

8.11: When Is the Reaction S_N1 SN1 , S_N2 SN2 , E1 E1 , or E2 E2 ?

Having discussed the many factors that influence nucleophilic substitution and elimination reactions of alkyl halides, we must now consider the practical problem of predicting the most likely outcome when a given alkyl halide is reacted with a given nucleophile. As we noted earlier, several variables must be considered, **the most important being the structure of the alkyl group and the nature of the nucleophilic reactant.** In general, in order for an S_N1 or E1 reaction to occur, the relevant carbocation intermediate must be relatively stable. Strong nucleophile favor substitution, and strong bases, especially strong hindered bases (such as tert-butoxide) favor elimination.

The nature of the halogen substituent on the alkyl halide is usually not very significant if it is Cl, Br or I. In cases where both S_N2 and E2 reactions compete, chlorides generally give more elimination than do iodides, since the greater electronegativity of chlorine increases the acidity of beta-hydrogens. Indeed, although alkyl fluorides are relatively unreactive, when reactions with basic nucleophiles are forced, elimination occurs (note the high electronegativity of fluorine).

The following table summarizes the expected outcome of alkyl halide reactions with nucleophiles. It is assumed that the alkyl halides have one or more beta-hydrogens, making elimination possible; and that low dielectric solvents (e.g. acetone, ethanol, tetrahydrofuran & ethyl acetate) are used. When a high dielectric solvent would significantly influence the reaction this is noted in red. **Note that halogens bonded to sp² or sp hybridized carbon atoms do not normally undergo substitution or elimination reactions with nucleophilic reagents.**

Nucleophile	Anionic Nucleophiles (Weak Bases: I ⁻ , Br ⁻ , SCN ⁻ , N ₃ ⁻ , CH ₃ CO ₂ ⁻ , RS ⁻ , CN ⁻ etc.) pK _a 's from -9 to 10 (left to right)	Anionic Nucleophiles (Strong Bases: HO ⁻ , RO ⁻) pK _a 's > 15	Neutral Nucleophiles (H ₂ O, ROH, RSH, R ₃ N) pK _a 's ranging from -2 to 11
Primary RCH ₂ -	Rapid S _N 2 substitution. The rate may be reduced by substitution of β-carbons, as in the case of neopentyl.	Rapid S _N 2 substitution. E2 elimination may also occur. <i>e.g.</i> ClCH ₂ CH ₂ Cl + KOH → CH ₂ =CHCl	S _N 2 substitution. (N ≈ S >>O)
Secondary R ₂ CH-	S _N 2 substitution and / or E2 elimination (depending on the basicity of the nucleophile). Bases weaker than acetate (pK _a = 4.8) give less elimination. The rate of substitution may be reduced by branching at the β-carbons, and this will increase elimination.	E2 elimination will dominate.	S _N 2 substitution. (N ≈ S >>O) In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be formed slowly.
Tertiary R ₃ C-	E2 elimination will dominate with most nucleophiles (even if they are weak bases). No S _N 2 substitution due to steric hindrance. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be expected.	E2 elimination will dominate. No S _N 2 substitution will occur. In high dielectric ionizing solvents S_N1 and E1 products may be formed.	E2 elimination with nitrogen nucleophiles (they are bases). No S _N 2 substitution. In high dielectric ionizing solvents S_N1 and E1 products may be formed.

Allyl $\text{H}_2\text{C}=\text{CHCH}_2-$	Rapid $\text{S}_{\text{N}}2$ substitution for 1° and 2°-halides. For 3°-halides a very slow $\text{S}_{\text{N}}2$ substitution or, if the nucleophile is moderately basic, E2 elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, $\text{S}_{\text{N}}1$ and E1 products may be observed.	Rapid $\text{S}_{\text{N}}2$ substitution for 1° halides. E2 elimination will compete with substitution in 2°-halides, and dominate in the case of 3°-halides. In high dielectric ionizing solvents $\text{S}_{\text{N}}1$ and E1 products may be formed.	Nitrogen and sulfur nucleophiles will give $\text{S}_{\text{N}}2$ substitution in the case of 1° and 2°-halides. 3°-halides will probably give E2 elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents $\text{S}_{\text{N}}1$ and E1 products may be formed. Water hydrolysis will be favorable for 2° & 3°-halides.
Benzyl $\text{C}_6\text{H}_5\text{CH}_2-$	Rapid $\text{S}_{\text{N}}2$ substitution for 1° and 2°-halides. For 3°-halides a very slow $\text{S}_{\text{N}}2$ substitution or, if the nucleophile is moderately basic, E2 elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, $\text{S}_{\text{N}}1$ and E1 products may be observed.	Rapid $\text{S}_{\text{N}}2$ substitution for 1° halides (note there are no β hydrogens). E2 elimination will compete with substitution in 2°-halides, and dominate in the case of 3°-halides. In high dielectric ionizing solvents $\text{S}_{\text{N}}1$ and E1 products may be formed.	Nitrogen and sulfur nucleophiles will give $\text{S}_{\text{N}}2$ substitution in the case of 1° and 2°-halides. 3°-halides will probably give E2 elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents $\text{S}_{\text{N}}1$ and E1 products may be formed. Water hydrolysis will be favorable for 2° & 3°-halides.

Contributors

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