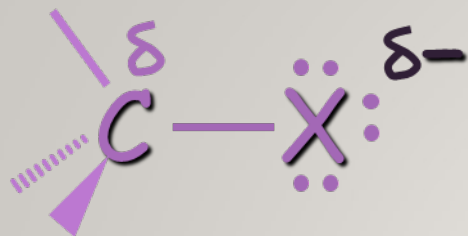


CHM-134 ORGANIC CHEMISTRY

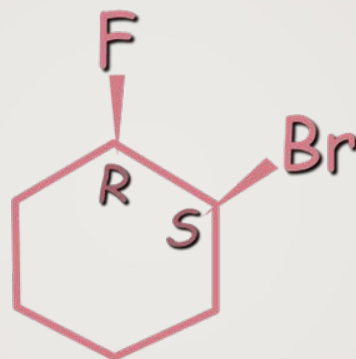
CHAPTER-6: ORGANIC HALOGEN COMPOUNDS



Names: Halo- is a substituent to alkane stem



1-Chlorobutane



(1*S*,2*R*)-1-Bromo-2-fluorocyclohexane



2-Iodo-2-methylpropane

6.1 PHYSICAL PROPERTIES OF HALOALKANES

- ❑ The bond strength of C-X decreases as the size of X increases.
- ❑ A halogen uses a p orbital to overlap a sp^2 orbital on a carbon atom.
- ❑ As the size of the halogen p orbital increases ($F < Cl < Br < I$), the percentage overlap with the smaller sp^2 carbon orbital is less and the bond strength decreases.

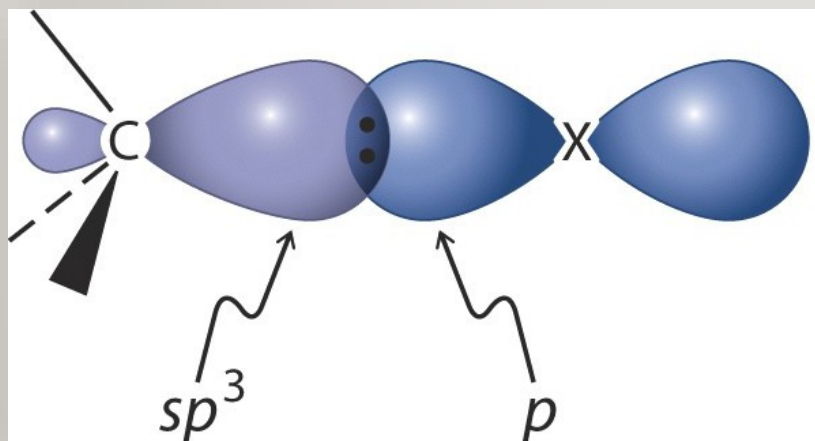


TABLE 6-1

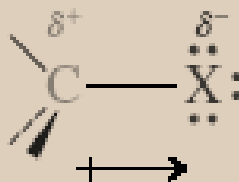
C-X Bond Lengths and Bond Strengths in CH_3X

Halo-methane	Bond length (Å)	Bond strength (kcal mol ⁻¹)
CH ₃ F	1.385	110
CH ₃ Cl	1.784	85
CH ₃ Br	1.929	70
CH ₃ I	2.139	57

6.1 NAMES AND PHYSICAL PROPERTIES OF ETHERS

- ❖ The C-X bond is polarized.
- ❖ Because halogens are more electronegative than carbon, carbon-halogen bonds are polarized.
- ❖ The halogen atom possesses a partial negative (δ^-) and the carbon atom a partial positive (δ^+) charge.

The Polar Character of the C-X Bond



The electrophilic δ^+ carbon atom is subject to attack by anions and other nucleophilic species. Cations and other electron-deficient species attack the halogen atom.

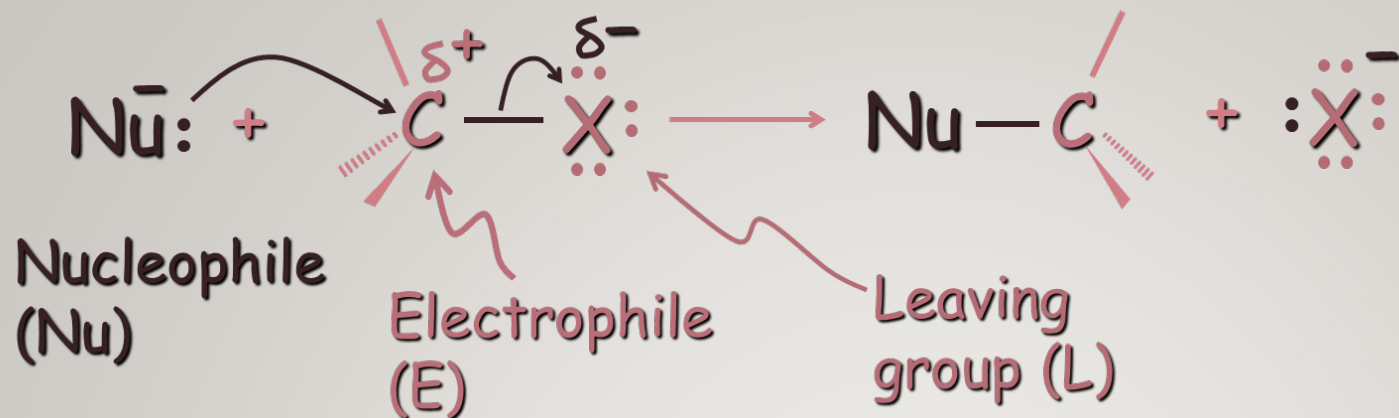
- ✓ Haloalkanes have higher boiling points than the corresponding alkanes.
- ✓ Boiling points of haloalkanes are higher than those of the parent alkanes mainly due to dipole-dipole interactions between the haloalkane molecules:

Dipole-Dipole Attraction

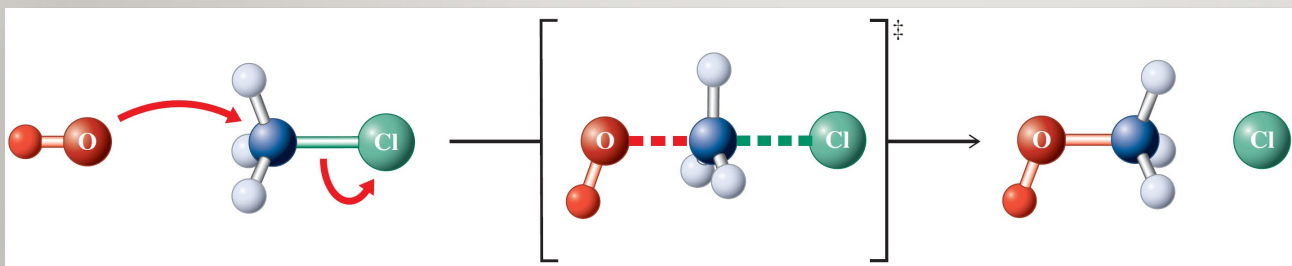


- ❖ As the size of the halogen increases there are also larger London forces between the haloalkane molecules.
- ❖ Larger atoms are more polarizable and interact more strongly through London forces.

6.2 NUCLEOPHILIC SUBSTITUTION

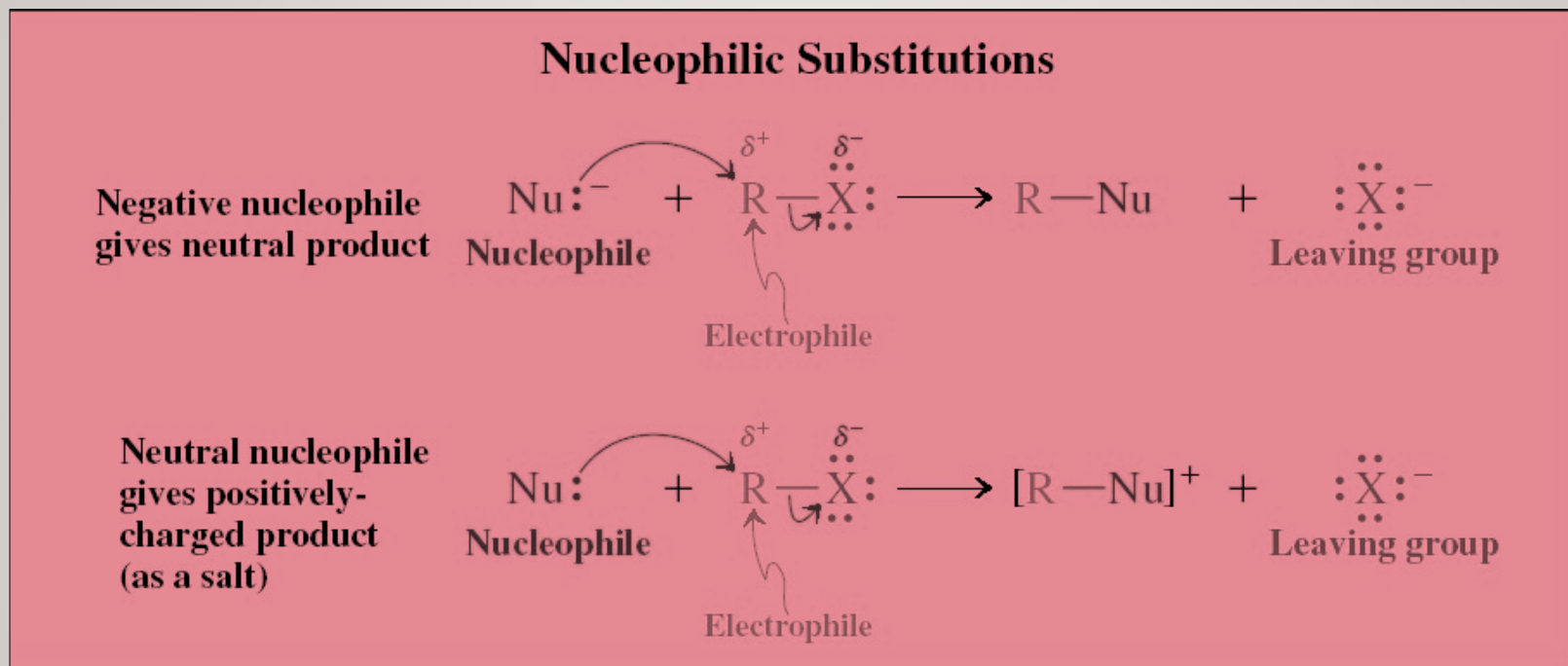


Backside attack: Inversion of configuration.



6.2 NUCLEOPHILIC SUBSTITUTION

- ✓ Haloalkanes can react with nucleophiles at their electrophilic carbon atom.
- ✓ The nucleophile can be charged, as in :OH^- or neutral, as in :NH_3 .
- ✓ In nucleophilic substitution of haloalkanes, the nucleophile replaces the halogen atom.



- ✓ In both cases, the leaving group is the halide anion, X^- .
- ✓ In describing reactions, the organic starting material is called the substrate of the reaction.
- ✓ Here, the substrate is being attacked by a nucleophile.

6.2 NUCLEOPHILIC SUBSTITUTION

Nucleophilic substitution exhibits considerable diversity.

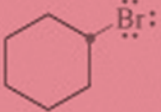
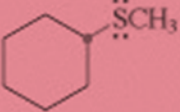
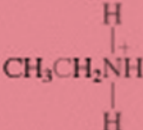
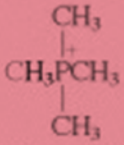
TABLE 6-3 The Diversity of Nucleophilic Substitution

Reaction number	Substrate	Nucleophile	Product	Leaving group
1.	$\text{CH}_3\ddot{\text{C}}\text{Cl}:$ Chloromethane	+ $\text{H}\ddot{\text{O}}:^-$	$\text{CH}_3\ddot{\text{O}}\text{H}$ Methanol	+ $:\ddot{\text{C}}\text{I}^-$
2.	$\text{CH}_3\text{CH}_2\ddot{\text{I}}:$ Iodoethane	+ $\text{CH}_3\ddot{\text{O}}:^-$	$\text{CH}_3\text{CH}_2\ddot{\text{O}}\text{CH}_3$ Methoxyethane	+ $:\ddot{\text{I}}^-$
3.	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\ \\ :\text{Br}: \end{array}$ 2-Bromobutane	+ $:\ddot{\text{I}}^-$	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\ \\ :\text{I}: \end{array}$ 2-Iodobutane	+ $:\ddot{\text{Br}}^-$
4.	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CCH}_2\ddot{\text{I}}: \\ \\ \text{CH}_3 \end{array}$ 1-Iodo-2-methylpropane	+ $:\text{N}\equiv\text{C}:^-$	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CCH}_2\text{C}\equiv\text{N}: \\ \\ \text{CH}_3 \end{array}$ 3-Methylbutane-nitrile	+ $:\ddot{\text{I}}^-$

Note: Remember that nucleophiles are red, electrophiles are blue, and leaving groups are green.

6.2 NUCLEOPHILIC SUBSTITUTION

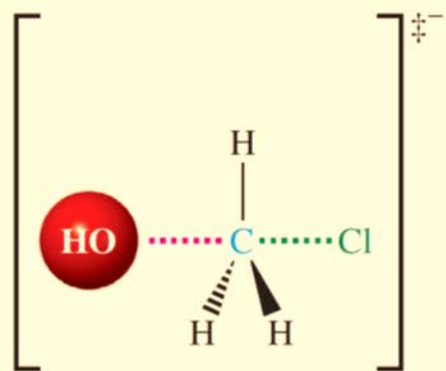
Nucleophilic substitution exhibits considerable diversity.

Reaction number	Substrate	Nucleophile	Product	Leaving group	
5.	 Bromocyclohexane	+ $\text{CH}_3\ddot{\text{S}}:^-$	\longrightarrow	 Methylthiocyclohexane	+ $:\ddot{\text{Br}}:^-$
6.	$\text{CH}_3\text{CH}_2\ddot{\text{I}}:$ Iodoethane	+ $:\text{NH}_3$	\longrightarrow	 Ethylammonium iodide	+ $:\ddot{\text{I}}:^-$
7.	$\text{CH}_3\ddot{\text{Br}}:$ Bromomethane	+ $:\text{P}(\text{CH}_3)_3$	\longrightarrow	 Tetramethylphosphonium bromide	+ $:\ddot{\text{Br}}:^-$

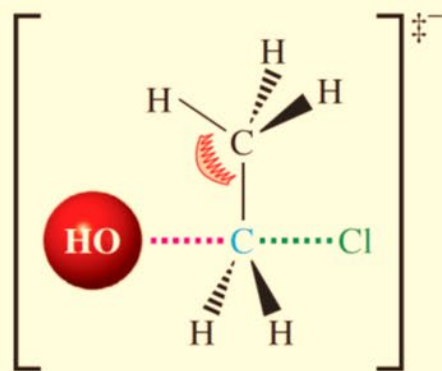
Note: Remember that nucleophiles are red, electrophiles are blue, and leaving groups are green.

6.2 NUCLEOPHILIC SUBSTITUTION

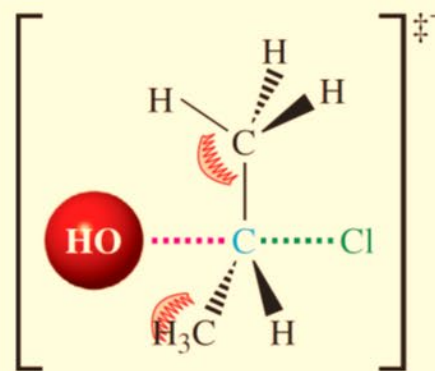
Alpha Branching



Methyl

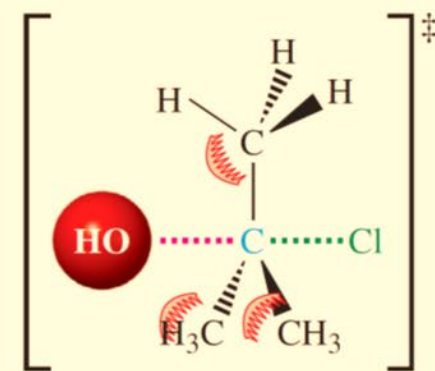


Primary



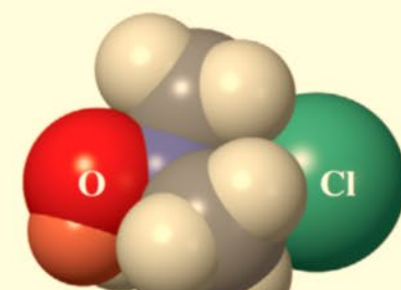
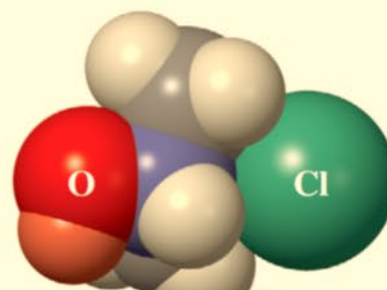
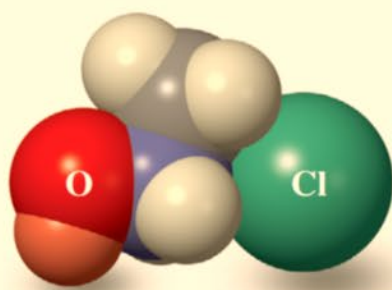
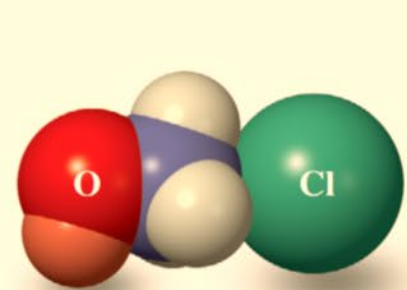
Secondary

(Slow reaction: hydrogens on two methyl groups interfere)



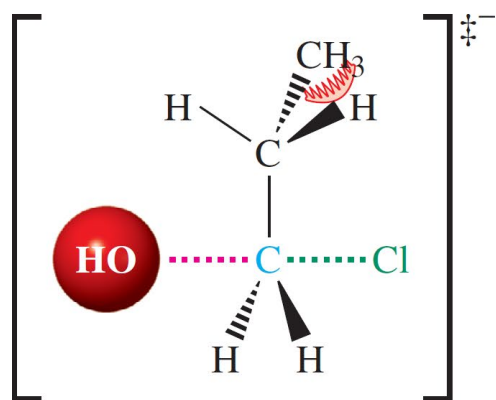
Tertiary

(Negligible S_N2 reaction; too much steric hindrance)

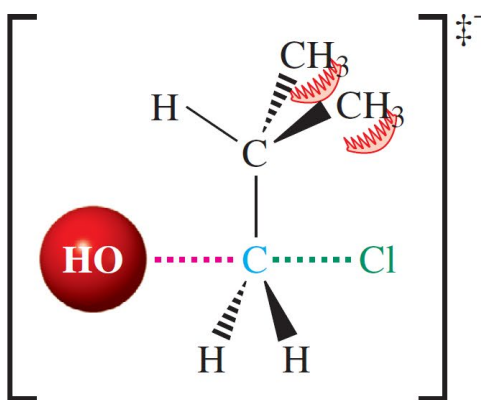


6.2 NUCLEOPHILIC SUBSTITUTION

Beta Branching

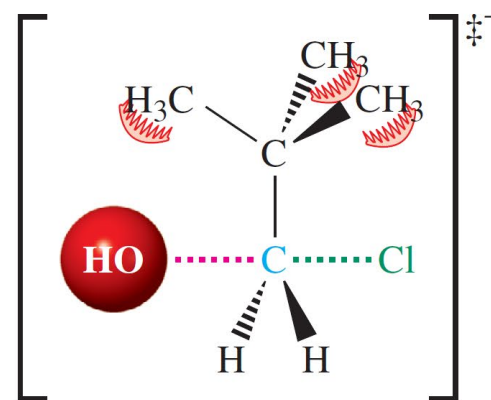


1-Propyl
(*gauche* CH₃ and Cl)



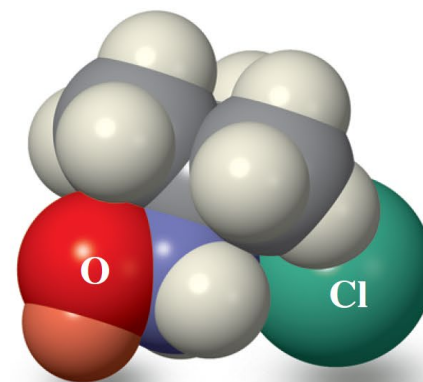
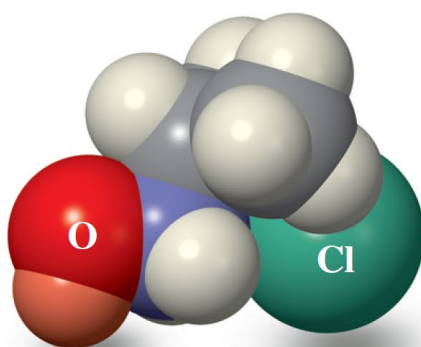
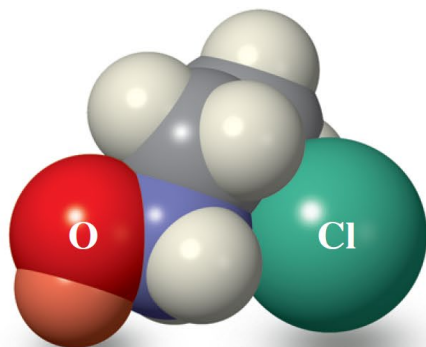
2-Methyl-1-propyl
(two *gauche* CH₃ and Cl)

(High energy transition state:
reaction is slower)

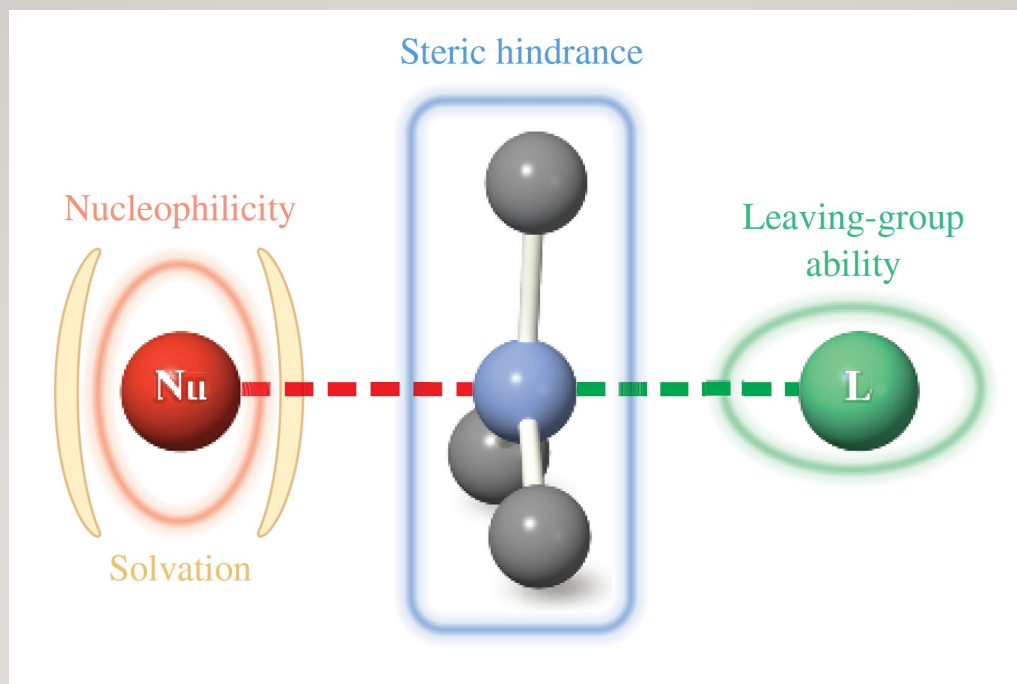


2,2-Dimethyl-1-propyl

(All conformations experience
severe steric hindrance)



6.2 NUCLEOPHILIC SUBSTITUTION



Nucleophilicity

Increases to the left (more basic Nu) and down (more polarizable Nu) the periodic table.

Solvation

Impedes nucleophilicity by forming a solvent shell around Nu, particularly with protic solvents and for charged, small Nu^- . Solvation is much attenuated with aprotic solvents.

Steric hindrance

Slows the reaction through substituents at and adjacent to the reacting center.

Leaving-group ability

Increases with decreasing basicity of L.