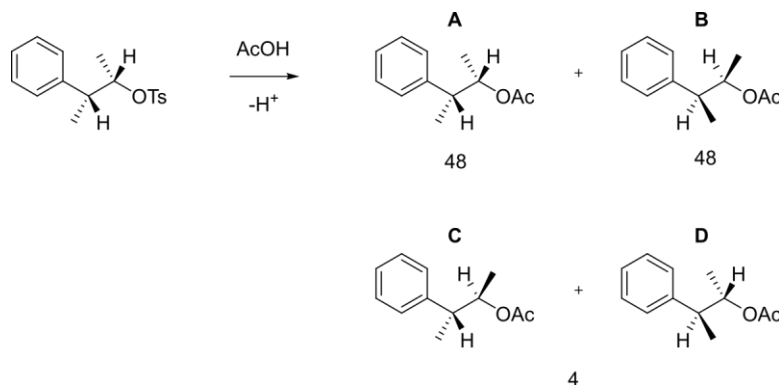


Furthermore, the raise in the  $S_N2$  reaction rate of allyl bromide with a nucleophile relative to the treatment with *n*-propyl bromide is due to the  $\pi$ -bond's orbitals-overlap with transition state's counterparts. Therefore, we can say that the alkene orbitals overlap with the  $S_N2$ -transition-state's orbitals in the allyl systems.

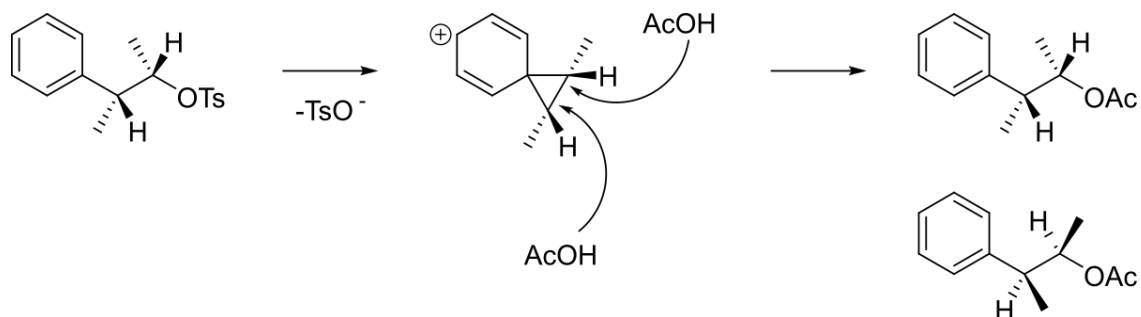
**2. Neighbouring group participation by an aromatic ring:** Just like allyl systems, higher reactivity for benzyl halide is observed because the  $S_N2$  transition state benefits from a similar overlapping effect. Similarly, many aromatic rings support the formation of an carbocation by delocalizing the positive charge density.



If the tosylate given below reacts with acetic acid via solvolysis instead of the normal  $S_N2$  pathway forming B, a 48:48:4 mixture of A, B (i.e., enantiomers), and C+D was formed.



The mechanism which forms A and B is shown below.

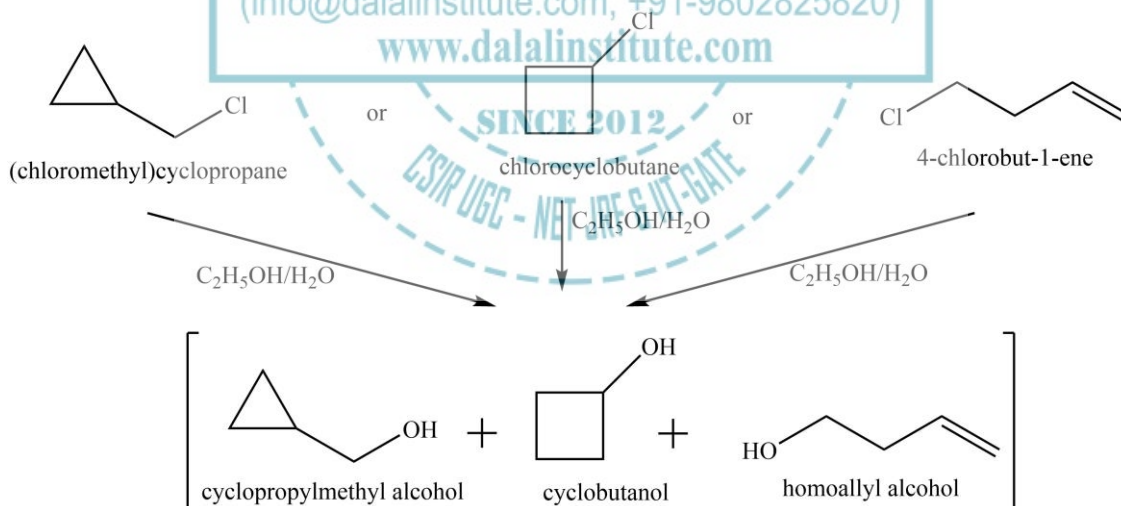


It is obvious from the above routes that the configuration would have changed if the reaction had taken place via the normal  $S_N2$  route.

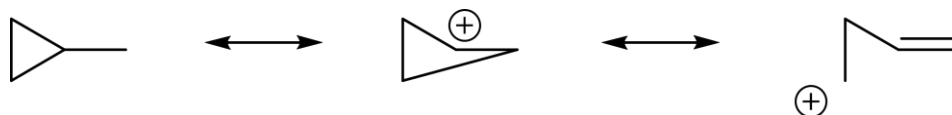
➤  **$\sigma$  Bond as Neighbouring Group**

This type of neighboring group participation can primarily be classified into two categories as discussed below.

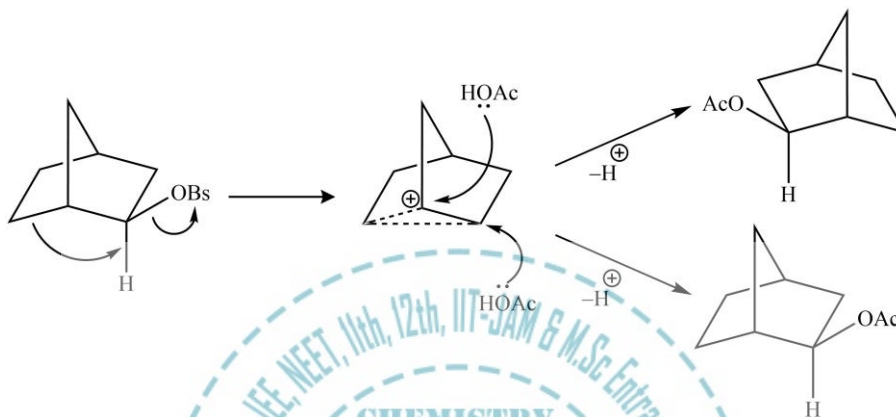
**1. Neighbouring group participation by cyclopropylmethyl, cyclobutyl, or a homoallyl group:** The treatment of cyclopropylmethyl chloride with dilute ethyl alcohol yields a mixture of 5% homoallyl alcohol, 47% cyclobutanol, and 48% cyclopropylmethyl alcohol. Similar results were obtained if we use cyclobutyl chloride or homoallyl chloride instead of cyclopropylmethyl chloride.



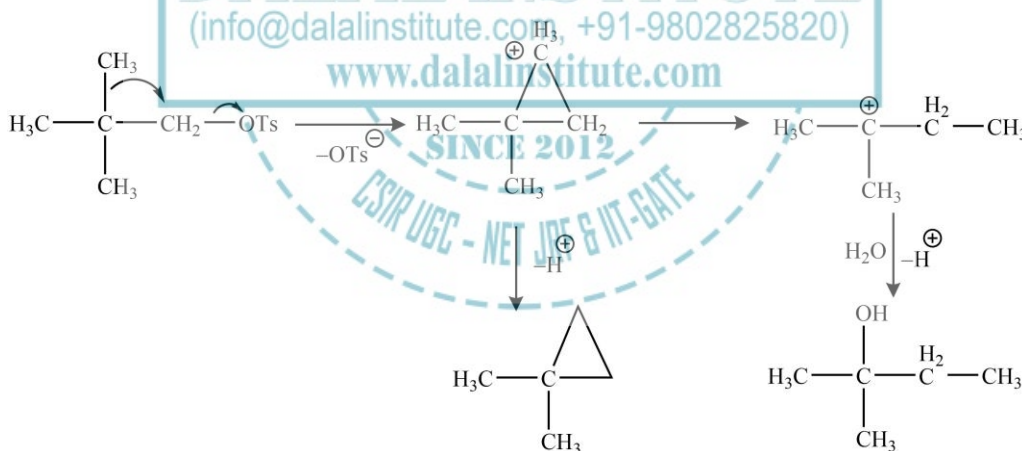
All this suggests that the carbocationic intermediate present in all three reactions must be the same, which in turn, is responsible for the same resulting products.



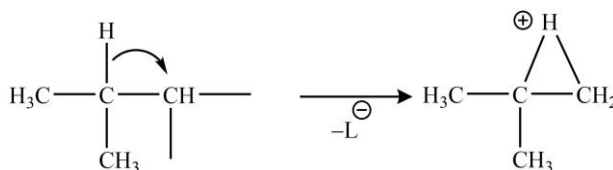
**2. Neighbouring group participation by aliphatic C-C or C-H bonds:** The aliphatic C-H or C-C bonds can also give rise to delocalization of charge if these bonds are close enough and antiperiplanar to the leaving group. The intermediates corresponding to these mechanisms are nonclassical in nature; and 2-norbornyl system is the most popular of such type. More precisely, the acetolysis of exo-2-norbornyl brosylate yields a racemic mixture of exo-acetates only and no endo product; suggesting neighboring group participation from  $\sigma$ -bond. Furthermore, a very slow rate is observed if we use endo-2-norbornyl brosylate confirming our guess.



Another example of such neighboring participation by aliphatic bonds is the methyl system where C-H gives rise to the original configuration as depicted below.



Another example of such neighboring group participation by aliphatic bonds is the methyl system where C-C gives rise to the original configuration as depicted below.



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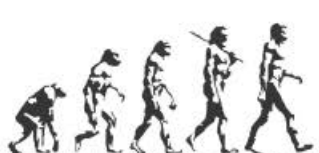
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# A TEXTBOOK OF ORGANIC CHEMISTRY

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**MANDEEP DALAL**



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