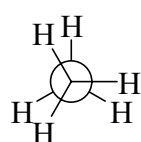
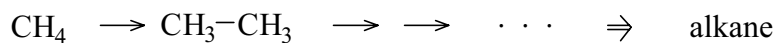


## Chapter 3



eclipsed

(Newman projection)



energy barrier ; 3kcal/mole



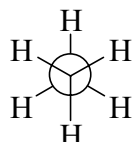
not quite free but rotate freely at RT



not from van der Waals repulsion but from repulsion between C—H bonds



tortional energy, tortional strain

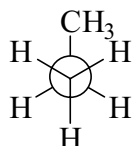
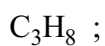


staggered

skew conformation

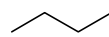
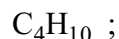


different arrangements of atoms by rotation about single bonds



3.3kcal/mole  
energy barrier

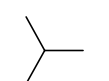
(due mainly to the same factor as in ethane)



↪ six isomeric  $\text{C}_4\text{H}_8\text{Cl}_2$

n-butane

isomers



isobutane

↪ three isomeric  $\text{C}_4\text{H}_8\text{Cl}_2$

anti , gauche

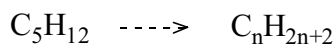


Fig 3.8 ⇒ van der Waals repulsion (steric repulsion)

van der Waals strain (steric repulsion)



still freely rotate at RT



homologous series, homolog

$\left( \begin{array}{l} \text{n-butane} \\ \text{isobutane} \end{array} \right) \left( \begin{array}{l} \text{n-pentane} \\ \text{isopentane} \\ \text{neopentane} \end{array} \right) \Rightarrow \text{much increase in isomers} \Rightarrow \text{systematic name}$

$C_nH_{2n+1}X = RX \Rightarrow \text{alkyl group}$

$\downarrow$

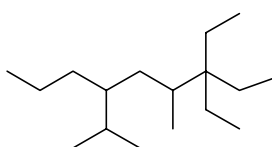
IUPAC name

$\left( \begin{array}{l} \text{n-propyl} \\ \text{isopropyl} \end{array} \right) \left( \begin{array}{l} \text{n-butyl} \\ \text{sec-butyl} \\ \text{tert-butyl} \\ \text{iso-butyl} \end{array} \right)$

$\downarrow$   
 (up to six carbons)

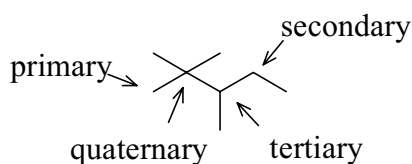
1) longest chain    2) numbering    3) di, tri, tetra...

ex)



4) alkyl

5) fluoro, chloro, bromo, iodo...

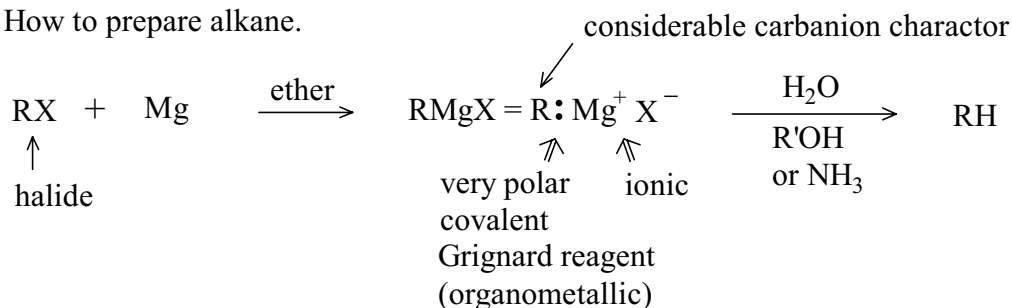


alkane  $\Rightarrow$  non-polar  $\Rightarrow$  van der Waals force  $\Rightarrow$  weak, very short range

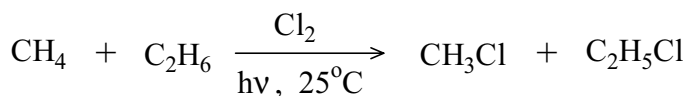
$\downarrow$

less dense than $H_2O$ (due to C&H)	$\Leftarrow$	a straight-chain isomer boils at a higher temp than a branched-chain isomer due to surface area	$\Leftarrow$	larger molecule $\rightarrow$ larger surface area
				$\rightarrow$ stronger intermolecular force
				$\rightarrow$ the higher mp & bp
				( gas $\rightarrow$ liq $\rightarrow$ solid)

How to prepare alkane.







( 1 : 1 ) (competition) 1 : 400

large excess

considering H numbers

1 : 270  $\Rightarrow$  the hydrogen of methane is less reactive than the primary hydrogen.

$\Delta E_a$  for chlorination : small Table 3.5  $\Leftarrow$

$\Delta E_a$  for bromination : large for  $E_a$

p 111  $\Rightarrow$  relative stability of free radicals  $3^\circ > 2^\circ > 1^\circ > \cdot\text{CH}_3$  ( Fig 3.12 relative to the parent alkane )

ease of abstraction of hydrogen atoms  $3^\circ > 2^\circ > 1^\circ > \cdot\text{CH}_3$

= ease of formation of free radicals

factors to stabilize the free radical tend to stabilize the incipient free radical in the transition state.

$\Downarrow$

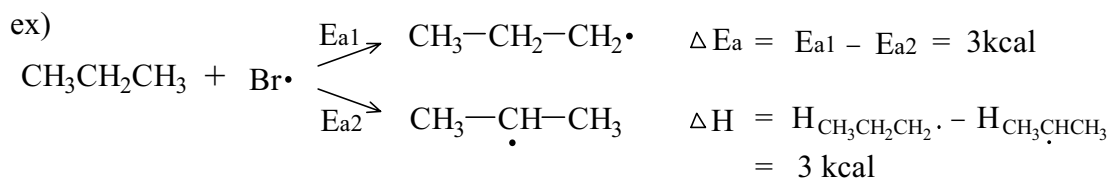
$\Uparrow$

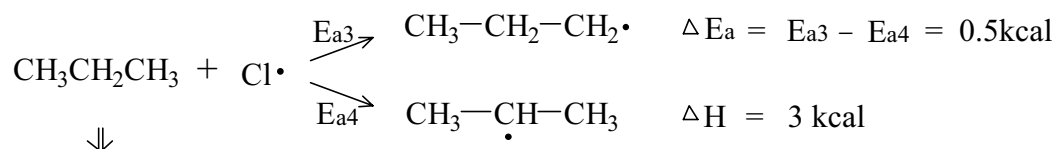
$\Downarrow$

the more stable the free radical, the more easily it is formed.

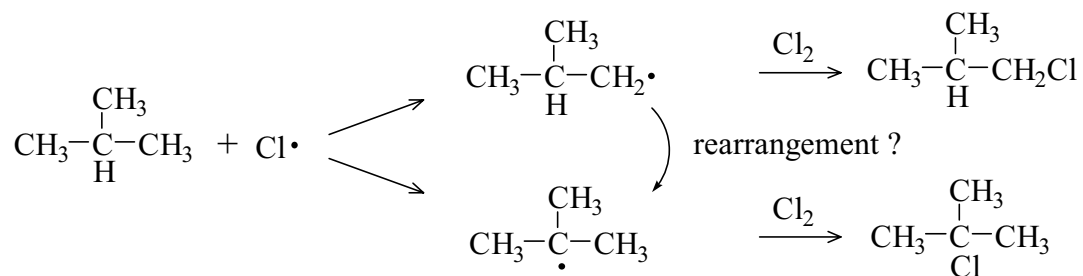
Fig 3.13

Br atom ; less reactive  $\rightarrow$  late t.s.  $\rightarrow$  more radical character  $\rightarrow$  the difference in  $E_a$   
 Cl atom ; more reactive  $\rightarrow$  early t.s.  $\rightarrow$  less radical character  $\approx$  the difference in radical stabilities

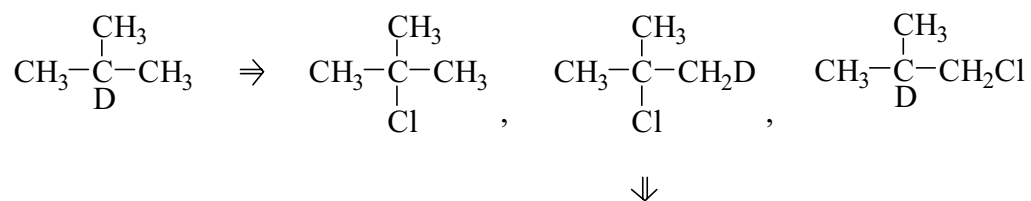




the less reactive  $\longrightarrow$  the more selective



How to prove no rearrangement.



it is not formed  $\Rightarrow$  no rearrangement