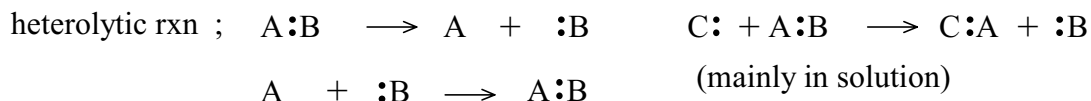
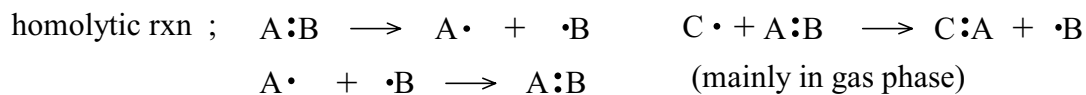


Chapter 5



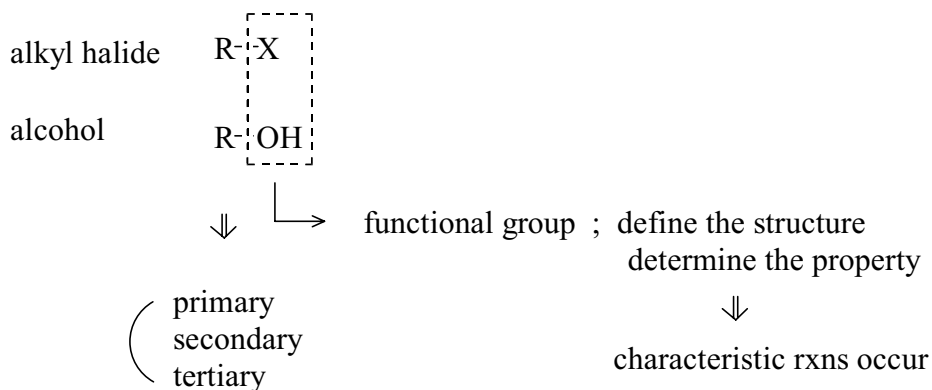
↓ cf) homolysis , heterolysis

nucleophilic (aliphatic) substitution

Which chemical rxn occurs ? \Rightarrow a matter of relative rates of competing rxns

ex) halogenation

What happens? Where does it happen? Does it happen?



IUPAC name for halide p168

alkyl halide ; van der Waals force or weak dipole-dipole interaction



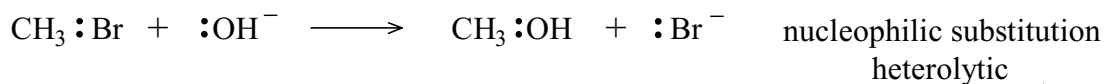
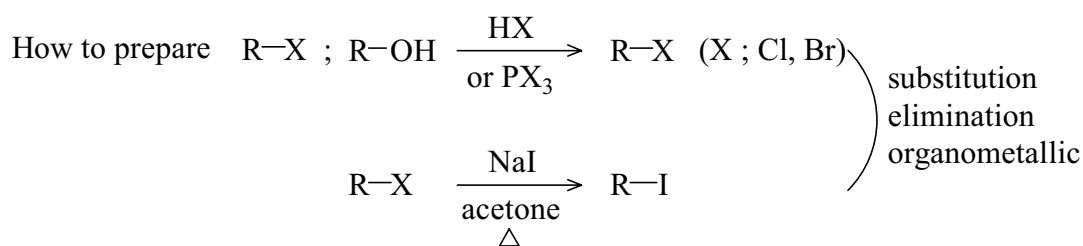
relatively low m.p & b.p

soluble in non-polar solvents

insoluble in H₂O

denser than H₂O (not for mono-chlorides)

from alkane (mixture, not practical)



substrate nucleophile

leaving group



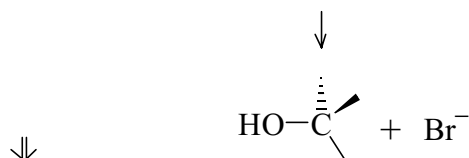
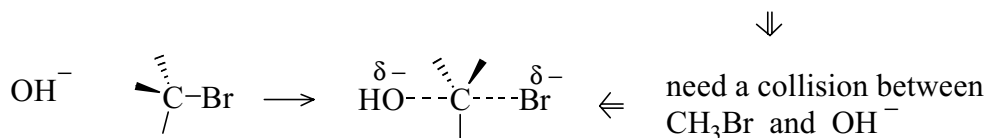
anion or neutral (containing an unshared pair of electrons)



basic

p173 – p174

→ compete with elimination



at the face most remote from Br
with sufficient energy

→ the rxn occurs

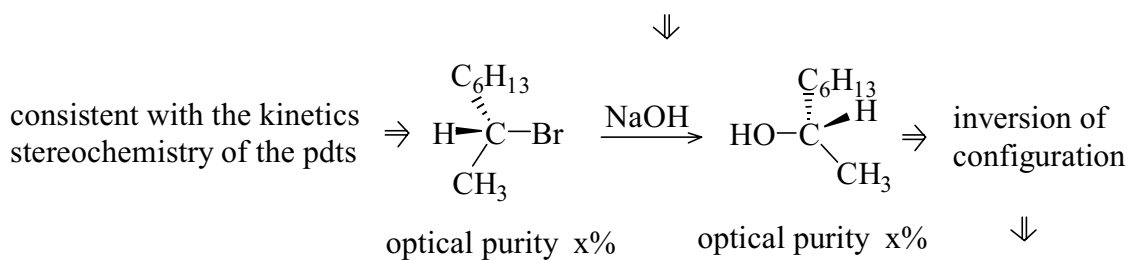
⇒ transition state

↓
partially bonded C-OH
C-Br

all bond angles ; 120° ← OH ; diminished negative charge
Br ; developed a partial
negative charge

partially formed C-OH
partially broken C-Br

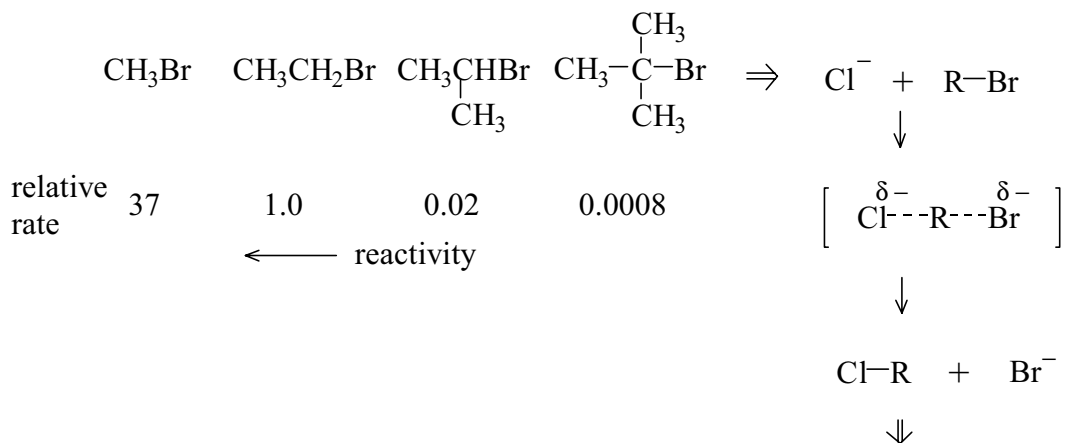
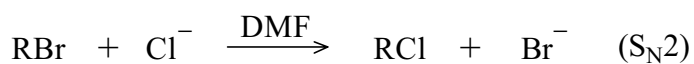
⇒ S_N2, mechanism (substitution nucleophilic bimolecular) ⇒ what evidence?



occurs in a single step

↓
bond-making &
bond-breaking
occur simultaneously

↓
in a concerted fashion



the polar effects of the substituent groups are not expected to be important due to nearly no charge on carbon in the transition state

\Leftarrow the factors to stabilize them are not expected to stabilize the transition state

\Leftarrow transition state is different from the structures of the reactants and the products.

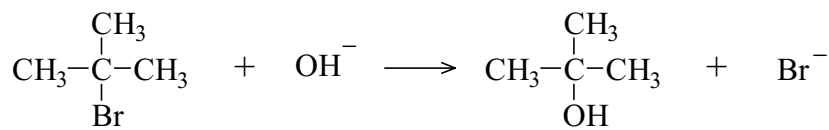
\Downarrow

shape \Rightarrow the different rates are mainly due to steric factors

\Rightarrow Fig 5.3 & 5.4

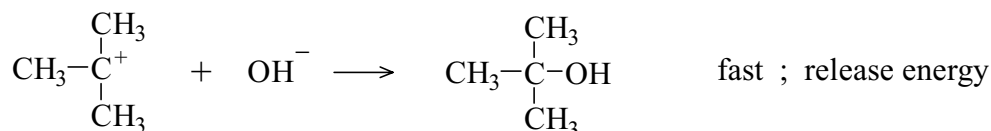
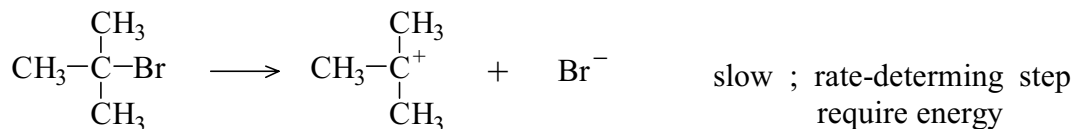
\Downarrow

p188 (relative rate)



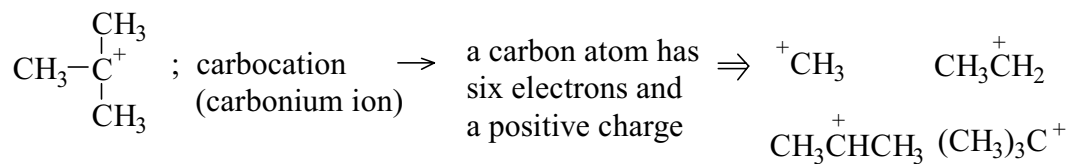
$$\text{rate} = k [\text{tBuBr}]$$

↓

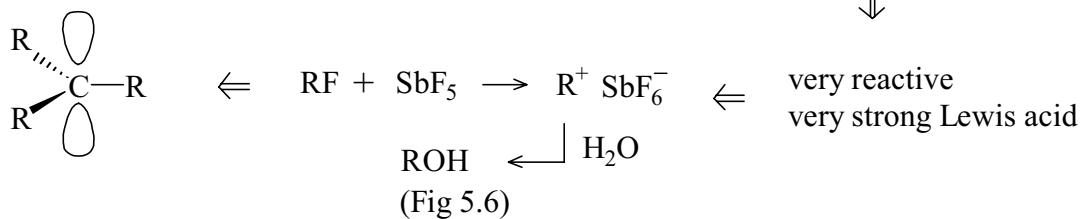


↓

$\text{S}_{\text{N}}1$ (substitution nucleophilic unimolecular)

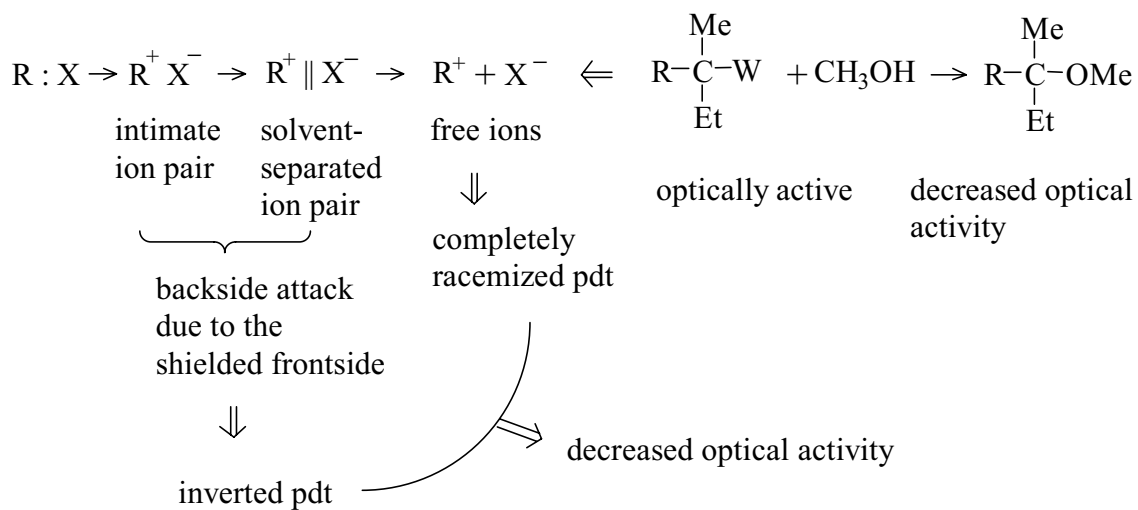


↓

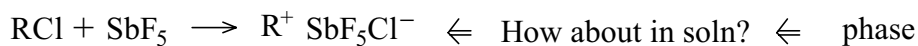


What evidence for $\text{S}_{\text{N}}1$? \Rightarrow first-order kinetics.
the stereochemistry of pds.

↓



relative stability of carbocation \Rightarrow p197 \Rightarrow $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$ \Rightarrow heterolytic bond dissociation in gas



the differences in stability are much the same

the greater the number of alkyl groups, the more stable the carbocation \Rightarrow alkyl groups should release electrons to disperse the positive charge on carbon

\Downarrow

inductive effect ; the intrinsic tendency of a substituent to release or withdraw electrons

resonance effect ; delocalize electrons (π electrons)

\Downarrow

not clear for alkyl groups.

may be an inductive effect.

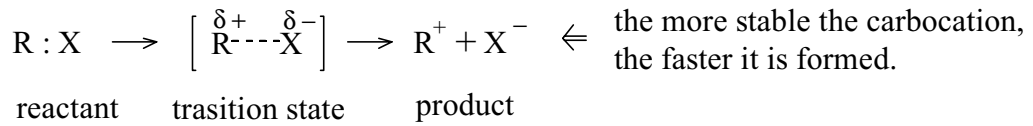
\Rightarrow may be a combination of the two

may be a resonance effect.

(overlap of σ bonds with the empty p orbital ; hyperconjugation)

relative reactivity for S_N1 = rate of formation carbocations \Rightarrow carbocation stability
 $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{W}$ (p200) $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

\Downarrow



\Downarrow

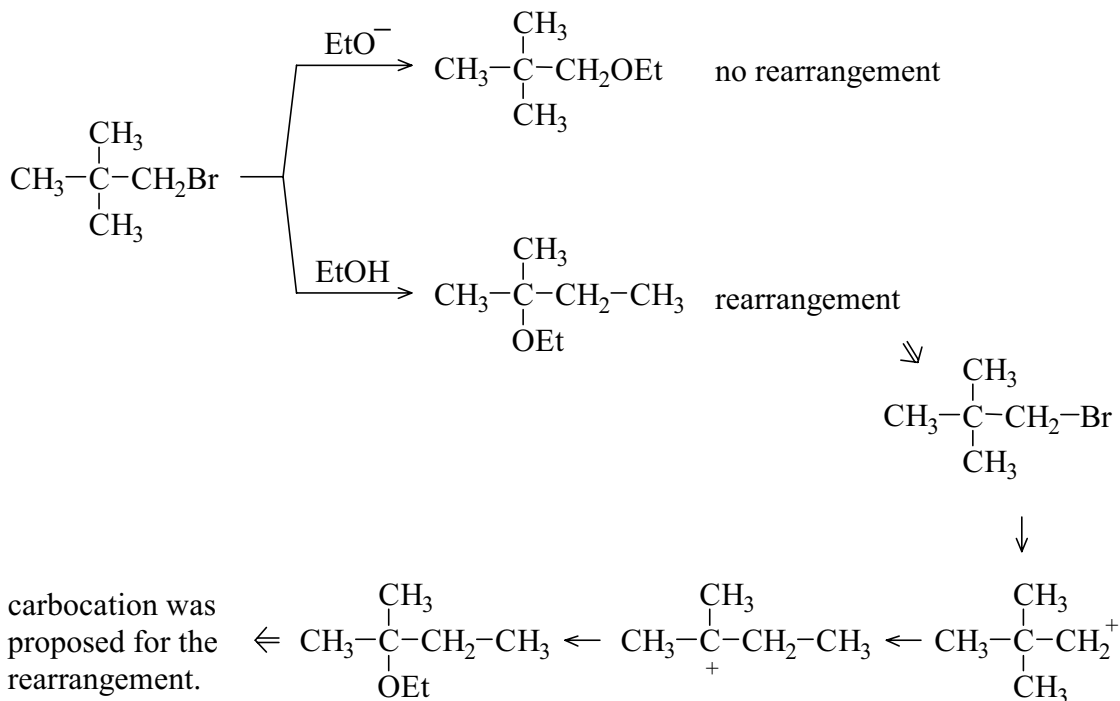
carbon has partly gained the positive charge. \Rightarrow electron-releasing groups disperse the partial positive charge

\Downarrow

faster rxn \Leftarrow lower E_a \Leftarrow stabilize the transition state

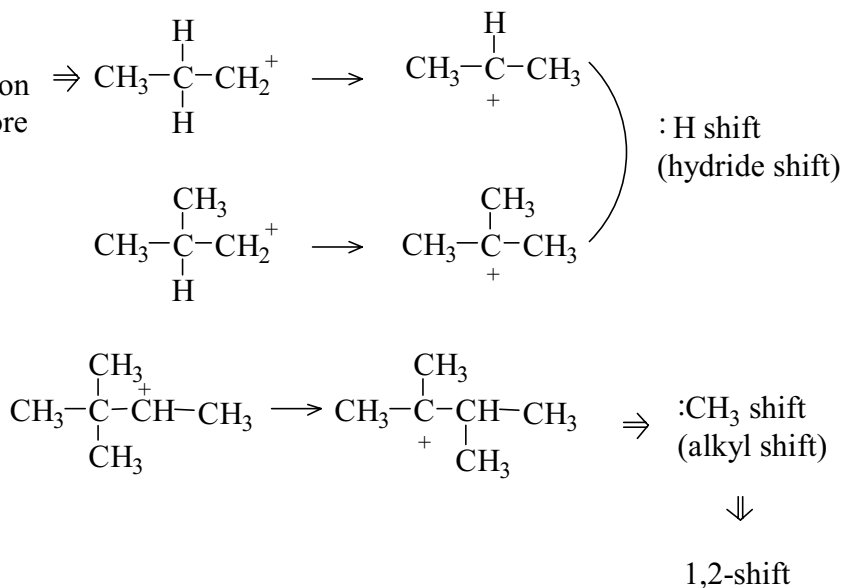
\Downarrow

Fig 5-10



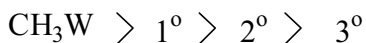
\Downarrow

in the rearrangement,
a less stable carbocation
is converted into a more
stable



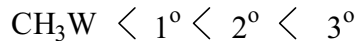
S_N2

second-order kinetics
complete stereochemical inversion
no rearrangement



S_N1

first-order kinetics
racemization
rearrangement



which mechanism will predominate for a given substrate
under a given set of conditions?

a matter of relative rates of competing rxns

1) substrate

leaving group ; the bond to the leaving group is broken in r.d.s.

a better leaving group speeds up rxn by both mechanisms
to about the same degree.

little effect on which mechanism is predominant

alkyl group ; steric effect

the ability to stabilize a positive charge



a profound effect on which mechanism is predominant.

2) nucleophile

S_N2 ; involved in r.d.s.

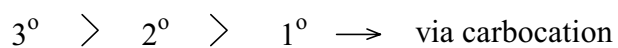
S_N1 ; involved after r.d.s.

$[Nu] \uparrow$ rate of $S_N2 \uparrow$ high $[Nu]$ favors S_N2 .
rate of $S_N1 \rightarrow$ no effect low $[Nu]$ favors S_N1 .

stronger Nu ; rate of S_N2 is faster strong Nu favors S_N2 .
no effect on S_N1 weak Nu favors S_N1 .

alcoholic $AgNO_3$ is used for the detection of alkyl halides.

reactivity



allylic & benzylic halides are very reactive.

vinyl & aryl halides are unreactive.

