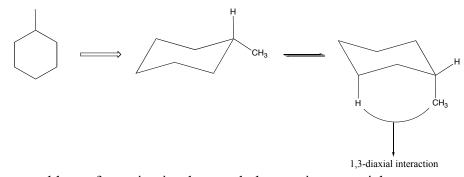
## **REVIEW: Cyclohexane – conformations**

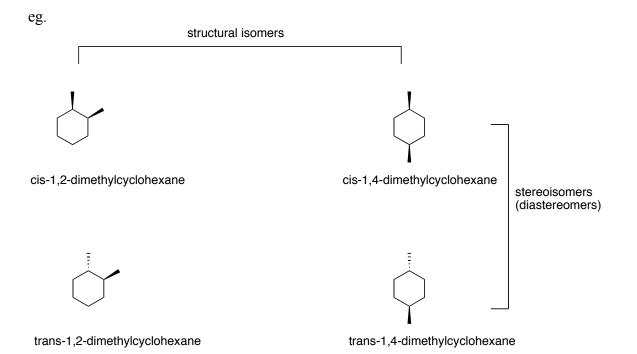


- most stable conformation is when methyl group is equatorial -
- when methyl group is placed axial, less stable conformation due to 1,3-diaxial interaction (as shown above)

**Isomers** - different compounds with same molecular formula – 2 basic types 1. structural/constitutional isomers

- compounds with same molecular formula and different names, numbers
- 2. Stereoisomers have normally same name but different 3-D structure 2 sub-types (a) diastereomers/diastereoisomers (geometric isomers)

  - (b) enantiomers (non-superposable mirror images of same molecule)

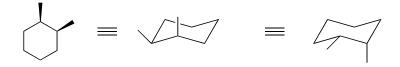


#### **Conformations**:

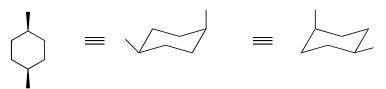
- different 3-D shapes a molecule can assume by rotation around single bonds

eg. Same conformation can be depicted in several ways

cis-1,2-cyclohexane

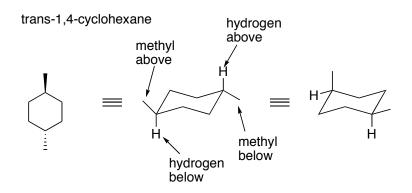


cis-1,4-cyclohexane



Note on drawing the most stable conformation of substituted cyclohexanes:

- generally, draw chair conformation of cyclohexane
- put the largest group in equatorial position
- draw the next group on the correct side (face) with respect to the largest group



- Reactions of alkanes: Two will be considered; combustion to  $CO_2$  and  $H_2O$  already discussed and....
  - 1) Halogenation of alkanes
  - $R-H + X_2 \rightarrow R-X + HX$

R= any alkane (group), R-X = alkyl halide / haloalkane (X=Cl, Br, F) ; I<sub>2</sub> fails

substitution reaction – replace one group by another (below, H is replaced by Cl) eg.

CH <sub>4</sub>	+	Cl <sub>2</sub>	hυ → CH <sub>3</sub> Cl +	HCI	
methane			methyl chloride chloromethane		
			light energy, $E = hv$		
			h = Planck's constant		
			v = frequency of light		
		CI	hu		
CH₃CI	+	Cl <sub>2</sub>		ICI	
			methylene chloride dichloromethane		
CH <sub>2</sub> Cl <sub>2</sub>	+	Cl <sub>2</sub>	hυ ────────────────────────────────────	HCI	
		-	chloroform trichloromethane		
CHCl <sub>3</sub>	+	Cl <sub>2</sub>	► CCl <sub>4</sub> + F	ICI	
011013	т	012			
			carbon tetrachloride tetrachloromethane		

### **Mechanism of reaction:**

- step by step description of what happens during a reaction (hypothesis)

homolytic reaction:  $R-R' \rightarrow R' + R'$  (one electron to each group) radical rxn heterolytic reaction:  $R-R' \rightarrow R^+ + :R'$  (both electrons on one group)

heterolytic reactions more common, but halogenation of alkanes involves homolytic reactions

 $CH_4 + X_2 \xrightarrow{hv} CH_3X + HX$ 

X = Cl, Br, I

Reactivity in organic chemistry is associated with:

- polarized bonds (electronegative elements)
- lone pairs of electrons
- multiple bonds

Mechanism of halogenation of CH<sub>4</sub>:

$$: \overset{\land}{\underset{h\nu}{\bigcirc}} \overset{\land}{\underset{h\nu}{\bigcirc}} 2 : \overset{\land}{\underset{h\nu}{\bigcirc}} initiation step$$

$$: \overset{\land}{\underset{h\nu}{\bigcirc}} + H - CH_3 \longrightarrow H \overset{\land}{\underset{l}{\bigcirc}} i + \cdot CH_3$$

$$a methyl radical$$

$$: \overset{\land}{\underset{h}{\bigcirc}} + : \overset{\land}{\underset{l}{\bigcirc}} - \overset{\land}{\underset{l}{\bigcirc}} i : \longrightarrow CH_3Cl + : \overset{\land}{\underset{l}{\bigcirc}} i \cdot$$

$$: \overset{\land}{\underset{h}{\bigcirc}} + : \overset{\land}{\underset{l}{\bigcirc}} i + : \overset{\land}{\underset{l}{\bigcirc}} i \to Cl_2$$

$$: \overset{\land}{\underset{h}{\bigcirc}} + \cdot CH_3 \longrightarrow CH_3CH_3$$

$$: \overset{\land}{\underset{l}{\bigcirc}} i + \cdot CH_3 \longrightarrow CH_3Cl$$

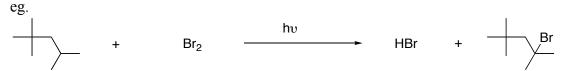
$$termination steps$$

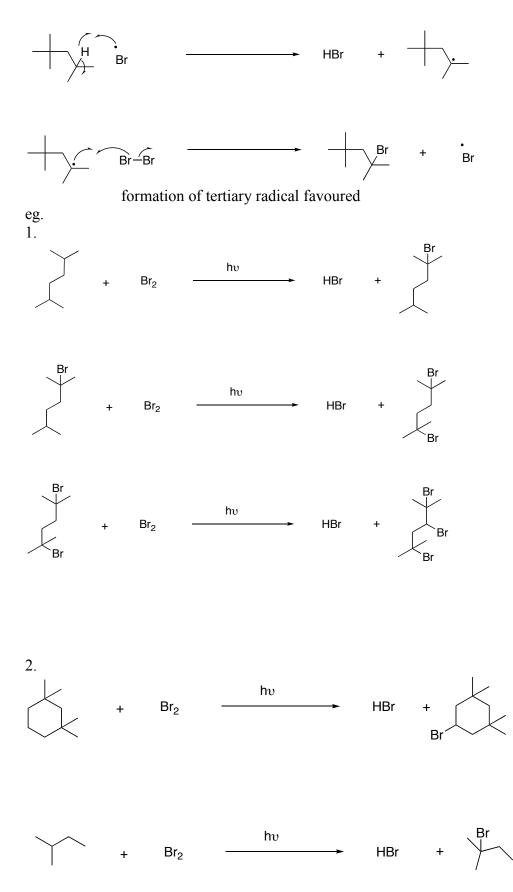
Note: above mechanism applies to other halogens (F, Cl, Br)

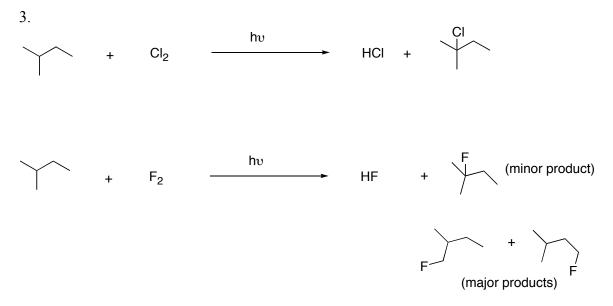
## **Stability of radicals:**

·CH <sub>3</sub> <	·CH <sub>2</sub> R	<	·CHR <sub>2</sub> <	·CR <sub>3</sub>
methyl	primary		secondary	tertiary
radical	radical		radical	radical
(least stable)				(most stable)

- alkyl groups donate electron density through single bonds  $\rightarrow$  inductive effect
- hydrogen can also donate by inductive effect but poor donation compared to alkyl groups







# WHY is fluorination different from chlorination or bromination – not selective for generation of tertiary (most stable) radical ?

- fluorine radical is most reactive radical, so goes for most accessible methyl hydrogen giving the primary alkyl radical
- -

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- "less reactive  $\rightarrow$  most selective"
- "most reactive  $\rightarrow$  less selective"
  - Will discuss Hammond Postulate