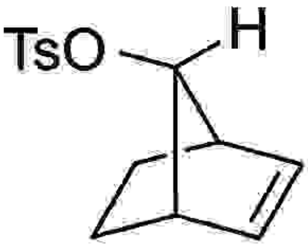
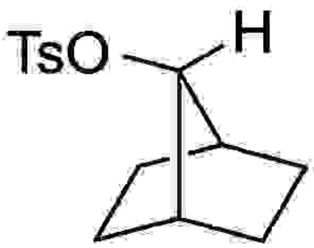
Neighbouring group participation

Neighbouring group participation (**NGP**) (also known as **anchimeric assistance**) in organic chemistry has been defined by IUPAC as the interaction of a reaction centre with a lone pair of electrons in an atom or the electrons present in a sigma bond or pi bond contained within the parent molecule but not conjugated with the reaction centre.[1][1][2][3] When NGP is in operation it is normal for the reaction rate to be increased. It is also possible for the stereochemistry of the reaction to be abnormal (or unexpected) when compared with a *normal* reaction. While it is possible for neighbouring groups to influence many reactions in organic chemistry (*e.g.* the reaction of a diene such as 1,3-cyclohexadiene with maleic anhydride normally gives the endo isomer because of a secondary effect {overlap of the carbonyl group π orbitals with the transition state in the Diels-Alder reaction}) this page is limited to neighbouring group effects seen with carbocations and S_N2 reactions.

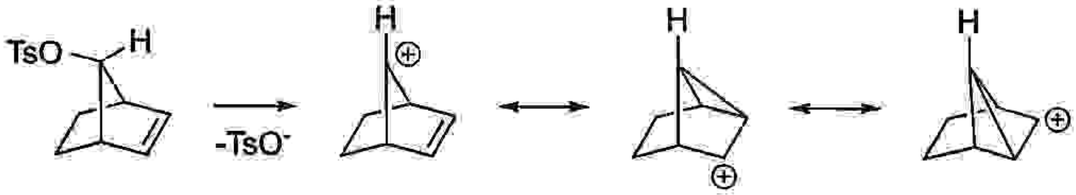
NGP by an alkene

The π orbitals of an alkene can stabilize a transition state by helping to delocalize the positive charge of the carbocation. For instance the unsaturated tosylate will react more quickly (10^{11} times faster for aqueous solvolysis) with a nucleophile than the saturated tosylate.

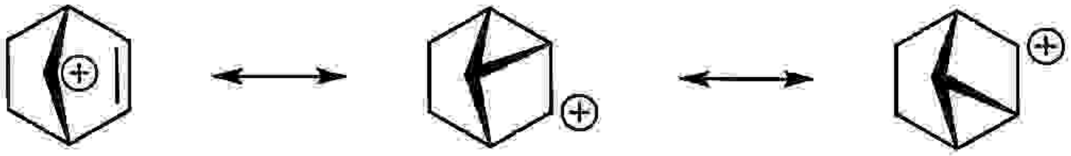




The carbocationic intermediate will be stabilized by resonance where the positive charge is spread over several atoms. In the diagram below this is shown.



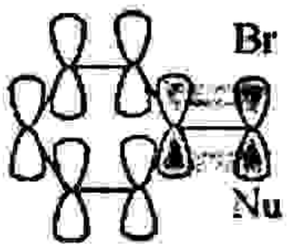
Here is a different view of the same intermediates.



Even if the alkene is more remote from the reacting center the alkene can still act in this way. For instance in the following alkyl benzenesulfonate the alkene is able to delocalise the carbocation.

NGP by an aromatic ring

In the case of a benzyl halide the reactivity is higher because the S_N2 transition state enjoys a similar overlap effect to that in the allyl system.



An aromatic ring can assist in the formation of a carbocationic intermediate called a **phenonium ion** by delocalising the positive charge.

When the following tosylate reacts with acetic acid in solvolysis then rather than a simple S_N2 reaction forming B, a 48:48:4 mixture of A, B (which are enantiomers) and C+D was obtained [2] [3].