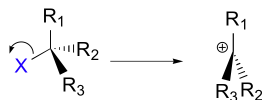


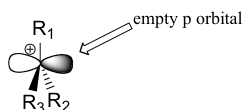
7.13: The S_N1 SN1 Mechanism

The S_N1 mechanism

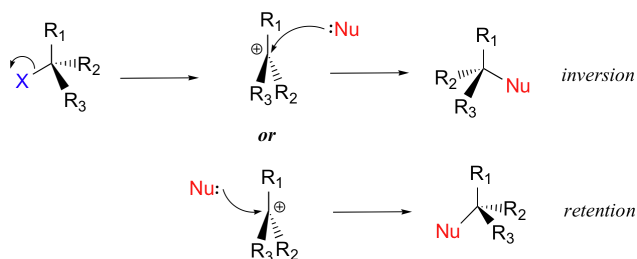
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



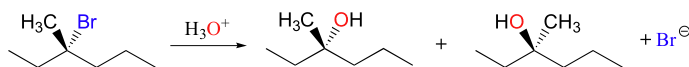
This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as sp^2 hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three sp^2 hybrid orbitals is an empty, unhybridized p orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' p orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.



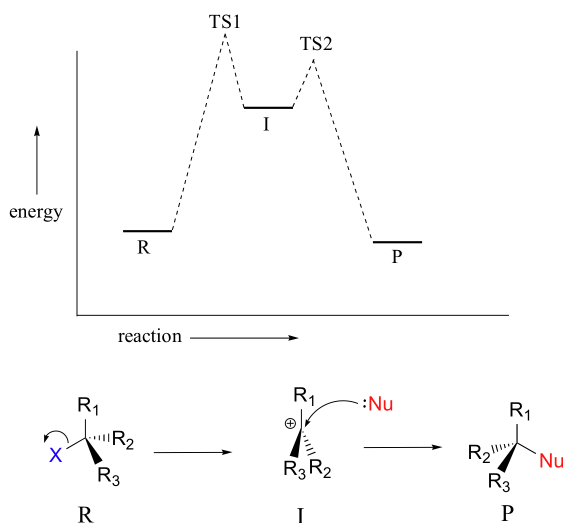
We saw that S_N2 reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of S_N1 reactions? In the model S_N1 reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar, sp^2 -hybridized carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an S_N1 reaction with water as the incoming nucleophile.



Exercise

Draw the structure of the intermediate in the two-step nucleophilic substitution reaction above.

The S_N1 reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity. Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discrete bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the S_N1 reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an S_N1 reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



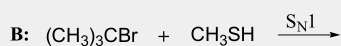
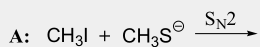
Exercise

Draw structures representing TS1 and TS2 in the reaction above. Use the solid/dash wedge convention to show three dimensions.

Recall that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for the first step is higher than that for the second step. Also recall that an S_N1 reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding.

Exercise

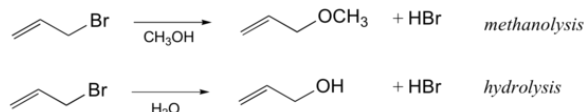
Consider two nucleophilic substitutions that occur uncatalyzed in solution. Assume that reaction A is S_N2 , and reaction B is S_N1 . Predict, in each case, what would happen to the rate of the reaction if the concentration of the nucleophile were doubled, while all other conditions remained constant.



Influence of the solvent in an S_N1 reaction

Since the hydrogen atom in a polar protic solvent is highly positively charged, it can interact with the anionic nucleophile which would negatively affect an S_N2 , but it does not affect an S_N1 reaction because the nucleophile is not a part of the rate-determining step. Polar protic solvents actually speed up the rate of the unimolecular substitution reaction because the large dipole moment of the solvent helps to stabilize the transition state. The highly positive and highly negative parts interact with the substrate to lower the energy of the transition state. Since the carbocation is unstable, anything that can stabilize this even a little will speed up the reaction.

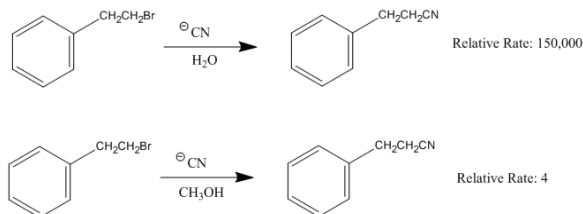
Sometimes in an S_N1 reaction the solvent acts as the nucleophile. This is called a solvolysis reaction. The S_N1 reaction of allyl bromide in methanol is an example of what we would call **methanolysis**, while if water is the solvent the reaction would be called **hydrolysis**:



The polarity and the ability of the solvent to stabilize the intermediate carbocation is very important as shown by the relative rate data for the solvolysis (see table below). The dielectric constant of a solvent roughly provides a measure of the solvent's polarity. A dielectric constant below 15 is usually considered non-polar. Basically, the dielectric constant can be thought of as the solvent's ability to reduce the internal charge of the solvent. So for our purposes, the higher the dielectric constant the more polar the substance and in the case of S_N1 reactions, the faster the rate.

Solvent	Dielectric Constant	Relative Rate
<ul style="list-style-type: none"> • $\text{CH}_3\text{CO}_2\text{H}$ • CH_3OH • H_2O 	<ul style="list-style-type: none"> • 6 • 33 • 78 	<ul style="list-style-type: none"> • 1 • 4 • 150,000

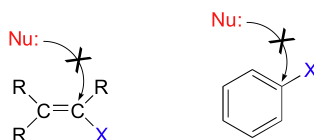
Below is the same reaction conducted in two different solvents and the relative rate that corresponds with it.



Exercise

Draw a complete curved-arrow mechanism for the methanolysis reaction of allyl bromide shown above.

One more important point must be made before continuing: nucleophilic substitutions as a rule occur at sp^3 -hybridized carbons, and *not* where the leaving group is attached to an sp^2 -hybridized carbon::



Bonds on sp^2 -hybridized carbons are inherently shorter and stronger than bonds on sp^3 -hybridized carbons, meaning that it is harder to break the C-X bond in these substrates. $\text{S}_{\text{N}}2$ reactions of this type are unlikely also because the (hypothetical) electrophilic carbon is protected from nucleophilic attack by electron density in the p bond. $\text{S}_{\text{N}}1$ reactions are highly unlikely, because the resulting carbocation intermediate, which would be sp -hybridized, would be very unstable (we'll discuss the relative stability of carbocation intermediates in a later section of this module).

Before we look at some real-life nucleophilic substitution reactions in the next chapter, we will spend some time in the remainder of this module focusing more closely on the three principal partners in the nucleophilic substitution reaction: the nucleophile, the electrophile, and the leaving group.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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