Organic Chemistry

Alkyl halides

by

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http://ocw.ump.edu.my/course/view.php?id=491

Chapter Description

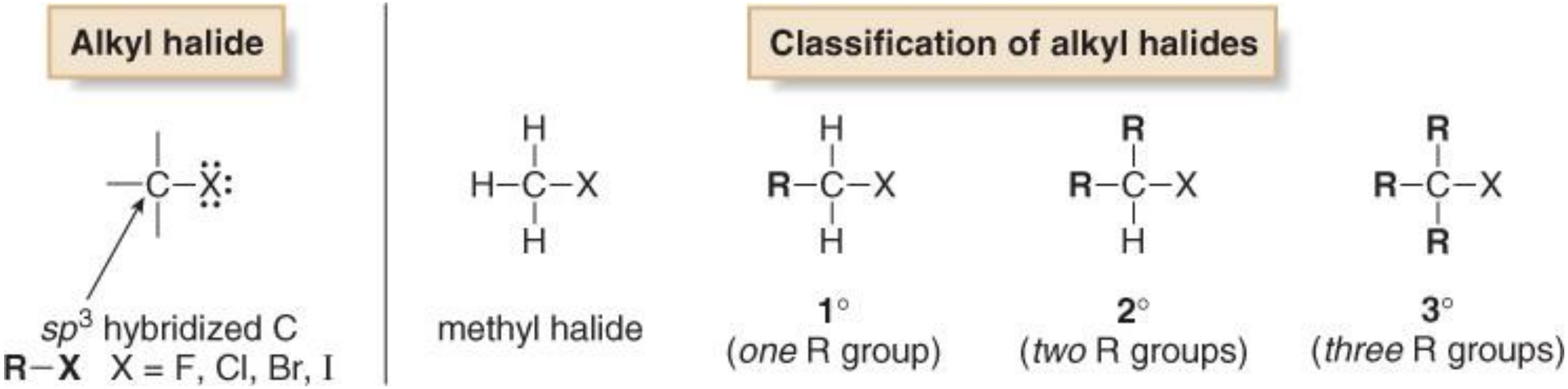
- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of alkyl halides
  - The students should be able to **explain** the fundamental of organic chemistry in terms of alkyl halides

- Expected Outcomes
  - Explain the basic knowledge in alkyl halides
  - Describe the chemical reactions and conditions for alkyl halides reactions
  - Describe the alkyl halides reactions for SN1 and SN2 reaction

- References
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

Introduction to Alkyl Halides

- Alkyl halides are organic molecules containing a halogen atom bonded to an *sp*^{3} hybridized carbon atom.
- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom in halides is often denoted by the symbol “X”.

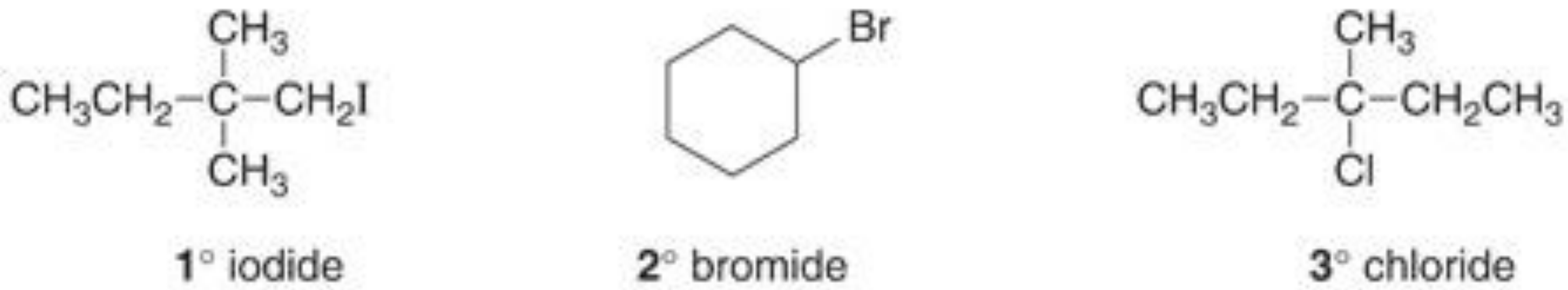


Introduction to Alkyl Halides

- There are other types of organic halides. These include vinyl halides, aryl halides, allylic halides and benzylic halides.
- Vinyl halides have a halogen atom (X) bonded to a C—C double bond.
- Aryl halides have a halogen atom bonded to a benzene ring.
- Allylic halides have X bonded to the carbon atom adjacent to a C—C double bond.
- Benzylic halides have X bonded to the carbon atom adjacent to a benzene ring.

Introduction to Alkyl Halides

Figure 9.1 Examples of 1°, 2°, and 3° alkyl halides

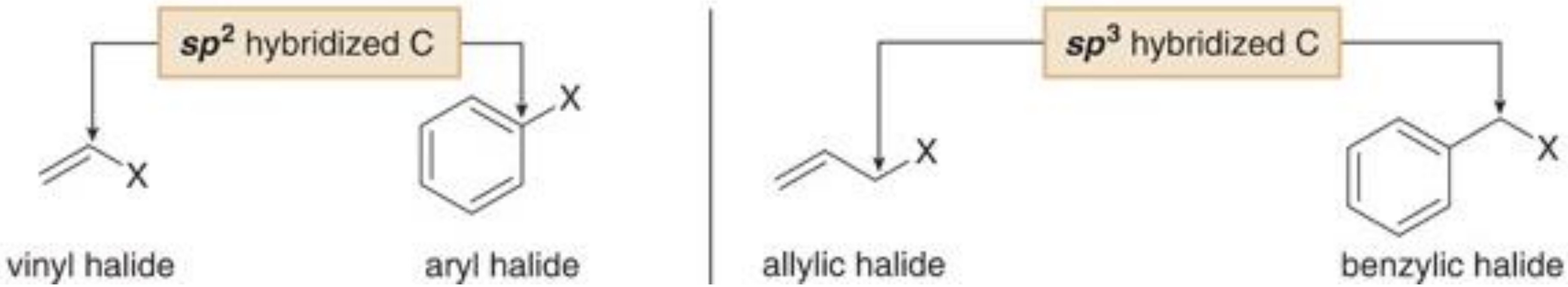


$CH_3CH_2-C(CH_3)_2-CH_2I$

$CH_3CH_2-C(CH_3)(Cl)-CH_2CH_3$

1° iodide **2° bromide** **3° chloride**

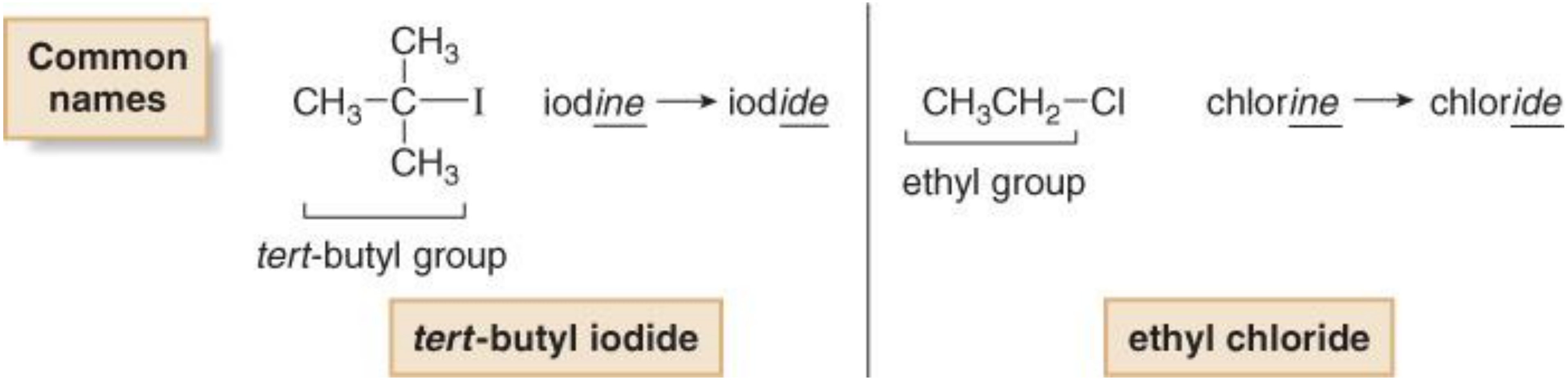
Figure 9.2 Four types of organic halides (RX) having X near a π bond



vinyl halide aryl halide allylic halide benzylic halide

Nomenclature

- Common names are often used for simple alkyl halides. To assign a common name:
    - Name all the carbon atoms of the molecule as a single alkyl group.
    - Name the halogen bonded to the alkyl group.
    - Combine the names of the alkyl group and halide, separating the words with a space.



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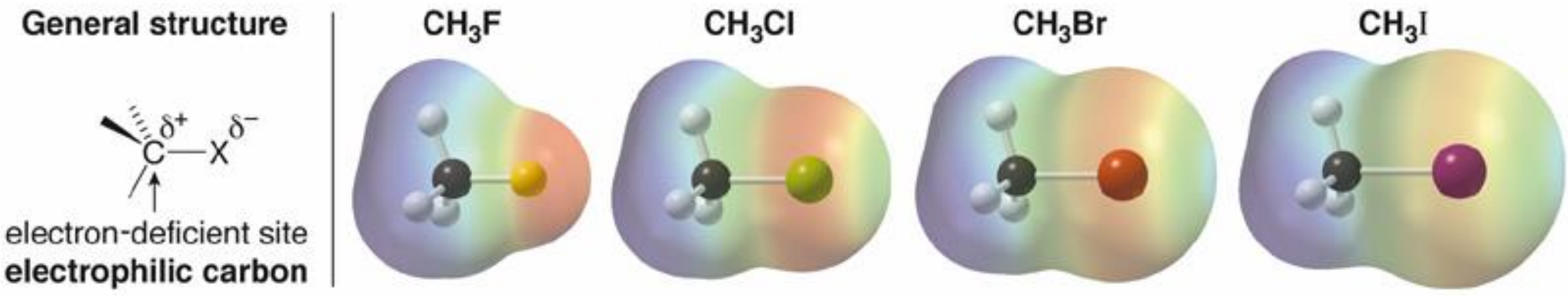
The Polar Carbon-Halogen Bond

- The electronegative halogen atom in alkyl halides creates a polar C—X bond, making the carbon atom electron deficient. Electrostatic potential maps of four simple alkyl halides illustrate this point.

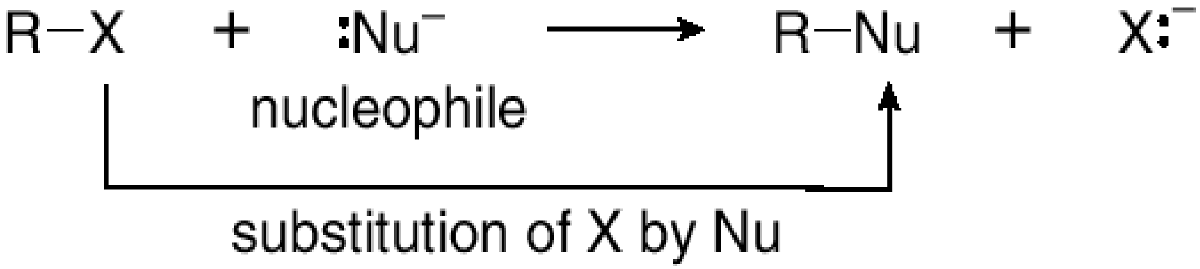
Electrostatic potential maps of four halomethanes (CH_3X)



- The polar C–X bond makes the carbon atom *electron deficient* in each CH_3X molecule.

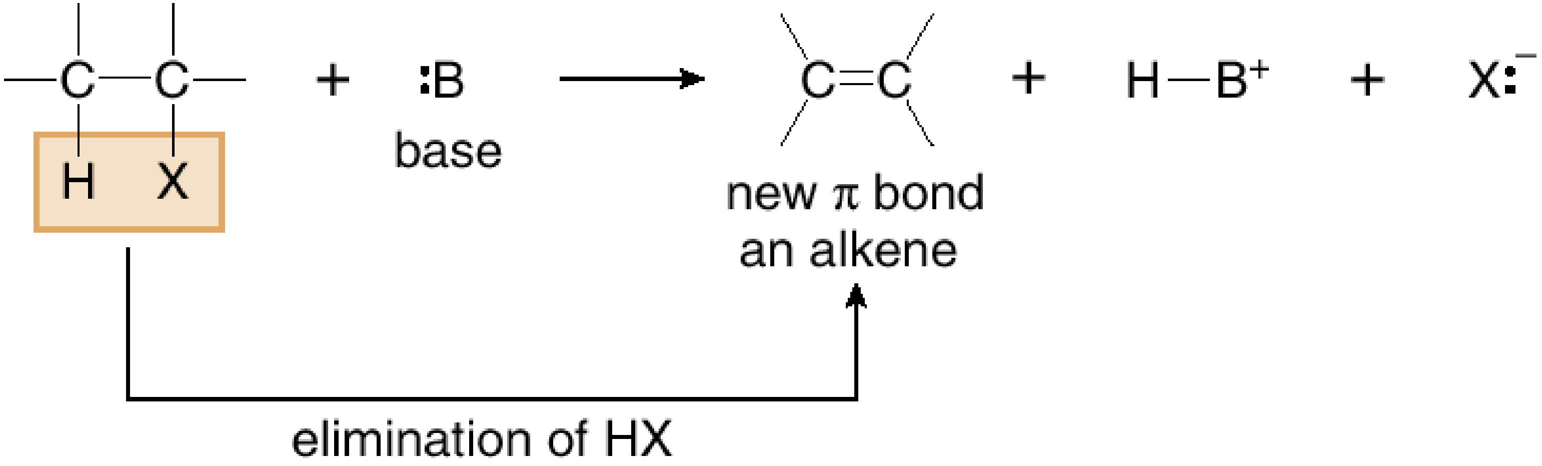
The Polar Carbon-Halogen Bond

Alkyl halides undergo substitution reactions with nucleophiles.



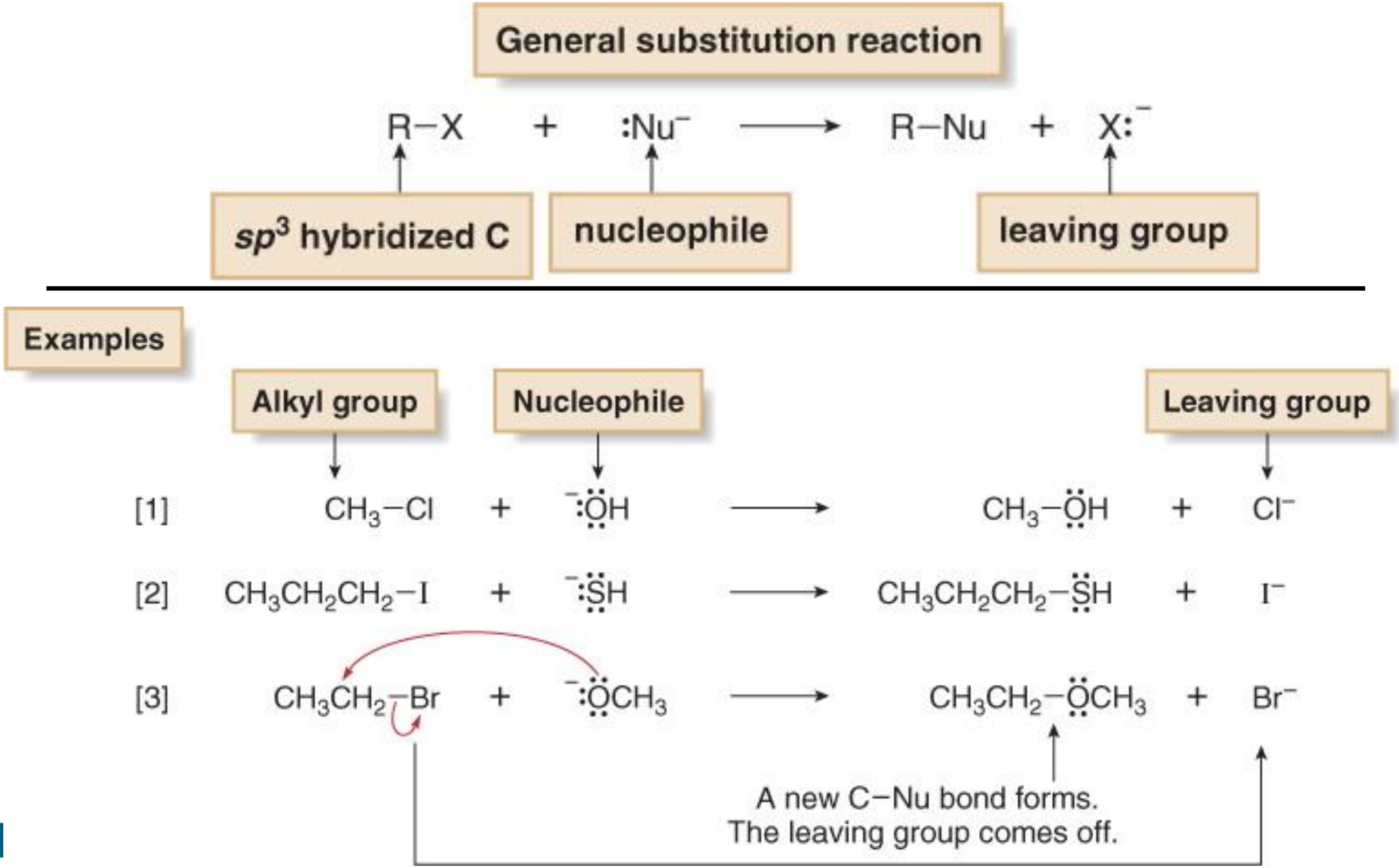
$$R{-}X \; + \; :Nu^- \longrightarrow R{-}Nu \; + \; X:^-$$

Alkyl halides undergo elimination reactions with Brønsted–Lowry bases.



General Features of Nucleophilic Substitution

- Three components are necessary in any substitution reaction.



$$R{-}X \quad + \quad :Nu^- \longrightarrow R{-}Nu \quad + \quad X:^-$$

$$[1] \quad CH_3{-}Cl \quad + \quad ^-:\ddot{O}H \longrightarrow CH_3{-}\ddot{O}H \quad + \quad Cl^-$$

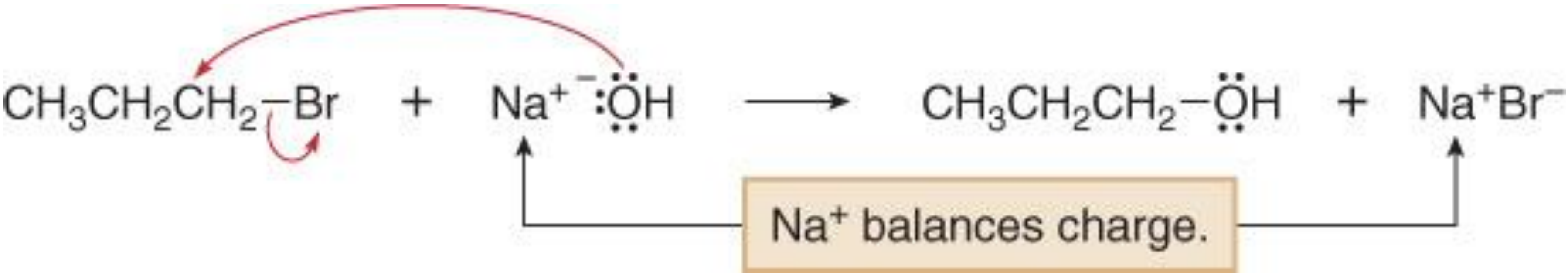
$$[2] \quad CH_3CH_2CH_2{-}I \quad + \quad ^-:\ddot{S}H \longrightarrow CH_3CH_2CH_2{-}\ddot{S}H \quad + \quad I^-$$

$$[3] \quad CH_3CH_2{-}Br \quad + \quad ^-:\ddot{O}CH_3 \longrightarrow CH_3CH_2{-}\ddot{O}CH_3 \quad + \quad Br^-$$

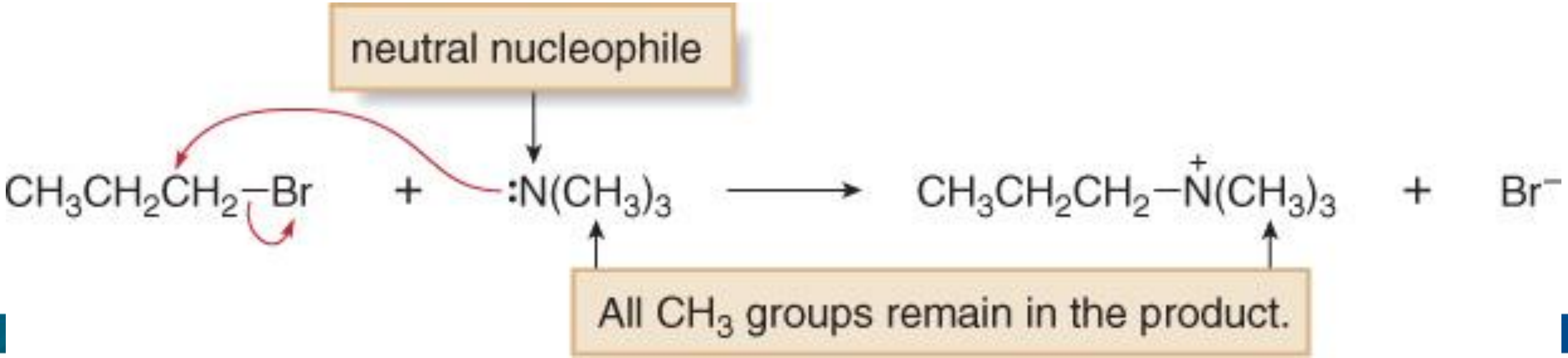
A new C–Nu bond forms.
The leaving group comes off.

General Features of Nucleophilic Substitution

- Negatively charged nucleophiles like HO^- and HS^- are used as salts with Li^+, Na^+, or K^+ counterions to balance the charge. Since the identity of the counterion is usually inconsequential, it is often omitted from the chemical equation.

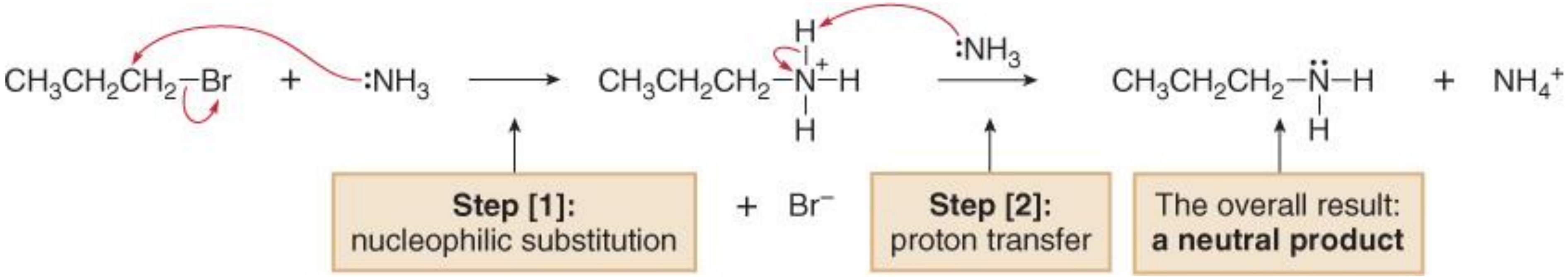


- When a neutral nucleophile is used, the substitution product bears a positive charge.



General Features of Nucleophilic Substitution

- Furthermore, when the substitution product bears a positive charge and also contains a proton bonded to O or N, the initially formed substitution product readily loses a proton in a Brønsted-Lowry acid-base reaction, forming a neutral product.



- To draw any nucleophilic substitution product:
  - Find the *sp*^{3} hybridized carbon with the leaving group.
  - Identify the nucleophile, the species with a lone pair or π bond.
  - Substitute the nucleophile for the leaving group and assign charges (if necessary) to any atom that is involved in bond breaking or bond formation.

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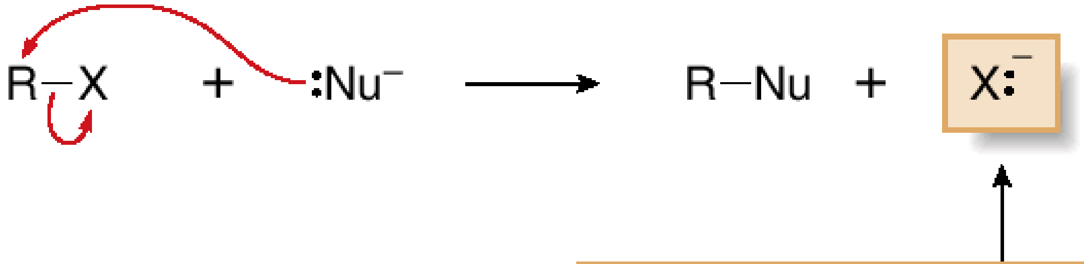
The Leaving Group

- In a nucleophilic substitution reaction of R—X, the C—X bond is heterolytically cleaved, and the leaving group departs with the electron pair in that bond, forming X:⁻. The more stable the leaving group X:⁻, the better able it is to accept an electron pair.

In comparing two leaving groups, the better leaving group is the weaker base.



$$R{-}X + :Nu^- \longrightarrow R{-}Nu + X:^-$$

Nucleophilic substitution occurs with **leaving groups that are weak bases.**

- For example, H_2O is a better leaving group than HO^- because H_2O is a weaker base.

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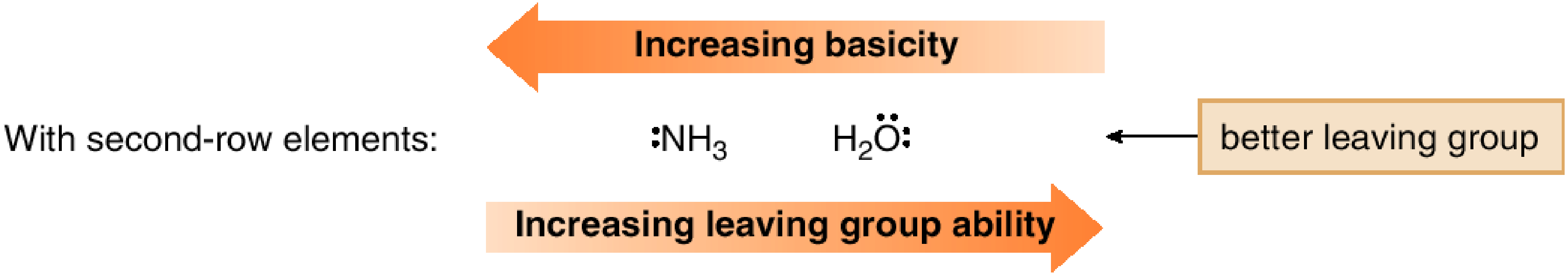
The Leaving Group

Left-to-right across a row of the periodic table, basicity *decreases* so leaving group ability *increases.*



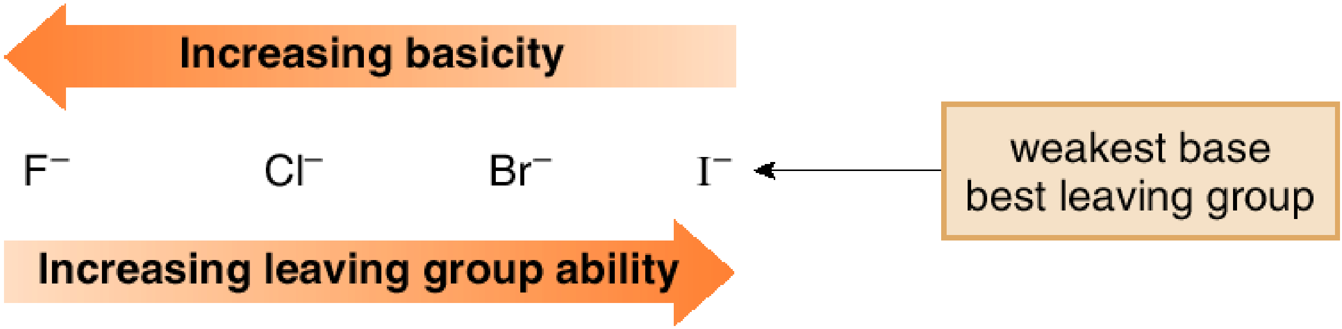
Increasing basicity

With second-row elements: $:NH_3$ $H_2\ddot{O}:$

better leaving group

Increasing leaving group ability

Down a column of the periodic table, basicity *decreases* so leaving group ability *increases.*



Increasing basicity

F^- Cl^- Br^- I^-

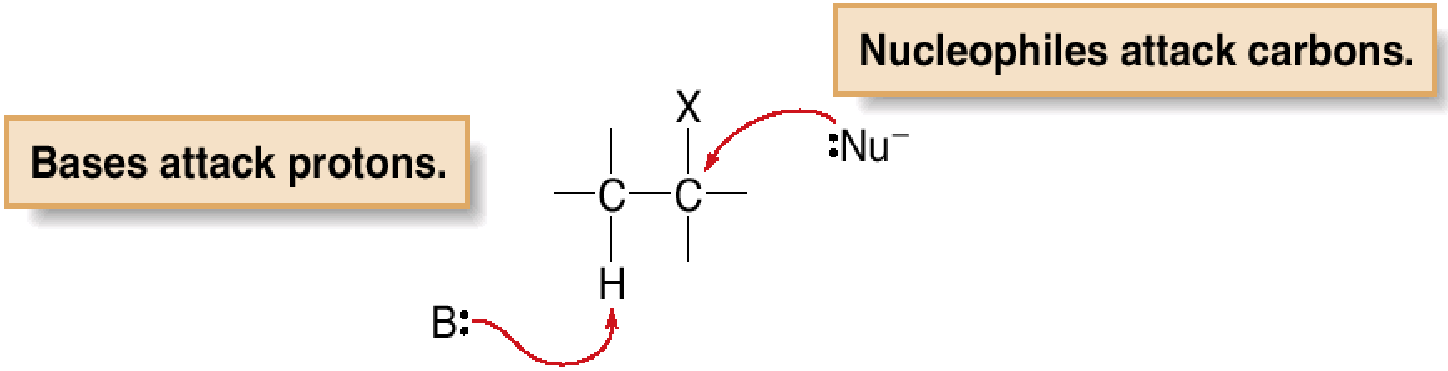
weakest base
best leaving group

Increasing leaving group ability

The Nucleophile

- Nucleophiles and bases are structurally similar: both have a lone pair or a π bond. They differ in what they attack.

- Bases attack protons. Nucleophiles attack other electron-deficient atoms (usually carbons).



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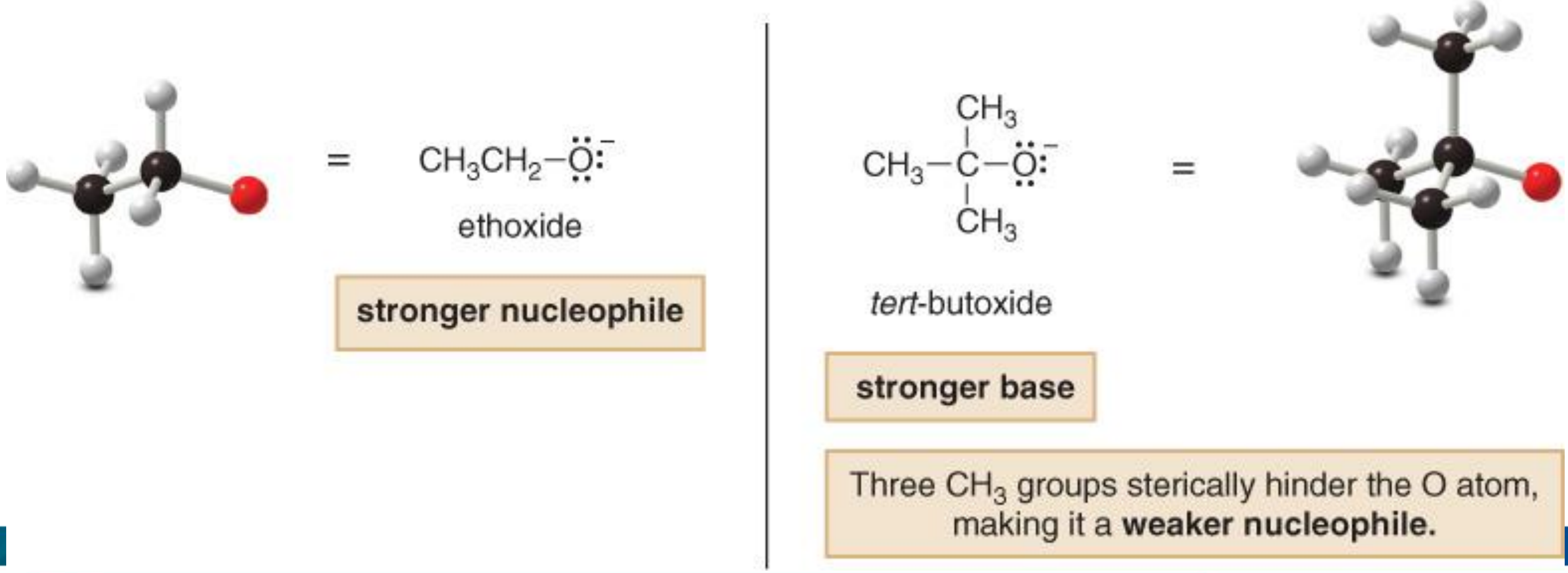
The Nucleophile

- Although nucleophilicity and basicity are interrelated, they are fundamentally different.
  - Basicity is a measure of how readily an atom donates its electron pair to a proton. It is characterized by an equilibrium constant, K_a in an acid-base reaction, making it a thermodynamic property.
  - Nucleophilicity is a measure of how readily an atom donates its electron pair to other atoms. It is characterized by a rate constant, k, making it a kinetic property.

The Nucleophile

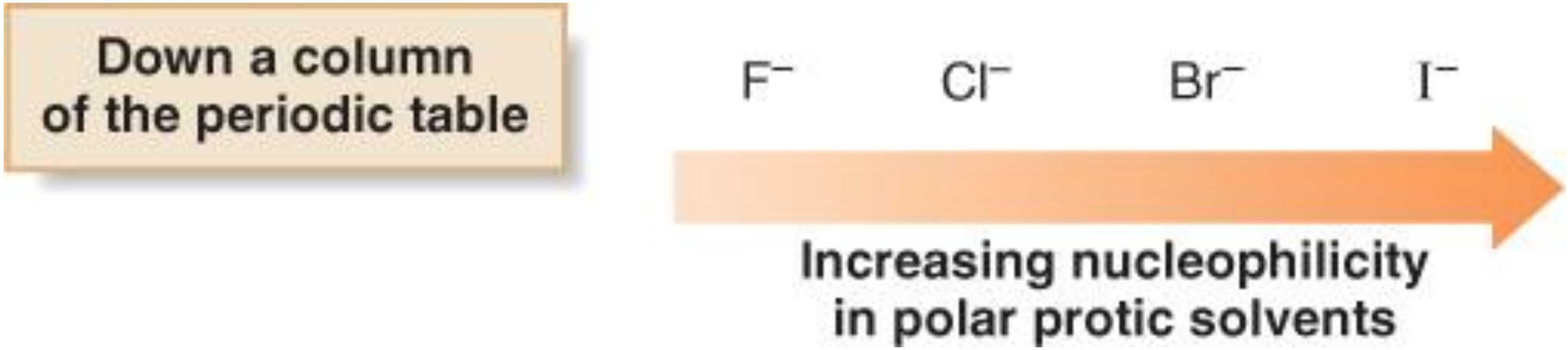
- Nucleophilicity does not parallel basicity when steric hindrance becomes important.
- Steric hindrance is a decrease in reactivity resulting from the presence of bulky groups at the site of a reaction.
- Steric hindrance decreases nucleophilicity but not basicity.
- Sterically hindered bases that are poor nucleophiles are called nonnucleophilic bases.



Three CH_3 groups sterically hinder the O atom, making it a **weaker nucleophile.**

The Nucleophile

- In polar protic solvents, nucleophilicity increases down a column of the periodic table as the size of the anion increases. This is the opposite of basicity.



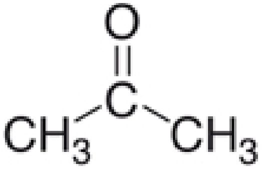
H_2O	CH_3OH	CH_3CH_2OH	$(CH_3)_3COH$	CH_3COOH
	methanol	ethanol	*tert*-butanol	acetic acid

Figure 7.6 Example of polar protic solvents

The Nucleophile

- Polar aprotic solvents also exhibit dipole—dipole interactions, but they have no O—H or N—H bonds. Thus, they are incapable of hydrogen bonding.

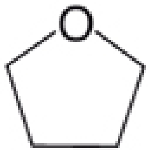
Figure 7.7 Examples of polar aprotic solvents



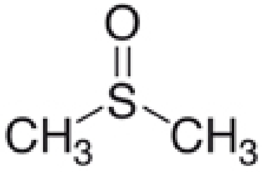
acetone

$CH_3-C\equiv N$

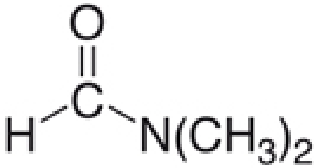
acetonitrile



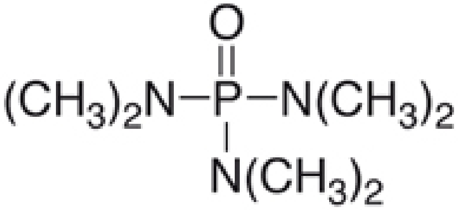
tetrahydrofuran
THF



dimethyl sulfoxide
DMSO



dimethylformamide
DMF



hexamethylphosphoramide
HMPA

Conclusion of The Chapter

- Conclusion #1
  - The fundamental of alkyl halides with its nomenclature were understandable.
- Conclusion #2
  - The fundamental of alkyl halides included its reactions involves were practically explained.
- Conclusion #3
  - The information of SN1 and SN2 were practically described

Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

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