Chapter 10 - Alkyl Halides

Alkyl halides are common

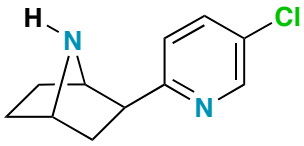
Organic halogen compounds are found in many places from common solvents for chemistry and industry, to refrigerants (largely banned for their ozone destruction properties) and natural products.

CH_2Cl_2
$CHCl_3$
$CH_2Cl\text{-}CH_2Cl$

common solvents

CF_2Cl_2

CFCs (chlorofluorocarbons)



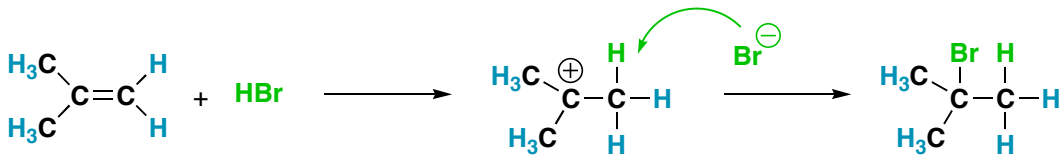
natural products (epibatidine)

The chemistry of alkyl halides is dominated by the fact that the carbon-halogen bond is polarized toward the more electronegative halogen. Thus, the carbon is electrophilic. Organic fluorides are the most stable whereas the iodides are the most reactive. This correlates to the change in bond length.

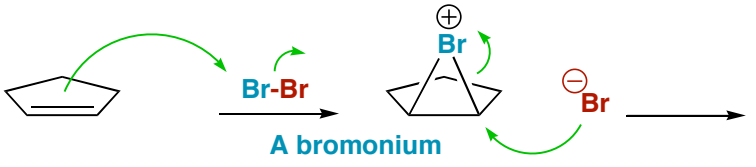
		diopole moment (Debyes)	bond length (Å)	bond strength (kcal/mol)
fluoromethane	$CH_3\text{-}F$	1.85	1.39	108
chloromethane	$CH_3\text{-}Cl$	1.87	1.78	84
bromomethane	$CH_3\text{-}Br$	1.81	1.93	70
iodomethane	$CH_3\text{-}I$	1.62	2.14	56

Preparation of Alkyl Halides - addition reactions

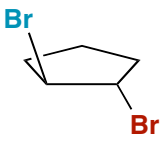
Recall that alkyl halides can be prepared by addition reactions of alkenes.



Most stable intermediate
Lower energy pathway



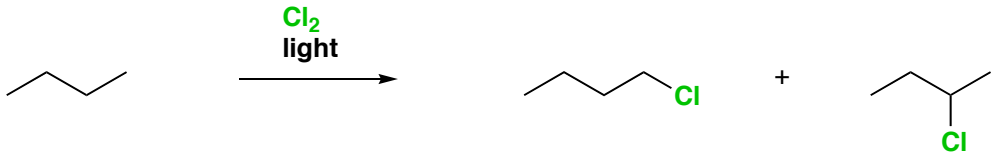
A bromonium



Bromide can only come from the bottom and kick off the bromine on the top. This reaction forms the trans product selectively.

Preparation of Alkyl Halides - free radical halogenation

Free radical halogenation of alkanes will produce alkyl halides, however, the reaction usually produces a mixture of products. Note that the reaction proceeds via carbon radical intermediates and similar to carbocations, a carbon radical is more stable if it is more substituted. Thus, tertiary hydrogens are more reactive than secondary hydrogens, which are more reactive than primary hydrogens in this process.



expected statistical ration from six 1° H's and four 2° H's **6 : 4**

actual ration observed **30 : 70**

=> secondary H's are 3.5 times more reactive than primary H's for radical chlorination

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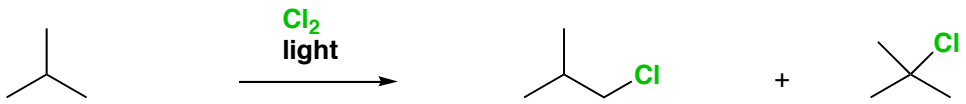

expected statistical ration from nine 1° H's and one 2° H **9 : 1**

actual ration observed **65 : 35**

=> tertiary H's are 5 times more reactive than primary H's for radical chlorination

Allylic Bromination - free radical

Allylic radicals are strongly stabilized by resonance. Thus, radical halogenation of molecules with an alkene will selectively substitute one of the allylic hydrogens. For example, bromine radicals, generated by the photolysis of NBS, will generate allylic bromides.