

Substitution Reactions

1 – Alkyl halides: Nomenclature, Properties and Applications

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Alkyl Halides - Nomenclature - 1

Alkyl halides is the general nomenclature of haloalkanes (IUPAC). In this functional group, one or more hydrogen in an alkanes has been substituted with a halogen (any element in group VII: fluorine, chlorine, bromine or iodine). The sp^3 bonding does not change, alkanes are still saturated.

Naming follows similar IUPAC rules covered so far. Below is the nomenclature of some of the small and simple haloalkanes. The genera names below are in *italics*.

- Smallest alkyl halides are from methane. Substitute a hydrogen with a halide.



chloromethane

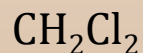


bromomethane



iodomethane

- Two and three substitutions of halide



Dichloromethane



dibromomethane



trichloromethane

Methylene chloride

chloroform

- In case there are different halo substituents, name them alphabetically.

CHClBrF - bromochlorofluormethane

Alkyl Halides - Nomenclature - 2

For ethane, the halogen can be on the same carbon or both carbons. Again, the general names are in *italics*.



Chloroethane

ethylchloride



1,1-dichloroethane



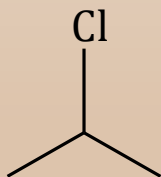
1,2-dichloroethane

When there are two different halogens, name them alphabetically.



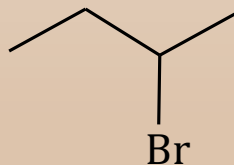
1-bromo-2-chloroethane

For longer alkanes, as below, there can be both IUPAC and general names.



2-chloropropane

Isopropylchloride



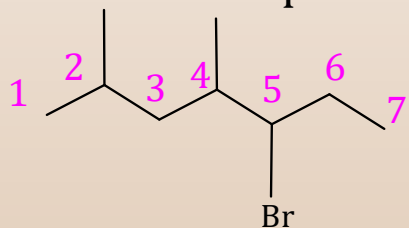
2-bromobutane

Sec-butylbromide

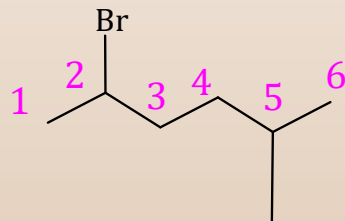
Alkyl Halides - Nomenclature - 3

For longer chain alkanes:

- find longest chain, name it as parent chain,
- Number from end nearest any substituent (alkyl or halide).
- Branching gets preference (not an alkyl or halide substituent).
- Name all substituents alphabetically.

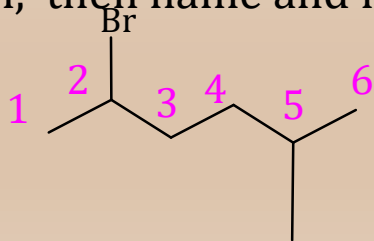


5-bromo-2,4-dimethylheptane



2-bromo-4,5-dimethylheptane

- If two substituents present with low numbers of carbon on either side of chain, then name and number alphabetically.

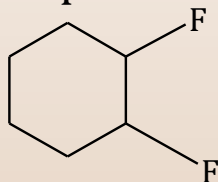


2-bromo-5-methylhexane

(**Not** 5-bromo-2-methylhexane)

Cycloalkylhalides – Nomenclature

In cycloalkylhalides also no precedence is given to alkyl groups over halides. Follow numbering from branching and alphabetical rules. Give all substituents lowest numbers possible.

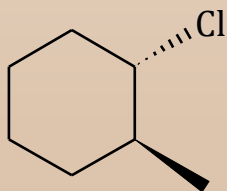


1,2-difluorocyclohexane

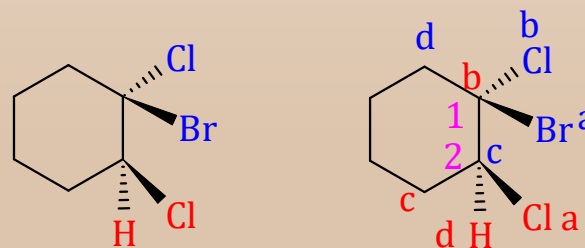


1-bromo-1-chlorocyclopentane

There is no rotation possible in single bonds of cyclic compounds, so bonds are stuck where they are, so substituents can be on the same side or opposite side. When Hs are on the same side compound is cis, and if on opposite side, then trans. When there are no H to determine cis/trans then use R/S for direction.



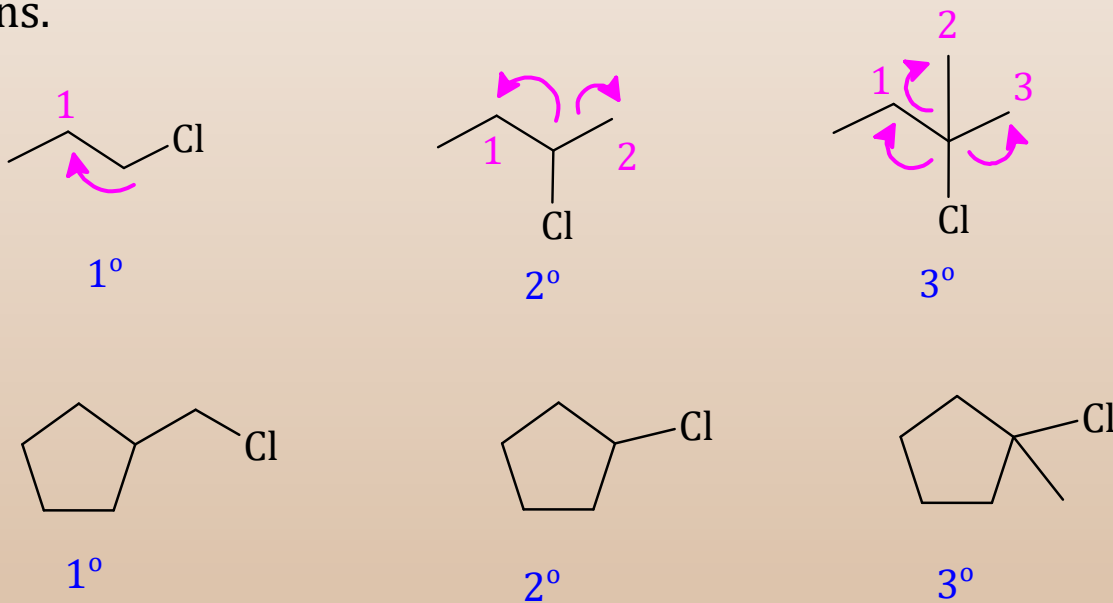
Trans-1-chloro-2-methylcyclohexane



(1R, 2S)-1-bromo-1,2-dichlorocyclohexane

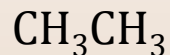
Classification of Halides

Halides can be classified as primary (1°), secondary (2°) and tertiary (3°), depending on how many carbon it is bonded to. This is similar to how we classified hydrogens in simple alkanes. The pink arrows shown below the connections of the number of carbons that is connected to the carbon that has the halogens.

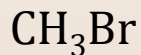


Alkyl Halides - Physical Properties - 1

1) **Boiling points** – Higher than alkanes because of dipole-dipole interactions and dispersion forces because of higher mass of halogens.



Bpt. -89°C



Bpt. 4°C

All haloalkanes have dipole moment depending on the halide.

Haloalkane	dipole moment
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CH_3F	1.85
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CH_3Cl	1.87
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CH_3Br	1.81
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CH_3I	1.62
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Alkyl Halides - Physical Properties - 2

2) **Solubility in Water** – Very little. The only intermolecular force common is dipole-dipole which also is not very much in alkyl halides. Solubility decreases as mol wt gets higher.

3) **Density** – Haloalkanes have higher density than alkanes because of higher molecular weight of the halogens.

Haloalkane	Density (g/mL) at 25°C		
	X=Cl	X=Br	X=I
CH ₂ X ₂	1.37	2.497	3.325
CHX ₃	1.48	2.890	4.008
CX ₄	1.59	3.273	4.23

4) **Odor** – All halo compounds smell, usually not a bad smell.

Applications of Alkyl Halides

- Solvents e.g. dichloromethane, chloroform.
- Good starting materials for substitution reactions.
- Chlorofluorocarbons – used as refrigerants, propellants for aerosols.
- Dry cleaning (chlorofluorocarbons) as solvents for dry cleaning and as a general degreasing agent.
- Starting material for polymers (vinylchloride, tetrafluorethane).
- Fire retardant.
- Most halogenated compounds are toxic in nature.

Key Concepts

- Nomenclature of haloalkanes
- Physical properties